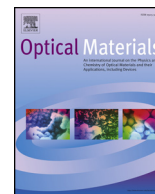




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journal homepage: www.elsevier.com/locate/optmatThe search for defects in undoped SrAl₂O₄ materialVirginija Vitola^{a,*}, Donats Millers^{a,b}, Krisjanis Smits^a, Ivita Bite^a, Aleksejs Zolotarjovs^a^a Institute of Solid State Physics, University of Latvia, Riga, Latvia^b ELGoo Tech, Latvia

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ABSTRACT

SrAl₂O₄:Eu,Dy is a very efficient long afterglow phosphor with wide range of possible applications. The luminescence properties and the possible luminescence mechanism of this material have been studied extensively, but there is almost no information available about the undoped material. Therefore, this article deals with the luminescence and thermally stimulated luminescence of an undoped SrAl₂O₄, revealing the possible defects that might be involved in the creation of the long afterglow in doped material. We conclude that undoped material exhibits some luminescence under X-ray irradiation in low temperature; close to room temperatures luminescence is almost fully thermally quenched in comparison to low temperatures. We can observe F and F₂ center luminescence as well as trace metal luminescence in the emission spectrum. TSL glow curve yields the peaks that are close to those observed in material with Eu and Dy doping; therefore these peaks are clearly related to intrinsic defects. The peak at around 400 K, that is shifting with rare earth doping, might be due to dopant interaction with intrinsic defects.

1. Introduction

The alkali-earth aluminates doped with Eu and some other rare earth as a co-dopant, for example, SrAl₂O₄: Eu, Dy, exhibit a very strong and long lasting luminescence. At least the 18 Eu doped compounds are known as long lasting (persistent) luminescence materials [1]. The luminescence from these materials covers blue to red region of visible spectrum, making them a very popular research subject during the last decade [1], [2]. There have been many different opinions on the mechanism governing the persistent luminescence in this material group [2–6], but the common opinion is that electrons are promoted from the occupied 4f levels of Eu²⁺ to the empty 5d levels located near to conduction band or even in the conduction band and some are then trapped at the intrinsic defect levels located in close proximity of the photo-generated Eu³⁺ cations. The characteristic luminescence of Eu²⁺ is then observed after the thermally assisted migration [2] or tunneling of the electron [6] to the luminescence center. That implies that there are some intrinsic defect levels in the material and these defects should also be present in undoped material.

Surprising is the lack of trustable information that can be found in literature about the luminescence of undoped SrAl₂O₄, that might be helpful in acknowledging the defects that participate in the long lasting luminescence process of the activated material. Most articles do not deal with the undoped material at all. There are several articles that report no detectable luminescence from the undoped material under UV

excitation [7], [8]. Some other articles describe a broad band emission with maximum at about 450 nm [9]. In one article sharp lines in the photoluminescence spectrum were observed [10], not characteristic for a solid material intrinsic defects, it seems the source of these lines might be some trace amount of transition metals or rare earths present in the material. As for different excitation sources - a broad, possibly complex, band luminescence revealing 450 and 500 nm maxima has been reported under X-ray irradiation [11] [12], that in our opinion could be the luminescence of SrAl₂O₄ intrinsic defects, however these bands are close to those known for Eu²⁺ in this material. Also, thermally stimulated luminescence (TSL) of an undoped SrAl₂O₄ after excitation with electrons has been reported in Ref. [13], although the spectrum of the luminescence within glow peak has not been published, leaving a question – what kind of luminescence was detected and what defects might be present in the material to act as trapping as well as recombination centers. To deal with these unclaritys and ambiguities, we have conducted a study on the luminescence of the undoped SrAl₂O₄ with different excitation sources and under different temperatures.

2. Experimental

Strontium nitrate (Sr(NO₃)₂, purity 98%, Sigma Aldrich), aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, purity 99,6%, VWR Prolabo Chemicals) were used as the starting materials. Urea (NH₂CONH₂, purity 99,5%, Sigma Aldrich) was used as a chelating and a complexing

* Corresponding author.

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agent. Analytical grade chemicals were used without any further purification. In the present work, non-doped SrAl_2O_4 was synthesized by sol-gel method. The appropriate amount of $\text{Sr}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in deionized water. After the $\text{Sr}(\text{NO}_3)_2$ and the $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved completely, an appropriate amount of urea was added to the solution (the molar ration of all metals ions and urea was 1:20, respectively). Also an appropriate amount of deionized water was added so the molar concentration of all metals ions in the solution would be 0.2 M. Then this mixture was heated at 90 °C until white gel was formed. When the gel consistence was obtained, then this gel was heated at 400 °C in an open oven for 2 h for nitric oxides elimination and white powder was obtained. After synthesis, obtained sample was calcined at 1200 °C for 2 h and white powders were obtained. The structure of non-doped strontium aluminate sample after heat treatment was characterized by X-ray powder diffraction (XRD, PANalytical X'Pert Pro diffractometer) using a cathode voltage of 45 kV and current of 40 mA with $\text{Cu K}\alpha$ radiation (1.5418 Å). The estimated grain size from the XRD data was 30 nm.

