

# Multisite formation in gadolinium doped SrF<sub>2</sub> nanoparticles

Andris Antuzevics\*, Meldra Kemere, Guna Kriekē  
Institute of Solid State Physics, University of Latvia

\* Corresponding author  
E-mail: andris.antuzevics@gmail.com

**Abstract.** Gadolinium doped SrF<sub>2</sub> nanoparticles have been synthesized by the precipitation method and characterized by site-selective optical spectroscopy and electron paramagnetic resonance (EPR) spectroscopy methods at cryogenic temperatures. The type of Gd<sup>3+</sup> centres present in SrF<sub>2</sub> is strongly dependent on the heat treatment parameters – the chosen temperature and gas composition during the annealing. Gd<sup>3+</sup> ions in SrF<sub>2</sub> annealed at temperatures up to 400 °C are mainly incorporated into sites with cubic symmetry. Higher annealing temperatures enable charge compensators to locate in a closer vicinity of the Gd<sup>3+</sup> ion lowering the site symmetry. Oxygen compensated Gd<sup>3+</sup> centres form after heating in air atmosphere, whereas for samples heated at an identical temperature in inert atmosphere interstitial fluorine ions serve as charge compensators. A comparison with previous studies of transparent glass ceramics containing SrF<sub>2</sub>:Gd<sup>3+</sup> shows similar patterns in gadolinium centre formation with the precipitated nanoparticles annealed in inert atmosphere here. The obtained results give a fundamental insight in trivalent defect formation mechanisms in nanostructured SrF<sub>2</sub> systems.

**Keywords:** nanostructured materials; point defects; gadolinium; electron paramagnetic resonance; optical spectroscopy; site-selective spectroscopy.

## Introduction

Due to the low phonon energies necessary for efficient luminescent performance fluorides serve as promising hosts for rare earth activators. In addition to that, strontium fluoride (SrF<sub>2</sub>) is also stable and non-hygroscopic, therefore, SrF<sub>2</sub> phosphors have attracted significant fundamental and practical interest. The recent advances in nanotechnology have stimulated in depth investigations of nanofluoride systems important for various technological applications. In particular, studies of singly and doubly doped SrF<sub>2</sub> nanoparticles show promising results for designing novel luminescent materials [1–4], thermoluminescent dosimeters [5], infrared radiation up-converters [6,7] and bioimaging nano-probes

[8,9]. Another field of growing interest is transparent glass-ceramic composites, where SrF<sub>2</sub> nanocrystals can be precipitated in a chemically and thermally stable glass matrix [10–17].

The seemingly simple cubic fluorite structure of SrF<sub>2</sub> offers a great diversity of possible ways to ensure charge neutrality when a trivalent rare earth ion substitutes the Sr<sup>2+</sup> ion. Based on the charge compensator's orientation the initial cubic crystal field symmetry around the impurity may be distorted, which in most cases also affects the optical properties of the site. Studies of electron paramagnetic resonance (EPR) spectra angular variations in single crystals have allowed to identify the possible site symmetries for gadolinium ions in SrF<sub>2</sub> [18–23]. The cubic site symmetry is retained only in the case if the charge compensation is not local [18]. A charge compensator in the vicinity of Gd<sup>3+</sup> ion causes an axial distortion in the crystal field – for example, an interstitial ion along the [100] direction lowers the site symmetry to tetragonal [19]. When co-doping SrF<sub>2</sub>:Gd with Na<sup>+</sup>, Li<sup>+</sup>, Rb<sup>+</sup> or Ag<sup>+</sup> formation of orthorhombic Gd<sup>3+</sup>-M<sup>+</sup> complexes is also possible [20]. Various Gd<sup>3+</sup> centres with trigonal site symmetry have also been observed in SrF<sub>2</sub> single crystals treated in different conditions [21–23]. The effect of crystal field symmetry on the Gd<sup>3+</sup> 4f<sup>7</sup> configuration energy level positions has been thoroughly investigated from experimental optical spectra measurements as well as theoretical calculations [24–29].

As can be seen, local structure of Gd<sup>3+</sup> in SrF<sub>2</sub> single crystals has been studied extensively, however, to our best knowledge, the formation of gadolinium centres has not been characterized in nanosized SrF<sub>2</sub> particles. Due to the half-filled 4f electron shell Gd<sup>3+</sup> serves as an excellent optical and paramagnetic probe to analyse the formation of different site symmetries. Ability to control site symmetry around the luminescent rare-earth ion could help to achieve the desired optical properties of nanostructured materials.

In this paper we report the multisite formation of gadolinium in nanocrystalline SrF<sub>2</sub> particles obtained by a simple precipitation method. The effect of heat treatment on Gd<sup>3+</sup> local environment is analysed. EPR and site-selective spectroscopy measurements at low temperatures reveal that the annealing temperature as well as the chosen gas composition during heat treatment procedure strongly influence Gd<sup>3+</sup> local structure.

## 1. Materials and methods

SrF<sub>2</sub> with 0.1 mol% Gd<sup>3+</sup> was synthesized using the precipitation method which is commonly used for obtaining nanostructured fluorides [30]. A total of 10 mmol of analytical grade SrCO<sub>3</sub> and Gd<sub>2</sub>O<sub>3</sub> were dissolved in concentrated HCl by heating at the boiling point. After cooling the system down 86 mmol of NH<sub>4</sub>F aqueous solution were added to the system dropwise causing the formation of white precipitates. The solution was mixed for 30 minutes, filtered, washed with water and dried at room temperature for 48 h.

Two sets of samples were prepared – the as prepared (AP) powder was annealed for 1 hour in either air or inert argon atmosphere. The sample abbreviation includes the annealing temperature and the gas composition during heating (A – air; I - inert). For example, A400 stands for the precipitated SrF<sub>2</sub> sample annealed at 400 °C in air atmosphere. The temperature precision during the annealing was estimated to be ± 20 °C.

