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INSIGHT IN ALUMINATE SYNTHESIS FOR PIEZOLUMINESCENT APPLICATIONS

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> Thesis proposed to obtain the degree of MASTER OF SCIENCE IN CHEMISTRY

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Insight in Aluminate Synthesis for Piezoluminescent Applications

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Abstract

In composites, the damage mechanisms are numerous, can initiate very early in time and are typically associated with decrease of strength until the point of structural failure. Over the years, many approaches have been suggested to monitor damage in composites. However, the need for in-situ sensors for self-sensing composites emerges from the critical limitations of the insufficient state-of-the-art monitoring techniques. We investigated the synthesis of mechanoluminescent materials on nanocrystal level to provide an integrated optical sensor for internal damage. This paper reports an insight in the synthesis of strontium aluminate, a piezoluminescent host material. The investigated solvothermal benzyl alcohol method was not able to produce this host material due to the low reactivity of the aluminium precursors. As a consequence, more reactive aluminium precursors needs to be obtained, so they match the reactivity of the strontium precursor. Although, there is no certainty that it is possible to synthesize strontium aluminate nanocrystals using the benzyl alcohol route which will be the focus of future work.

1. INTRODUCTION

It is well known that damage mechanisms in structural fiber-reinforced composites differ from the typical damage mechanisms involved in common isotropic materials. In composites, the damage mechanisms are numerous (e.g. fiber/matrix debonding, matrix cracking, tearing and crazing, fiber tensile failure and buckling, intra-ply and inter-plydelaminations), show complex interactions and have many associated variables (e.g. strain rate, temperature). Moreover, even in long-lasting structural components (e.g. wind turbine blades), damage can initiate very early in time, before 10% of the life span, and grow gradually. Structural internal damage is typically associated with decrease of strength but, different from other materials, the stiffness gives rise to continuous internal stress redistribution. Because reliable life-time predictions cannot be made from simple laboratory tests, and because at the same time they are of great concern to operational reliability and human safety, much research effort is currently being spent on the combined use of numerical simulations of the momentary structural behaviour and continuous monitoring of the actual damage state.¹

Over the years, many approaches have been suggested to monitor damage in composites. However, there is currently no 'universal' technique that allows predicting the health of structural composite materials. Current standard inspection techniques such as visual surveillance, ultrasonic inspection and radiography do not answer the need for continuous in-service and in-situ monitoring. Moreover, these techniques are labour-intensive and therefore expensive. A wide range of surface mounted and in rare cases embedded sensors have already been studied for structural health monitoring applications, including strain gauges, accelerometers, fiber optic sensors, active ultrasonic sensors, passive acoustic sensors and infrared cameras.^{1,2,3}

Damage in structural elements is often deducted from strain measurements. Indeed the presence of damage (i.e. the different possible mechanisms mentioned) gives rise to local strain concentrations and changes in the strain gradients. For strain monitoring, strain gauges and fiber optic sensors are currently the main choice. Externally applied strain gauges are now the obvious choice, but their wiring poses significant challenges to sensor deployment and limits the number of points that can be monitored in a large structure. Even by using surface monitoring techniques, such as classic strain gauges, it remains difficult or impossible to detect important internal damage mechanisms, such as delaminations or fiber debonding, because such damage in not 'visible' at the exterior of the structure or can only be sensed at the micro-scale level. When embedded, optical fiber Bragg or Fabry-Perot sensors show affinity with the host material (they are small, lightweight, chemically inert and have intrinsic multi-plexing capabilities) and are therefore considered valuable for in-situ strain monitoring, but they equally suffer from critical limitations.⁴

Emerging self-sensing composites take an alternative approach, namely by using intrinsic, multifunctional properties of the (adapted or modified) constituents of the composite, thereby acting themselves as the sensing element. This approach has already been demonstrated, using the electrically conductive properties of carbon-fiber composites, or using the inherent optical properties of reinforcing glass fibers.⁵ Other routes to self-sensing may be for example coating of the fibers or stacking layers with ultra-thin sensing films^{6,7,8} or adding a specific component (e.g. a stable suspension or a powder) to the matrix. In the latter context, the use of mechanoluminescent films has been demonstrated.^{9,10} These films are able to emit light when exposed to stress or strain.

Strontium aluminate $(SrAl_2O_4)$ is the best host material for persistent luminescent known

until today.^{11, 12} Although $SrAl_2O_4:Eu^{2+},Dy^{3+}$ is known to show very strong persistent luminescence, these values are mostly reported for the material where particles are of millimeter or micrometer size. Materials of this size are often made by aqueous based methods (i.e. sol-gel^{13, 14} or combustion^{15, 16, 17, 18}) and display low processability. This makes its employment in further applications difficult, such as printing on or homogeneously mixing in a substrate.

For the synthesis of SrAl₂O₄, we design a novel synthetic route based on the benzyl alcohol route which has already proven its use in many syntheses.^{19, 20, 21} The benzyl alcohol route, a non-aqueous non-surfactant assisted method, seems to be a very interesting reaction approach for the synthesis of crystalline metal oxide nanoparticles.²² It is an one pot solvothermal reaction where the benzyl alcohol is acting as solvent, ligand and reactant. This route has already been proven to be very versatile with good control over particle size, shape, crystallinity, solubility and assembly behavior.²¹ Niederberger et al.^{19, 20} reported the first syntheses using this method for titanium, tungsten and vanadium oxides in 2002. The following years synthesis of various binary and ternary metal oxide nanoparticles (e.g. SrTiO₃²¹ , (Ba,Sr)TiO₃²¹ , ZnAl₂O₄²² , BaTiO₃^{21, 23} , BaAl₂O₄²⁴ , CaAl₄O₇²⁴ and SrAl₄O₇²⁴) were published. This novel synthetic route will be groundbreaking research on account of multimetaloxide nanocrystal chemistry which become very recently a hot topic.^{22, 23, 25, 24}

2. SYNTHESIS

Materials. All chemicals have been used without further purification. Strontium acetate $(Sr(ac)_2, -)$, aluminium isopropoxide $(Al(OiPr)_3, 98\%)$, benzyl alcohol (BnOH, 99.8%), oleic acid (HOle, 90%), basic aluminium acetate $(Al(ac)_2(OH), -)$ and metallic strontium (Sr, 99.0%) were supplied by Sigma Aldrich. Diethyl ether (DEE, 99.5%) was purchased from Fiers. Chloroform (CHCl₃, 99.8%) was supplied by Carlo Erba. Acetonitrile (CH₃CN, 99.0%) was purchased from Acros Organics.

Autoclave synthesis. In a Teflon autoclave, 0.1029 g (0.5 mmol) $Sr(ac)_2$, 0.2043 g (1 mmol) $Al(OiPr)_3$ and 20 mL BnOH is stirred. Upon dissolution, the autoclave is sealed and placed in a muffle furnace at 200°C for 72 hours. When the autoclave is naturally cooled to room temperature, the reaction mixture is centrifuged and the white precipitation is washed 3 times with DEE. The precipitation can be dried in air or the surface can be modified with organic ligands. For modification, the precipitation is suspended in 4 mL CHCl₃ with 100 μ L HOle. The cloudy suspension is mildly centrifuged to remove the remaining precipitation. The suspension is purified by precipitating with CH₃CN and re-suspending in CHCl₃ (repeat 3 times). The autoclave synthesis can vary in reaction time (48h-168h) and reaction temperature (200°C-260°C). Instead of Sr(ac)₂, Al(ac)₂(OH) (0.1621 g) can be used as well as aluminium precursor.

Microwave synthesis. In a 5 mL microwave tube, 0.1029g (0.5 mmol) $Sr(ac)_2$, 0.2043 g (1 mmol) $Al(OiPr)_3$ and 5 mL BnOH is stirred. The tube is introduced in the microwave and submitted to a microwave heating program of 50°C (5 min), 100°C (5 min), 150°C (5 min), 200°C (5 min) to dissolve the precursors and is followed by the reaction step at 250°C for 10 hours. After completion the reaction mixture is centrifuged and washed 3 times with DEE. The white precipitation can be dried in air or the surface can be modified with organic ligands. For modification, the precipitation is suspended in 4 mL CHCl₃ with 100 μ L HOle. The cloudy suspension is mildly centrifuged to remove the remaining precipitation. The suspension is purified by precipitating with CH₃CN and re-suspending in CHCl₃ (repeat 3 times). The microwave synthesis can be varied in the use of precursors. Instead of Sr(ac)₂, Sr (0.0438g) can be used when working in a glovebox. Instead of Al(OiPr)₃, Al(ac)₂(OH) (0.1621g) can be used as well.

Analysis. The obtained materials are subjected to XRD analysis (a Thermo Scientific ARL X'tra X-ray diffractometer is used with the Cu K_{α} line as the primary source) and TEM analysis (a JEOL JEM-2200FS TEM is used with Cs corrector).

3. RESULTS AND DISCUSSION

Autoclave synthesis. The different syntheses performed in the autoclave are summarized in table 1, alterations in temperature, time and aluminium precursor are tested.

Table 1: Syntheses performed via the conventional (autoclave) method, listed with alternated conditions.

Synthesis	Temperature	Time	Strontium precursor	Aluminium precursor
GOA-48	$200^{\circ}\mathrm{C}$	48h	acetate	isopropoxide
GOA-49	$200^{\circ}\mathrm{C}$	168h	acetate	isopropoxide
GOA-5 3	$260^{\circ}\mathrm{C}$	72h	acetate	acetate, basic
GOA-55	$200^{\circ}\mathrm{C}$	72h	acetate	acetate, basic



Figure 1: (left) X-ray diffraction patterns of the syntheses performed in the autoclave in a regular muffle furnace. (right) Database X-ray diffraction patterns of aluminium hydroxide oxide (ICSD 27865) and strontium carbonate (ICSD 27293) and X-ray diffraction pattern of the synthesis GOA-53.

The reaction duration is predicted to have an influence on the degree of crystallinity whereas the temperature and the used precursors could also have an influence on the crystal phase formation itself due to temperature/pressure change and precursor reactivity. From the XRD patterns (figure 1, left graph), one can distinguish two different results. A group with two different crystalline phases (GOA-48, GOA-49 and GOA-55) and a synthesis with only one main crystalline phase (GOA-53). The XRD measurements can only be interpreted qualitative, a Rietveld measurement (not included) is needed for quantitative analysis.

The syntheses of this group (GOA-48, GOA-49 and GOA-55) show similar diffraction patterns and result in two different materials, small particles (broad XRD peaks) and large particles (small XRD peaks). Comparing the peaks from the XRD pattern with different databases, we can determine that the small particles are strontium carbonate (figure 1). The crystallites have an estimated size of 5.9, 7.1 and 18.0 nm according to the Scherrer equation (equation 1) for samples GOA-48, GOA-49 and GOA-55 respectively.

$$d = \frac{K\lambda}{\beta \cos(2\theta)} \tag{1}$$

with d the mean size of the ordered domains (mean crystallite size), K a dimensionless shape factor, λ the X-ray wavelength, β the line broading at half the maximum intensity and θ the Bragg angle.

The large particles are not identified and have an estimated crystallite size of 44.1, 33.8 and 36.0 nm for samples GOA-48, GOA-49 and GOA-55 respectively. The unidentified peaks are believed to be from a diffraction pattern originating from one material as a result that the peak intensities relative to another stay constant. A limited off-size estimation of the particles by the Scherrer calculations can be expected and explained by merging together of peaks close to one another or/and by peak interference of the different materials.

The synthesis of two different materials is confirmed by TEM analysis of synthesis GOA-48, shown in figure 2, showing small particles of 3 nm in diameter and the large particles as clusters of nanowires. In nanowires, the atomic layers perpendicular to the growth direction will be favored in the XRD pattern, leading to misrepresented or eliminations of certain XRD peaks of the material compared to the databases. The mismatch of the size estimation by the Scherrer equation can be explained by the shape factor which is defined for spherical particles. For the reason that the synthesis did not yield solely a strontium aluminate phase, no further effort is done to identify the clusters of nanowires.

Duration of the synthesis has no influence on the composition of the material, as it is



Figure 2: TEM images of GOA-48 consisting of unidentified nanowire clusters (left) and 3nm strontium carbonate nanoparticles (right).

the only difference between synthesis GOA-48 and GOA-49. Also, the use of other metal precursors does not influence the composition of the material, as for synthesis GOA-55 basic aluminium acetate is used instead of aluminium isopropoxide.

The most remarkable difference with respect to this group is synthesis GOA-53. For GOA-53, a higher temperature is employed resulting in a higher pressure as well. Here, only the small strontium carbonate nanoparticles are produced and a small quantity of aluminium hydroxide oxide nanoparticles (figure 1, right graph).

Microwave synthesis. The different syntheses performed in the microwave are summarized in table 1, alterations in temperature, time and metal precursors are tested.

Table 2: Syntheses performed via the microwave method, listed with alternated conditions.

Synthesis	Temperature	Time	Strontium precursor	Aluminium precursor
GOA-4 4	$250^{\circ}\mathrm{C}$	10h	acetate	isopropoxide
GOA-45	$250^{\circ}\mathrm{C}$	10h	metallic	isopropoxide
GOA-56	$200^{\circ}\mathrm{C}$	48h	acetate	isopropoxide
GOA-57	$250^{\circ}\mathrm{C}$	10h	acetate	acetate, basic

From the XRD patterns (figure 3, left graph), it is visible that only one crystalline phase is obtained. First, different strontium precursors are tested and no difference is observed between metallic strontium and strontium acetate, both resulting in the production of strontium carbonate. Secondly, basic aluminium acetate is used instead of the aluminium isopropoxide precursor, the same unidentified large particle sized material (figure 3, left graph) is obtained as with the autoclave synthesis but this time no strontium carbonate is formed. It is therefore concluded that the selective production of either small strontium carbonate particles or large unidentified particles is dependent on the reactivity properties of the used aluminium precursor.



Figure 3: (left) X-ray diffraction patterns of the syntheses performed in the microwave furnace. (right) X-ray diffraction patterns of the identical synthesis GOA-48 (autoclave synthesis) and GOA-56 (microwave synthesis).

Because of this difference between the conventional autoclave syntheses (a mix of crystalline phases) and the microwave syntheses (selective production synthesis of strontium carbonate or the unidentified crystal phase), an identical synthesis to GOA-48 is performed (GOA-56). The XRD patterns of both syntheses are compared (figure 3, right graph) and shows that the microwave synthesis (GOA-56) only produces small strontium carbonate particles. No aluminium oxide hydroxide is detected next to the strontium carbonate as it is the case with GOA-53.

4. CONCLUSION

The benzyl alcohol route is chosen as a result that it is proven to be a very versatile method to produce multi metal oxide nanocrystals. Two different approaches are exploited, the conventional autoclave and the microwave synthesis. Using an autoclave synthesis, two crystalline materials are produced with 3 nm small strontium carbonate particles. In the samples, a material with a nanowire cluster morphology or a small quantity of aluminium hydroxide oxide could also be detected. Different reaction times and aluminium precursors were tested but no influence on the product composition could be found. The aluminium hydroxide oxide side product is only formed at higher temperatures (260°C) whereas at 200°C the unidentified material is obtained.

The microwave synthesis results in one crystalline phase. Different strontium precursors (metallic and acetate) and aluminium precursors (isopropoxide and acetate) were tested. Strontium acetate in combination with basic aluminium acetate results in a large fraction of unidentified material as also obtained from the autoclave synthesis. All other precursor combinations result in small strontium carbonate particles.

In conclusion, neither the autoclave nor the microwave synthesis result in a crystalline strontium aluminate material. Strontium reacts rather fast into strontium carbonate nanocrystals whereas aluminium react not at all or in the best case very limited to form separately aluminium hydroxide oxide. More research must be conducted for more reactive aluminium precursors and to investigate the feasibility to produce alumina nanocrystals. At second hand, the compatibility between different strontium precursors and the found aluminium precursors needs to be investigated to come to a conclusion whether the strontium aluminate material is still a suitable choice for the use of internal damage sensors.

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Chapter 1

Introduction

1.1 ENCLOSE Project

This master thesis is part of a larger ENCLOSE project which is carried out by a collaboration of several research teams (MMS, DRAFT, LumiLab and SCRiPTS) at the University of Ghent. The physics research group LumiLab investigates mechanoluminescence properties of existing materials and exploits new promising materials. The physics research group DRAFT (Dedicated Research on Advanced Films and Targets) focuses on physical deposition methods of the sensor materials on composite substrates. This thesis is executed under supervision of the chemical research group SCRiPTS (Sol-gel Centre for Research on Inorganic Powders and Thin films Synthesis) which is responsible for the synthesis and chemical deposition of the sensor materials into and onto composite substrates. The engineering research group MMS (Mechanics of Materials and Structures) brings the work of all the groups together and intensively tests the impact of the integrated sensor on the composite material and vice versa. This is investigated to completely understand the performance of the internal sensor and exploitation of the obtained signal.

The 'state-of-the-art' in the field of self-sensing composites is clearly not sufficiently advanced to address current industrial requirements. The ENCLOSE (Embedded sensor Network in Composites for LOcal SEnsing) project (Special Research Fund/Concerted Research Actions n° : BOF2015/GOA/007) aims at the development of a new generation of embedded sensors for structural composites, based on additional intrinsic and multifunctional properties (as result of local modifications or adaptations) and leading to performing, sustainable and cost effectively produced self-sensing composites. The ENCLOSE project focuses on the detection of damage in structural composites by specially developed sensors. Two classes of sensors are envisaged. The first class is based on an electrical output (strain gauge and piezoelectric materials). The second group uses mechanoluminescent materials. The sensors are produced by reactive sputter deposition, inkjet printing and solid state synthesis.

1.1.1 General

It is well known that damage mechanisms in structural fiber-reinforced composites differ from the typical damage mechanisms involved in common isotropic materials. In composites, the damage mechanisms are numerous (e.g. fiber/matrix debonding, matrix cracking, tearing and crazing, fiber tensile failure and buckling, intra-ply and inter-plydelaminations), show complex interactions and have many associated variables (e.g. strain rate, temperature). Moreover, even in long-lasting structural components (e.g. wind turbine blades), damage can initiate very early in time, before 10% of the life span, and grow gradually. Structural internal damage is typically associated with decrease of strength but, different from other materials, the stiffness gives rise to continuous internal stress redistribution. Because reliable life-time predictions cannot be made from simple laboratory tests, and because at the same time they are of great concern to operational reliability and human safety, much research effort is currently being spent on the combined use of numerical simulations of the momentary structural behaviour and continuous monitoring of the actual damage state.¹

Over the years, many approaches have been suggested to monitor damage in composites. However, there is currently no 'universal' technique that allows predicting the health of structural composite materials. Current standard inspection techniques such as visual surveillance, ultrasonic inspection and radiography do not answer the need for continuous in-service and insitu monitoring. Moreover, these techniques are labour-intensive and therefore expensive. A wide range of surface mounted and in rare cases embedded sensors have already been studied for structural health monitoring applications, including strain gauges, accelerometers, fiber optic sensors, active ultrasonic sensors, passive acoustic sensors and infrared cameras.^{1, 2, 3}

Damage in structural elements is often deducted from strain measurements. Indeed the presence of damage (i.e. the different possible mechanisms mentioned) gives rise to local strain concentrations and changes in the strain gradients. For strain monitoring, strain gauges and fiber optic sensors are currently the main choice. Externally applied strain gauges are now the obvious choice, but their wiring poses significant challenges to sensor deployment and limits the number of points that can be monitored in a large structure. Even by using surface monitoring techniques, such as classic strain gauges, it remains difficult or impossible to detect important internal damage mechanisms, such as delaminations or fiber debonding, because such damage in not 'visible' at the exterior of the structure or can only be sensed at the micro-scale level. When embedded, optical fiber Bragg or Fabry-Perot sensors show affinity with the host material (they are small, lightweight, chemically inert and have intrinsic multi-plexing capabilities) and are therefore considered valuable for in-situ strain monitoring, but they equally suffer from critical limitations.⁴

The main weaknesses of all available monitoring technologies, based on extrinsic sensors, are the insufficient compatibility with the host material, creating a potential source of damage onset by itself and the bulkiness of the sensor elements that prevents easy and reliable embedding within a composite. Furthermore, only a limited number of point measurements can be performed and the resolution is too low to be able to detect specific damage types.