Photoluminescence excitation was carried out with optical parametric oscillator pulsed NT342/3UV EKSPLA laser (pulse length ~ 5 ns, repetition frequency 10 Hz). The samples were cooled down using Janis closed cycle refrigerator CCS-100 operating within temperature range ~9–325 K. The Lake Shore 331 Temperature controller was used for temperature control as well as for sample heating (6 deg/min) during thermally stimulated luminescence (TSL) measurements up to 320 K. A self-made heating equipment was used for TSL measurements within 295–650 K. Luminescence spectra were recorded using Andor Shamrock B303-I spectrometer. The integration time was set 1 ms for each spectrum recording. For radioluminescence measurements as well as for trap filling before TSL measurements the excitation source was X-ray tube with W target. The voltage of tube can be varied within 14kV–35kV and the current within 1–15 mA range, thus providing variable X-ray energy and intensity. The voltage and current were set 30 kV and 10 mA for radioluminescence spectra recording, as well as for trap filling for TSL measurements.

3. Results and discussion

3.1. Sample characteristics

The analysis of obtained XRD patterns of SrAl_2O_4 powder (Fig. 1) and the comparison of these XRD patterns with data from International Center for Diffraction Data (ICDD) Inorganic Crystal Structure Database [00-034-0379] confirms the dominant phase of the sample is

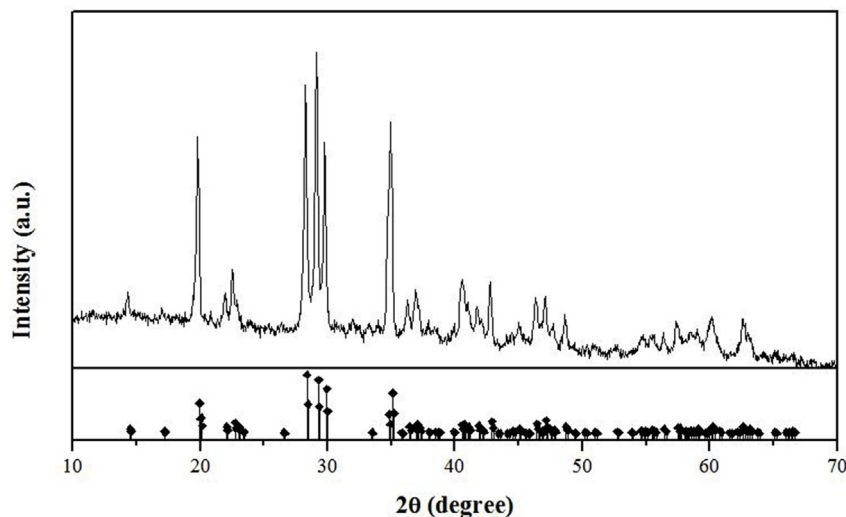


Fig. 1. The X-ray diffraction pattern of undoped SrAl_2O_4 , the data base pattern is shown underneath the experimental data.

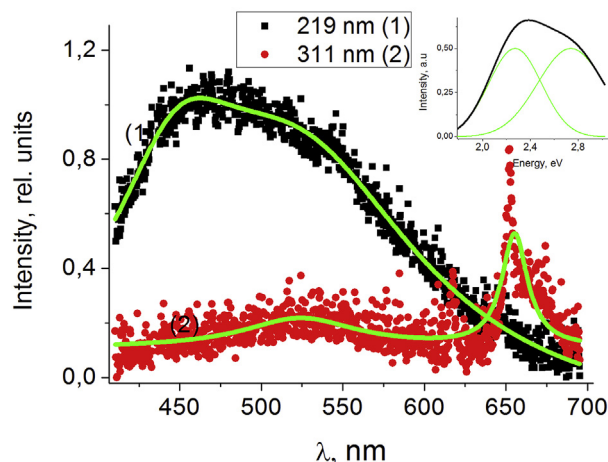


Fig. 2. Photoluminescence spectra at 10 K under different excitation wavelengths.

monoclinic SrAl_2O_4 , and other phases, if present, are under the limits of detection.