SrF<sub>2</sub> crystalline phase was identified by X-ray diffraction (XRD) measurements with PANalytical X'Pert Pro X-ray diffractometer using Cu K<sub>α</sub> radiation (40 kV; 30 mA). The morphology of the samples was analysed by scanning electron microscopy (SEM) with Tescan Lyra microscope operated at 15 kV and transmission electron microscopy (TEM) with Tecnai G2 F20 microscope operated at 200 kV. The samples for TEM measurements were prepared as described in [31].

Photoluminescence spectra were measured by Andor DU-401-BV CCD camera coupled to Andor SR-303i-B spectrometer. Pulsed tunable solid state laser Ekspla NT342/3UV with pulse duration of 4 ns and linewidth of 4.3 cm<sup>-1</sup> was used as the excitation source. For low temperature measurements a cold finger type Advanced Research Systems DE202 N helium cryostat was used.

Conventional X-band ( $f \approx 9.18$  GHz with 0.001 GHz precision) spectrometer RE 13-06 was used for EPR spectra measurements at 77 K. The magnetic field was calibrated from the resonance line of polycrystalline DPPH standard at  $g = 2.0036 \pm 0.0002$ . Spectra simulations were performed in EasySpin simulation toolbox for MATLAB [32].

## 2. Results and discussion

### 3.1. Material characterization

XRD data of the prepared samples are shown in figure 1. All of the studied samples contain single phase SrF<sub>2</sub> with fluorite structure. Crystallography Open database [33] and Vesta software [34] were used for the calculated curve. The average crystallite size estimated from the 111 peak using the Scherrer equation [35] is  $\approx 20$  nm for the AP sample,  $\approx 30$  nm and  $\approx 35$  nm for the A400 and I400 samples respectively. After heat treatment at 800 °C rapid growth of the crystals is detected and microcrystals with average size of 200-300 nm are formed (see figure 2).

Electron microscopy analysis of the morphology of the samples is shown in figure 2. SEM image shows that the AP sample consists of nanosized plate-like structures. After the annealing the particle size increases. The morphology of the samples after heat treatment at the same temperature is similar for both A and I series, therefore, only one is shown here. TEM analysis in figure 2.d reveals that SrF<sub>2</sub> nanocrystals with the average size determined from XRD are typical, however, there are also regions consisting of smaller particles as well as some larger structures. The limited control of obtained particle size distribution is known to be a common disadvantage of the co-precipitation synthesis method [36].

The XRD data in combination with electron microscopy analysis confirm that the samples studied consist of single phase SrF<sub>2</sub> particles with the average size ranging from  $\approx 20$  nm for AP to several hundred nanometers for samples heated at 800 °C.

### 3.2. Optical spectroscopy analysis

Like most rare-earth elements, gadolinium incorporates materials in the 3+ valence state. The [Xe]4f<sup>7</sup> electron configuration leads to optical spectra consisting of relatively narrow f-f transitions. The ground state of Gd<sup>3+</sup> is <sup>8</sup>S<sub>7/2</sub>, which in the presence of external magnetic field can be split and studied by magnetic resonance spectroscopy. Characteristic <sup>6</sup>P<sub>7/2</sub> → <sup>8</sup>S<sub>7/2</sub> Gd<sup>3+</sup> photoluminescence is usually excited by UV radiation induced <sup>8</sup>S<sub>7/2</sub> → <sup>6</sup>I transitions [37–39]. An illustration of Gd<sup>3+</sup> 4f energy levels is given in figure 3.

Figure 4 shows photoluminescence spectra of SrF<sub>2</sub>:Gd<sup>3+</sup> samples under a 273 nm excitation measured at room temperature. Crystal field components of the <sup>6</sup>P<sub>7/2</sub> → <sup>8</sup>S<sub>7/2</sub> transition are sensitive to the sample treatment procedure – while the AP sample as well as the samples heated at 400 °C have similar spectra

to each other, the samples annealed at 800 °C have additional spectral features indicating the formation of new Gd<sup>3+</sup> centres.

To separate the contributions from multiple Gd<sup>3+</sup> sites selective laser excitation spectra measurements at 8 K were performed. The excitation (for  $\lambda_{em} = 312.7$  nm) and luminescence (for  $\lambda_{exc} = 275.6$  nm) spectra of the AP sample are shown in figure 5. The transitions in the excitation spectrum have been identified according to [26]. The  ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$  peak lacks structure if we compare it to the spectra of the annealed samples shown in figure 6. This effect is most likely caused by gadolinium ions distributed in slightly different environments after the precipitation leading to a luminescence behaviour one could expect from an amorphous system. The effect of Gd<sup>3+</sup> local structure disorder is also apparent in the EPR spectra in figures 7 and 8 analysed in the next section of the article.

Site-selective spectra of the samples annealed at 400 °C are shown in figure 6.a. As identified in the EPR section of the article the dominant contribution for both samples annealed at 400 °C comes from the cubic SrF<sub>2</sub>:Gd<sup>3+</sup> centre. The additional Gd<sup>3+</sup> position of the I400 sample has maximum emission at a lower wavelength value and could be caused by a fluorine charge compensator located closer to the impurity.

The A800 sample in figure 6.b has at least three different Gd<sup>3+</sup> sites. The line at 311.6 nm is similarly positioned as the second signal of the I400 sample. There are two new emission lines which are shifted to longer wavelengths by approximately 2 nm. As the sample was annealed in air atmosphere it is likely that those are due to strong crystal fields caused by O<sup>2-</sup> charge compensators in a close vicinity of Gd<sup>3+</sup> ions. Shift of  ${}^6P_{7/2}$  Stark manifolds for Gd<sup>3+</sup>-O<sup>2-</sup> centres to lower energies has been previously reported in SrF<sub>2</sub> and BaF<sub>2</sub> crystals [24]. If we compare absolute intensities of all three signals in the A800 sample, the line at 314.5 nm is an order of magnitude more intense than the other lines, which most likely indicates that this site is dominant after annealing SrF<sub>2</sub> at 800 °C in air atmosphere.