Emerging self-sensing composites take an alternative approach, namely by using intrinsic, multifunctional properties of the (adapted or modified) constituents of the composite, thereby acting themselves as the sensing element. This approach has already been demonstrated, using the electrically conductive properties of carbon-fiber composites, or using the inherent optical properties of reinforcing glass fibers.⁵ Other routes to self-sensing may be for example coating of the fibers or stacking layers with ultra-thin sensing films^{6,7,8}, or adding a specific component (e.g. a stable suspension or a powder) to the matrix. In the latter context, the use of mechanoluminescent films has been demonstrated.^{9,10} These films are able to emit light when exposed to stress or strain. These are the routes that we want to exploit within the ENCLOSE project.

Problems that have to be overcome are the creation and the integration of such sensing elements, as well as the fundamental understanding and interpretation of the very complex stress/strain transfer mechanisms within typical composite laminates. The resulting composites should allow for well performed sensing of the onset and development of local and distributed damage.

1.1.2 Aim of the ENCLOSE Project, related to this work

The optical sensors developed in ENCLOSE, will be based on mechanoluminescent materials. These materials are a special class of persistent phosphors, emitting light when pressure is applied to them. The research proposal aims at the synthesis of new mechanoluminescent powders which can be embedded in the composite. The mechanoluminescent materials will serve as starting point to deposit thin films by inkjet printing and magnetron sputter deposition. Monitoring the stress can occur in on-line and off-line mode. Accurate on-line monitoring of mechanoluminescence is complicated by possible afterglow emission just after the excitation. Specific design of the distribution of trap depths allows suppressing fading, limiting afterglow intensity and reducing stress response times. Therefore, measurement procedures will be designed together with modification of the phosphors behaviour. With the design of the off-line measurement methods, the occurrence of excessive stress in a particular place in the composite before the actual measurement will be investigated. The approach will be based on optically stimulated luminescence of these materials, resulting in an entirely novel approach for repeatable stress sensing with a memory function. An important part of the project will focus on the effective processing of self-sensing composite specimens. The actual integration of the sensors in the composite laminate will be investigated. Also basic compatibility issues will be investigated, answering questions related to the persevering of the sensors as well of the host composite. To be able to study the sensor input/output signal initial solutions of the so-called ingres/egress problems will be developed. The effective processing of self-sensing composites allows to correlate the damage generation to the signal output of the sensors. The complex mechanical behaviour of actual self-sensing composites will be studied and the sensor output will be evaluated when loading and damaging structural composite specimens. Combined experimental observation and numerical finite element simulations will be applied to well know load cases. Postmortem evaluation of the damage will be performed by sectioning, optical/electronic microscopy, and nondestructive computed tomography. To assist in unraveling these complex relationships, in-depth characterization of the sensor or sensor material is a necessity as it will deliver more information on the influence of the embedding process. Moreover, it will yield a better fundamental understanding of the relationship between the deformation and the signal output.

1.2 Objective of the Thesis

The main study during this master thesis is the development of a mechanoluminescent material. A mechanoluminescent material is a phosphor which releases previously stored energy under pressure. The energy, originating from earlier excitation, is stored in traps in the crystal lattice of the material (more detailed explained in appendix section C). Mechanoluminescence measurements are very complex and as a result that most of the mechanoluminescent phosphors show persistent luminescence, measuring the afterglow of the phosphor gives a first impression of its mechanoluminescent properties. First, we must make a decision which material will be most suitable for the purpose of this project. The material needs to have piezoluminescent properties with a very long afterglow duration (more detailed explained in section 1.4). The choosing and optimization of the persistent phosphor will lead to a large storage capacity material that needs to be printable. The optimization include the synthesis of the material in the correct crystallographic structure, the degree of crystallinity, the optimal doping percentages and the particle size.

A lot of materials are already identified and characterized as persistent luminescent. Several reviews^{11,12} are available, yet not all persistent photoluminescent materials have mechanoluminescent properties, such as $CaSi_2O_2N_2$:Eu. But, if the material has mechanoluminescent properties, they generally increase with the persistent luminescent properties.¹³

Two main categories of persistent luminescent materials can be distinguished: divalent europium¹¹ and non-europium¹² doped compounds. The latter uses other elements (mostly other lanthanide or transition metals) as activator (electron donating center) for the persistent luminescence but can still contain europium when it is not the activator. Nevertheless, there is a wide variety of host materials for luminescence, but the number of hosts which provide the basis for persistent luminescence is relatively low. Besides aluminates, silicates

and sulfides also phosphates, stannates, titanates and germanates can be a good host material. Table 1.1 gives an overview of some host materials with their dopants and their emission properties.^{11,12}

We make the prior assumption that the intensity increase contributed from the mechanical stress, is proportional to the intensity of the persistent luminescence. Consequently the intensity difference between the stressed and non-stressed material can be measured significantly. The investigation whether this assumption is correct, is not included in this thesis research but is being tackled within the ENCLOSE project.

On this basis, we choose the material with the longest afterglow duration as the most suited material for the synthesis of internal damage sensors. It is clear that the aluminates exhibit a very long afterglow duration, and in particular strontium aluminate scores the best with a reported afterglow duration of more than thirty hours when doped with divalent europium and codoped with trivalent dysprosium. Strontium aluminate can occur in many different crystalline phases, see table 1.2, all build out of a different strontium to aluminium ratio. SrAl₂O₄, which has the best optical properties, can exist in two different crystalline phases, the desired monoclinic phase and the hexagonal one. Although $SrAl_2O_4:Eu^{2+},Dy^{3+}$ is known to show very strong persistent luminescence, these values are mostly reported for the material where particles are of millimeter or micrometer size. Materials of this size display low processability and therefore it is difficult to employ them for further applications, such as printing on or mixing in a substrate. Reducing the size of the material to nano- or submicrosize would increase its processability and therefore research on efficient synthetic routes for synthesizing $SrAl_2O_4:Eu^{2+}, Dy^{3+}$ nanoparticles is being carried out.¹⁴ A short review of all the existing synthetic routes for $SrAl_2O_4:Eu^{2+},Dy^{3+}$ is listed in section 2.1 with analysis what their shortcomings are. The most common one is the addition of an extra annealing step, due to the synthesis of initially amorphous material which leads to sintering.

For the synthesis of $SrAl_2O_4:Eu^{2+},Dy^{3+}$, we will need to design a novel synthetic route which will meet all the desired properties. This novel route is based on existing methods for metal oxide nanocrystal synthesis. The benzyl alcohol route will be used to synthesize strontium aluminate (discussed in section 2.2.1). Non-aqueous surfactant assisted methods will be used to synthesize, at first, aluminium oxide for the reason that multi-metal oxides have not been made with this method (discussed in section 2.3). In future work, the aluminium precursors will be mixed with strontium precursors to synthesize the desired strontium aluminate host. These novel synthetic routes will be groundbreaking research on account of multi-metaloxide nanocrystal chemistry which is a very recently hot topic.¹⁵

The strontium aluminate material must be crystalline to have piezoluminescent properties, preferably the monoclinic phase.^{11,14} The size is of extreme importance as it must be small enough to process perfectly into or onto the substrate but still as large as possible to prevent

Host material	Dopants	Fluorescence maximum (nm)	Afterglow duration
$CaAl_2O_4$	Ce^{3+}	400 (blue)	>10h
$CaAl_2O_4$	Eu^{2+}, Nd^{3+}	440 (blue)	>5h
$\operatorname{Zn}_3(\operatorname{PO}_4)_2$	Mn^{2+}	$616 \pmod{10}$	>2h
Lu_2O_3	Tb^{3+}	490 + 550 (green)	5-8h
SrO	Pb^{2+}	390 (violet)	>1h
CaO	Eu^{3+}	594 + 616 (orange)	>2h
$SrMgAl_{10}O_{17}$	Eu^{2+}, Dy^{3+}	460 (blue)	>3min
$\mathrm{SrAl}_2\mathrm{O}_4$	Eu^{2+}, Dy^{3+}	520 (green)	>30h
$\mathrm{Sr}_4\mathrm{Al}_{14}\mathrm{O}_{25}$	Eu^{2+}, Dy^{3+}	490 (blue)	>20h
$\mathrm{SrAl}_4\mathrm{O}_7$	Eu^{2+}, Dy^{3+}	480 (blue)	>3h
$CaWO_4$	Eu^{3+}	592 + 616 (red)	$40 \min$
HfO_2	intrinsic	480 (blue)	>1min
$ m ZrO_2$	Ti^{4+}	$470 + 500 \; (\text{green})$	$1\mathrm{h}$
$ZnGa_2O_4$	Cr^{3+}	$650-750 \ (red)$	>1h
YPO_4	Pr^{3+}	600 + 620 (orange/red)	>30min
$\mathrm{Cd}_{2}\mathrm{Ge}_{7}\mathrm{O}_{16}$	Mn^{2+}	585 (yellow)	>3h
$CaZnGe_2O_6$	Mn^{2+}	648	>3h
$CaMoO_4$	Eu^{3+}	$616 \pmod{10}$	>5min
ZnS	Cu^+	530 (green)	>3h
Y_2O_2S	Tb^{3+}	417 + 546 (green)	>20min

Table 1.1: Overview of a few persistent luminescence host materials.^{11,12}

Table 1.2: Overview of all possible crystalline phases of strontium aluminate obtained from the FindIt database.

Crystalline System
monoclinic
hexagonal
monoclinic
cubic
hexagonal
cubic
trigonal/rhombohedral
orthorhombic
monoclinic
orthorhombic
trigonal/rhombohedral

loss of the mechanoluminescence intensity (discussed in next paragraphs). The ideal size would be in the submicron range of 400 to 500 nm. Here it is important to make a distinction between the size of the nanoparticle and the crystallite size. A nanoparticle is defined as a microscopic particle with at least one dimension less than 100 nm. These nanoparticles or bigger particles can exist out of smaller crystalline domains (crystallites), which can be calculated out of the XRD patterns.¹⁶

For the processability, the size of the particles is very important, for the piezoluminescence intensity, the size of the crystallites is important. The morphology is generally dependent on the crystal structure but can be somewhat influenced with the use of ligands. The desired morphology of the particles is preferential spherical, but especially not rod- or wire-like due to the difficult processability. As a final step, investigation on the surface chemistry must be executed to fully exploit the stabilization capacity of the particles in suspension. With the surface chemistry knowledge, we will be able to bring the (nano)particles in a stable suspension for further processing.

After the synthesis of the material and the optimization of the crystal phase, size and surface chemistry, the particles can be spin-, dip-coated or printed onto the composite substrate. Optimization, by tuning various parameters (e.g. solvent, pH, organic ligands, etc.), is required to obtain a stable ink with good contact angle and wettability. The mixing in of these particles during the hardening out of the polymer based composite material is also a possibility to obtain homogeneous randomly distributed particles within the composite material.

As is known with a change in size and shape of a material also its properties, including optical properties, can change. Unfortunately, when reducing the size of the particles, it is expected that it will reduce their persistent luminescence properties.¹⁴ As a secondary occupation during this master thesis, the influence of the crystallite size on the persistent luminescence is investigated. For 'normal' luminescence, the emitted light originates from the surface of the crystal (the intensity increases with a smaller crystallite size). The emitted light of persistent luminescence originates from the de-excitation of the doped activator which is located inside the crystal lattice (the intensity increases with the crystallite size). As the particles get smaller, leading to a larger surface to volume ratio, it is observed that persistent luminescence intensity decreases. Therefore it is important to find a balance between the size of the particles (suitable for further processing in applications) and its optical properties.

It is reported that hafnium and zirconium oxide are intrinsic persistent luminescent materials, presumably due to presence of titanium as a trace element in the hafnium and zirconium precursors.¹² Titanium will be build in the crystal lattice of hafnia and zirconia and act as activator. The persistent luminescent properties (afterglow duration and intensity) of hafnia and zirconia are much lower than strontium aluminate, as reported in table 1.1. Hafnium and zirconium oxide doped with titanium will be made with different crystallite sizes to

investigate the influence of the size on the persistent luminescence. This specific choice of materials is based on the in-house knowledge of SCRiPTS to synthesize these materials on nanoscale. $^{17, \, 18, \, 19}$

1.3 Historical Background of Persistent Luminescence

Persistent luminescence from natural materials has been observed and fascinated people for centuries. The first written reference of this mysterious afterglow effect dates back to the Sung Dynasty of China. The notes of the Sung monk Tsan-Ning from the 11th century describe a painting presented to the second emperor of the Sung Dynasty. In the painting, there was a cow which appeared as eating grass during the daytime but was resting at night. The ink, visible at night, was mixed with a special kind of pearl shell.²⁰

These natural persistent luminescent materials were described as 'magic' minerals glowing in the dark. In 1568, Cellini Benvenuto described in the book "Due Trattati dell'Orifieera" a diamond which emit light after exposure during the day. Another example described by Joseph Priestley in 1772, by Cesare Beccaria in 1744 and by B. Wilson in 1775 was Jan Baptista van Helmont's flint stone. This stone 'retained' the light of the sun up to three hours.²¹

The first scientifically documented persistent luminescent material was the Bolognian Stone. In 1603, an Italian shoemaker, who also engaged in alchemy, found by chance a mineral, from Monte Paterno close to Bologna, which glowed in the dark after calcination. The rumor of this magic stone circulated quickly but the preparation method remained a secret. Since the mechanism or reason of persistent luminescence remained a secret, alchemists had hoped for the discovery of the Philosopher's Stone. A legendary alchemical substance said to be capable to create perfection which was every true alchemists goal. They believed when the Bolognian Stone was correctly made, it could attract the golden light of the sun and convert ignoble metals into gold or the less perfect silver. Although they never succeeded, it aroused great interest among the educated and the layman alike. Galileo Galilei was one of them who tried to explain the phenomenon as a reflection of sunlight from the Earth to the Moon. Before the electron concept, the explanations of persistent luminescence were beliefs and myths described by La Galla, Ovidio Montalbani and many more. Finaly, the Bolognian Stone was identified as barium sulphate. The luminescence is related to the reduction of the barite to barium sulfide. The impurities in the crystal lattice are responsible for the variations of the afterglow.^{20, 21}

At the beginning of the 20th century, synthetic persistent luminescent materials arose. The first developed materials was a zinc sulfide doped with copper $(ZnS:Cu^+)$.²² Codoping this ZnS:Cu⁺ material with Co²⁺ doubled the afterglow duration. These materials found many

applications as night vision materials but were sensitive to moisture. The cobalt codoped materials are initially strong but have a small energy storage capacity. The afterglow is stimulated by adding environmentally unsafe isotopes like tritium or radium.

The next generation persistent luminescent materials were alkaline earth sulfides such as CaS and SrS. These materials, also known as Lenard's phosphors, were studied in the 1930s and re-discovered by Lehmann et al. in the early 1970s. Lehmann doped these materials with different ions, like Bi^{3+} , Eu^{2+} or Ce^{3+} . These materials can be excited by sunlight but are also chemically unstable.²³

The next big step for (long) persistent luminescent materials arrived in 1996. In this year Matsuzawa et al.²⁴ reported (at the same time of Takasaki et al.²⁵) a new type of afterglow phosphor: $SrAl_2O_4:Eu^{2+},Dy^{3+}$ developed from the already known $SrAl_2O_4:Eu^{2+}$. Together with a first proposed mechanism, this discovery started a new wave of research on persistent luminescence and the understanding of its mechanism (discussed in the appendix chapter C).

1.4 What is Persistent Luminescence?

Luminescence is emission of light, electromagnetic radiation positioned in or near the visible region, by a substance not resulting from heat. It is thus a form of cold body radiation. When a material is thermally excited, it is called incandescence, from the Latin verb incandescere (to glow white), which refers specifically to visible light. While thermal radiation refers also to other electromagnetic radiation. The term 'luminescence' was introduced in 1888 by Eilhard Wiedermann.

There are many origins that are able to result in luminescence. The most important types of luminescence are:

- Chemiluminescence
- Crystalloluminescence
- Electroluminescence
- Mechanoluminescence
- Photoluminescence
- Radioluminescence
- Thermoluminescence

Luminescence is generally divided in fluorescence and phosphorescence. There is still some discussion about what the definition is. In terms of organic and inorganic (or in this case also called phosphors) chemistry they have a slightly different connotation, schematically shown in figure 1.1.



Figure 1.1: Schematic representation of the meaning of the use of different naming.

Persistent luminescence can be understood as phosphorescence but instead of storing the absorbed energy in the form of an excited electron in metastable states, it is stored in trap levels, see figure 1.2. Any imperfection of a perfect crystal lattice can give rise to additional energy levels which can be located in the band gap. The caught electron in such a trap level cannot directly recombine with the created hole. A certain amount of energy is required to release the electron again. This trapping and detrapping process can occur via the conduction band but is also possible by localized transitions.²⁶ Because of this, the recombinant luminescence process will be delayed. The evolution of the persistent luminescence model is briefly discussed in the appendix chapter C. Until today, there is no entirely proven persistent luminescence model, but the present model gives an idea how this kind of luminescence works.



Figure 1.2: Schematic representation of trap levels. Deep trap levels require more (thermal) energy to overcome the energetic barrier and will have a longer delayed afterglow.²⁶

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Persistent luminescent is initiated by photoexcitation, absorption of a photon, and relaxes back by emitting a photon, mostly somewhat of the energy will be transferred into heat (phonons). This means that the wavelength of the absorbed photon will be smaller than the wavelength of the emitted photon. Therefore most luminescent materials can be excited by UV-light.

Mechanoluminescence, a general term for the phenomenon in which light emission occurs during any mechanical action on a solid, can be divided roughly into two classes: destructive mechanoluminescence and non-destructive mechanoluminescence. Depending on the type of mechanical action stimulating the emission, mechanoluminescence phenomena are given specific names. The term fractoluminescence is used when the emitted light is generated through the breaking of chemical bonds by fracture of the material. This has been observed in various organic and inorganic compounds such as sugars, molecular crystals, alkali halides, quartz and minerals. Triboluminescence is light emission caused by rubbing a material, but actually the emission is generated because the material breaks upon rubbing. Fractoluminescence and triboluminescence are thus often used as synonyms for this destructive type of mechanoluminescence. This destructive type of mechanoluminescence is obviously not suitable for the use as intrinsic damage sensors considering they could only be used once. Piezoluminescence is light emission caused by pressure which results only in elastic deformation and is often referred to as elasticomechanoluminescence. As such, piezoluminescence is a non-destructive and, therefore, a repeatable mechanoluminescent phenomenon and finds applications in pressure sensing devices. Piezoluminescence has been observed in different classes of compounds such as colored alkali halide crystals, II-VI semiconductors, quartz and some polymers, but the most efficient mechanoluminescent materials reported, are persistent luminescent materials. Nowadays, the suggested mechanism for piezoluminescence is based on the same principles as persistent luminescence, similar traps are responsible for both phenomena. Energy stored in the material is released by emission after detrapping of the charge carriers. The detrapping in piezoluminescence, however, is induced by the pressure applied on the material, see figure $1.3.^{13}$

To release electrons from a trap (figure 1.4), the mechanical stimulation somehow has to reduce the depth of the trap or has to provide an extra amount of energy which helps to overcome the thermal barrier associated with the trapped charges. The most recent model for piezoluminescent emission, the piezoelectrically induced detrapping model for piezoluminescence, ascribes the faster release of the trapped charges to the piezoelectric effect: (i) the application of pressure produces a piezoelectric field, which can be high near defects and activator ions, (ii) the piezoelectric field either lowers the trap depth or causes band bending, (iii) the decrease of trap depth implies that less energy is needed to release the trapped electrons and causes a faster transfer of electrons from the trap to the ionized activator ion. For the case of $SrAl_2O_4:Eu^{2+},Dy^{3+}$, the divalent europium ions to form excited Eu^{2+} ions in

the $4f^{6}5d^{1}$ state, while band bending might cause direct tunneling from the trap to the Eu²⁺ $4f^{6}5d^{1}$ state or to another trap, (iv) the de-excitation of the created Eu²⁺ ions from $4f^{6}5d^{1}$ to the $4f^{7}5d^{0}$ ground state through emission of light.¹³



Figure 1.3: (A) Piezoluminescence stimulated in BaSi₂O₂N₂:Eu by (a) an applied external force (pressure) and (b) the release of the external force. (B) Mechanoluminescence stimulated in BaSi₂O₂N₂:Eu by a periodically applied external force of 20 kN (64 MPa). The mechanoluminescence intensity on a linear scale (solid line) follows the 0.25 Hz square wave profile of the external force (dashed line).¹³



Figure 1.4: Energy level scheme for the persistent luminescence and piezoluminescence.¹³

Chapter 2

Synthesis

In 1968, Palilla et al.²⁷ and Blasse and Brill²⁸ were the first to synthesize $SrAl_2O_4:Eu^{2+}$ by use of a solid state reaction between $SrCO_3$, Al_2O_3 and Eu_2O_3 in a reducing atmosphere at a temperature between 1400-1700°C. Matsuzawa et al.²⁴ used the same recipe with the addition of B_2O_3 as a flux to make $SrAl_2O_4:Eu^{2+},Dy^{3+}$. The solid state synthesis results in millimeter sized particles which are too big to use in further applications for internal damage sensors.