3.2. Luminescence of SrAl_2O_4

We recorded SrAl_2O_4 luminescence spectra at different temperatures. Fig. 2 shows photoluminescence spectra of the undoped sample under two different wavelengths laser excitation at 10 K temperature. Although the luminescence is not strong, there is a clearly distinguishable shape consisting of two bands peaking at 2.43 eV and 2.85 eV (510 and 435 nm) under 219 nm excitation and a 652 nm peak under 311 nm excitation. This narrow line probably is emission from Mn^{4+} since in Ref. [14] is shown that these transient metal ions in SrAl_2O_4 polymorphs are responsible for lines within 652–657 nm. As mentioned in Ref. [14], traces of transition metals are present even in material that has been synthesized from high purity grade precursor materials.

In search of the defects that are responsible for bands at 510 nm and 435 nm, we checked the available information on defect luminescence in Al_2O_3 . The luminescence of F^- centers in pure α - Al_2O_3 is at ~440 nm (2.8 eV) [15–17], in turn the luminescence of F_2^- centers is at 517 nm (2.4 eV) [18]. Important is the F_2^- centers luminescence band position is found the very close, even the same in both α - Al_2O_3 and γ - Al_2O_3 [19,20] showing weak influence from the structure. There is a strong possibility, that in the SrAl_2O_4 material these defects might

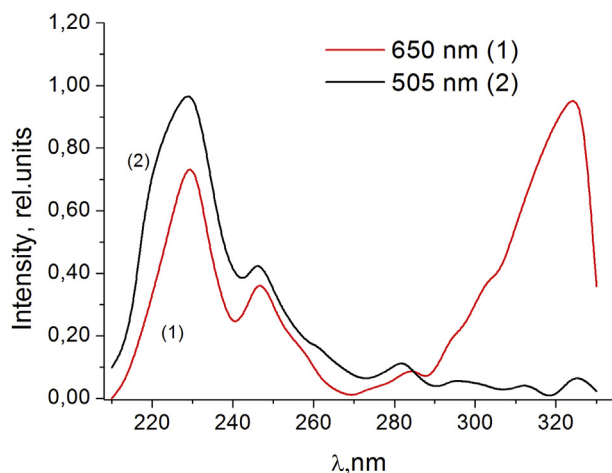


Fig. 3. Excitation spectra in two maxima of emission.

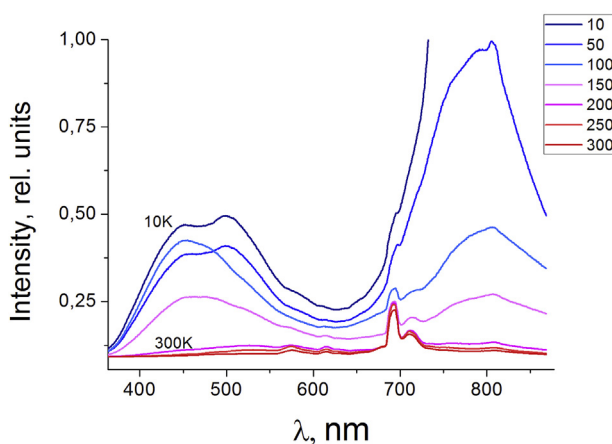


Fig. 4. X-ray induced luminescence at different temperatures (10–300 K).

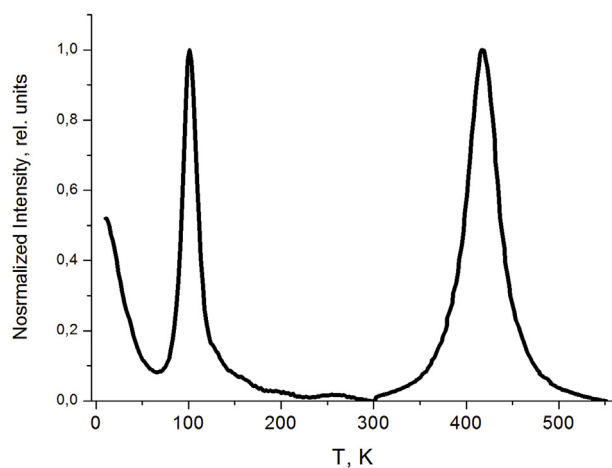


Fig. 5. TSL measurement at 790 nm (two measurements: 10–300 K and 300–700 K).

be present as well and the F – centers and F_2 – centers could be responsible for luminescence bands peaking at 440 nm and 510 nm.

The photoluminescence intensity at RT is low and equipment used was not sensitive enough for spectrum recording.

