

SYNTHESIS OF $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ BY COMBUSTION METHOD AND INVESTIGATION ITS LUMINESCENCE PROPERTIES AT VARIOUS TEMPERATURES

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Safer and more energy effective Combustion synthesis method yields homogenic, stable phase and dimension phosphors and in contrast to more conventional solid-state reaction - a process that takes just 5-10 minutes. In order to get information on the crystal structure, X-ray diffraction analysis of the obtained luminescent material was conducted. The optical properties were explored by measuring emission and excitation spectra at room, low and high temperatures. We also have measured afterglow properties of these nanophosphors and compared their afterglow time with the results in literature.

Keywords: nanophosphor, combustion method .

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1. INTRODUCTION

Phosphors are the most important materials in lighting. In our work we used oxide based phosphor - $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ (1%) doped with divalent europium ion because of its high brightness, high chemical and thermal stability and low toxicity properties [1]. In this work we obtained these oxide phosphors by combustion method, as by this method oxide phosphors are prepared in a safer, energy-efficient way and in a short period of time [2]. Divalent Eu^{2+} is a widely applied rare earth element, which gives a very intense and broad emission band in the visible region [3]. Inter-configurational electronic $f^7(8s_{7/2})-f^6d$ transition causes broad emission band. Unlike 4f electrons the 5d electron is not shielded by the $5s^25p^6$ electrons, so their energy levels are split by the crystal field into t_{2g} and e_g components. At room and high temperatures there is only one broad emission band, but at low temperatures (e.g. 77-150K), emission spectrum is split into two bands. There are a lot of hypotheses for explaining this situation.

2. EXPERIMENTAL SECTION

All reagents were commercially purchased and used without further purification. For the synthesis, stoichiometric amounts of $\text{Sr}(\text{NO}_3)_2$ (99,99%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99,99%), $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99,99%), $\text{CO}(\text{NH}_2)_2$ (99,3%) and H_3BO_3 (99,9%) were dissolved together in 20ml of deionized water to obtain a transparent solution. Small amount of boric acid was used as flux and urea was used as fuel [4, 5].

The components were mixed together and the solution was stirred using a magnetic bar at 70°C for two hours. And in every 15 minutes the temperature of the solution was raised by 10°C up to 130°C. We got white viscous gel. The gel was placed in a preheated muffle furnace at 600°C. At this temperature the solution evaporated, generating large amounts of gases, e.g. oxides of carbon and nitrogen. The combustion process lasted for about 5 to 10 minutes and resulted in white ash. At the

next step, the precursor was annealed at 1000°C for 1 and 2 hours under an Ar /H₂ reductive atmosphere for the purpose reducing Eu^{3+} to Eu^{2+} .

Photoluminescence (PL) excitation and emission spectra were recorded between 77 and 350K on the FS 920 fluorescent spectrometer (Edinburgh Instruments) equipped with a Hamamatsu R928P red-sensitive photomultiplier (wavelength range from 200 to 850 nm). An Oxford Optistat CF cryostat was used to cover a measurement temperature range from 4 to 500K and to record the TL properties.

X-ray diffraction patterns were recorded using a Bruker 5000 diffractometer in standard θ -2 θ geometry using Cu K α radiation.