To reduce the size of the particles, research teams started to create novel synthesis routes which were often in solution, whereof most of these routes are water based. As a result of the high reactivity with water, the material requires an additional annealing step to crystallize. Due to the oxidizing nature of water an extra step to reduce trivalent europium to divalent europium often needs to be added. This can be done with a reducing atmosphere of active carbon, H_{2} - or argon gas.¹⁴

2.1 Overview of State-of-the-art Synthesis Methods

In this section, a short review is provided on all the syntheses of strontium aluminate doped with Eu^{2+} and codoped with Dy^{3+} available in literature.

2.1.1 The Sol-gel Method

The starting point in this method is to prepare a homogeneous solution containing all the cationic ingredients. The solution is gradually dried and, depending on the species present, it may transform to a viscous sol containing particles of colloidal dimensions and finally to a transparent, homogeneous, amorphous solid known as a gel without precipitation of any crystalline phases. The gel is heated to remove various volatile components trapped in the pores of the gel or chemically bonded organic side groups and to crystallize the final product. Often, the reagents for sol-gel synthesis are metal-organic compounds, especially

alkoxides. These are usually covalent liquids, but can be powders as well, which are mixed in appropriate ratios, often with an alcohol to promote miscibility of the alkoxide and water. Water is a key reagent since it hydrolyses the alkoxides, usually in the presence of either acid or base as a catalyst to speed up the reaction. Other methods based on nitrates, acetates, tartrates etc. are also explored. Here, the process can be completely water based. The composition, structure and viscosity of the reaction products depend very much on the degree of hydrolysis/condensation and careful control of the reaction variables is required to achieve the desired product. For the synthesis of complex oxides containing more than one cation, cross-condensation is required and clearly it is essential to achieve this instead of condensation of the components separately.²⁹

The following describes the different steps in the alkoxy method. Hydrolysis may be regarded as occurring in two steps or more. First, the replacement of -OR group(s) by -OH occurs, given by equation 2.1. Second, condensation polymerization with the elimination of water occurs, given by equation 2.2.²⁹

$$M(OR)_n + xH_2O \longrightarrow (RO)_{n-x}M(OH)_x + xROH$$
 (2.1)

$$-M-OH + HO-M'- \longrightarrow -M-O-M'- + H_2O$$
 (2.2)

The final stage of the synthesis is to heat, or calcine the gel, burning off all organic matter and leaving an oxide product. The sol-gel method is extremely versatile and can incorporate most elements of the periodic table.²⁹

The sol-gel synthesis allows the intimate mixture of reactants, an easier composition control and a lower processing temperature compared to solid state reactions. Advantages of this synthesis are also the control of particle size and homogeneous morphology. Wang et al. reported enlargement of the particle size with increasing annealing temperature.³⁰ Disadvantages include long reaction time and sintering at higher temperatures to obtain the desired crystalline phase.¹⁴ After the additional heat treatment steps, for crystallization and reduction which sinters the independent particles together, we will not be able to make a stable suspension again.

2.1.2 The Combustion Method

In contrast to solid state reactions, that often require heating for several days at high temperatures to complete a synthesis, controlled explosions in reactions known variously as combustion synthesis, self propagating high temperature synthesis (SHS) and solid state metathesis (SSM) can give reaction products in minutes or even seconds. This method is usually applied for the preparation of highly crystalline complex oxide ceramics. In the SHS technique pioneered by Merzhanov and co-workers in Russia, starting materials that react together highly exothermically are chosen. Consequently, once a reaction is initiated, enough heat is generated leading to very high temperatures and complete reaction occurs rapidly. The starting materials may be classified as either 'fuels' or 'oxidants'.²⁹ Because no complexing agents are added and a lot of gas is produced, the reaction will produced very thin and porous material.

2.1.3 The Solvothermal Method

Solvothermal synthesis is a method for preparing a variety of materials such as metals, semiconductors, ceramics, and polymers. If water is used as the solvent, the method is called hydrothermal synthesis. This method involves heating the reactants in water/steam at high pressures and temperatures. The solvent has two functions, as a pressure-transmitting medium and as a dissolving medium, in which the solubility of the reactants is P, T-dependent.²⁹ The process can be used to prepare many geometries including thin films, bulk powders, single crystals and nanocrystals. In addition, the morphology (sphere (3D), rod (2D) or wire (1D)) of the crystals formed, is controlled by manipulating the solvent supersaturation, the chemical of interest, the concentration and the kinetic control. The method can be used to prepare thermodynamically stable and metastable states including novel materials that cannot be easily formed from other synthetic routes.³¹ The solvothermal synthesis can be carried out using a conventional heating system (with an autoclave) or a microwave heating system, both explained in more detail in section 2.2.1.

Ishigaki et al.³² describe a hydrothermal microwave synthesis of strontium aluminate preformed in a domestic microwave. The results are comparable with those of the sol-gel method (millimeter sized, porous material) and for the same reasons not usable for the purpose of this thesis research.

2.1.4 The Microemulsion Method

Microemulsions consist of mixtures of two or more non-miscible liquids in which one liquid forms microdroplets (dispersed phase), surrounded by the other liquid (continuous phase). The aqueous formed droplets contain the reagents necessary for particle formation and act as microreactors.¹⁴

Lu et al.³³ describe a strontium aluminate synthesis where they proposed an ideal ratio of surfactant and co-surfactant to oil and an ideal ratio of oil to water. After synthesis, the material needs an additional calcination step at 900°C. The material is indeed in the nanosize range (<100 nm) but to crystallize the material again a calcination step is required leading to sintering of the particles.

2.1.5 The Coprecipitation Method

Coprecipitation consists of one of the most simple preparation methods in this context, in which the reagents react in solution, generating precipitation of the nanoparticles. For successful synthesis, two conditions must be fulfilled: (i) just highly dissociable reactions can be applied, excluding oxides from the appropriate starting materials and (ii) the precipitate particles must be removed from the reacting solution to avoid further growth.¹⁴ Cheng et al.³⁴ described a recipe which resulted in the synthesis of micro-size, rod-like strontium aluminate. The rod-like material has a diameter of approximately 100 nm but the length is in the microsize range which makes the material too large to make a stable suspension out of it. Chang et al.³⁵ investigated by DSC-TG the different reactions that take place during the synthesis of nanosized particles and concluded that different phases of strontium aluminate can be selectively formed at specific heating temperatures. The desired crystal phase can be obtained out of the amorphous material by tuning the temperature of the annealing step, nevertheless the heat treatment step is still required which leads to sintering of the particles.

2.1.6 The Ultrasonic Spray Pyrolysis Method

Spray pyrolysis is a commonly used method of drying a liquid feed through a hot gas. Typically, this hot gas is air but sensitive materials such as pharmaceuticals and solvents like ethanol require oxygen-free drying and nitrogen gas is used instead. The liquid feed varies depending on the material being dried and is not limited to food or pharmaceutical products and may be a solution, colloid or suspension. This process of drying is a one step rapid process and eliminates additional processing. The liquid feed is pumped through an atomizer device that produces fine droplets into the main drying chamber. Atomizers vary with rotary, single fluid, two-fluid, and ultrasonic designs. These different styles have different advantages and disadvantages depending on the application of the spray drying required. The hot drying gas can be passed as a co-current or counter-current flow to the atomizer direction. The co-current flow enables the particles to have a lower residence time within the system and the particle separator (typically a cyclone device) operates more efficiently. The counter-current flow method enables a greater residence time of the particles in the chamber and usually is paired with a fluidized bed system.²⁹

Li et al.³⁶ used a system consisting of an ultrasonic atomizer with a 2.4 MHz transducer, a horizontal reaction furnace and an electrostatic precipitator for collecting the strontium aluminate particles. Acetylacetonate salts are used as precursors dissolved in acetylacetone and water to obtain the desired spherical nanoparticles instead of submicrometer sized aggregated powders. The synthesized particles are hollow spheres which is an enormous disadvantage for persistent luminescence considering it is based on the size of the crystallites.¹⁴
2.1.7 The Molten Salt Method

The molten salt method is recently published as synthesis method by Rojas-Hernandez et al.³⁷ for strontium aluminate. In this method the raw materials are mixed together with a salt, then the mixture is heated to a temperature higher than the melting point of the salt. The molten salt fluxes have been employed to enhance the reactivity and promote crystal growth in systems such as complex oxides powders. The molten salt process has similarities to single crystals prepared by the seeded method but extended to particle synthesis. Nevertheless, only little information has been reported regarding the mechanisms of the reaction assisted by molten salts. It is based on the 'dissolution-precipitation' (dissolution in the molten salt which behaves as an ionic liquid) and the 'template formation' (formation and precipitation of the material) mechanisms.³⁷ Generally speaking, the molten salts behave as an ionic liquid in which the dissolution of a metal cation is very limited.³⁸ Thus, the strong and promising advantages of the molten salt method are frustrated by the lack of knowledge in the field.³⁷

2.1.8 Other Methods

To complete the list, many other methods (ceramic synthesis, pulsed laser deposition, template assisted method, electrospinning technique, solid state reaction, etc.) are described in literature but were not considered from the beginning. Those methods do not result in particles with the desired properties (size, morphology, structure, stability, etc.) as described in section 1.2.¹⁴

2.2 New Synthetic Pathways

The existing methods which are listed above all fail to produce strontium aluminate with the desired properties (desired size, crystallinity, morphology), discussed in detailed in section 3.1. That is the reason why we needed to design new synthesis routes. Inspiration was found in existing synthetic routes described in literature but which have never been used to produce nanosized, monoclinic strontium aluminate doped with divalent europium and codoped with trivalent dysprosium.

2.2.1 Benzyl Alcohol Route

Non-aqueous (or non-hydrolytic) sol-gel processes in organic solvents under exclusion of water are able to overcome some of the major limitations of aqueous systems. The advantages are closely related to the multiple role of the organic components in the reaction mixture. These components not only act as the oxygen-supplying agent for the metal oxide but also strongly influence particle size, shape, surface and assembly properties, and, in selected cases, even composition and crystal structure. Highly crystalline products are obtained via the slow reaction rates mainly as a consequence of the moderate reactivity of the C-O bond, in combination with the stabilizing effect of the organic species. These highly crystalline products are often characterized by uniform particle morphologies and crystallite sizes in the range of just a few nanometers.³⁹

The benzyl alcohol route, a non-aqueous non-surfactant assisted method, seems to be a very interesting reaction approach for the synthesis of crystalline metal oxide nanoparticles.¹⁵ It is a one pot solvothermal reaction where the benzyl alcohol is acting as solvent, ligand and reactant. This route has already been proven to be very versatile with good control over particle size, shape, crystallinity, solubility and assembly behavior.⁴⁰ Niederberger et al.^{41,42} reported the first syntheses using this method for titanium, tungsten and vanadium oxides in 2002. The following years synthesis of various binary and ternary metal oxide nanoparticles (e.g. $ZnAl_2O_4^{15}$, $SrTiO_3^{40}$, $(Ba,Sr)TiO_3^{40}$, $BaTiO_3^{40,43}$, $BaAl_2O_4^{44}$, $CaAl_4O_7^{44}$ and $SrAl_4O_7^{44}$) were published. With all this literature information, we will try to synthesize a stable suspension of monoclinic $SrAl_2O_4:Eu^{2+},Dy^{3+}$ nanocrystals.

The SCRiPTS-group has already a lot of experience with hafnium oxide and zirconium oxide synthesized by use of the benzyl alcoholo route. The entire synthesis recipe is explored and optimized, including surface chemistry and modification, by De Keukeleere et al.¹⁸ and De Roo et al.¹⁷ By means of this excellent in-house knowledge, we will try to synthesize monoclinic HfO_2 :Ti and ZrO_2 :Ti nanocrystals in different sizes to investigate the size impact of the nanocrystal on the intensity of the persistent luminescence.

The starting materials are often metals, metal halides or metal organic species (e.g. metal alkoxides and metal acetates), the reaction can be performed in the conventional (autoclave) way as well as in the microwave. First, alcoholysis of the metal takes place, given by equation 2.3, 2.4 and 2.5 respectively. Second, a condensation takes place, resulting in either alkyl halide, ether or ester elimination, given by equation 2.6, 2.7 and 2.8.

$$M + xBnOH \longrightarrow M(OBn)_x + \frac{1}{2}xH_2$$
 (2.3)

$$M(X)_n + xBnOH \longrightarrow (X)_{n-x}M(OBn)_x + xHX$$
 (2.4)

$$M(OR)_n + xBnOH \longrightarrow (RO)_{n-x}M(OBn)_x + xHOR$$
 (2.5)

$$-M-X + R-O-M^- \longrightarrow M-O-M^- + RX$$
 (2.6)

$$-M-OR + RO-M^- \longrightarrow -M-O-M- + ROR$$
 (2.7)

$$-M-O-C(O)R' + RO-M^- \longrightarrow -M-O-M- + ROC(O)R'$$
 (2.8)

Autoclave Synthesis

The method is quite simple, the reactants and the solvent are placed inside a Teflon-lined cylinder or autoclave, see figure 2.1 which is either sealed or connected to an external pressure control. The autoclave is then placed in a furnace, usually at a temperature in the range 100- 300° C. These conditions, in which the pressure is raised above atmospheric pressure and the temperature is raised above the boiling point of the solvent (benzyl alcohol stays liquid above 478 K at higher pressures), but where the temperatures to be used are not as high as in the solid state reaction methods. Under these conditions, starting materials will more easily dissolve. The nutrient is placed in a muffle furnace in order to create two temperature zones. The nutrient dissolves in the hotter zone and the saturated aqueous solution in the lower part is transported to the upper part by convective motion of the solution. The cooler and denser solution in the upper part of the autoclave descends while the counter flow of solution ascends. The solution becomes supersaturated in the upper part as the result of the reduction in temperature and crystallization sets in.²⁹



Figure 2.1: Autoclave in (A) side-view, (B) top-view without cover.⁴⁵

Microwave Synthesis

Traditional heating methods make use of an external heat source. This is a slow and inefficient method for transferring heat to the system under study, as this is dependent on the thermal conductivity of the different materials which must be penetrated. This results in a reaction vessel which has a higher temperature than the reaction mixture inside the vessel until enough time has passed, so that a thermal equilibrium can be established. This process can take several hours. Using a microwave treatment the microwaves interact directly with the (solvent) molecules which are present in the reaction mixture, which leads to a more rapid increase in temperature, as illustrated in figure 2.2. This method is not dependent on the thermal conductivity of the reaction vessel, as microwave transparent materials are used, such as borosilicate glass, Teflon or quartz. A microwave process possesses the ability to increase the crystallization kinetics of a hydrothermal process. A much debated statement in literature is whether the microwave radiation only supplies additional energy to overcome the energy barrier and thus complete the reaction more quickly than conventional heating, or does it also have an effect on the activation energy of a reaction. Microwaves will transfer energy in 10^{-9} s with each cycle of electromagnetic energy, the kinetic molar relaxation of this energy is about 10^{-5} s. This means that the energy is transferred more quickly than that the molecules can relax, resulting in non-equilibrium conditions with high temperatures that immediately affect the kinetics of the system. This will, in turn, increase the product yield within the same unit of time.⁴⁶



Figure 2.2: Illustration of the heating difference between the conventional, autoclave method and the microwave method.⁴⁷

Microwaves are electromagnetic waves in the 300 to 300 000 MHz frequency range or have a wavelength from 1 meter to 1 millimeter respectively. The energy of the microwave photons (0.155 kJ/mol) is low in comparison with the typical energy required to break chemical bonds (335 to 502 kJ/mol). This means that the microwaves will not affect the structure of the molecules in the reaction mixture, but will only affect the molecular rotations of the molecules in the reaction mixture. The 2.45 GHz frequency, that is being used, has the correct penetration depth to work on laboratory scale in the reaction mixtures used. The result of microwave irradiation is a direct localized super-heating of all the molecules in the reaction is an interaction or ionic conduction. Dipole rotation is an interaction in which polar molecules are trying to align with a rapidly changing electric field of the microwaves, illustrated in figure 2.3.



Figure 2.3: Illustration of the interaction between the dipoles of the (solvent) molecule and the microwave electromagnetic radiation.

The coupling capacity of this mechanism is related to the polarity of the molecule. The field changes very rapidly (4.9 10^6 times per second), generating a phase difference between the orientation of the field and the orientation of the dipole. This phase difference causes an energy loss of the dipole by molecular friction and collisions, which leads to dielectric heating. Ionic conduction is achieved if ions or ionic species are present in the reaction mixture. The ions will move through the solution under the influence of the applied electric field, resulting in an energy consumption caused by increased impact speed, whereby kinetic energy is converted into heat. The ability of a specific solvent to convert microwave energy into heat at a given frequency and temperature is determined by the loss factor (tan δ), given by equation 2.9.⁴⁶

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \tag{2.9}$$

With ϵ " the dielectric loss and ϵ ' the dielectric constant. The higher the dielectric loss, the more efficient the solvent converts microwave energy into thermal energy and thus the faster temperature will increase.⁴⁶

2.3 Non-aqueous Surfactant Assisted Method

The non-aqueous surfactant assisted route is an organic synthesis route in which already a surfactant is added so that no post-modification is necessary. It is a bottom-up synthesis method for nanocrystals done with the Schlenk line deployment, shown in figure 2.4.



Figure 2.4: Schematic illustration of the set-up for hot-injection and heating-up synthesis. (a) tap, (b) coil condenser, (c) thermocouple, (d) septum, (e) insertion for thermocouple, (f) three-neck round-bottom flask with reaction mixture, (g) stirring bar, (h) heating mantle.

The hot-injection mechanism to obtain monodisperse colloids was proposed by La Mer et al.⁴⁸ The La Mer model explains that the nucleation stage should be extremely short in order that additional nucleation does not occur, or in other words the nucleation process occurs homogeneously. As a consequence, monodisperse colloidal particles are formed via uniform growth on the existing nuclei, shown in figure 2.5. Based on this La Mer model, a lot of theoretical and experimental research has been conducted on the underlying mechanism of the hot-injection method. It is a kinetically driven process, in which highly reactive reactants are rapidly injected into a hot solution, which immediately induces a high supersaturation in the reaction mixture. With it, a burst of nucleation starts, followed by a size focusing growth process.^{49, 50} When the initial concentration of the precursors in a solution is high,

case, the nucleation process dominates the crystal growth, thereby yielding small nanocrystals. Conversely, a low concentration of the precursors in solution will drastically limit the number of nuclei which form in the initial stage of the reaction. In this case, the concentration of the monomer in solution is still high after the nucleation process and the diffusion-mediated growth process is dominant, thereby leading to the formation of larger nanoparticles.⁵¹

the solution becomes quickly supersaturated leading to a large number of nuclei. In such a

The heating-up mechanism underlying the control of the size distribution during this process cannot be satisfactorily explained by the theory used to explain the hot-injection process, in which high initial supersaturation is necessary for the formation of uniform nanocrystals.^{49, 50} The heating-up synthesis method can only be used when less reactive precursors are at hand, becayse very reactive precursors will undergo multiple nucleation bursts. The precursor is added to a high boiling solvent together with a surfactant. By heating the reaction mixture, the precursor will transform into monomer and reach at a certain point supersaturation, which means that the solubility limit is exceeded. When the nucleation threshold is exceeded, small clusters of the final product are formed (nucleation regime). After the seeds are formed, the monomer concentration is dropped beneath supersaturation which means no additional seeds will be formed even though there is still monomer in solution. The remaining monomer will react with the existing seeds with growth as result (growth regime). During this regime, the monomer will react preferably with the smallest particles because these are thermodynamically most unstable (focusing regime).⁴⁵

2.3.1 Thermal Decomposition

The thermal decomposition route is a synthetic method that produces uniform nanocrystals. This synthesis can be either performed via the hot-injection or the heating-up method.