The excitation spectrum of photoluminescence (Fig. 3) shows excitation energies within 3.8–5.9 eV (\sim 330–210 nm). These energies are well below the band gap of $SrAl_2O_4$ matrix. The band gap of $SrAl_2O_4$ is

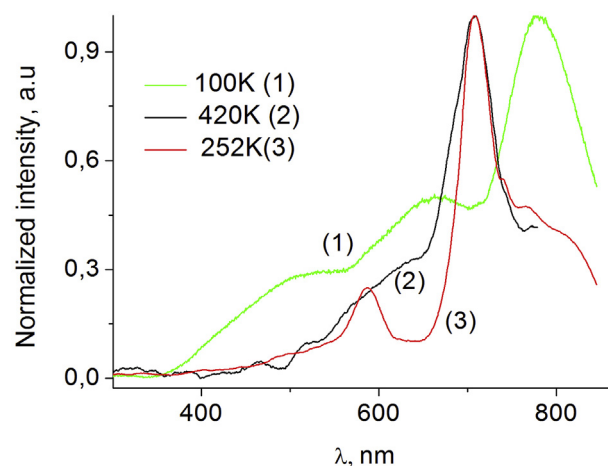


Fig. 6. Emission spectra during TSL measurement at 100, 252 and 420 K.

estimated to be around 6.6 eV [21], meaning that under laser excitation electron – hole pairs over the band gap were not created – therefore we can assume the presence of some defect levels in the band gap. Unfortunately, our equipment limits photoluminescence excitation spectra recording at wavelengths above 340 nm.

The 652 nm narrow band luminescence excitation peak close to the 325 nm could be related to Mn^{4+} excitation [14]. The two excitation peaks at \sim 230 nm and \sim 246 nm are common for the broad luminescence band at 500 nm and for the narrow band at 652 nm. Since the F – centers are probably responsible for the broad band luminescence and Mn^{4+} – for the narrow band at 652 nm, the same excitation bands for both exclude the direct excitation of these centers, we can assume that energy transfer takes place. The possible hypothesis would be as follows. The initial step of excitation could be the charge transfer between oxygen and F – or F_2 – center (excitation band peaking at \sim 229 nm), similar to that described for α - Al_2O_3 by Surdo et al. [15]. The other excitation band peaking at \sim 246 nm possibly is of the same nature, since both F – and F_2 – centers could be involved. The step where energy is transferred to Mn^{4+} needs a separate study. Therefore the photoluminescence spectra and corresponding excitation spectra show the intrinsic defects and trace impurity is present in $SrAl_2O_4$ sample. It will be noted the F – type centers can act as electron as well as hole traps. The study of charge traps in $SrAl_2O_4:Eu,Dy$ by Botterman et al. [22] showed that traps in vicinity of Eu ion are deeper than those at larger separation and it is possible that interaction of F-type centers with dopant ion changes the trap depth. Thus the incorporation of dopant somewhat is related to defects in the host. Therefore we propose the intrinsic defects are presented in rare earth doped $SrAl_2O_4$ also and incorporation of Eu^{3+} as well as followed reduction to Eu^{2+} can strongly depend on presence of F type centers.

The luminescence spectra under X – ray excitation differ from those under photo excitation. The main differences are in the longer wavelength region of the spectra and in the luminescence intensity. Under X-ray irradiation the luminescence spectrum at 10 K is more intense than that of photoluminescence and it was possible record the spectra at different temperatures (Fig. 4). There are clearly distinguishable maxima at 440 and 510 nm (similar that those in photoluminescence under laser 219 nm excitation) that decrease in intensity due to thermal quenching at RT. The wide and intense luminescence band at low temperatures was recorded within 650 nm–900 nm. This band quenches at RT; however, above 150 K a narrow band at 692 nm and a side band at 713 nm is revealed.

The relative narrow luminescence bands of Cr^{3+} are known to be within 650–850 nm for several aluminates as well as for Al_2O_3 [22–29]. Therefore the narrow bands recorded at 692 nm and 713 nm under X-ray irradiation are due to spin-forbidden ${}^2E - {}^4A_2$ transition in Cr^{3+} , at

low temperature these narrow bands are strongly overlapped with more intense 790 nm band. The Cr usually present in aluminum, therefore Cr can be incorporated in SrAl_2O_4 from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ that is used as the raw material in synthesis. The 790 nm band might also be attributed to Cr luminescence and this consideration is based on fact that in alkaline earth aluminate crystals Cr^{3+} ion substitutes two different crystallographic sites if substituting for Sr^{2+} [30], and also can substitute Al^{3+} , as the ionic radii of all the ions are quite similar. Therefore the X-ray excited luminescence confirms the presence of intrinsic defects responsible for overlapping bands between ~ 350 and 600 nm as well as presence of trace impurities in undoped SrAl_2O_4 .