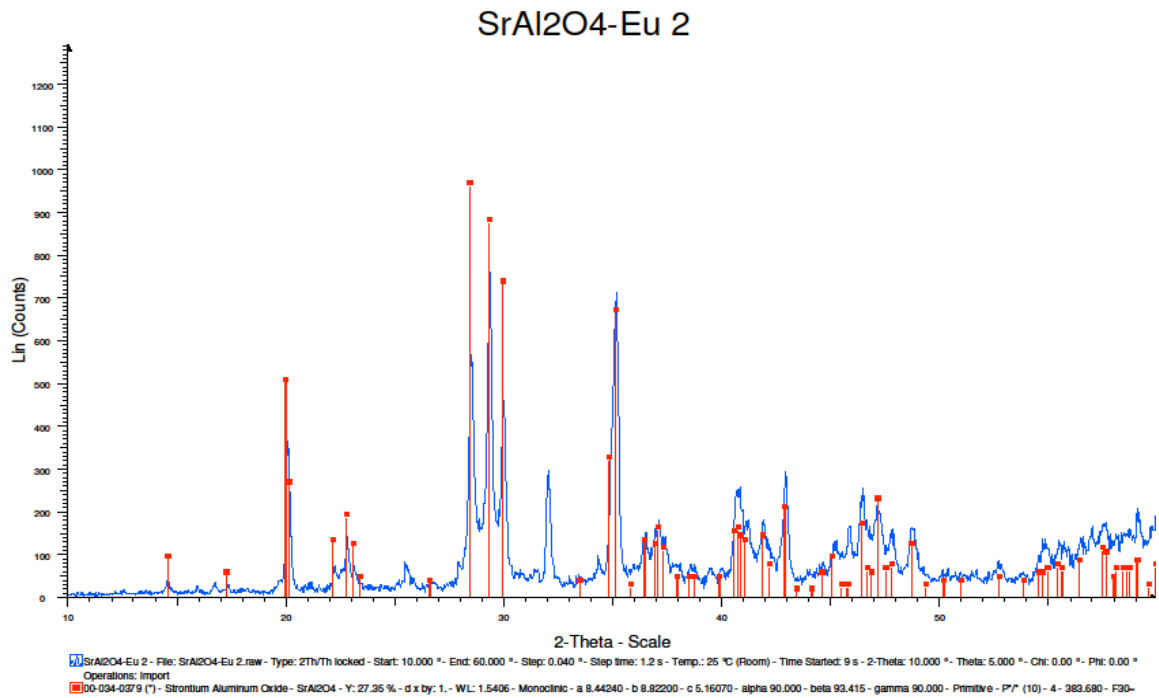
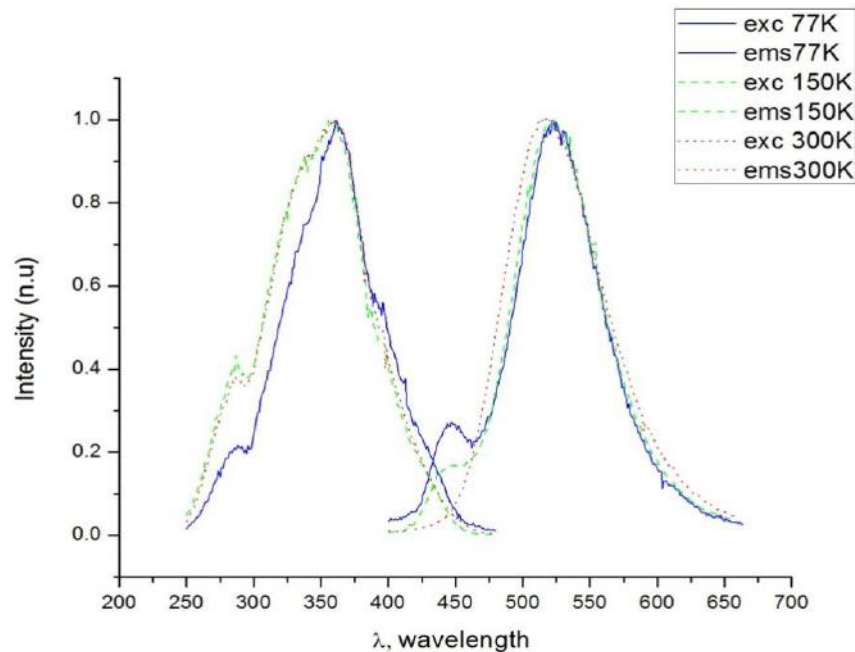
3. RESULTS AND DISCUSSION

3.1 XRD analysis

Fig.1 shows the XRD of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ (1%). From this X-ray diffraction analysis we can tell that our sample is not absolutely mono-phase. One of those is the main monoclinic SrAl_2O_4 phase and the other one is orthorhombic $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase. But there are no any lines of combination of other elements. It means that all nitrates, boric acid and urea were dissolved and during 5-10 minutes the combustion process absolutely finished. This proves once again that combustion method is really energy effective method.

3.2. PL properties of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$

The photoluminescence spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ was observed at different temperatures (77-400K). At room temperature (T=300K) we observe one symmetric broad band centered at 517 nm (FWHM=100 nm). This emission is characteristic for 5d-4f transitions in divalent europium. But at low temperatures (77, 150K) emission spectrum is split into two bands. These two bands are centered at approximately 445nm and 521 (FWHM=79nm) at 77K; 442 nm and 521 nm (FWHM= 80nm) at 150K.

Fig 1. XRD for SrAl₂O₄:Eu²⁺Fig. 3. The excitation and emission spectra of SrAl₂O₄:Eu²⁺ at different temperatures.

As shown in the figure 3 with increasing temperature the intensity of the blue emission band decreases and only green emission band remains. There are a lot of hypothesis to explain this situation. For example Clabau et al. explained this situation with charge transfer from level of $4f^7$ configuration to the valence band associated with a holetrapping mechanism [6]. Other two hypothesis are associated with crystal structure

of SrAl₂O₄:Eu²⁺, which has a three-dimensional network (fig. 4) formed by corner sharing AlO₄ tetrahedra with the Sr²⁺ ions in its a-, b-, c-directed channels. The Eu²⁺ ions replace the Sr²⁺ ions in such lattice in both seven-coordination sites (Sr1 and Sr2, C1 site symmetry for both) since the average Sr-O distances are similar (2,695 and 2,667 Å). Plus, Eu²⁺ and Sr²⁺ ions have very similar ionic sizes (1.20 Å and 1.21 Å, respectively). Poort et al.

explained this situation like that: There are two nonequivalent strontium sites with different coordination numbers in the SrAl_2O_4 crystal [7]. So the distances between the strontium ion and its neighboring oxygen ions are different for these strontium sites.