When a metal organic complex is heated in a solvent (e.g. 1-octadecene or trioctylphosphine oxide) until approximately 300-400°C, the complex will degrade into free radicals, given by equation 2.10 and 2.11. These radicals can recombine, decompose into smaller molecules or



Figure 2.5: Schematic representation of the La Mer growth model for the hotinjection synthesis. It shows the start of the particle reaction with nucleation followed by growth and its evolution over time.⁴⁵

react with another metal oleate complex. The latter will start a propagation reaction, given by equation 2.12.

$$-M-OOCR \longrightarrow -M^{\bullet} + RCOO^{\bullet}$$
(2.10)

$$-M-OOCR \longrightarrow -MO^{\bullet} + RC^{\bullet}O$$
 (2.11)

$$-M^{\bullet} + -MO^{\bullet} \longrightarrow -M-O-M-$$
 (2.12)

Using the thermal decomposition route several nanocrystals (TiO₂⁵², Fe₃O₄^{53,54}, MnO⁵³, Co₃O₄⁵³, NiO⁵³, Cr₂O₃⁵³, MnFe₂O₄⁵⁴ and CoFe₂O₄⁵⁴) have been successfully made. In a first stage we will try to synthesize alumina (Al₂O₃) and then develop an equal reactive strontium precursor to synthesize finally the monoclinic SrAl₂O₄ host material, for the reason that no aluminate has already been synthesized.

2.3.2 Aminolysis

The amidification route is a very similar method like the thermal decomposition route. Instead of increasing the reaction temperature until the metal oleate complex decomposes and by this propagate the reaction, as described in the above section, an amine (e.g. oleyl amine) is added to the reaction mixture. This amine can react with the oleate carboxylate group with the formation of a much stabler amide, shown in equation 2.13. Therefore, the reaction temperature can be lowered compared to the thermal decomposition route. The amidification method can be used either with a hot-injection or a heating-up mechanism.⁵⁵

$$-M-O(O)CR + H_2NR \longrightarrow -M-OH + RC(O)N(H)R$$
 (2.13)

2.3.3 Alcoholysis

The esterification route also makes use of a chemical reaction based reaction mechanism, just as the amidification route described in the above section. Instead of an amine, an alcohol (e.g. oleyl alcohol) is added to the mixture, forming an ester, shown in equation 2.14. In this synthesis method, the alcohol is used as a reactant as well as the solvent, so there is a total conversion of the metal oleate to the ester compound. Here as well because of the esterification, the reaction temperature can be lowered compared to the thermal decomposition route. The esterification method can be used either with a hot-injection or a heating-up mechanism. ^{56, 57}

$$-M-O(O)CR + HOR \longrightarrow -M-OH + RC(O)OR$$
 (2.14)

Chapter 3

Experimental

3.1 Aqueous Methods

Many methods are described in literature to produce doped strontium aluminate, see section 2.1. Almost all state-of-the-art methods for strontium aluminate particles are water based, which means, due to the high reactivity of water, microsized particles will be obtained. The synthesized material will originally be amorphous as well, so an extra annealing step is inevitable to produce a crystalline material, leading to an agglomerated material.

In this section, the two most popular and frequently published methods (i.e. sol-gel and combustion) are reproduced as a starting point to obtain the strontium aluminate host material. Due to the lack of control of the size and crystallinity, we investigate the sol-gel method by changing the synthesis and heat treatment procedures but also by adding ligand(s) and a flux material (boron). An overview of all sol-gel syntheses is given in table A.3. The combustion method is investigated by changing the metal precursors, the synthesis procedure and the used fuel and its added excess. An overview of all combustion syntheses is given in table A.2.

3.1.1 Sol-gel Synthesis

The used recipe, based on literature research $^{58, 59}$, is described in section A.2.1. The metal precursors (strontium, europium and dysprosium acetate and aluminium isopropoxide) and the ligand(s) (glycerol, tartaric acid, ethylenediaminetetraacetic acid, malonic acid and/or ethyl acetoacetate) solutions are mixed together to form a gel. This gel is calcined, annealed and the europium in the obtained powders is reduced under hydrogen atmosphere. The obtained powders always results in the desired monoclinic strontium aluminate crystalline phase with sometimes different alumina crystal phases as side product, shown in XRD patterns figure 3.1. The crystallite size is 42 nm which is calculated by the Scherrer equation, shown in equation 3.1.



Figure 3.1: Database X-ray diffraction patterns of monoclinic strontium aluminate (ICSD 26466), aluminium (II) oxide (ICSD 28919), aluminium (III) oxide (ICSD 33639) and aluminium hydroxide (ICSD 181006). X-ray diffraction patterns of the normal sol-gel synthesis (GOA-4), GOA-4 brought in ethanol (GOA-4S) with oleic acid and the sol-gel synthesis with addition of boric acid as a flux agent (GOA-10).

$$d = \frac{K\lambda}{\beta \cos(2\theta)} \tag{3.1}$$

with d the mean size of the ordered domains (mean crystallite size), K a dimensionless shape factor, λ the X-ray wavelength, β the line broading at half the maximum intensity and θ the Bragg angle.

The material is microsized and has a porous morphology, shown in figure 3.3. The sol-gel method obtains nanosized cristallites which sinter together during the heat treatment steps, resulting in microsized particles. This can be illustrated on the basis of figure 3.2. After evaporation of the solvent, the amorphous material, obtained from the cations in solution, consists out of small spheres which are connected to one another to form a xerogel. To purge out the remaining ligands and their counter ions, a calcination step is followed by an annealing step. During these steps, all the residual organic material is removed and the particle spheres crystallize but because the spheres are connected to each other they will also sinter together thus forming particles in the microsized range consisting of nanosized crystallites. All the tested changes in synthesis, heat treatment procedures and used ligands (overview A.3) have no significant influence on the material morphology, the particle size or the crystallite size.

To bring the material partially suspended in ethanol with the use of oleic acid and oleyl amine is not possible. The crystal phase (figure 3.1) and morphology (figure 3.4) change and the luminescence partly or completely disappears (figure 3.7). Although the strontium aluminate phosphors are more resistant to moisture, it is know that they still degrade in direct contact.⁶⁰



Figure 3.2: Schematic illustration of the different stages during the sol-gel method.



Figure 3.3: SEM image of the monoclinic strontium aluminate material obtained by the sol-gel synthesis with the use of tartaric acid as ligand (GOA-4).

The reported influence of boric $\operatorname{acid}^{61, 62}$ on the improved persistent luminescence is reproduced as well. The boric acid is added in different concentrations together with the aluminium precursor during the synthesis. The obtained material always results in monoclinic strontium aluminate (figure 3.1) and the crystallite size according the Scherrer equation (eq. 3.1) is 48 nm. The particles are microsized and have a block-shaped morphology, shown in figure 3.5, as a result of the flux properties (improving the mobility of the different ions within the crystal lattice during heating steps) of boron.

Figure 3.6 shows the persistent luminescence measurements of the obtained monoclinic strontium aluminate with (GOA-10) and without (GOA-4) added boric acid during the sol-gel synthesis. The afterglow of the material with boric acid is more intense and emits very long.



Figure 3.4: SEM image of the monoclinic strontium aluminate material obtained by the sol-gel synthesis with the use of tartaric acid as ligand and brought in ethanol with oleic acid and oleyl amine (GOA-4S).



Figure 3.5: SEM image of the monoclinic strontium aluminate material obtained by the sol-gel synthesis with the use of tartaric acid as ligand and 5% added boric acid (GOA-10).



Figure 3.6: Persistent luminescence measurements of the monoclinic strontium aluminate material obtained by the sol-gel synthesis with the use of tartaric acid as ligand with 5% added boric acid (GOA-10) and without added boric acid (GOA-4). The left graph contains the different measurements with a blank measurement (black line), the right graph contains the different measurements where the blank is subtracted from.



Figure 3.7: Photo of (left) GOA-4 and (right) GOA-4 brought in ethanol with oleic acid and oleyl amine (GOA-4S).

3.1.2 Combustion Synthesis

The used recipe, based on literature research $^{63, 64, 65, 66}$, is described in section A.2.2. The metal precursors (strontium nitrate and carbonate, aluminium nitrate) and the reaction fuel (urea, glycine or glycylglycine) are dissolved in a minimum of water. The crucible is put in a muffle furnace preheated at 600°C where the reaction is finished in less then 10 minutes. In general, the obtained products are crystalline immediately after the combustion synthesis, without the need for further high temperature treatment. Due to the large amount of produced CO_2 and N_2 , it is assumed that under such conditions the trivalent europium will be reduced to divalent europium (when the lanthanides are added to the synthesis). 63 Before lanthanides are added to the synthesis, the host material is synthesized to investigate whether it has the desired properties (crystal phase and size), as described in section 1.2. However, the obtained products are not crystalline, thus an annealing step is added to obtain the crystalline material (figure 3.8). The peak visible for the non-heat treated sample (GOA-7) is originating from the used silicon measuring platform. The reason why the strontium aluminate is not crystalline can be found in the very fast reaction, the ions have no time to create the crystal lattice. After the annealing step, the strontium aluminte material has a crystallite size of 36 nm according to the Scherrer equation (eq. 3.1). The obtained material has a morphology of very thin sheets clustered together (figure 3.10) and is very airborne. The strontium aluminate material crafted by use of the combustion method, results in microsized layered particles which again are not suitable for employing for using as internal damage sensors in composites.



Figure 3.8: Database X-ray diffraction pattern of monoclinic strontium aluminate (ICSD 26466), X-ray diffraction pattern of the combustion synthesis before (GOA-7) and after (GOA-7B) the extra annealing step. The peak indicated with (*) at 33.2° is originating from the used silicon measuring platform.



Figure 3.9: SEM image of the monoclinic strontium aluminate material obtained by the combustion synthesis with the use of strontium nitrate, aluminium nitrate and a 20-fold stoichiometric excess of urea without an additional annealing step (GOA-7).



Figure 3.10: SEM image of the monoclinic strontium aluminate material obtained by the combustion synthesis with the use of strontium nitrate, aluminium nitrate and a 20-fold stoichiometric excess of urea with an additional annealing step at a temperature of 1100°C for 4 hours (GOA-7B).

3.2 Benzyl Alcohol Method

The benzyl alcohol route is a method which has already proven its robustness in the synthesis of various ceramic materials with a good control of crystallinity, size and morphology as described in section 2.2.1. This method can be used in a conventional way (autoclave) or via a microwave heating system.

3.2.1 Autoclave Synthesis

Based on the procedure described by Pinna et al.¹⁵, a synthetic approach is designed with a strontium and an aluminium precursor with molar concentration of 0.025 and 0.05 respectively (described in section A.3.1). The reaction duration is predicted to have an influence on the degree of crystallinity whereas the temperature and the used precursors could also have an influence on the crystal phase formation itself due to temperature/pressure change and precursor reactivity. The differences of the syntheses are shown in table 3.1. From the XRD patterns (figure 3.11), one can distinguish two different results. A group with two different crystalline phases (GOA-48, GOA-49 and GOA-55) and a synthesis with only one main crystalline phase (GOA-53). The XRD measurements can only be interpreted qualitative, a Rietveld measurement (not included) is needed for quantitative analysis.

The syntheses of this group (GOA-48, GOA-49 and GOA-55) show similar diffraction patterns and result in two different materials, small particles (broad XRD peaks) and large particles (small XRD peaks). Comparing the peaks from the XRD pattern with different databases, we can determine that the small particles are strontium carbonate (figure 3.11). The crystallites have an estimated size of 5.9, 7.1 and 18.0 nm according to the Scherrer equation (eq. 3.1) for samples GOA-48, GOA-49 and GOA-55 respectively. The large particles are not identified and have an estimated crystallite size of 44.1, 33.8 and 36.0 nm for samples GOA-48, GOA-49 and GOA-55 respectively. The unidentified peaks are believed to be from a diffraction pattern originating from one material as a result that the peak intensities relative to another stay constant. A limited off-size estimation of the particles by the Scherrer calculations can be expected and explained by merging together of peaks close to one another or/and by peak

Table 3.1: Syntheses performed via the conventional (autoclave) method, listed with alternated conditions.

Synthesis	Temperature	Time	Strontium precursor	Aluminium precursor
GOA-48	$200^{\circ}\mathrm{C}$	48h	acetate	isopropoxide
GOA-49	$200^{\circ}\mathrm{C}$	168h	acetate	isopropoxide
GOA-53	$260^{\circ}\mathrm{C}$	72h	acetate	acetate, basic
GOA-55	$200^{\circ}\mathrm{C}$	72h	acetate	acetate, basic



Figure 3.11: X-ray diffraction patterns of the syntheses performed in an autoclave in a regular muffle furnace. Peaks originating form the unidentified material are indicated by '|'.

interference of the different materials. The synthesis of two different materials is confirmed by TEM analysis of synthesis GOA-48, shown in figure 3.13, showing small particles of 3 nm in diameter and the large particles as clusters of nanowires. In nanowires, the atomic layers perpendicular to the growth direction will be favored in the XRD pattern, leading to misrepresented or eliminations of certain XRD peaks of the material compared to the databases. The mismatch of the size estimation by the Scherrer equation can be explained by the shape factor which is defined for spherical particles. For the reason that the synthesis did not yield solely a strontium aluminate phase, no further effort is done to identify the clusters of nanowires.

Duration of the synthesis has no influence on the composition of the material, as it is the only difference between synthesis GOA-48 and GOA-49. Also, the use of other metal precursors does not influence the composition of the material, as for synthesis GOA-55 basic aluminium acetate is used instead of aluminium isopropoxide. The most remarkable difference with respect to this group is synthesis GOA-53. For GOA-53, a higher temperature is employed resulting in a higher pressure as well. Here, only the small strontium carbonate nanoparticles are produced and a small quantity of aluminium hydroxide oxide nanoparticles, as shown in figure 3.12.



Figure 3.12: Database X-ray diffraction patterns of aluminium hydroxide oxide (ICSD 27865), strontium carbonate (ICSD 27293) and X-ray diffraction pattern of the synthesis GOA-53.



Figure 3.13: TEM images of GOA-48 consisting of unidentified nanowire clusters (left) and 3 nm strontium carbonate nanoparticles (right).

A final autoclave synthesis is performed, a recipe by Karmaoui et al.⁴⁴ (see recipe A.3.2) where a strontium (metallic) to aluminium (isopropoxide) ratio of 3:7 is used.¹⁵ In contrast to the reported monoclinic SrAl₄O₇, the synthesis mainly results in strontium carbonate particles (figure 3.14) with an crystallite size of 28 nm according the Scherrer equation (eq. 3.1). Together with another unidentified crystalline phase with an intense diffraction peak at 17.7°. SEM analysis (figure 3.15) confirms the synthesis two different materials. EDX mapping shows that one contains a high concentration of strontium while the other consists mostly out of aluminium.



Figure 3.14: Database X-ray diffraction patterns of strontium carbonate (ICSD 27293), monoclinic SrAl₂O₄ (ICSD 26466) and monoclinic SrAl₄O₇ (ICSD 2817) and X-ray diffraction pattern of the Karmaoui synthesis (GOA-68).



Figure 3.15: SEM image of the material obtained by the Karmaoui synthesis (GOA-68).



Figure 3.16: EDX analysis on the SEM image of the material obtained by the Karmaoui synthesis (GOA-68).

3.2.2 Microwave Synthesis

The used recipe is described in section A.3.3. Table 3.2 gives an overview of the microwave syntheses with their specific alterations and figure 3.17 shows the XRD patterns of the different syntheses. The strontium precursor is dissolved in benzyl alcohol before the aluminium precursor is added. First, different strontium precursors are tested and no difference is observed between metallic strontium and strontium acetate, both resulting in the production of strontium carbonate. Secondly, basic aluminium acetate is used instead of the aluminium isopropoxide precursor, the same unidentified large particle sized material (figure 3.17) is obtained as with the autoclave synthesis but this time no strontium carbonate is formed as side product. It is therefore concluded that the selective production of either small strontium carbonate particles or large unidentified particles is dependent on the reactivity properties of the used aluminium precursor.



Figure 3.17: X-ray diffraction patterns of the syntheses performed in the microwave furnace.

 Table 3.2: Syntheses performed via the microwave method, listed with alternated conditions.

Synthesis	Temperature	Time	Strontium precursor	Aluminium precursor
GOA-4 4	$250^{\circ}\mathrm{C}$	10h	acetate	isopropoxide
GOA-45	$250^{\circ}\mathrm{C}$	10h	metallic	isopropoxide
GOA-56	$200^{\circ}\mathrm{C}$	48h	acetate	isopropoxide
GOA-57	$250^{\circ}\mathrm{C}$	10h	acetate	acetate, basic

Because of this difference between the conventional autoclave syntheses (a mix of crystalline phases) and the microwave syntheses (selective production synthesis of strontium carbonate or the unidentified crystal phase), an identical synthesis to GOA-48 is performed (GOA-56). The XRD patterns of both syntheses are compared in figure 3.18 and shows that the microwave synthesis (GOA-56) only produces small strontium carbonate particles with an estimated crystallite size of 14 nm according the Scherrer equation (eq. 3.1). No aluminium hydroxide oxide is detected next to the strontium carbonate as it is the case with GOA-53 (figure 3.12).



Figure 3.18: X-ray diffraction patterns of the identical synthesis GOA-48 (autoclave synthesis) and GOA-56 (microwave synthesis).

3.3 Non-aqueous Surfactant Assisted Method

The fatty acid salt method is a non-aqueous method where the extra fatty acid is added to a solvent or the solvent itself will bind to the surface of the formed particles to stabilize them, yielding a stable suspension. The formation of a precipitate is not intended and thus unwanted.

This method is frequently used to produce metal oxide nanocrystals as described in section 2.3. Oleic acid as fatty acid (HOle) is often used as stabilizing agent in the solvent 1-octadecene (ODE). The use of trioctylphosphine oxide (TOPO) is also frequently used as both stabilizing agent and solvent. Metal oleate precursors are already used a lot in literature for the production of metal oxide nanocrystals.^{54, 67} First, the investigation to obtain pure aluminium oleate precursors is pursued. Secondly, the synthesis of aluminium oxide (alumina) from the aluminium oleate precursor is investigated with different reaction protocols. In follow-up research, production of strontium, europium and dysprosium precursors with equal reactivity properties to the aluminium oleate precursor is required. The final step of this research line is to produce strontium aluminate nanocrystals doped with divalent europium and trivalent dysprosium.

3.3.1 Precursor Optimization

Literature describes a few ways to prepare oleate precursors. Kovalenko et al.⁶⁷ reported the production of iron oleate from hydrated iron chloride, oleic acid and sodium hydroxide in methanol for the synthesis of spinel iron oxide. Cabrera et al.⁵⁴ made use of a two phase reaction mixture (water and hexane) with a third exchange solvent (ethanol) to prepare iron, cobalt and manganese oleate out of their hydrated metal chloride for the synthesis of MFe₂O₄ (M = Fe, Mn and Co). Adapted from the publications of Kovalenko et al. and Cabrera et al., aluminium oleate recipes are designed and referred to as the Kovalenko precursor (recipe A.4.1) and the Cabrera precursor (recipe A.4.2).

Infrared measurements of both the precursors are shown in figure 3.20. The Kovalenko precursor shows that estrification of oleic acid with methanol takes place. This problem is avoided by the use of ethanol in the Cabrera precursor. The longer the alkyl chain of the alcohol, the lower its esterification reactivity. However, unreacted oleic acid is still observed in the Cabrera precursor. The purification of both precursor methods is not obvious because aluminium oleate is a waxy solid which has the tendency to stick very easily to the walls of the used glass equipment, resulting in a high loss (low yield) with increasing purification steps when a pure precursor is desired.