Site-selective spectroscopy results of the I800 sample are presented in figure 6.c. Multiple Gd<sup>3+</sup> sites have been detected, including the cubic SrF<sub>2</sub>:Gd<sup>3+</sup> signal as well as lower symmetry signals most likely caused by F<sup>-</sup> charge compensators in various orientations in respect to the gadolinium impurity. Further

interpretation on the formation of different Gd<sup>3+</sup> site symmetries based on EPR spectra analysis is continued in the next section of the article.

### 3.3. EPR analysis

The splitting of <sup>8</sup>S<sub>7/2</sub> ground state into Stark components is already achieved when Gd<sup>3+</sup> incorporates the lattice and from the EPR point of view is called zero field splitting (ZFS). ZFS sublevels are further split into a total of 8 components in the presence of external magnetic field as illustrated above in figure 3.

Thus, if the Zeeman splitting is much larger than ZFS (strong magnetic field case), 7 characteristic lines are expected in a typical Gd<sup>3+</sup> EPR spectrum. The resonance positions depend strongly on the local site symmetry around the impurity, therefore, Gd<sup>3+</sup> is an ideal paramagnetic probe to investigate activator local structure in solids [40]. The experimental EPR spectra shown in figure 7 consist of numerous resonances in a wide magnetic field range characteristic for a high spin system in a strong crystal field.

The EPR spectra of the AP as well as the A400 and I400 samples consist of a signal with a maximum at around 0.33 T. While this signal is still present in the I800 sample, another set of lines located at lower magnetic field values emerges after annealing the sample at 800 °C in inert atmosphere. Heat treatment in air atmosphere also produces new resonances in the EPR spectrum, however, they are caused by Gd<sup>3+</sup> ions in a different crystal field environment. Variations in the EPR spectra are in a good agreement with the changes in the photoluminescence spectra in figure 4.

The averaging of angle-dependent resonance positions in polycrystalline systems often leads to wide EPR spectra. In addition, there are several Gd<sup>3+</sup> site symmetries present in our samples resulting in spectra which are a superposition of all signals, therefore, an unambiguous interpretation is complicated.

We base EPR spectra analysis on simulations of the experimental curves with spin-Hamiltonian (SH) parameter sets available in literature obtained from single crystal SrF<sub>2</sub>:Gd studies [18–23,40,41]. In this article the SH notation from [42] in the absence of hyperfine structure has been adopted:

$$H = \beta B \cdot g \cdot S + \sum_{k,q} B_k^q O_k^q \quad (1)$$

where  $\beta$  is the Bohr magneton,  $B$  is the magnetic field value,  $S$  is the effective spin of the system and  $O_k^q$  – Steven operator equivalents. The adjustable parameters in EPR spectra simulations are the spectroscopic splitting factor  $g$  and ZFS parameters  $B_k^q$ . There is a lot of ambiguity and confusion in literature about the ZFS term and its parameters in the SH [43]. Here ZFS parameters  $B_k^q$  in the units of MHz are chosen as used in simulations with EasySpin [32].

First, we analyse the signal of the samples heated at 400 °C. When  $Gd^{3+}$  substitutes  $Sr^{2+}$ , the initial cubic site symmetry may be preserved if the charge compensator is located outside the nearest neighbourhood. In cubic symmetry the SH (1) can be reduced to [40,41]:

$$H = \beta B \cdot g \cdot S + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4 \quad (2)$$

Moreover, for cubic centres  $B_4^4/B_4^0 = 5$  and  $B_6^4/B_6^0 = -21$ . EPR spectra of  $SrF_2$  annealed in air atmosphere and a simulation with cubic  $SrF_2:Gd^{3+}$  centre parameters from [18] summarized in table 1 are shown in figure 8. The 6<sup>th</sup> order ZFS parameters have not been reported in [18]. For the samples heated at higher temperatures peaks become better resolved and their resonance fields match well with the simulation curve. The wider spectra of the samples annealed at lower temperatures could be explained by a slight ZFS parameter distribution, where each  $Gd^{3+}$  ion is located in a slightly different crystal field environment. A trace of the cubic signal is also present in the AP sample, however, a broad Gaussian-like curve superimposes the spectrum. Previous studies of gadolinium doped fluorite structure  $CeO_2$  nanoparticles have shown a contribution from at least three different paramagnetic centres in the EPR spectrum besides the cubic  $Gd^{3+}$  signal [44]. There is an additional signal in our AP sample at 0.1 T, which is absent in all of the annealed samples. A resonance at  $g_{eff} \approx 6$  is common for amorphous materials such as glasses [45–48]. In our case this signal could originate from  $Gd^{3+}$  ions with a disordered local environment possibly at the surface of the nanoparticles in the initially precipitated sample. Our results show that regardless of the gas composition predominantly cubic symmetry  $Gd^{3+}$  centres form when nanostructured  $SrF_2$  is annealed at relatively low temperatures.

As shown in the EPR spectra of figure 7, the chosen gas composition plays a critical role in the formation of  $Gd^{3+}$  centres in  $SrF_2$  if the annealing temperature is increased to 800 °C. At high temperatures the

efficiency of ionic diffusion in the lattice is increased [49], therefore, the charge compensators can locate closer to the  $Gd^{3+}$  impurity distorting the cubic site symmetry. Depending on the annealing conditions the charge compensator can be either  $O^{2-}$  or  $F^-$ . Our observation is validated from EPR spectra simulations in figures 9 and 10 as the resonance positions of the experimental signals can be simulated using SH parameters values previously reported for  $SrF_2:Gd$ .