The electron – hole pairs were created in SrAl_2O_4 under X – ray irradiation and at low temperatures these charge carriers could be trapped, thus the TSL measurements were conducted. The TSL curves show a well resolved maximum at 100 K, that appears also in the SrAl_2O_4 : Eu, Dy and SrAl_2O_4 : Dy material [31]. This can be attributed to the electrons release from intrinsic defects of the SrAl_2O_4 crystal. The weak glow peak was at ~ 260 K, at the same temperature the glow peak is in the rare earth doped SrAl_2O_4 [31]. The third well resolved peak is located above RT at around 400 K. This is also visible in the Eu and Dy doped material [31,32], although this peak is slightly shifted to lower temperatures when adding the dopants. As glow peaks at the similar temperatures were observed in rare earth doped and undoped SrAl_2O_4 , we would like to state that the defects that act as trapping centers in the long lasting luminescence of SrAl_2O_4 : Eu, Dy are intrinsic defects nearby to dopant, not the dopant impurities directly. The Dy co-doping clearly shifts the TSL peak at 400 K to lower temperature [31], suggesting that intrinsic defects could be perturbed by dopant or by trace impurities, thus contributing to more intensive afterglow.

Also, it is possible to see that the 790 nm peak exhibits an afterglow at low temperatures (Fig. 5). We have already stated in our former studies, that tunneling luminescence is present in SrAl_2O_4 and this afterglow of Cr^{3+} might also be related to creation of excited Cr^{3+} via electron tunneling.

When analyzing TSL spectra at different temperatures (Fig. 6), we can observe different spectra – and all of them might be explained with Cr and intrinsic defect luminescence. The spectrum recorded within 100 K glow peak reveals three broad luminescence bands peaking at 780 nm, 660 nm and around 500 nm. The long wavelength band is from Cr^{3+} spin-allowed transition ${}^4\text{T}_2 - {}^4\text{A}_2$ and ${}^4\text{T}_2 - {}^4\text{A}_1$ [27,28], the band at ~ 660 nm might be due to Cr^{3+} ${}^4\text{T}_2 - {}^4\text{A}_1$ transition, however other origin of this band cannot be excluded. The luminescence band peaking around 500 nm seems complex one however a good deconvolution on the components was not possible due to the strong overlap with the 660 nm band. As the luminescence band around 500 nm covers the same spectral range as X-ray induced luminescence bands of F – and F_2 – centers (Fig. 4) it could be that luminescence band around 500 nm is emerging from F – type centers. The support for this assumption is that F – centers luminescence was not quenched at 100 K (Fig. 4). As mentioned above the relatively narrow Cr^{3+} luminescence bands were overlapped with strong band peaking at 790 nm. This 790 nm band partially undergoes quenching at RT, and the narrow Cr^{3+} bands became dominant (Fig. 4). Within glow curve peaking at ~ 260 K the before mentioned narrow Cr^{3+} luminescence bands are also dominant (Fig. 6). The origin of luminescence band peaking at ~ 590 nm is unclear. Thus the narrow Cr^{3+} bands in TSL spectra above 150 K are dominant and origin of this luminescence is the electron recombination with Cr^{4+} . The spectrum above RT (420 K) shows similar features as the 252 K spectrum – with the Cr^{3+} emission as the dominant peak.

4. Conclusions

The analysis of luminescence is a helpful tool to understand the long lasting luminescence processes in Eu and Dy doped material. We report a clearly distinguishable luminescence of undoped SrAl_2O_4 material under X-ray excitation up to RT. The luminescence of undoped SrAl_2O_4

consists of two main parts – trace impurity metals, namely, Mn^{4+} and Cr^{3+} luminescence, and intrinsic defects luminescence – F – centers and F_2 – centers. The intensities of broad bands of this luminescence are low at RT due to partial quenching and narrow luminescence bands of Cr^{3+} became dominant. There is a strong possibility, that in the rare earth doped SrAl_2O_4 material these defects might be present as well and we propose that the presence of these defects is stimulating the Eu^{3+} ion incorporation. TSL shows two strong glow peaks – a peak under RT at ~ 100 K, emerging from intrinsic defects of the SrAl_2O_4 crystal and this peak also present in the doped materials, as well as a peak above RT at ~ 420 K, that might be attributed to the defects perturbed by trace impurities, and it is also present in the doped material, but its position depends on the dopant incorporation.

Acknowledgements

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