Because of the importance of a pure and easy approach to make precursor with high yield, a novel method is designed which does not require a purification step due to the absence of byproducts. First, the aluminium oleate precursor is prepared from basic aluminium acetate and a stoichiometric quantity of oleic acid by heating the reaction mixture and applying vacuum (recipe A.4.4). When the reaction between the solid basic aluminium acetate and the high viscous oleic acid propagated, the reaction mixture becomes even more viscous until the point that the mixture cannot be stirred anymore. According to the infrared spectrum, shown in figure 3.20, the reaction is still not completely finished but due to the extreme high viscosity the reaction time would be infinite.

Considering the aluminium oleate precursor will always be dissolved in high boiling solvent (e.g. ODE or TOPO) for further reaction, the production of a pure precursor can be made as a stock solution. The recipe methodology is the same but the reaction mixture is diluted with ODE to a 0.5 molar concentration of aluminium (recipe A.4.5). Two different metal precursors are tested, the good soluble basic aluminium acetate and the less soluble aluminium isopropoxide. The chemical reactions are given in equations 3.2 and 3.3 respectively and infrared analysis as a function of the reaction time is shown in figures 3.21 and 3.22 respectively.

$$Al(OAc)_2(OH) + 3HOle \longrightarrow Al(Ole)_3 + 2AcOH + H_2O (3.2)$$
$$Al(OiPr)_3 + 3HOle \longrightarrow Al(Ole)_3 + 3iPrOH (3.3)$$

The reaction with basic aluminium acetate (figure 3.21) takes place in two steps. The first step takes place within an hour, where most of the aluminium oleate is formed. During the second step where still some free acid is present, either from oleic acid or from the formed acetic acid. This carboxylic acid peak (at 1710 cm⁻¹) disappears after 6 hours which is visual noticeable when the reaction mixture stops boiling. This delayed peak at 1710 cm⁻¹ that corresponds to a carbonyl stretch of a carboxylic acid can be interpreted in three ways or a combination of them. (i) A delayed boiling effect of the formed acetic acid due to the viscosity of the reaction mixture. (ii) This peak still corresponds to free oleic acid and can be explained from the delayed reaction due to increasing steric hindrance. (iii) This peak still corresponds to free oleic acid and is due to slower reaction kinetics of one of the groups (hydroxyl or acetate).

The reaction with aluminium isopropoxide (figure 3.22) is very fast. Even at the beginning where the reagents are mixed without heating, at the starting point of the measurements (0 minutes), the reaction starts and is finished within 30 minutes. The end of the reaction is again noticed when the reaction mixture stops boiling due to evaporation of all the produced isopropanol, which has a boiling temperature of approximately 85°C at atmospheric pressure.

As a result of the precursor stock solution in ODE, the reaction temperature can not rise

higher than 350°C in the higher boiling solvent TOPO (410°C), see next section. Preparation of the stock solution in TOPO is a possibility but because TOPO is solid under 60°C, it is not easy to handle. Therefore, a solid pure aluminium oleate precursor is still ideal. A new recipe is designed (recipe A.4.6), in which aluminium isoproxide and oleic acid are dissolved in toluene (figure 3.19). Two problems emerge due to the use of a lower boiling solvent. (i) Due to evaporation, extra toluene must be added during the synthesis therefore making it a high consuming synthesis of a toxic and hazardous solvent. (ii) Due to this evaporation, the reaction mixture becomes, at times, very viscous and local stirring is not always possible anymore. This results in local overheating, leading to unwanted esterification side reaction between oleic acid and isopropanol, visible in the transmission infrared spectrum shown in figure 3.19. Both problems can be avoided when making use of aluminium hydroxide, which will produce water with oleic acid and forms an azeotropic mixture with toluene, in combination with the use of a Dean-Stark deployment.



Figure 3.19: Transmittance infrared measurements of reaction mixture of a 0.5 molar concentration aluminium isopropoxide in toluene at 100°C under argon atmosphere after 3 hours. With peaks (a) C=O stretch of the esterification of oleic acid with isopropanol at 1735 cm⁻¹, (b) C=O stretch of aluminium oleate at 1585 cm⁻¹ and (c) C-H bend of the different alkanes chains in the reaction mixture at 1465 cm⁻¹.



Figure 3.20: Transmittance infrared measurements of (bottom to top) oleic acid, the Kovalenko precursor, the Cabrera precursor and precursor obtained directly out of basic aluminium acetate and oleic acid. With peaks (a) C=O stretch of methyl oleate at 1740 cm⁻¹, (b) C=O stretch of oleic acid at 1710 cm⁻¹, (c) C=O aluminium oleate at 1585 cm⁻¹ and (d) C-H bend of the different alkanes chains in the reaction mixture at 1465 cm⁻¹.



Figure 3.21: Transmittance infrared measurements of reaction mixture of a 0.5 molar concentration basic aluminium acetate in 1-octadecene at 150°C under vacuum progressing over time (0, 30, 60, 90, 120, 180, 240, 300 and 360 minutes). With peaks (a) C=O stretch of oleic acid at 1710 cm⁻¹, (b) -C=C- stretch of 1-octadecene at 1640 cm⁻¹, (c) C=O stretch of aluminium oleate at 1585 cm⁻¹ and (d) C-H bend of the different alkanes chains in the reaction mixture at 1465 cm⁻¹.



Figure 3.22: Transmittance infrared measurements of reaction mixture of a 0.5 molar concentration aluminium isopropoxide in 1-octadecene at 120°C under vacuum progressing over time (0, 30, 60, 90, 120, 180, 240, 300 and 360 minutes). With peaks (a) C=O stretch of oleic acid at 1710 cm⁻¹, (b) -C=C- stretch of 1-octadecene at 1640 cm⁻¹, (c) C=O stretch of aluminium oleate at 1585 cm⁻¹ and (d) C-H bend of the different alkanes chains in the reaction mixture at 1465 cm⁻¹.

3.3.2 Thermal Decomposition

The first thermal decomposition reaction, described in section A.4.3, is based on literature descriptions of thermal decomposition of spinel iron oxide by Kovalenko et al.⁶⁷ and MFe₂O₄ (M = Fe, Mn and Co) by Cabrera et al.⁵⁴. The synthesis results in a fluorescent greenyellow gel instead of the expected white alumina powder. To enhance the crystallization of the reaction mixture to produce the desired alumina nanocrystals, the reaction duration is changed to 6, instead of 3 hours for GOA-50 and the synthesis concentration of GOA-51 is changed to 0.035M instead of 0.155M (synthesis differences are summarized in table 3.3). After this, the obtained materials also did not result in the white powder as expected from alumina, but in a brown and yellow coloured gel.

Thermogravimetric analysis (figure 3.26) of the precursors reveals that the used temperature of 320°C (boiling point of 1-octadecene (ODE)) is below the thermal decomposition temperature of aluminium oleate. The thermogravimetric and differential temperature analysis curves are not what is expected from a pure combustion reaction of the metal oleate precursor. A first mass reduction is observed around 360°C which is the boiling point of free, unreacted oleic acid. For the aluminium oleate precursor this first loss of mass accounts already for approximately 50% of the total mass. This confirms what is discussed in the section of precursor optimization, the reaction between basic aluminium acetate and oleic acid propagates till the point that the reaction mixture becomes to viscous and the reaction stops (would take infinite time to complete).

The next stage in the TGA curves (figure 3.26) is a second and steep loss of mass (for the aluminium oleate precursor, a steep exothermic peak is observed) presumed to be of the degradation of the metal oleate compound. A final stage is observed only for the Kovalenko and Cabrera precursors presumed to be a secondary reaction with left impurities. The loss of mass percentage for the Kovalenko, Cabrera and aluminium oleate precursor are 91.43%, 89.85% and 88.85% respectively. The theoretical loss of mass percentage is calculated to be 94.21%.

After the precursor optimization (described in the previous section) the thermal decomposition synthesis is repeated in trioctylphosphine oxide (TOPO) (recipe A.4.7). The aimed reaction temperature of 410° C is not reached due to the ODE present in the precursor stock solution which limits the boiling point of the reaction mixture to 350° C.

3.3.3 Aminolysis

A method to decrease the reaction temperature is to mix the aluminium oleate (carboxylate) stock solution with an amine to facilitate an amidification reaction. The followed recipe is described in section A.4.9. It results in a sand-coloured powder with a crystallite size of

Synthesis	Time	Concentration	Extra added HOle
GOA-46	3h	$0.155 \mathrm{M}$	1 eq. (732 μL)
GOA-5 0	6h	$0.155 \mathrm{M}$	1 eq. (732 $\mu {\rm L})$
GOA-5 1	3h	$0.035 \mathrm{M}$	3 eq. (926 $\mu {\rm L})$

 Table 3.3: Syntheses performed via thermal decomposition method, listed with alternated conditions.

around 1.7 nm calculated according the XRD pattern (figure 3.23) using the Scherrer equation (eq. 3.1). As a result of the very small crystallite size and no recognizable peaks in the XRD pattern, we can conclude that the obtained material is amorphous.



Figure 3.23: X-ray diffraction pattern of the aminolysis reaction.

3.3.4 Alcoholysis

A similar method to aminolysis is to mix the aluminium oleate (carboxylate) stock solution with an alcohol to facilitate an esterification reaction, based on publications of Ito et al.⁵⁶ and Della Gaspera et al.⁵⁷ (recipe A.4.8. It results in a sand-coloured powder with a crystallite size of around 30 nm calculated according the XRD pattern (figure 3.24) using the Scherrer equation (eq. 3.1). The TEM-images (figure 3.25) show that the particles have a size in the (sub-) microsize range. The material cannot be identified as an aluminium oxide.



Figure 3.24: X-ray diffraction pattern of the alcoholysis reaction. The peak indicated with (*) at 33.2° is originating from the used silicon measuring platform.



Figure 3.25: TEM images of GOA-59 (alcoholysis) consisting of unidentified (sub)-microsized particles.



Figure 3.26: Thermogravimetric analysis (left axis, light colours) and differential temperature analysis (right axis, dark colours) of the Kovalenko precursor (red lines), the Cabrera precursor (blue lines) and the aluminium oleate percursor (green lines).

3.4 Size Dependency of Persistent Luminescence

Hafnium and zirconium oxide are reported the have persistent luminescence properties.¹² The underlying reason for persistent luminescence is ascribed to the presence of titanium as an impurity in the crystal lattice.^{68,69} The choice for these two materials in particular is due to the in-house knowledge of the synthesis to obtain hafnia¹⁷ and zirconia¹⁸ nanocrystals but also the in-house knowledge of titanium.⁷⁰

Hafnium and zirconium oxide nanocrystals are obtained according the synthesis method A.3.4 and A.3.5 respectively. Samples are prepared with an extra added titanium doping concentration of 4%, 0.5% and 0%. From the first synthesis of zirconia doped with a 4% titanium concentration, a lower crystallinity is observed in the XRD pattern (figure 3.27) and the post modification to stabilize the zirconia nanocrystals with oleic acid and oleyl amine is not possible as well. For those two reasons we decide to continue only with the hafnia nanocrystals.



Figure 3.27: Database X-ray diffraction pattern of zirconia (ICSD 41010) and X-ray diffraction pattern of the zirconia doped with 4% titanium. The peak indicated with (*) at 33.2° is originating from the used silicon measuring platform.

Persistent luminescence is correlated to the volume of the crystalline domains (crystallite sizes). To investigate the dependence of the crystallite size on the persistent luminescence properties, the synthesized hafnia samples are partly subjected to an annealing step of 1000°C for 3 hours to enlarge the crystallite size. The XRD patterns (figure 3.28) show that monoclinic hafnia is synthesized and no titania phase is observed. The unidentified peak at 33.2° that is visible, is a peak originating from the used silicon XRD measuring platform. The crystallite size is calculated with the Scherrer equation (eq. 3.1), for the non-annealed samples (independently of their titanium doping concentration) the crystallites have a size of 5 nm. For the annealed samples a crystallite size of 25 nm is calculated. TEM analysis of the

non-annealed samples shows that the increasing titanium concentration has no effect on the morphology of the particles (figure 3.29 - 3.31). The particle sizes correspond to the crystallite sizes calculated from the XRD patterns. The particles are stabilized by oleyl amine and oleic acid to obtain a clear suspension, shown in figure 3.32.



Figure 3.28: Database X-ray diffraction patterns of hafnia (ICSD 187015) and X-ray diffraction patterns of the hafnia doped with 0%, 0.5% and 4% titanium doping concentration. The annealed samples are noted as 0%-T, 0.5%-T and 4%-T. The peaks indicated with (*) at 33.2° is originating from the used silicon measuring platform.



Figure 3.29: TEM images of hafnia doped with an extra added 0.0% titanium consisting of stabilized nanoparticles.



Figure 3.30: TEM images of hafnia doped with an extra added 0.5% titanium consisting of stabilized nanoparticles.



Figure 3.31: TEM images of hafnia doped with an extra added 4.0% titanium consisting of stabilized nanoparticles.



Figure 3.32: Photo of the stable suspensions of hafnia samples with different titanium doping concentration.

The titanium doping has also no influence on the morphology of the hafnia. SEM analysis of the morphology for the non-annealed and the annealed material is shown in figure 3.33 and 3.34 respectively. It is visible that after the annealing step multiple nanocrystals coalesce and fuse together in a larger nanocrystal (crystallite size increases from 5 nm to 25 nm according the Scherrer calculation). As a result of this annealing step, the new formed nanoparticles also sinter together. Thus bringing the hafnia material back in a stable suspensions after annealing, is not possible.



Figure 3.33: SEM image of hafnium oxide particles with 0.5% extra added titanium and without extra annealing step (GOA-64).


Figure 3.34: SEM image of hafnium oxide particles with 0.5% extra added titanium and with extra annealing step (GOA-64X).

The combined excitation and emission spectra for the 0%, 0.5% and 4% extra added titanium are given in figures 3.35, 3.36 and 3.37 respectively. The emission spectra of the different samples have a broad range, resulting in the emission of (bluish) white light. The maxima of the excitation and emission peaks are summarized in table 3.4. A recent study by Villa et al.⁶⁹ demonstrated that the incorporated titanium is responsible for the excitation peak at 4.4 eV (280 nm) and the emission peak at 2.5 eV (490 nm). They found also an excitation peak at 3.5 eV (360 nm) due to intrinsic defects. Emission peaks at 2.1 eV (580 nm), 2.5 eV (490 nm), 2.9 eV (430 nm) and 3.6 eV (310 nm) were ascribed to intrinsic defects as well.⁶⁹ The titanium present in the hafnia lattice is presumed to be trivalent.^{68, 69} Although the used titanium precursors are tetravalent, the titanium is reduced due to the reducing nature of the reaction. The intrinsic lattice defects are responsible for fast emission whereas the afterglow originates from the titanium centers.^{68, 69}

A shift in relative intensity is detected for the non-annealed samples. The 0% doped sample absorbs more energy with a wavelength of 380 nm (3.3 eV) which is linked to intrinsic defects absorbing around 3.5 eV. When extra titanium is added, the peak at 380 nm (which is linked to the excitation energy of titanium) becomes more intense. The emission peak responsible from the titanium centers at 500 nm (2.5 eV) becomes more intense while the emission peak resulting from intrinsic defects is not detectable anymore. The annealing step restores the defects in the crystal lattice, resulting in higher crystallinity and crystallite size. This leads to a higher intensity of the combined excitation and emission spectra in comparison with the non-annealed samples (visible in figure 3.38). Both the excitation and emission peak originate from the titanium centers. The higher intensity of the excitation and emission peak from the annealed 4% extra added titanium sample cannot be explained and this result is in contradiction with our visual observation.



Figure 3.35: The excitation (blue) and emission (red) spectra of hafnia doped with an extra added 0.0% titanium, left after synthesis and right after an extra annealing step. Emission spectra are recorded upon excitation at 288 nm (left) and 281 nm (right) while excitation spectra are obtained by monitoring the emission at 460 nm (left) and 470 nm (right).



Figure 3.36: The excitation (blue) and emission (red) spectra of hafnia doped with an extra added 0.5% titanium, left after synthesis and right after an extra annealing step. Emission spectra are recorded upon excitation at 288 nm (left) and 315 nm (right) while excitation spectra are obtained by monitoring the emission at 500 nm (left) and 475 nm (right).

The persistent luminescence measurements of the different hafnia samples are given in figure 3.39. From the left graph it is clear that the samples (annealed or not) emit significant more afterglow than the blank measurement (black line). The 0% doped, annealed sample (dark red) shows the best persistent luminescence result with a comparable afterglow duration as reported in literature^{12,71,72}. All the annealed samples are characterized with better



Figure 3.37: The excitation (blue) and emission (red) spectra of hafnia doped with an extra added 4.0% titanium, left after synthesis and right after an extra annealing step. Emission spectra are recorded upon excitation at 290 nm (left) and 290 nm (right) while excitation spectra are obtained by monitoring the emission at 500 nm (left) and 485 nm (right).

 Table 3.4: Summary of the hafnia syntheses with the maximum excitation and emission peaks.

Sample	Excitation	Emission	
0.0% Ti	280-380 nm (1:2)	$440~\mathrm{nm}$	
$0.5\%~{ m Ti}$	280-380 nm (1:1)	500 nm	
4.0% Ti	280-380 nm (1:1)	500 nm	
0.0% Ti, T	$288~\mathrm{nm}$	$475~\mathrm{nm}$	
0.5% Ti, T	288-315 nm (1:1)	$475~\mathrm{nm}$	
4.0% Ti, T	288-315 nm (1:2)	$580 \mathrm{~nm}$	

persistent luminescence which is also visual observed and in literature reported by Pejaković.⁷² The reason of this enhanced afterglow can be explained by an increase in crystallite size or an increase in crystallinity (crystallinity percentage can be calculated by Rietveld analysis, not included). The reason that the other annealed hafnia samples do not improve equally as the 0% doped can have multiple explanations. It is believed that titanium is the activator in the hafnia material but it is not proven so far. After synthesis, it is unknown where the titanium is located, it can be on the surface and penetrate or grow into the crystal during the annealing step. A possible explanation is that the extra added titanium concentration is to high and therefore responsible for faster emission of the stored energy. This statement is supported by visual observation, where the 0.5% and 4% doped samples emit intenser during excitation but has a shorter afterglow duration in comparison with the 0% doped sample.⁷¹



Figure 3.38: Photo of the different hafnia samples during excitation by UVirradiation of 302 nm.



Figure 3.39: Persistent luminescence measurements of the hafnia doped with 0%, 0.5% and 4% titanium doping concentration (light colours). The annealed samples (dark colours) are noted with 'T'. The left graph contains the different measurements with a blank measurement (black line), the right graph contains the different measurements where the blank is subtracted from.

Chapter 4

Conclusion

The first part of this thesis describes the state-of-the-art synthesis methods for monoclinic strontium aluminate doped with europium and dysprosium ($SrAl_2O_4:Eu^{2+},Dy^{3+}$). The investigation what their shortcomings are for the application as integrated sensors for the detection of internal damage of composite materials. In the second part, the synthesis of (undoped) strontium aluminate nanocrystals through the design of a novel non-aqueous non-surfactant synthesis method (the benzyl alcohol route) is tested. The conventional (autoclave) and microwave heating are compared. The third part describes the synthesis of alumina through a novel non-aqueous surfactant assisted synthesis method. The final part investigates the influence of the crystallite size on the persistent luminescence properties.

The sol-gel synthesis results in monoclinic strontium aluminate with excellent persistent luminescence properties with only a crystallite size of 42 nm and 48 nm when boron is added. The influence of the used ligand (tartaric acid, glycerol, ethylenediaminetetraacetic acid, malonic acid and ethyl acetoacetate) on the crystal phase, morphology and size (both the crystallite and particle) is minimal. The addition of boron to the synthesis mixture has a big influence on the morphology and on the persistent luminescence properties. The particles change from a porous material to a much denser material with a block-shaped morphology. The observed afterglow is more intense and lasts longer in comparison with the non-boron added syntheses, although both the crystallite and the particle size are comparable. Nevertheless, the particle size stays in the micro- and millimeter range, which makes these materials not processable for the desired integrated sensors.