The most intense features of the A800 spectrum in figure 9 can be simulated with the trigonal centre “T2” parameters from [22] and a trigonal site symmetry SH [40,41]:

$$H = \beta B \cdot g \cdot S + B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + B_6^0 O_6^0 + B_6^3 O_6^3 + B_6^6 O_6^6 \quad (3)$$

The weaker resonances of the A800 spectrum have been satisfactorily simulated using the tetragonal centre parameters from [19] and a tetragonal site symmetry SH [40,41]:

$$H = \beta B \cdot g \cdot S + B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4 \quad (4)$$

The above mentioned tetragonal centres with  $F^-$  charge compensators located along the [100] direction are dominant in the I800 sample. A contribution from the “weak” trigonal centres where the charge compensators are  $F^-$  ions oriented in the [111] direction [21] has also been identified from spectra simulations.

All  $SrF_2:Gd^{3+}$  centres observed in this study and their simulation parameters are summarized in table 1. The annealing temperature after which the corresponding EPR spectrum is first observed has been determined with a precision of 50 °C.

Table 1. A summary of  $Gd^{3+}$  centres observed in  $SrF_2$  nanoparticles.

$SrF_2:Gd^{3+}$ centre	Annealing conditions	SH	SH parameters	Reference
Cubic	As prepared	(2)	$g = 1.992$ $B_4^0 = 2.05$ MHz $B_4^4 = 10.25$ MHz	[18]
T2 trigonal	600 °C (air atmosphere)	(3)	$g = 1.991$ $B_2^0 = -1814$ MHz $B_4^0 = 1.12$ MHz $B_4^3 = -28.7$ MHz $B_6^0 = -0.0005$ MHz $B_6^3 = -0.0071$ MHz $B_6^6 = -0.0024$ MHz	[22]
Tetragonal	600 °C (inert atmosphere) 750 °C (air atmosphere)	(4)	$g = 1.992$ $B_2^0 = -1218$ MHz	[19]



			$B_4^0 = -0.98$ MHz $B_4^4 = -7.34$ MHz $B_6^0 = -0.0023$ MHz $B_6^4 = 0.0095$ MHz	
Weak trigonal	750 °C (inert atmosphere)	(3)	$g = 1.992$ $B_2^0 = -151$ MHz $B_4^0 = 1.44$ MHz $B_4^3 = -40.8$ MHz $B_6^0 = -0.0007$ MHz $B_6^3 = -0.0024$ MHz $B_6^6 = -0.0071$ MHz	[21]

In precipitated SrF<sub>2</sub> nanoparticles cubic symmetry Gd<sup>3+</sup> centres are formed if the annealing temperature is relatively low. On the other hand, the results of our study suggest that lower symmetry centres, with the charge compensator located in the vicinity of Gd<sup>3+</sup>, are energetically more favourable and form when the samples are heated at higher temperatures. Previous studies of yttrium and barium fluoride systems have shown that thermodynamically unstable nanofluoride phases can be obtained using the co-precipitation synthesis method [50] and similar effects could be expected with the formation of metastable Gd<sup>3+</sup> centres in the investigated samples during the precipitation of SrF<sub>2</sub>. Additional experimental and first principle calculation studies could provide a better insight into the formation of different SrF<sub>2</sub>:Gd centres.

To summarize the results so far, we have observed that the cubic SrF<sub>2</sub>:Gd<sup>3+</sup> centre is dominant after annealing SrF<sub>2</sub> nanoparticles at 400 °C. After annealing at 800 °C in air atmosphere oxygen ions incorporate in the SrF<sub>2</sub> lattice mainly forming trigonal symmetry Gd<sup>3+</sup>-O<sup>2-</sup> centres. Oxygen ions create strong crystal field distortions causing a shift of optical transitions to longer wavelengths by a few nanometers. Heating in inert atmosphere at 800 °C produces at least 4 different Gd<sup>3+</sup> sites with similar optical properties, which are caused by interstitial F<sup>-</sup> charge compensators located in different positions of the SrF<sub>2</sub> lattice. A site-selective spectroscopy study at 77 K of europium doped SrF<sub>2</sub> nanoparticles reported two possible sites for Eu<sup>3+</sup> ions [3]. The ability to perform measurements at 8 K in combination with thorough EPR analysis with gadolinium probes in our study reveals that there are even more ways trivalent rare earth ion defects in nanostructured SrF<sub>2</sub> systems can be formed.

### 3.4. Comparison with gadolinium doped glass ceramics

In this section of the article we compare the obtained results with our previous study of gadolinium local structure in oxyfluoride glass ceramics containing SrF<sub>2</sub> nanocrystals [15]. Oxyfluoride glass ceramics are composite materials where fluoride nanoparticles are embedded inside an oxide glass matrix [51]. In principle this material class could combine the chemical and thermal stability as well as transparency of a glass with highly efficient luminescence properties from rare earth ions incorporated in fluoride nanoparticles, therefore, rare earth doped glass ceramics is a field of growing scientific and practical interest [10–17,52–56].

It has been reported that Gd<sup>3+</sup> incorporates SrF<sub>2</sub> and CaF<sub>2</sub> crystalline phases of glass ceramics in a cubic site symmetry [15,48]. In addition, increasing the annealing temperature in SrF<sub>2</sub> composition glass ceramic may also produce tetragonal symmetry fluorine ion compensated Gd<sup>3+</sup> sites [15], which correlates with the SrF<sub>2</sub> nanoparticles annealed in inert atmosphere here.