The combustion synthesis described in literature, does not yield a crystalline material. The used fuel (urea, glycine or glycylglycine) and its ratio (stoichiometric or excess) has no influence on the formation of crystalline material and the synthesis always results in amorphous material. An extra annealing step results in a crystallite size of 36 nm. The obtained monoclinic strontium aluminate has a clustered sheet morphology which results in microsized layered particles that are not processable for the desired integrated sensors.

Two different approaches are exploited for the benzyl alcohol route, the conventional autoclave and the microwave synthesis. Using an autoclave synthesis, two crystalline materials are produced with 3 nm small strontium carbonate particles. In the samples, a material with a nanowire cluster morphology or a small quantity of aluminium hydroxide oxide could also be detected. Different reaction times and aluminium precursors were tested but no influence on the product composition could be found. The aluminium hydroxide oxide side product is only formed at higher temperatures (260°C) whereas at 200°C the unidentified material is obtained.

The microwave synthesis results in one crystalline phase. Different strontium (metallic and acetate) and aluminium (isopropoxide and acetate) precursors were tested. Strontium acetate in combination with basic aluminium acetate results in a large fraction of unidentified material as also obtained from the autoclave synthesis. All other precursor combinations result in small strontium carbonate particles. In conclusion, neither the autoclave nor the microwave synthesis result in a crystalline strontium aluminate material. More research must be conducted to have a better insight in the synthesis of strontium aluminate (nano)particles.

The use of the non-aqueous surfactant assisted method is often used for the synthesis (mono-) metal oxides. First, the synthesis of alumina is investigated before the synthesis with mixed metal precursors is designed. Due to impure aluminium oleate precursor and a too low reaction temperature, we were not able to produce alumina nanoparticles using the thermal decomposition route. The optimization to obtain a pure aluminium oleate precursor is finished. Future research will clarify whether it is successful to produce alumina nanoparticles from this pure aluminium oleate using thermal decomposition. Other high boiling solvents (>400°C) to make the aluminium precursor stock solution and other aluminium precursors are another possibility for future research. Aminolysis between the aluminium oleate precursor stock and oleyl amine results in an amorphous material. Alcoholysis with oleyl alcohol results in a crystalline material. The identity of the compound still needs to be identified. As well for the aminolysis as for the alcoholysis, an amine and an alcohol with a smaller alkyl chain is an option to enhance the reaction kinetics. In conclusion, neither thermal decomposition, aminolysis or alcoholysis results in alumina nanoparticles More research must be conducted to have a better insight in the synthesis of alumina (nano)particles.

Hafnia is selected as the ideal material for the investigation of the minimum crystallite size to still obtain good persistent luminescence intensity. Hafnia is chosen as a result of its already reported persistent luminescence properties and the in-house knowledge of its nanocrystal synthesis. The hafnia nanocrystals are successfully made with different extra added titanium concentrations (0%, 0.5% and 4%) and have a crystallite size of 5 nm. To enlarge the crystallite size an extra annealing step is used after which the crystallite size of all samples is increased to 25 nm as a result of coalescence and fusion. However, during this step it is observed

that the nanocrystals also sinter together. The small hafnia nanoparticles almost do not emit any afterglow in comparison to the annealed samples. The non-doped annealed hafnia sample shows the best persistence luminescent properties which match the same afterglow duration as reported in literature. This could be realised with a lower crystallite size of 25 nm. The crystallite size is suspected to be the underlying cause for the increase in intensity and afterglow duration, knowing that the crystallinity will have improved as well during the annealing step. To make any definitive conclusion on the impact of each independent parameter, more research and tests must be executed.

The preliminary conclusion of this master thesis is that the crystallite size is not such a big issue as first believed. We have proven that the persistent luminescence is still good when the crystallite is nanosized (50 nm <crystallite size <100 nm). The crystallite size of the strontium aluminate obtained by the aqueous methods are nanosized but they sinter together resulting in microsized particles. These cannot be brought in suspension and are to large to be printed, spin- or dip-coated. Therefore it is necessary to design a novel synthetic route to produce strontium aluminate nanocrystals in suspension but it tends to be a very hard process due to the large difference in reactivity between strontium and aluminium. Strontium reacts rather fast into strontium carbonate nanocrystals whereas aluminium react not at all or in the best case very limited to form separately aluminium hydroxide oxide.

The next big step in the chemical story of this ENCLOSE-project, is to search for more reactive aluminium precursors and to investigate the feasibility to produce alumina nanoparticles. At second hand, the compatibility between different strontium precursors and the found aluminium precursors needs to be investigated to come to a conclusion whether the strontium aluminate material is still a suitable choice for the use of internal damage sensors.

Appendix A

Chemicals and Synthesis methods

A.1 Chemicals

Product	CAS	Supplier	Purity	Hazard symbols
Metallic strontium	7440-24-6	Sigma Aldrich	99.0%	
Aluminium chloride	7446-70-0	Fluka	99.0%	AL POINT
Hafnium chloride	ium chloride 13499-05-03 Alfa-Aesar		99.9%	()
Zirconium chloride	10026-11-6	Sigma Aldrich	99.9%	()
Aluminium nitrate	7784-27-2	Sigma Aldrich	98.0%	(1)
Dysprosium(III) nitrate	10031-49-9	Sigma Aldrich	99.9%	(!) 📀
Europium(III) nitrate	63026-01-7	Sigma Aldrich	99.9%	(!) 📀
Strontium nitrate	10042-76-9	Acros Organics	99.0%	٢
Strontium carbonate	1633-05-2	Sigma Aldrich	98.0%	-
Aluminium isopropoxide	555 - 31 - 7	Sigma Aldrich	98.0%	۲
Titanium(IV) butoxide	5593-70-4	Fluka	97.0%	(1)
Aluminium acetate, basic	142-03-0	Sigma Aldrich	-	-
Strontium acetate	543 - 94 - 2	Sigma Aldrich	-	-
Ethyl acetoacetate	141-97-9	Acros Organics	99.0%	-
Boric acid	10043-35-3	ucb	-	٠

Table A.1: Overview of the used chemicals.

Product	CAS	Supplier	Purity	Hazard symbols
Malonic acid	141-82-2	Sigma Aldrich	99.0%	
Tartaric acid	133-37-9	Sigma Aldrich	99.0%	(1)
ТОРО	78-50-2	STREM	99.0%	
MEA	16024-58-1	Sigma Aldrich	technical grade	
Dodecanoic acid	143-07-7	Sigma Aldrich	99.0%	-
Oleic acid	112-80-1	Sigma Aldrich	90.0%	(1)
EDTA	60-00-4	Sigma Aldrich	99.4%	(1)
Sodium hydroxide	1310-73-2	Roth	99.0%	and the second s
Methanol	67-56-1	Fiers	99.8%	۵ 🗇 🚯
Ethanol	64-17-5	VWR	99.8%	۲
2-methoxyethanol	203-713-7	Sigma Aldrich	99.0%	۵ 🔅 🗞
Isopropanol	67-63-0	Fiers	99.7%	(ا) 🚯
Glycerol	56 - 81 - 5	Sigma Aldrich	99.0%	-
Benzyl alcohol	100-51-6	Sigma Aldrich	99.8%	(1)
Oleyl alcohol	143-28-2	Sigma Aldrich	85%	(1)
Toluene	108-88-3	Fiers	99.8%	۵۰ 🗞
Hexane	110-54-3	Acros Organics	95.0%	
Chloroform	67-66-3	Carlo Erba	99.8%	(!)
Acetone	67-64-1	Fiers	99.0%	(!) (*)
Acetonitrile	75-05-8	Acros Organics	99.0%	(ا) 🚯
Diethyl ether	67-64-1	Fiers	99.5%	(!) 🚸
Dibenzyl ether	103-50-4	Sigma Aldrich	98.0%	
1-octadecene	112-88-9	Alfa Aesar	90.0%	٠
Oleyl amine	112-90-3	Sigma Aldrich	98.0%	
Urea	57-13-6	Roth	99.5%	-
Glycine	56-40-6	Chimica	99.0%	-
Glycylglycine	556-50-3	Sigma Aldrich	98.0%	()

A.2 Aqueous Based Methods

A.2.1 Sol-gel Synthesis

The sol-gel syntheses are carried out using different types of additives or combinations of them: tartaric acid, glycerol, ethylenediaminetetraacetic acid (EDTA), malonic acid and ethyl acetoacetate. A number of synthesis and heat treatment procedures are also altered (gelation procedure, crystalline phase forming temperature and time, reduction time and exclusion of residual carbon content).

In the general procedure first 0.92 mmol of strontium acetate and 0.04 mmol of europium nitrate and dysprosium nitrate each are mixed in a 250 mL beaker with 15 mL of water. The additive(s) is/are added (always 4 mmol additive in total), here also the boric acid is added when the synthesis describes this. Then 2 mmol (or minus the quantity of added boric acid when used) of aluminium isopropoxide dissolved separately in 10 mL of 2-methoxyethanol at a temperature of 100°C is mixed into the solution forming a sol-gel. The mixture is stirred for one hour at room temperature before it is put in an oven at 75°C overnight. Next the obtained gel (when the ligand is liquid) or moist powder (when the ligand is a powder) is put in a ceramic crucible and kept at 180°C in a muffle furnace for 24 hours before it is heat treated at 1100°C for 4 hours to obtain the monoclinic crystalline phase. The final reduction step happens also at 1100°C for 4 hours but with a 5% hydrogen/argon-gas flow at 0.5 L/min for 12 hours in a tube furnace. Between all the steps the sample is cooled naturally.

A.2.2 Combustion Synthesis

In the general followed procedure stoichiometric amounts of $Al(NO_3)_3 \cdot 9H_2O$, $Sr(NO_3)_2$ or $SrCO_3$ and fuel/reducer are mixed with a minimum of water. No lanthanides are added. First of all, research is needed to establish whether this synthesis method works or not. The gel-like paste is stirred for 30 minutes to ensure a homogeneous mixture and is then put in a preheated muffle oven of 600°C for 10 minutes. Urea, glycine and glycylglycine are used as fuel in the reactions, the stoichiometric reactions are shown respectively in equation A.1, A.2 and A.3.

$$\begin{split} 3\,{\rm Sr}({\rm NO}_3)_2 + 6\,{\rm Al}({\rm NO}_3)_3 &\cdot 9\,{\rm H}_2{\rm O} + 20\,{\rm CO}({\rm NH}_2)_2 \\ & \longrightarrow 3\,{\rm SrAl}_2{\rm O}_4 + 32\,{\rm N}_2 + 94\,{\rm H}_2{\rm O} + 20\,{\rm CO}_2 \quad ({\rm A}.1) \end{split}$$

$$\begin{split} 9\,\mathrm{Sr}(\mathrm{NO}_3)_2 + 18\,\mathrm{Al}(\mathrm{NO}_3)_3 &\cdot 9\,\mathrm{H}_2\mathrm{O} + 40\,\mathrm{H}_2\mathrm{NCH}_2\mathrm{COOH} \\ & \longrightarrow 9\,\mathrm{SrAl}_2\mathrm{O}_4 + 56\,\mathrm{N}_2 + 262\,\mathrm{H}_2\mathrm{O} + 80\,\mathrm{CO}_2 \quad (\mathrm{A.2}) \end{split}$$

$$\begin{split} 9\,\mathrm{Sr}(\mathrm{NO}_3)_2 + 18\,\mathrm{Al}(\mathrm{NO}_3)_3 &\cdot 9\,\mathrm{H}_2\mathrm{O} + 20\,\mathrm{H}_2\mathrm{NCH}_2\mathrm{CONHCOOH} \\ & \longrightarrow 9\,\mathrm{SrAl}_2\mathrm{O}_4 + 56\,\mathrm{N}_2 + 98\,\mathrm{H}_2\mathrm{O} + 60\,\mathrm{CO}_2 \quad \mathrm{(A.3)} \end{split}$$

Name	Deviation	Colour	Monoclinic	Morphology
GOA7B	20 fold excess urea ⁶³	white	yes	microsized porous
GOA8B	20 fold excess urea	white	yes	microsized porous
	$ m SrCO_3$			
GOA14B	20 fold excess urea	white	-	-
	$gelation^{64}$			
GOA15B	$1.5 \text{ fold excess glycine}^{65}$	white	-	-
GOA16B	NO_3 :urea 1:1.5 ⁶⁶	white	-	-
GOA17B	1.5 fold excess	white	-	-
	glycylglycine			

Table A.2: Overview of all the different experiments of the combustion method with a brief overview of the properties.

Name	Deviation	Colour	Monoclinic	Morphology	Luminescence
GOA1X	G^{59} , old oven	gray	yes	microsized	+
				porous (mp)	
GOA2X	old oven	white	yes	mp	+
GOA3X	G:TA 1:1	white	yes	mp	++
	old oven				
GOA4X	/	gray	yes	mp	+
GOA5X	G:TA 3:1	yellow	yes	mp	++
GOA6X	G:TA 1:3	yellow	yes	mp	++
GOA9X	2.5% boron ⁶²	yellow	yes	mp	+++
GOA10X	5% boron ⁶²	yellow	yes	mp	+++
GOA11X	$7.5\% \text{ boron}^{62}$	yellow	yes	-	+++
GOA12X	5% boron ⁶² , G	yellow	yes	-	+++
GOA13X	5% boron	yellow	yes	-	+++
	G:TA 1:1				
GOA18X	EDTA	white	-	-	++
GOA19X	MA	black	-	-	_
GOA20X	$\mathrm{EAA}^{62,58}$	gray	-	-	_
GOA21X	ice bath gelation $^{62, 58}$	gray	yes	-	—
GOA22X	red: 2h	white	-	mp	+
GOA23X	phase: 0h	black	yes	-	no
GOA24X	phase: 2h	white	yes	mp	+
GOA25X	phase: $500^{\circ}C^{58}$	black	yes	-	no
GOA26X	phase: $800^{\circ}C^{58}$	dark gray	yes	mp	
GOA34X	tube furnace	white	yes	mp	+
	pure oxygen gas				
GOA35X	phase: $12h^{58}$	white	-	-	+
GOA36X	phase: 24h	white	yes	mp	+
GOA37X	furnace S1	white	_	mp	+
GOA39X	0.5% boron	white	yes	-	++
GOA41	molton salt	white	yes	-	not applicable

Table A.3: Overview of all the different experiments of the sol-gel method with a brief overview of the properties.

A.3 Benzyl Alcohol Method

A.3.1 Autoclave Synthesis

In a Teflon autoclave, 0.1029 g (0.5 mmol) strontium acetate, 0.2043 g (1 mmol) aluminium isopropoxide and 20 mL benzyl alcohol is stirred. Upon dissolution, the autoclave is sealed and placed in a muffle furnace at 200°C for 72 hours. When the autoclave is naturally cooled to room temperature, the reaction mixture is centrifuged and the white precipitation is washed 3 times with diethyl ether. The precipitation can be dried in air or the surface can be modified. For modification, the precipitation is suspended in chloroform with 100 μ L oleic acid. The cloudy suspension is purified by precipitating with acetonitrile and re-suspending in chloroform (repeat 3 times).

The autoclave synthesis can vary in reaction time (48 - 168 hours) and reaction temperature (200°C-260°C). Instead of strontium acetate, basic aluminium acetate (0.1621 g) can be used as aluminium precursor.

A.3.2 The Karmaoui Synthesis

In the glovebox, 0.1551 g (1.77 mmol) metallic strontium in a 25 mL glass vial with 20 mL benzyl alcohol is stirred and heated to 90°C for 15 hours (overnight). When the metallic strontium is completely dissolved, the temperature is lowered to 50°C. 0.8456 g (4.14 mmol) aluminium isopropoxide is added and the vial brought out of the glovebox. The reaction mixture is introduced in a Telfon autoclave and put under inert argon atmosphere. The autoclave is sealed and placed in the muffle furnace at 275°C for 48 hours. When the autoclave is naturally cooled to room temperature, the reaction mixture is centrifuged.^{44,15} The precipitation is three times washed with diethyl ether (2000 rpm, 2') and two times washed with chloroform (4000 rpm, 4') to remove all organic waste. The sheeny white precipitate can be dried in air or the surface can be modified. For modification, the precipitate is redissolved in 4 mL chloroform with 200 μ L 2-[2-(2-Methoxyethoxy)ethoxy]acetic acid (MEA).

The particles can also be modified with oleyl amine and oleic acid using the same protocol but this results in a less stable suspension (less material is stabilized).

A.3.3 Microwave Synthesis of Strontium Aluminate

In a 5 mL microwave tube, 0.1029 g (0.5 mmol) strontium acetate, 0.2043 g (1 mmol) aluminium isopropoxide and 5 mL benzyl alcohol is stirred. The tube is introduced in the microwave and submitted to a microwave heating program of 50° C (5'), 100° C (5'), 150° C (5'), 200° C (5') followed by the reaction step at 250°C for 10 hours. After completion the reaction mixture is centrifuged and washed 3 times with diethyl ether. The white precipitation can be dried in air or the surface can be modified. For modification, the precipitation

is suspended in chloroform with oleic acid. The cloudy solution is purified by precipitating with acetonitrile and re-suspending in chloroform (repeat 3 times).

The microwave synthesis can be varied in the use of precursors. Instead of strontium acetate, (0.0438 g) metallic strontium can be used when working in a glovebox. Instead of aluminium isopropoxide, (0.1621 g) basic aluminium acetate can be used.

A.3.4 Microwave Synthesis of Hafnium Oxide

The precursor preparation is executed in a 10 mL microwave vial under argon gas flow. Under vigorous stirring, 0.5 mL of dibenzyl ether is added to 0.13 g (0.4 mmol) of hafnium chloride in a 10 mL microwave vial. Then quickly, 4 mL of benzyl alcohol is added, yielding a clear and colorless solution after 5 minutes of stirring with the aid of the ultrasonic bath. The solution is subjected to microwave heating with the following temperature settings: 5 minutes at 60°C and 3 hours at 220°C. After synthesis, the phase-separated mixture is transferred to a plastic tube and 3 mL of diethyl ether is added. After mild centrifugation (2000 rpm, 2'), two clear and transparent phases are observed. The organic (top) phase is removed, and ethanol is added to the aqueous (bottom) phase, yielding 2 mL of a clear suspension. The particles are precipitated and washed once with diethyl ether. Finally, the particles are either redispersed in chloroform, and typically, 50 μ L oleic acid and 50 μ L oleyl amine are added to transform the milky suspension to a clear suspension. The particles can be purified by adding a non-solvent (acetonitrile or acetone), followed by centrifugation and resuspension in chloroform.⁷³ Alternatively the particles are dried at the air for XRD and PL-measurements.

The titanium doped hafnium oxide nanocrystals are synthesized according the same recipe but the percentage of added titanium is subtracted from the quantity of hafnium chloride. Titanium butoxide is used as precursor which is added in a 4%, 0.5% and 0% (blanco) concentration.

A.3.5 Microwave Synthesis of Zirconium Oxide

The precursor preparation is executed in a 10 mL microwave vial under argon gas flow. Under vigorous stirring, 0.5 mL of dibenzyl ether is added to 0.13 g (0.56 mmol) of hafnium chloride in a 10 mL microwave vial. Then quickly, 4 mL of benzyl alcohol is added, yielding a clear and colorless solution after 5 minutes of stirring with the aid of the ultrasonic bath. The solution is subjected to microwave heating with the following temperature settings: 5 minutes at 60°C and 4 hours at 220°C. After synthesis, the phase-separated mixture is transferred to a plastic tube and 3 mL of diethyl ether is added. After mild centrifugation (2000 rpm, 2'), two clear and transparent phases are observed. The organic (top) phase is removed, and ethanol is added to the aqueous (bottom) phase, yielding 2 mL of a clear suspension. The particles are precipitated and washed once with diethyl ether. Finally, the particles are redispersed

in chloroform, and typically, 50 μ L oleic acid and 50 μ L oleyl amine are added to transform the milky suspension to a clear suspension. The particles can be purified by adding a nonsolvent (acetonitrile or acetone), followed by centrifugation and resuspension in chloroform.⁷³ Alternatively the particles are dried at the air for XRD and PL-measurements.

The titanium doped hafnium oxide nanocrystals are synthesized according the same recipe but the percentage of added titanium is subtracted from the quantity of hafnium chloride. Titanium butoxide is used as precursor which is added in a 4% concentration.

A.4 Non-aqueous Surfactant Assisted Method

A.4.1 The Kovalenko Precursor

In a 50 mL flask, 0.6400 g (4.8 mmol) anhydrous aluminium chloride, 12 mL methanol (production of gaseous hydrochloric acid) and 4.54 mL (14.4 mmol) oleic acid is stirred. Under vigorous stirring, 36 mL of a 0.4 mol/L (14.4 mmol) sodium hydroxide solution in methanol is added dropwise. After 1 hour, the reaction mixture is transferred to a plastic tube and centrifuged, 3 times washed with methanol and dissolved in hexane. The hexane phase is washed 3 times with water heated to 50°C by use of a separatory funnel. It si dried in air and under vacuum to obtain a waxy powder.⁶⁷

A.4.2 The Cabrera Precursor

In a 50 mL flask, 0.7014 g (12 mmol) sodium hydroxide, 6 mL water, 4.24 mL (12 mmol) oleic acid, 8 mL ethanol and 14 mL hexane is stirred. 0.5334 g (4 mmol) anhydrous aluminium chloride (production of gaseous hydrochloric acid) is added. The reaction mixture is refluxed for 4 hours at a temperature of 70°C. After cooling to room temperature, the organic phase is washed three times with water by the use of a separatory funnel. It is dried it in air and under vacuum to obtain a waxy powder.⁵⁴

A.4.3 Literature Based Thermal Decomposition

In a 50 mL three-necked flask, 2.0216 g (2.32 mmol) of the Kovalenko or Cabrera precursor, 0.732 mL oleic acid and 15 mL 1-octadecene is stirred. The flask is installed at the Schlenkline and is three times degassed (applying vacuum followed by introduction of argon) to remove air from the reaction mixture. The reaction mixture is heated to 320°C under vacuum, after 3 hours the reaction mixture is cooled down to room temperature and transferred to plastic tubes. Aceton is added, the precipitate is centrifuged at 3000 rpm for 3 minutes and the liquid phase is removed. Isopropanol is added and put in the ultrasonic bath for 10 minutes. The precipitate is centrifuged at 3000 rpm for 3 minutes and the liquid phase is removed. Aceton is added, the precipitate is centrifuged at 3000 rpm for 3 minutes and the liquid phase is removed.

phase is removed (repeat 3 times). The obtained precipitate is dried in air or suspended in chloroform.

A.4.4 Aluminium Oleate Precursor

In a 25 mL glass vial, 2.026 g (12.5 mmol) basic aluminium acetate and 9.5 mL (37.5 mmol) oleic acid is stirred. The vial is heated to 150°C under vacuum for two days and cooled to room temperature.

A.4.5 Aluminium Oleate Precursor Stock Solution

In a 50 mL three-necked flask, 2.026 g (12.5 mmol) basic aluminium acetate, 9.5 mL (37.5 mmol) oleic acid and 25 mL 1-octadecene in stirred. The flask is installed at the Schlenkline and is three times degassed (applying vacuum followed by introduction of argon) to remove air from the reaction mixture. The reaction mixture is heated to 150°C under vacuum, after 6 hours the reaction mixture is cooled to room temperature.

When it is made from aluminium isoproposide, 2.5531 g (12.5 mmol) is added and heated to 120° C.

A.4.6 Aluminium Oleate Precursor

In a 50 mL three-necked flask, 2.5531 g (12.5 mmol) aluminium isopropoxide, 9.5 mL (37.5 mmol) oleic acid and 25 mL toluene is stirred. The flask is installed at the Schlenkline and is three times degassed (applying vacuum followed by introduction of argon) to remove air from the reaction mixture. The reaction mixture is heated to 100°C under argon atmosphere, after 3 hours the reaction mixture is cooled to room temperature. The reaction mixture is recast in a 25 mL glass vial and put in an oven at 75°C for 2 weeks with frequently bursting the surface to evaporate all the solvent.

A.4.7 Thermal Decomposition Synthesis

In a 50 mL three-necked flask, 2.75 mL of the aluminium oleate precursor stock solution and 22.5 g trioctylphosphine oxide (TOPO) is stirred. The flask is installed at the Schlenkline, heated to 70°C to melt the TOPO and degassed three times (applying vacuum followed by introduction of argon) to remove air from the reaction mixture. The temperature is increased to 410°C. After 3 hours, the reaction mixture is cooled down to 80°C and transferred to plastic tubes. Aceton is added, the precipitate is centrifuged at 4000 rpm for 4 minutes and the liquid phase is removed (repeat 3 times). The obtained precipitate is dried in air or suspended in chloroform.

A.4.8 Alcoholysis Synthesis

In a 50 mL three-necked flask, 2.75 mL of the aluminium oleate precursor stock solution, 2.50 mL (6 equivalents) oleyl alcohol and 20 g trioctylphosphine oxide (TOPO) is stirred. The flask is installed at the Schlenkline, heated to 70°C to melt the TOPO and degassed three times (applying vacuum followed by introduction of argon) to remove air from the reaction mixture. The temperature is increased to 320°C. After 3 hours, the reaction mixture is cooled to 80°C and transferred to plastic tubes. Aceton is added, the precipitate is centrifuged at 4000 rpm for 4 minutes and the liquid phase is removed (repeat 3 times). The obtained precipitate is dried in air or suspended in chloroform.

A.4.9 Aminolysis Synthesis

In a 50 mL three-necked flask, 2.75 mL of the aluminium oleate precursor stock solution, 2.50 mL (6 equivalents) oleyl amine and 20 g trioctylphosphine oxide (TOPO) is stirred. The flask is installed at the Schlenkline, heated to 70°C to melt the TOPO and degassed three times (applying vacuum followed by introduction of argon) to remove air from the reaction mixture. The temperature is increased to 320°C. After 3 hours, the reaction mixture is cooled to 80°C and transferred to plastic tubes. Aceton is added, the precipitate is centrifuged at 4000 rpm for 4 minutes and the liquid phase is removed (repeat 3 times). The obtained precipitate is dried in air or suspended in chloroform.

Appendix B

Techniques

B.1 Thermogravimetric Analysis - Differential Thermal Analysis

These techniques are thermal analysis techniques that provide information about the various reactions at the completion of the thermal process.

ThermoGravimetric Analysis (TGA) measures the mass loss of the sample which is plotted as a function of the temperature.

Differential Thermal Analysis (DTA) is a technique in which a reference sample and the sample of interest is given the same amount of heat. The difference in temperature between the reference and sample is plotted as a function of the temperature. TGA and DTA can therefore be recorded simultaneously. In an exothermic reaction, the temperature of the sample will increase which is displayed in the thermogram by a peak. For an endothermic reaction a valley is then obtained.²⁹

For TGA-DTA analysis a Netsch Model STA 449 F3 Jupiter system was used.

B.2 Dynamic Light Scattering

Dynamic Light Scattering (DLS) is an analysis technique in which the particle size and the particle distribution of a suspension is determined on the basis of interaction with a laser beam. A monochromatic helium-neon laser with a wavelength of 633 nm is used as radiation source. Before the radiation enters the sample, it is reduced with the aid of a size attenuator. When light interacts with a particle, scattering will occur (see figure B.1).²⁹

Both the intensity and the scattering angle are influenced by the particle size. In case of relatively small particles (d = λ / 10), the intensity in all directions is uniform. By making



Figure B.1: Possible interactions of light with a particle.

use of Rayleigh (elastic) scattering, it can be derived that the measured scattered intensity (I) is proportional to the diameter of the particle (d) and inversely proportional to the wavelength of the beam (λ) (see equation B.1).²⁹

$$I \sim d^6 \sim 1/\lambda^4$$
 (B.1)

When the particle size approaches the wavelength, a complex function is obtained with several minima and maxima. In reality, the rate of diffusion of the particles is measured. Depending on the movement of the particles the interference pattern will vary and the detected intensity will undergo a change in a very short time scale. Small, fast diffusing particles will cause rapid fluctuations in intensity. In contrast to large, slow diffusing particles which will cause a slower fluctuation of the intensity. The fluctuation of the scattered light will be displayed by using the correlation function given by equation B.2.²⁹

$$G(t) = \frac{1}{\beta} \left(\frac{I(t) * I(0)}{I(t)^2} - 1 \right)$$
(B.2)

In this β is a constant determined by the available optical elements and I(t) is the intensity at time t. If there is a monodisperse distribution, equation B.3 holds.²⁹

$$G(t) = A(1 + Be^{-tDq^2})$$
(B.3)

A represents the baseline of the correlation function, B is the intercept of the correlation function, D is the diffusion coefficient and q is the scattering vector. The scattering vector q is shown in equation B.4, where η is the refractive index of the medium, λ the wavelength of the incident light in vacuum and θ the angle of the scattering.²⁹

$$q = \frac{4\pi\eta}{\lambda}\sin(\frac{\theta}{2}) \tag{B.4}$$

On the basis of the data correlation functions it is possible to determine the diffusion coefficient. If the diffusion coefficient is known, it is possible to determine the particle size via the Stokes-Einstein relation, given by equation B.5. In the Stokes-Einstein equation k_B represents the Boltzmann constant, T the temperature, ν the viscosity of the medium and R_h the hydrodynamic radius of the particle.²⁹

$$D = \frac{k_B T}{6\pi\nu R_h} \tag{B.5}$$

When these calculations are performed, the particle diameter is shown as a function of the intensity. Since the measurements obtain the hydrodynamic radius, it is impossible to know the exact particle size. Namely, the hydrodynamic radius is the radius of the particle and its surrounding mantle.²⁹

The above equations are only valid if there two assumptions are met. Namely, (1) the particles should be spherical and (2) they undergo a Brownian motion. Brownian motion is the random movement of the particles as a result of bombardment by the solvent molecules that surround them. The Brownian motion is related to the diffusion coefficient. It is important to carry out the measurements at a constant temperature because it influences both the viscosity and the Brownian motion.²⁹

The source and the equipment which is responsible for the image formation are positioned relative to each other in a fixed angle of 90° or 173° . Both of these set-ups are shown in figure B.2.²⁹



Figure B.2: The key elements of a DLS system are (1) the laser, (2) the measurement cell, (3) the detector, (4) the attenuator, (5) the correlator and (6) data handling computer. Detectors can be placed at either 90° or at a 173° angle.

When an angle of 173° is employed, there may be a wider interval for the measured concentration. Since the particles are measured close to the cuvette's wall, the scattered light will take a shortcut through the sample thus avoiding multi-scattering. As a result, it is possible to measure higher concentrations, with respect to the 90° set-up. The scattered light is collected by a photomultiplier.²⁹

For dynamic light scattering (DLS) measurements, a Malvern Nano ZS was used in backscattering mode (173°) .

B.3 X-Ray Diffraction

X-Ray Diffraction (XRD) analysis is a technique that can determine the texture of a thin film or powder, as well as the crystal structure of a material on the basis of the obtained reflections.

If an X-ray descend on an atom, the incident beam is scattered uniformly in all directions. If the material, which is irradiated with X-rays, is amorphous, the scattered rays will exhibit destructive interference in all directions and disappear. If there is an order in the material (i.e. being crystalline), the scattered rays will exhibit in certain directions constructive interference. Although this mathematical model is difficult to describe, it is similar to X-ray reflections at series of parallel planes in a crystal. The orientation of a set of parallel atomic planes with respect to the unit cell and the interplanar spacing are determined by the Miller indices. In order to obtain constructive interference on a plane with equally spaced atoms, the angle of the incident light and the outgoing beam should be equal. To obtain constructive interference at a set of parallel planes, the phase difference between the outgoing rays are equal to an integer times the wavelength (Bragg's Law). This is described mathematically in equation B.6 and is illustrated in figure B.3.^{16,74}

$$2d_{hkl}\sin\theta = n\lambda\tag{B.6}$$

In this formula, d_{hkl} is the distance between the lattice planes, θ the angle of the exiting beam with respect to the lattice plane, n is an integer and λ is the wavelength.^{16,74}



Figure B.3: Principle of diffraction according to Bragg's Law.

In the source, X-rays are generated by accelerating electrons in an electric field (for a copper anode typically 9 kV) to strike the anode material. A hot tungsten filament is used as electron source. An X-ray source is shown schematically in figure B.4.^{16,74}



Figure B.4: Schematically representation of a X-ray source.

The interaction of the electron with the anode material gives rise to two types of X-radiation. Bremsstrahlung is generated by the inelastic interaction when the electron collides with an anode atom. As a result, the electron is delayed and sends the excess energy out as a photon, illustrated in figure B.5 at the left. Characteristic radiation is obtained when the incident electron strikes an electron from one of the inner shells of the anode atom away, followed by relaxation. During this relaxation an electron from a higher shell is filling the vacancy in the inner shell. In this relapse a photon is emitted whose wavelength is correlated with the energy difference between the higher and the lower shell, illustrated in figure B.5 at the right.^{16,74}



Figure B.5: Schematically representation Bremsstrahlung (left) and characteristic radiation (right).

The generated X-ray spectrum consists of the continuous Bremsstrahlung with superposed very strong intensities of the characteristic wavelengths as illustrated in figure B.6. Because diffraction is typically performed with a single wavelength (typically the most intense K α -wavelength), a part of the spectrum is eliminated with the aid of a suitable filter.^{16,74}



Figure B.6: The X-ray spectrum of copper with a nickel absorption filter.⁷⁴

The goniometer is the technical platform on which the source, the detector and the sample are mounted. There are two types of goniometers, the θ -2 θ and the θ - θ goniometer. With the θ -2 θ deployment, the source is fixed and the sample and detector are rotated with a θ and 2θ angle respectively. With a θ - θ deployment, the sample position is fixed and both the source and the detector are rotated with a θ angle, as depicted in figure B.7.^{16,74}



Figure B.7: Illustration of the θ - 2θ deployment (left) and the θ - θ deployment (right).

For the detectors a first distinction can be made between those that detect all photons regardless of the wavelength and detectors which are capable of detecting photons of a particular wavelength. An example of the first type are scintillator detectors. In these detectors the X-ray photon is in phase with a scintillator crystal frequency. This results in the fluorescence of the crystal and the crystal emits light that can be detected by a photomultiplier and is transformed into an electrical signal. Because these detectors detect all incident X-rays, there must be a monochromator in front of the detector in order to let only the desired wavelength through. At very intense reflections, it is possible that the monochromator also allows other characteristic wavelengths. This gives rise to forbidden reflections.^{16, 74}

Depending on the geometry of the X-rays, there are two types of geometry of the radiation beam: the Bragg-Brentano geometry (see figure B.8 left) and the parallel beam geometry (see figure B.8 right). With the Bragg-Brentano geometry the X-ray beam starts to diverge before diffraction and converge back on the detector. In this geometry it is of crucial importance that the distance between the source and the sample is exactly the same as between the sample and the detector. In addition also the height of the sample plays a role. In a parallel beam geometry a parallel X-ray beam is created with the aid of a parabolic mirror. This mirror can also serve as a monochromator. In this geometry the mutual distances and the height of the sample play no major role, but the resulting intensities are lower.^{16,74}



Figure B.8: Illustration of the Bragg-Brentano geometry (left) and the parallel beam geometry (right).

For X-ray diffraction (XRD) characterization, a Thermo Scientific ARL X'tra X-ray diffractometer was used with the Cu K_{α} line as the primary source.

B.4 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is a surface analytical technique that allows to examine the morphology of a layer. For this purpose, the surface of the sample is scanned point by point with a primary electron beam. By interaction of these electrons with the sample surface radiation will be emitted under various forms. These different forms of interaction are shown in figure B.9.⁷⁵



Figure B.9: Illustrations of the potential interaction of the primary electron beam with the sample.⁷⁵

A first type of interaction is the reflection of the primary electron beam through elastic collisions. These reflected electrons are referred to as backscattered electrons and have an energy that is approximately equal to that of the primary electrons. When inelastic collisions occur between the sample and the primary electrons or the backscattered electrons, electrons from the outer shell of the sample atoms may be washed away. The obtained electrons are then referred to as secondary electrons. These electrons have a much lower energy than the backscattered electrons and can therefore only escape from the top layer (about 5 nm depth) of the material, in contrast to the backscattered electrons which may escape from the bulk (about 100 nm depth) of the material.⁷⁵

As mentioned earlier in XRD analysis, the interaction between the sample atoms and the primary electrons also gives rise to X-rays. Again, one obtains two types of radiation: continuous Bremsstrahlung and the characteristic X-rays. The characteristic radiation includes information about the chemical composition of the sample. When the obtained X-rays, in turn, interact with the sample, the possibility exists to generate secondary fluorescence of the material.⁷⁵

A final occurring interaction is the emission of Auger electrons. When an electron from an atomic inner shell of the sample is washed away, this vacancy is normally filled by an electron coming from a higher shell free of characteristic X-rays. However, it is possible that the excess energy is released in the form of an electron, in this case called Auger electrons.⁷⁵

In principle, all of the above mentioned interactions may be used to characterize the material. However, in practice, the imaging in SEM is usually based on the secondary electrons. In practice, two types of electron sources are used frequently. The first type relates to the thermionic electron sources. Here, a metal (e.g.tungsten) is heated in such a way to free electrons from the metal by obtaining sufficient energy to leave the metal. These electrons are then accelerated towards the anode. Another type of ion source is the LaB₆ source. However, this source requires a higher vacuum and this is more expensive, but it gives higher brightness and smaller beam diameter than the tungsten source.⁷⁵

The second type concerns the Field Emission Gun (FEG). Here the electron beam is obtained by the application of a strong electric field between the tungsten tip and the first anode. The second anode, which is on the desired voltage, allows for the acceleration of the electrons. The different sources are displayed on figure B.10. The accelerating voltage at SEM is typically 30kV.⁷⁵

FEG source has the same important advantages over the thermionic electron sources. They deliver higher efficiency and better image clarity. Also, a greater resolution is obtained since the diameter of the obtained primary electron bundle and consequently the energy spread is smaller.⁷⁵



Figure B.10: Illustration of different primary electron sources. (a) a tungsten filament, (b) a LaB_6 tip and (c) a field emission gun (FEG).⁷⁵

The electron beam originating from the source is focused by means of different electromagnetic lenses and coils. The condenser lens provides for a narrowing of the electron beam, while the objective lens allows for the focusing of the beam on the specimen. The position of the beam on the sample is determined with the aid of grid coils which can deflect the electrons. Figure B.11 shows a schematic representation of the imaging in SEM.⁷⁵



Figure B.11: Schematic representation of the imaging in SEM.⁷⁵

As mentioned earlier, through interaction of the primary electron beam with the sample, secondary electrons are released and only these will be used for imaging. The released secondary electrons are detected by a scintillator (Everhardt-Thornley detector). By the impact of electrons flashes of light are generated in this scintillator, which is transferred to a photomultiplier via a light pipe. The obtained electric signal is digitally saved. For old models, the electric signal is then transported to the cathode ray tube. When the primary electron beam describes a raster and the electrical signal synchronously is fed to the cathode ray tube, a greatly magnified image of the surface structure of the sample can be obtained. The measured intensity at any point on the surface is correlated to the obtained gray value of that point on the screen. The obtained amount of secondary and backscattered electrons is highly dependent on the irradiation angle ϕ and to a lesser extent on the atomic number Z (small composition contrast). In addition, the contrast is also obtained by the location of the detector (see figure B.12). On the right side of rough surface ('mountain') will escape

many of the backscattered electrons (small irradiation angle), but these will not be able to reach the detector. On the other side of the 'mountain', they have yet to be sent to the additional detector by the slope. Through this imaging and detection a resolution of 1 nm can be achieved.⁷⁵



Figure B.12: Illustration on the origin of different intensity (contrast) of a SEM image.⁷⁵