Figure 11 shows a photoluminescence spectra comparison of gadolinium doped oxyfluoride glass and glass ceramic containing SrF<sub>2</sub> [15] and the nanoparticles investigated here. The spectra were measured at room temperature using 273 nm excitation. The main contribution in the photoluminescence spectra of both the glass and glass ceramic comes from a relatively wide band located at around 312.4 nm. Based on the lack of structure of this signal we can conclude that it originates from Gd<sup>3+</sup> ions residing in the disordered matrix. There is a slight change in the peak shape after the precipitation of SrF<sub>2</sub> nanoparticles in the glass ceramic producing an additional maximum located at approximately 312.0 nm as for the SrF<sub>2</sub> nanoparticles annealed at 400 °C. Site-selective spectroscopy analysis of the glass ceramic sample is shown in figure 12. Gd<sup>3+</sup> ions in the amorphous and crystalline environments were selectively excited. Two distinct Gd<sup>3+</sup> luminescence spectra with sharp and narrow luminescence bands similar to the I800 data presented in figure 6.c characteristic of Gd<sup>3+</sup> ions in crystalline SrF<sub>2</sub> have been distinguished. In addition a relatively wide band originating from gadolinium ions in the glass matrix was observed. The two distinct Gd<sup>3+</sup> positions observed in the A800 sample in figure 6.b which we have identified as oxygen compensated gadolinium centres are absent in the glass ceramic sample. Although the glass ceramic composition is abundant with oxygen, these ions do not serve as charge compensators for Gd<sup>3+</sup> in the SrF<sub>2</sub> phase of glass ceramics. This could be explained by the phase separation phenomenon which

occurs in oxyfluoride glass ceramics – the crystalline phase is formed by fluorine compounds, whereas oxygen is contained in the amorphous phase of the glass ceramic [51].

This is an interesting result that two different systems – precipitated SrF<sub>2</sub> nanoparticles annealed in inert atmosphere and oxyfluoride glass ceramics containing SrF<sub>2</sub> nanocrystals annealed in air – show similar patterns in Gd<sup>3+</sup> site formation.

### 3. Conclusions

Gadolinium doped nanocrystalline SrF<sub>2</sub> particles have been obtained by the precipitation method and characterized by site-selective optical spectroscopy and EPR spectroscopy methods. Formation of at least 6 Gd<sup>3+</sup> centres has been detected, which can be controlled by varying the thermal treatment parameters – temperature and gas composition. Regardless of the chosen gas composition, Gd<sup>3+</sup> ions in SrF<sub>2</sub> annealed at temperatures up to 400 °C are embedded mainly in a cubic site symmetry. Higher annealing temperatures enable charge compensators to locate in a closer vicinity of the Gd<sup>3+</sup> ion lowering the site symmetry. For SrF<sub>2</sub> annealed in air atmosphere formation of oxygen compensated Gd<sup>3+</sup> centres occurs. Oxygen ions cause strong **crystal** field perturbations and shift the gadolinium <sup>6</sup>P<sub>7/2</sub> → <sup>8</sup>S<sub>7/2</sub> transition to longer wavelengths. A comparison with previous results reveals that incorporation of Gd<sup>3+</sup> in **SrF<sub>2</sub> crystalline phase of oxyfluoride** glass ceramics is similar to precipitated SrF<sub>2</sub> nanoparticles annealed in inert atmosphere.

### Acknowledgements.

Authors thank prof. Uldis Rogulis for valuable discussions and suggestions **and Dr. Krisjanis Smits for TEM measurements**. Financial support provided by Scientific Research Project for Students and Young Researchers Nr. SJZ/2017/2 realized at the Institute of Solid State Physics, University of Latvia is greatly acknowledged. Institute of Solid State Physics, University of Latvia as the Center of Excellence has received funding from the European Union's Horizon 2020 Framework Programme H2020-WIDESPREAD-01-2016-2017-TeamingPhase2 under grant agreement No. 739508, project CAMART<sup>2</sup>

### References

- [1] Y. Su, M. Liu, D. Han, L. Li, T. Wang, X. Wang, Ce<sup>3+</sup> and Ln<sup>3+</sup> (Ln = Dy, Eu, Sm, Tb) Codoped SrF<sub>2</sub> Nanoparticles: Synthesis and Multicolor Light Emission, *J. Nanosci. Nanotechnol.* 16 (2016) 3956–3960. doi:10.1166/jnn.2016.11861.