B.5 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is a microscopy technique in which a primary electron beam incident on a (ultra) thin specimen and interacts while they are being transmitted. The accelerating voltage for TEM is about 100 to 300 kV, yielding a very small wavelength (0.0037 nm) of the electrons, resulting in a much higher resolution than in light microscopes or SEM. The same electron sources as with SEM are used for obtaining a primary electron beam (W-tip, LaB₆ or FEG). Again, any of several types of interactions can occur, but because of the very high accelerating voltage and the minimal thickness of the sample (about 100 nm) most of the electrons will be transmitted. The scattering obtained by the interaction of the electron beam with the specimen can be both forward and backward. With TEM, logically, the forward scattered electrons are used for analysis. The way in which the electrons are scattered, moreover, can then be done in several ways. This is illustrated in figure B.13: (1) coherent, this preserves the phase relationships; (2) incoherent, change of the phase relations; (3) elastic, the primary electron does not lose its energy; (4) inelastic, in the case of inelastic interaction of the electrons with the atoms to exhibit a measurable loss of energy.⁷⁵

Inelastic interactions are the basis for a variety of signals (such as X-rays, EELS, SE, CL,...) and beam damage. Moreover inelastic interactions are inconsistent and have a low scattering angle ($\theta < 1^{\circ}$). If these scattered electrons can pass through the objective aperture, they provide a background noise. In view of the energy losses of the electrons, consequently a larger chromatic aberration is obtained.⁷⁵



Figure B.13: Illustration on the origin of the different scatter possibilities which can occur during TEM imaging.⁷⁵

Elastic scattering is the dominant component in the total scattering process which occurs during a TEM analysis, in addition, it is one of the most important sources for contrast formation and change of intensity in diffraction mode. This kind of scattering can be understood by looking at the wave character of an electron.⁷⁵

Particle character: electron interactions cause a relatively low scattering angle and are principally a function of the applied accelerating voltage. The higher the accelerating voltage, the less interaction. Nucleus interaction results in a higher scattering angle, which is generally incoherent. Above about 5° can this kind of elastic scattering be considered inconsistent. This is promoted by the presence of atoms having a larger atomic number, lower accelerating voltages and greater thickness of the specimen.⁷⁵

Wave character: the electric wave can interact with different atoms in a crystalline specimen resulting in coherent scattering (diffraction). The diffraction is again described by Bragg's law.⁷⁵

In order to focus the electron beam on the specimen and on the phosphor screen electromagnetic lenses are used just as with SEM. These lenses consist of a copper coil inside an iron pole shoe. In addition, they are stationary but their strength can be varied by changing the current intensity through the coil. When an electron moves through this magnet, it will undergo a spiral movement as a result of the Lorentz force, so the image is rotated. This, however, is corrected in the current TEM architecture. In these electromagnetic lenses the field is homogeneous to the extent that it is weak in the center and it becomes stronger closer to the wall. Electrons near the center will thus be less strongly deflected.⁷⁵

The lenses can't be regarded as perfect lenses as described above. It is in fact not the case that all the rays coming from one point in the object plane also come back into the same focal point on the image plane. The lens errors occurring are (1) Spherical aberration, due to the homogeneous magnetic field described above, electrons are deflected more strongly to the wall than in the center. This results in a series of different focal points whereby the point source is depicted as a zone of minimum confusion with a certain diameter. These are circular holes in a metal disk in microscale. This allows the reduction of disk of minimum confusion but the beam current is also reduced. A too small aperture may give rise to a different lens error namely diffraction patterns. We therefore need an optimum to be found for the used aperture angle. In current TEM architectures an additional so-called C_s -correction is introduced; (2) Chromatic aberration, the energy beam obtained by the source will have a certain energy range. Electrons of different energies at the same location in a lens will also result in different forces whereby again a disk of minimum confusion is obtained; (3) Astigmatism, an electromagnetic lens which is used in TEM is not perfectly spherical. As a result the focus point is displayed oval instead of spherical, this again gives rise to a disk of minimum confusion.⁷⁵

The imaging in TEM can be done in two different ways: diffraction mode or imaging mode. In each case forward scattering takes place due to the interaction of the electron beam and the electrons are collected on the phosphor screen. In Imaging Mode the objective lens is brought into focus on the first intermediate imaging plane, which is used in turn as an object right in front of the magnifying lenses. Rays coming from a certain point in the object plane are focused to a point in the image plane. The scattering of the electrons by interaction with the specimen results in a non-uniform distribution of electrons coming from the specimen. This is the basis of the contrast producing mechanism. Contrast can be described as the distribution of the base signal, which is the brightness. There may be appearing different types of contrast: mass / thickness, diffraction and phase contrast. A mass / thickness contrast is due to differences in the atomic number, density and thickness of the sample, visualized in figure B.14.⁷⁵

The areas of the sample that are thicker or have a higher atomic number will cause proportionally more scattering. By introducing a specimen under the objective aperture, these scattered electrons will be filtered as it were, thereby giving these zones will have a dark colour. A consequence of this is that a smaller aperture has the effect of a greater mass / thickness contrast. This principle of imaging is known as Bright Field Imaging. However, it is also possible to form on image on the basis of the scattered electron beam (high θ), then we speak of Dark Field Imaging.⁷⁵

Transmission electron microscopy (TEM) images are taken on a JEOL JEM-2200FS TEM with Cs corrector.



Figure B.14: Illustration on the effect of mass and thickness on the intensity of the TEM signal.

B.6 Infrared Spectroscopy

Infrared (IR) spectroscopy is an indirect spectroscopic technique based on electromagnetic (EM) radiation in order to obtain information about the structure and composition of molecules. Molecules are characterized by electronic, vibrational and rotational states. In IR spectroscopy, one only has to consider the vibrational states within the electronic ground state.^{29, 76, 77}

A chemical bond is an equilibrium situation with a minimum of energy D_0 at a distance of r_e between the two atoms. The vibrational motion of a chemical can be described with a potential energy surface (PES) within the anharmonic oscillator model, called the Morse potential (see figure B.15). Each level is characterized by a vibrational quantum number ν .^{29,76,77}



Internuclear Separation (r)

Figure B.15: Schematic illustration of the Morse potential (anharmonic oscillator model) and a fitted parabolic oscillating harmonic curve with the different vibrational states.⁷⁶ To induce transitions between these vibrational states, one needs IR radiation from the mid-IR range, which has a wavelength between 3 and 60 μ m. One has to consider only the vibrational transitions from the ground state, as approximately only the vibrational ground state is populated. The most intense transition is the transition from ν_0 to ν_1 . The transitions to ν_2 and ν_3 , etc... are called the overtones and are less intense.^{29,76,77}

When a sample is irradiated with mid-IR radiation, the energy is absorbed by the vibrational motion of the molecules, when the frequency of the IR radiation is equal to the frequency of the vibrational motion. In this case, the oscillating electric field of the EM radiation is in resonance with the oscillating electric field of the dipole of the bond. This means that only vibrational motions with a change in electrical dipole moment are IR active and lead to an absorption peak in the IR spectrum. There are different types of vibrational modes, namely stretch, in-plane bend and out-of-plane bend vibrations. However, not all of these vibrational modes will be IR active, as explained before.^{29, 76, 77}

One can distinguish four regions in the IR spectrum, as illustrated in figure B.16. In region 1, one expects single bond vibrations with hydrogen. Region 2 contains the conjugated double bond vibrations, diazo, alkyn and nitril vibrations. In region 3, one can find carbonyl functions and double C-C bond vibrations. Region 4 is the fingerprint area, this region often shows peaks corresponding to molecular vibrations and is best interpreted together with the complementary Raman spectroscopy technique.^{29,76,77}



Figure B.16: The IR spectrum can be divided in four regions, each with their specific characteristic peaks.

An IR-spectrum is obtained by plotting the percentage of transmission as a function of the wave number between 400 and 4000 cm⁻¹. When the intensity of the incident and exiting light beam is measured, its transmission percentage can be calculated using equation B.7.^{29,76}

$$\%T = \frac{I}{I_0} * 100\% \tag{B.7}$$

with I and I_0 the intensity of the incoming and outgoing beam respectively.^{29,76}

B.7 Excitation and Emission

The emission and excitation spectra can be determined by making use of an accurate spectrometer fitted with the necessary monochromators. The emission spectrum is measured under standard continuous illumination of the sample. The wavelength of the excitation light can be chosen between approximately 250 nm and 800 nm. This wavelength range is derived from the usable emission spectrum of the exciting xenon arc lamp. The excitation wavelength is fixed and the detector measures the sequential emission at different wavelengths. If the measurement takes place under continuous illumination of the specimen, the fluorescence spectrum is being measured and not the persistent emission spectrum. Both of these are often very similar but not always coincident. The detection of the persistent spectrum is less easy since, in the ideal case, this require a quasi simultaneous measurement of all the wavelengths which is not possible with the used set-up. After switching off the excitation and a certain period of time, the emission intensity is limited but still present and decreases very slowly as a function of time. When repeating several times a rapid cyclus of excitation and followed by measuring, a good persistent emission spectrum can be obtained.⁷⁸

The excitation spectrum is obtained by varying the wavelength of the excitation light and simultaneously measure at a fixed wavelength. This type of measurement gives rise to the excitation spectrum with respect to fluorescent emission. However, the excitation spectrum for phosphorescent emission can deviate from this type of measurement.⁷⁸

To measure the excitation and emission spectrum a Edinburgh FS920 fluorescence spectrometer is used.

B.8 Persistent Luminescence

In addition to the previously discussed emission and excitation spectrum, is the afterglow of the phosphor of crucial importance for determining the quality and usefulness. The afterglow of decay time is defined as the time after stopping excitation before the intensity of the emitted light reach the 0.32 mcd/m^2 (milli candela per square meter) border. This limit is a frequently used threshold which corresponds approximately to 100 times the sensitivity of the human eye.⁷⁸

With the aid of the Edinburgh FS290 spectrometer the decay curve can be measured for a fixed emission wavelength. The disadvantage, this method yields an intensity in arbitrary unit and no value for the decay time can be defined. The possibility of quasi instantaneously detection of the decay after excitation is again an advantage of this spectrometer.⁷⁸

The measurement set-up which is mainly used in this thesis makes use of the calibrated photometer ILT 1700 International Light Technologies. The advantage of this arrangement is

the ability to measure absolute values of the intensity (e.g. expressed in candela per square meter). For this, a conversion of the measured spectral intensity to an absolute measurement value is needed which is characteristic for the full spectrum. This conversion is carried out with the aid of a standard photopic filter which takes the eye sensitivity curve into consideration in the photopic vision. During the experiment, the specimen is excited with an unfiltered xenon arc lamp of 1000 lux. After excitation, the powder must be properly positioned in front of the detector, either the specimen or the detector can be moved to this respect. At a consequence, the first few seconds of afterglow are not be measured.⁷⁸

In addition to the decay curve time (defined o the basis of the threshold value of 0.32 mcd/m^2), also other methods can be used to characterize the persistent luminescence (aferglow) decay. One tries to fit the afterglow to an exponential function, or combination of exponential curves, or to a power function. The persistent decay can rarely be described by a single exponential function and the endless combinations of exponential functions provide little meaningful information.⁷⁸

Appendix C

Suggested Mechanisms

C.1 The Nature of Defects

In this section we will give a short review on the defects²⁹ that can be present in the lattice of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphor in order to explain the suggested mechanisms described in the following sections.

Lattice defects and impurities introduce localized states in the band gap of the semiconductor or insulator due to the interruption of the long range translational symmetry of a perfect lattice. Through these lattice defects, ionic solids are able to trap holes and electrons in vacant ion sites. Two main defect categories exist: intrinsic and extrinsic defects. Intrinsic defects do not change the overall composition of the lattice (stoichiometric defects). There are two kinds of intrinsic defects: Schottky and Frenkel defects. Schottky are vacancies in the lattice and preserve the (local) electrical neutrality, shown in figure C.1. Frenkel defects are vacancies created because the ion, mostly a cation because they are much smaller than anions, moved to an interstitial position, shown in figure C.1.



Figure C.1: Schematic representation of (left) a Schottky defect and (right) a Frenkel defect.

Extrinsic defects occur when foreign elements are intentionally (doping) or unintentionally (impurity) build in on a lattice position. A divalent metal ion vacancy, e.g. a strontium vacancy, is considered as a point defect with a double negative charge in respect to a perfect lattice and is often symbolized with the Kröger-Vink notation. In a similar reasoning, an oxygen vacancy forms a double positive charge. Both vacancies types can trap charge carriers, electrons in the case of positive charge vacancies and holes in the case of negative charge vacancies.

C.2 Mechanisms

Since the discovery of persistent luminescence a theory that described the underlying mechanism of these phosphorescence materials was needed. Until then it was generally accepted that charge carriers could get caught by trap levels by exciting the material with for example UV-radiation. Study on these trap levels was preformed on the basis of thermoluminescence glow curves and how to derive information on the trap depth.

When Matsuzawa et al. announced the discovery of $SrAl_2O_4:Eu^{2+},Dy^{3+}$, different mechanisms where proposed varying from basic to very complex ones. In this section we discuss the most important mechanisms which have been proposed to described the long afterglow duration of persistent luminescence.

C.2.1 The Matsuzawa model

In 1996, Matsuzawa et al.²⁴ announced the discovery of a green emitting $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphor with very bright and long lasting phosphorescent properties. Matsuzawa et al. tried to explain the underlying mechanisms based on the earlier proposed model by Abbruscato et al.⁷⁹ for the non codoped $SrAl_2O_4:Eu^{2+}$ by modifying it to include the enhancement of the codoping with trivalent dysprosium. A schematic picture of the Matsuzawa model is shown in figure C.2. The model is based on the photoconductivity study of powder samples which showed that UV irradiation induces a hole-type photoconductivity. By this, the existence of hole trapping has been suggested. The excitation of an electron from the 4f⁷-orbital to the 4f⁶5d¹-orbital by UV irradiation creates a hole in the 4f⁷-orbital. The valence band can absorb this hole, thus creating an Eu⁺ ion and transport it to a dysprosium doping site where it relaxes to a more stable state creating a Dy^{4+} ion in the crystal lattice. The hole can be released back to the valence band by ambient temperature. The hole can recombine and emit the phosphorescent radiation. However, the highly unlikely assumptions, such as the creation of Eu⁺ and Dy⁴⁺ ions, were pointed out later.^{11, 21}



Figure C.2: Persistent lumisnescence mechanism of SrAl₂O₄:Eu²⁺,Dy³⁺ proposed in 1996 by Matsuzawa et al.²⁶

C.2.2 The Aitasalo model

In 2001, Aitasalo et al.⁸⁰ suggested a new mechanism which described a two photon absorption. In 2003, Aitasalo et al.⁸¹ revised that mechanism, schematically shown in figure C.3. In this model an electron is directly excited from the valence band into trap levels of unknown origin (and unknown energy level) by the absorption of a photon. The created (positive) hole can migrate freely throughout the valence band until they are trapped by alkaline earth metal vacancies. The trapped electrons can, with thermal energy, end up at oxygen vacancies and recombine. Since the conduction band lies energetically much higher to enable thermal assisted transition, they assumed that the energy is delivered directly by means of energy transfer. This assumption introduced the requirement of close proximity between the vacancies and the luminescent centers. In this model only holes are assumed to be charge carriers which is in line with the measurements preformed by Matsuzawa et al. Aitasalo et al. explained the influence of the codoping by suggesting that they increased the number of lattice defects for charge compensation (trivalent positive ion on the position of a divalent positive one).^{11,21}

C.2.3 The Beauger model

In 1999, Beauger et al.⁸² proposed a mechanism for $SrAl_2O_4:Eu^{2+},Dy^{3+}$ similar to that of Aitasalo et al. In contrast to the Aitasalo model, the electrons are not transferred to oxygen vacancies but the delay of recombination is due to the entrapment of the holes solely by alkaline earth metal vacancies. With regard to codoping, Beauger et al. suggested that UV irradiation leads to a metal to metal charge transfer with the effect of delayed emission.²¹


Figure C.3: Persistent lumisnescence mechanism of CaAl₂O₄:Eu²⁺,Dy³⁺ proposed in 2003 by Aitasalo et al.²⁶

C.2.4 The Dorenbos model

In 2005, Dorenbos formulated a new groundbreaking mechanism, shown in figure C.4, which was based on his research on the position of the lanthanides energy levels relative to the valence and conduction band of various compounds including $SrAl_2O_4:Eu^{2+}, Dv^{3+83,84,85,86}$. According to him the existence of Eu⁺ and Dy⁴⁺ ions was highly improbable, just like Aitasalo et al.^{80,81} and Beauger et al.⁸² concluded. Moreover he argued the hole conduction mechanism proposed by Matsuzawa et al.²⁴ and the validity to interpret the excited 4f state of europium as a real hole which can accept an electron from the valence band. His previous research pointed out that the energy level of Dy^{2+} (Dy^{3+} after capture of an electron) in $SrAl_2O_4$ lies approximately 0.9 eV below the conduction band. Which equals the same order energy of the earlier proposed trap level of unknown origin. The excited electron of divalent europium can escape via the conduction band, making it a trivalent europium ion. This electron can be trapped by a dysprosium ion and needs thermal energy again to escape to the conduction band in order to relax back to the ground state by emitting electromagnetic radiation. This model also explains why there is a decrease of the luminescent properties when codoping the $SrAl_2O_4:Eu^{2+}$ with other lanthanides which have a stable divalent state (e.g. Sm^{3+} and Yb³⁺). The trapped electron cannot escape back to the conduction band by thermal energy because it is energetically too stable. However the model can not explain persistent luminescence in non-codoped materials.^{11,21}

C.2.5 The Clabau model

In 2005, Clabau et al.⁸⁷ reviewed all existing mechanisms for persistent luminescence and revised it during the next two years. They, as well as Dorenbos and Aitasalo et al., rejected the Matsuzawa model. By using electron paramagnetic resonance (EPR) measurements which showed a decrease in Eu^{2+} concentration during UV irradiation and an increase as soon as the irradiation was stopped until the afterglow ends. They concluded that Eu^{2+} participated in



Figure C.4: Persistent lumisnescence mechanism of SrAl₂O₄:Eu²⁺,Dy³⁺ proposed in 2005 by Dorenbos.²⁶

the trapping process, this contradicted the energy transfer idea of Aitasalo et al. The model, see figure C.5, differs in two aspects from the Dorenbos model.

A first difference, the transport of the electrons between the traps and the luminescent centers occur through direct transfer instead of through the conduction band, which implies a close proximity.⁸⁷ This assumption was based on photoconductivity measurements under UV irradiation. It increased up to 250K and reached a plateau at 300K, meaning no free charge carriers are released at this temperature. Thermoluminescent measurements at 300K showed detrapping processes which led to the conclusion that the interaction between trap and luminescent center did not occur through the conduction band.

A second difference is the influence of the codoping material⁸⁸ described by the model. The peak shapes of the glow curves of the codoped and non-codoped materials are similar. Clabau et al. concluded that the chemical nature of the trap is not influenced by codoping, meaning that the defects in the crystal lattice, described in section C.1, and not the (co)doped ions act as traps in the material. The role of the codopant is to stabilize the oxygen vacancies.⁸⁹ The stabilizing influence depends on the ionization potential of the codoped lanthanide. A lower ionization potential of the codopant causes a stronger attraction of the oxygen vacancies, resulting in an increased trap depth, prolonging the afterglow duration.^{11, 21}

C.2.6 The renewed Aitasalo model

In 2006, Aitasalo et al. in view of criticism proposed a new model of persistent luminescence which integrates the findings of Dorenbos and Clabau et al. with addition of a thermoluminescence study⁹⁰ and a study on the influence of defects⁹¹. The codopants do not change the position of the thermoluminescent peak, only its intensity. This model suggests that when the material is irradiated with UV radiation, electrons from the Eu^{2+} ground state are excited into the excited f-d state where they can escape to the conduction band, see figure C.6. These



Figure C.5: Persistent lumisnescence mechanism of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ proposed in 2007 by Clabau et al.²⁶

electrons can be trapped by an oxygen vacancy which is aggregated with a strontium vacancy as well as an RE^{3+} ion. No clear correlation was found between the trap depth and the and RE^{2+} and RE^{3+} ground energy levels, since these defects can interact with each other and form complex aggregates. The assumption was introduced that the electrons can migrate from one trap to another. When the electron relaxes back through the conduction band to the ground state, persistent luminescence is observed.^{11,21}



Figure C.6: Persistent lumisnescence mechanism of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ proposed in 2006 by Aitasalo et al.²⁶

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