- [2] B. Ritter, P. Haida, F. Fink, T. Krahl, K. Gawlitza, K. Rurack, et al., Novel and easy access to highly luminescent Eu and Tb doped ultra-small CaF<sub>2</sub>, SrF<sub>2</sub> and BaF<sub>2</sub> nanoparticles - structure and luminescence, *Dalt. Trans.* 46 (2017) 2925–2936. doi:10.1039/C6DT04711D.
- [3] P. Cortelletti, M. Pedroni, F. Boschi, S. Pin, P. Ghigna, P. Canton, et al., Luminescence of Eu<sup>3+</sup> Activated CaF<sub>2</sub> and SrF<sub>2</sub> Nanoparticles: Effect of the Particle Size and Codoping with Alkaline Ions, *Cryst. Growth Des.* (2018) acs.cgd.7b01050. doi:10.1021/acs.cgd.7b01050.
- [4] M.Y.A. Yagoub, H.C. Swart, R.E. Kroon, E. Coetsee, Low temperature photoluminescence study of Ce<sup>3+</sup> and Eu<sup>2+</sup> ions doped SrF<sub>2</sub> nanocrystals, *Phys. B Condens. Matter.* (2017) 1–4. doi:10.1016/j.physb.2017.08.011.
- [5] M. Zahedifar, E. Sadeghi, M. Kashefi biroon, S. Harooni, F. Almasifard, Thermoluminescence dosimetry features of DY and Cu doped SrF<sub>2</sub> nanoparticles under gamma irradiation, *Appl. Radiat. Isot.* 105 (2015) 176–181. doi:10.1016/j.apradiso.2015.08.022.
- [6] M. Runowski, J. Marciniak, T. Grzyb, D. Przybylska, A. Shyichuk, B. Barszcz, et al., Lifetime Nanomanometry - High-Pressure Luminescence of Up-converting Lanthanide Nanocrystals - SrF<sub>2</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup>, *Nanoscale.* (2017). doi:10.1039/C7NR04353H.
- [7] J. Sun, J. Xian, X. Zhang, H. Du, Hydrothermal synthesis of SrF<sub>2</sub>:Yb<sup>3+</sup>/Er<sup>3+</sup> micro-/nanocrystals with multiform morphologies and upconversion properties, *J. Rare Earths.* 29 (2011) 32–38. doi:10.1016/S1002-0721(10)60396-1.
- [8] N.P. Singh, L.P. Singh, N.R. Singh, S.K. Srivastava, Photoluminescence properties of SrF<sub>2</sub>:3Tb@BaF<sub>2</sub> nanoparticles and improved hyperthermia temperature achieved by core-shell nanohybrid SrF<sub>2</sub>:3Tb@BaF<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> materials, *Colloid Polym. Sci.* (2018) 1–11. doi:10.1007/s00396-017-4257-8.
- [9] I. Villa, A. Vedda, I.X. Cantarelli, M. Pedroni, F. Piccinelli, M. Bettinelli, et al., 1.3 μm emitting SrF<sub>2</sub>:Nd<sup>3+</sup> nanoparticles for high contrast in vivo imaging in the second biological window, *Nano Res.* 8 (2015) 649–665. doi:10.1007/s12274-014-0549-1.
- [10] M. Walas, T. Lewandowski, A. Synak, M. Lapinski, W. Sadowski, B. Koscielska, Eu<sup>3+</sup> doped tellurite glass ceramics containing SrF<sub>2</sub> nanocrystals: Preparation, structure and luminescence properties, *J. Alloys Compd.* 696 (2017) 619–626. doi:10.1016/j.jallcom.2016.11.301.
- [11] Q. Luo, X. Qiao, X. Fan, S. Liu, H. Yang, X. Zhang, Reduction and luminescence of europium ions in glass ceramics containing SrF<sub>2</sub> nanocrystals, *J. Non. Cryst. Solids.* 354 (2008) 4691–4694. doi:10.1016/j.jnoncrysol.2008.07.019.
- [12] Q. Luo, X. Qiao, X. Fan, X. Zhang, Luminescence properties of Eu<sup>2+</sup>-doped glass ceramics containing SrF<sub>2</sub> nanocrystals, *J. Am. Ceram. Soc.* 93 (2010) 2684–2688. doi:10.1111/j.1551-2916.2010.03756.x.
- [13] X. Qiao, X. Fan, M. Wang, X. Zhang, Spectroscopic properties of Er<sup>3+</sup> and Yb<sup>3+</sup> co-doped glass ceramics containing SrF<sub>2</sub> nanocrystals, *J. Phys. D. Appl. Phys.* 42 (2009) 55103. doi:10.1088/0022-3727/42/5/055103.
- [14] C.R. Kesavulu, K. Kiran Kumar, C.K. Jayasankar, Upconversion properties of Er<sup>3+</sup> -doped oxyfluoride glass-ceramics containing SrF<sub>2</sub> nanocrystals, *SPIE Photonics West 2014-OPTO Optoelectron. Devices Mater.* 8987 (2014) 89871J. doi:10.1117/12.2039308.
- [15] A. Antuzevics, M. Kemere, R. Ignatans, Local structure of gadolinium in oxyfluoride glass matrices containing SrF<sub>2</sub> and BaF<sub>2</sub> crystallites, *J. Non. Cryst. Solids.* 449 (2016) 29–33. doi:10.1016/j.jnoncrysol.2016.07.015.
- [16] A. Antuzevics, M. Kemere, G. Krieke, R. Ignatans, Electron paramagnetic resonance and

- photoluminescence investigation of europium local structure in oxyfluoride glass ceramics containing SrF<sub>2</sub> nanocrystals, *Opt. Mater. (Amst)*. 72 (2017). doi:10.1016/j.optmat.2017.07.024.
- [17] A. Antuzevics, U. Rogulis, A. Fedotovs, A.I. Popov, Crystalline phase detection in glass ceramics by EPR spectroscopy, *Low Temp. Phys.* 44 (2018) 449–454.
- [18] J. Sierro, Paramagnetic resonance of Gd<sup>3+</sup> in SrF<sub>2</sub> and BaF<sub>2</sub>, *Phys. Lett.* 4 (1963) 178–180. doi:10.1093/jicru/ndp028.
- [19] W.-Q. Yang, Y. Zhang, Y. Lin, W.-C. Zheng, Spin-Hamiltonian parameters for the tetragonal centers in CaF<sub>2</sub> and SrF<sub>2</sub> crystals, *J. Magn. Reson.* 227 (2013) 62–65. doi:10.1016/j.jmr.2012.12.003.
- [20] E.J. Bijvank, A.G. Zandbergen-Beishuizen, H.W. Hartog, EPR of Orthorhombic Gd<sup>3+</sup>-M<sup>+</sup> Complexes in SrF<sub>2</sub>, *Solid State Commun.* 32 (1979) 239–244.
- [21] C. Yang, S. Lee, A.J. Bevolo, Investigations of the weak trigonal Gd<sup>3+</sup> ESR center in alkaline-earth fluoride crystals, *Phys. Rev. B.* 13 (1976) 2762–2767.
- [22] C. Yang, S. Lee, A.J. Bevolo, Investigations of two trigonal (T<sub>1</sub> and T<sub>2</sub>) Gd<sup>3+</sup> ESR centers in treated alkaline-earth-fluoride crystals, *Phys. Rev. B.* 12 (1975) 4687–4694.
- [23] S. Lee, C. Yang, A.J. Bevolo, Investigations of the new trigonal Gd<sup>3+</sup> ESR center produced in irradiated alkaline-earth fluoride crystals, *Phys. Rev. B.* 10 (1974) 4515–4522.
- [24] J. Makovsky, Optical Spectra of Gd<sup>3+</sup> in SrF<sub>2</sub> and BaF<sub>2</sub>, *J. Chem. Phys.* 46 (1967) 390–391. doi:10.1063/1.1840403.
- [25] P.P. Yaney, D.M. Schaeffer, J.L. Wolf, Fluorescence and absorption studies of Sr<sub>0.999-x</sub>Gd<sub>0.001</sub>Ce<sub>x</sub>F<sub>2.001+x</sub>, *Phys. Rev. B.* 11 (1975) 2460–2477.
- [26] J.A. Detrio, M.W. Ferralli, P.P. Yaney, D.M. Ware, V.L. Donlan, Concentration Study Determination of the 6 P, 6 I, and 6 D Energy Levels of Gd<sup>3+</sup> in SrF<sub>2</sub> at a C 4v Site, *J. Chem. Phys.* 53 (1970) 4372–4377. doi:10.1063/1.1673949.
- [27] J.M. O’Hare, J.A. Detrio, V.L. Donlan, Analysis of the Cubic Crystal-Field Parameters for Gd<sup>3+</sup> in the Alkaline Earth Fluorides, *J. Chem. Phys.* 51 (1969) 3937–3940. doi:10.1063/1.1672613.
- [28] J.A. Detrio, Line Strengths for Gd<sup>3+</sup> at a C4v Site in SrF<sub>2</sub>, *Phys. Rev. B.* 4 (1971) 1422–1427.
- [29] J.M. O’Hare, Calculations of the Spectra of SrF<sub>2</sub>:Gd<sup>3+</sup> in a Tetragonal Crystal Field, *Phys. Rev. B.* 3 (1971) 3603–3607.
- [30] P.P. Fedorov, A.A. Luginina, S. V. Kuznetsov, V. V. Osiko, Nanofluorides, *J. Fluor. Chem.* 132 (2011) 1012–1039. doi:10.1016/j.jfluchem.2011.06.025.
- [31] K. Smits, A. Sarakovskis, L. Grigorjeva, D. Millers, J. Grabis, The role of Nb in intensity increase of Er ion upconversion luminescence in zirconia, *J. Appl. Phys.* 115 (2014) 1–9. doi:10.1063/1.4882262.
- [32] S. Stoll, A. Schweiger, EasySpin, a comprehensive software package for spectral simulation and analysis in EPR, *J. Magn. Reson.* 178 (2006) 42–55.
- [33] S. Gražulis, A. Daškevič, A. Merkys, D. Chateigner, L. Lutterotti, M. Quirós, et al., Crystallography Open Database (COD): An open-access collection of crystal structures and platform for world-wide collaboration, *Nucleic Acids Res.* 40 (2012) 420–427. doi:10.1093/nar/gkr900.
- [34] K. Momma, F. Izumi, VESTA: A three-dimensional visualization system for electronic and

- structural analysis, *J. Appl. Crystallogr.* 41 (2008) 653–658. doi:10.1107/S0021889808012016.
- [35] A. Monshi, M.R. Foroughi, M.R. Monshi, Modified Scherrer Equation to Estimate More Accurately Nano-Crystallite Size Using XRD, *World J. Nano Sci. Eng.* 2 (2012) 154–160. doi:10.4236/wjnse.2012.23020.
- [36] M. Lin, Y. Zhao, S.Q. Wang, M. Liu, Z.F. Duan, Y.M. Chen, et al., Recent advances in synthesis and surface modification of lanthanide-doped upconversion nanoparticles for biomedical applications, *Biotechnol. Adv.* 30 (2012) 1551–1561. doi:10.1016/j.biotechadv.2012.04.009.
- [37] C.R. Kesavulu, H.J. Kim, S.W. Lee, J. Kaewkhao, E. Kaewnuam, N. Wantana, Luminescence properties and energy transfer from  $Gd^{3+}$  to  $Tb^{3+}$  ions in gadolinium calcium silicoborate glasses for green laser application, *J. Alloys Compd.* 704 (2017) 557–564. doi:10.1016/j.jallcom.2017.02.056.
- [38] Y.-C. Li, Y.-H. Chang, Y.-S. Chang, Y.-J. Lin, C.-H. Laing, Luminescence and Energy Transfer Properties of  $Gd^{3+}$  and  $Tb^{3+}$  in  $LaAlGe_2O_7$ , *J. Phys. Chem. C.* 111 (2007) 10682–10688. doi:10.1021/jp0719107.
- [39] Q. Su, Z. Pei, J. Lin, F. Xue, Luminescence of  $Dy^{3+}$  enhanced by sensitization, *J. Alloys Compd.* 225 (1995) 103–106.
- [40] H.A. Buckmaster, Y.H. Shing, A survey of the EPR spectra of  $Gd^{3+}$  in single crystals, *Phys. Status Solidi.* 12 (1972) 325–361. doi:10.1002/pssa.2210120202.
- [41] S.A. Al'tshulter, B.M. Kozyrev, *Electron Paramagnetic Resonance in Compounds of Transition Elements*, Wiley, 1974.
- [42] A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, 1970. doi:10.1017/CBO9781107415324.004.
- [43] C. Rudowicz, M. Karbowski, Disentangling intricate web of interrelated notions at the interface between the physical (crystal field) Hamiltonians and the effective (spin) Hamiltonians, *Coord. Chem. Rev.* 287 (2015) 28–63. doi:10.1016/j.ccr.2014.12.006.
- [44] R.M. Rakhmatullin, L.K. Aminov, I.N. Kurkin, R. Böttcher, A. Pöpl, S. Sen, Nature of size-dependent lattice distortions in doped  $CeO_2$ , *J. Appl. Phys.* 114 (2013). doi:10.1063/1.4834537.
- [45] B. Sreedhar, C. Sumalatha, K. Kojima, EPR and optical absorption spectra of some paramagnetic ions in lithium fluoroborate glasses, *J. Non. Cryst. Solids.* 192–193 (1995) 203–206. doi:10.1016/0022-3093(95)00438-6.
- [46] S. Rada, V. Dan, M. Rada, E. Culea, Gadolinium-environment in borate-tellurate glass ceramics studied by FTIR and EPR spectroscopy, *J. Non. Cryst. Solids.* 356 (2010) 474–479. doi:10.1016/j.jnoncrysol.2009.12.011.
- [47] M. Mohapatra, B. Rajeswari, N.S. Hon, R.M. Kadam, M.S. Keskar, V. Natarajan, An electron spin resonance and photoluminescence investigation of the effect of annealing temperature on Gd-doped  $La_2Zr_2O_7$  nano-ceramics, *Ceram. Int.* 41 (2015) 8761–8767. doi:10.1016/j.ceramint.2015.03.099.
- [48] A. Fedotovs, A. Antuzevics, U. Rogulis, M. Kemere, R. Ignatans, Electron paramagnetic resonance and magnetic circular dichroism of  $Gd^{3+}$  ions in oxyfluoride glass-ceramics containing  $CaF_2$  nanocrystals, *J. Non. Cryst. Solids.* 429 (2015) 118–121. doi:10.1016/j.jnoncrysol.2015.08.036.
- [49] H. Mehrer, *Diffusion in solids: fundamentals, methods, materials, diffusion-controlled processes*, Springer Ser. Solid-State Sci. (2007). doi:10.1007/978-3-540-71488-0.

- [50] P.P. Fedorov, M.N. Mayakova, S. V. Kuznetsov, V. V. Voronov, R.P. Ermakov, K.S. Samarina, et al., Co-precipitation of yttrium and barium fluorides from aqueous solutions, *Mater. Res. Bull.* 47 (2012) 1794–1799. doi:10.1016/j.materresbull.2012.03.027.
- [51] P.P. Fedorov, A.A. Luginina, A.I. Popov, Transparent oxyfluoride glass ceramics, *J. Fluor. Chem.* 172 (2015) 22–50. doi:10.1016/j.jfluchem.2015.01.009.
- [52] G. Krieke, A. Sarakovskis, M. Springis, Upconversion luminescence of a transparent glass ceramics with hexagonal Na(Gd,Lu)F<sub>4</sub> nanocrystals, *J. Alloys Compd.* 694 (2017) 952–958. doi:10.1016/j.jallcom.2016.10.156.
- [53] X. Fan, X. Qiao, D. Zhao, Q. Luo, X. Zhang, Nanocrystallization and photoluminescence of Ce/Dy/Eu-doped fluorosilicate glass ceramics, *J. Alloys Compd.* 511 (2012) 232–236. doi:10.1016/j.jallcom.2011.09.042.
- [54] R. Wang, D. Zhou, J. Qiu, Y. Yang, C. Wang, Color-tunable luminescence in Eu<sup>3+</sup>/Tb<sup>3+</sup> co-doped oxyfluoride glass and transparent glass-ceramics, *J. Alloys Compd.* 629 (2015) 310–314. doi:10.1016/j.jallcom.2014.12.233.
- [55] A.M. Kłonkowski, W. Wicz, J. Ryl, K. Szczodrowski, D. Wileńska, A white phosphor based on oxyfluoride nano-glass-ceramics co-doped with Eu<sup>3+</sup> and Tb<sup>3+</sup>: Energy transfer study, *J. Alloys Compd.* 724 (2017) 649–658. doi:10.1016/j.jallcom.2017.07.055.
- [56] M. Kemere, U. Rogulis, J. Sperga, Luminescence and energy transfer in Dy<sup>3+</sup>/Eu<sup>3+</sup> co-doped aluminosilicate oxyfluoride glasses and glass-ceramics, *J. Alloys Compd.* 735 (2018) 1253–1261. doi:10.1016/j.jallcom.2017.11.077.

Fig 1. XRD patterns of the studied samples.

Fig. 2. (a-c) SEM and (d) TEM images of the samples annealed at different temperatures.

Fig. 3. Illustration of  $Gd^{3+}$  4f shell energy levels.

Fig. 4. Room temperature photoluminescence spectra of the studied samples with 273 nm excitation.

Fig. 5. Low temperature site-selective spectroscopy excitation and photoluminescence spectra of the AP sample.

Fig. 6. Low temperature site-selective spectroscopy photoluminescence spectra of the (a) samples heated at 400 °C; (b) A800 sample; (c) I800 sample.

Fig. 7. Experimental EPR spectra of the studied samples at 77 K.

Fig. 8. EPR spectra shape comparison of the samples annealed in air atmosphere and simulation with the cubic  $SrF_2:Gd^{3+}$  centre SH parameters [18].

Fig. 9. Simulation of the A800 spectrum with trigonal “T2” [22] and tetragonal [19]  $SrF_2:Gd^{3+}$  centre SH parameters. The inset shows the defect model.

Fig. 10. Simulation of the I800 spectrum with tetragonal [19] and “weak” trigonal [21]  $SrF_2:Gd^{3+}$  centre SH parameters. Insets show the defect models.

Fig. 11. Room temperature photoluminescence spectra comparison of the samples studied here with gadolinium doped oxyfluoride glass ceramic containing  $SrF_2$  nanocrystals [15] with 273 nm excitation.

Fig. 12. Low temperature site-selective spectroscopy photoluminescence spectra of the gadolinium doped oxyfluoride glass ceramic containing  $SrF_2$  nanocrystals [15].