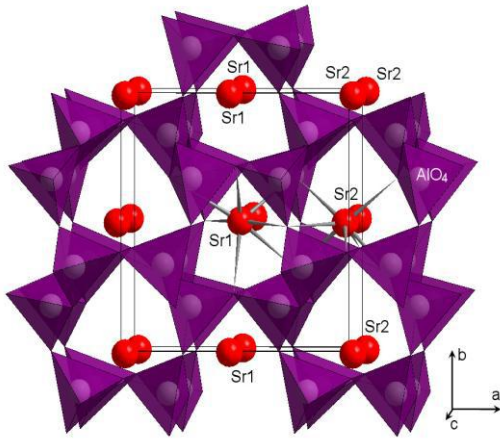


Fig. 4. Crystal structure of SrAl_2O_4 activated with Eu^{2+} ions.

If we look along the a axis, we can see that the oxygen ions are close to one Sr1 site, but far from other Sr2 site. So at the first site there is no any preferential orientation of *d* orbitals. But in the second case, because of the large distance between negative charges and Sr2 site, there is a preferential orientation of *d* orbitals present. Hence at low temperatures there are two emission bands in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ spectra [8]. Other hypothesis is also associated with two different independent Sr sites. Dopant Eu^{2+} ion occupy two Sr sites. So the bond length between the Eu ion and its nearest oxygen neighbors is very important. And these bond lengths are different for Sr1 and Sr2 sites. The excitation band of the green emission could be related to the Sr1 site, the excitation band of the

blue emission to the Sr2 site. We assume this hypothesis to be more plausible, because dopant Eu^{2+} ion causes redshift in the compound. And redshift arises as a result of the centroid shift and crystal field splitting. Dependence of these two quantities on the bond length between Eu ion and the nearest neighboring oxygen sites implies that they will also change in the Sr 1 and Sr2 sites. And it will be the main cause of blue emission band in emission spectrum at low temperatures [9].

We also made our experiments at lower temperature of about $T=20\text{K}$ but at different exciting wavelength ($\lambda=165\text{nm}$, $\lambda=206,6\text{nm}$).

When we excited the sample with 165nm (7,5eV) different bands were observed there. The first peak (250nm) appears due to the intrinsic emission of aluminate matrix. The second one is observed at 380nm and corresponds to inter-band transitions. Band at 410 nm can be explained as the one above (figure 3) for 445 nm.

We can see that at 206,6nm exciting wavelength (6,1eV) these two bands are diminished. We only can see band at 445nm and Eu^{3+} ion line.

3.3 Afterglow properties of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$

The persistent luminescence lifetime can be enhanced by adding some trivalent Re^{3+} ions. But in this work we measured decay time of afterglow for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ (1%). There are a lot of models for explaining the afterglow process. But we believe that in our situation it can be explained by Aitasalo model. As described in this model the long persistent luminescence of $\text{MAI}_2\text{O}_4:\text{Eu}^{2+}$ might be caused by alkaline earth vacancies. It is known from the literature that this time should be in microseconds. In comparison the afterglow decay time in the literature is nearly 2 minutes.

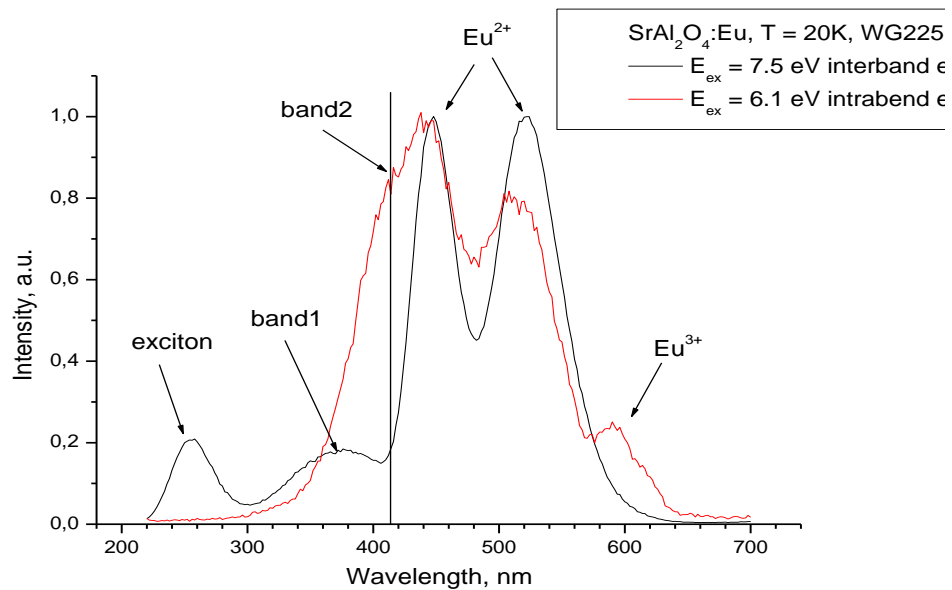


Fig.5. The excitation and emission spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ at low temperature (20K) in different wavelengths.

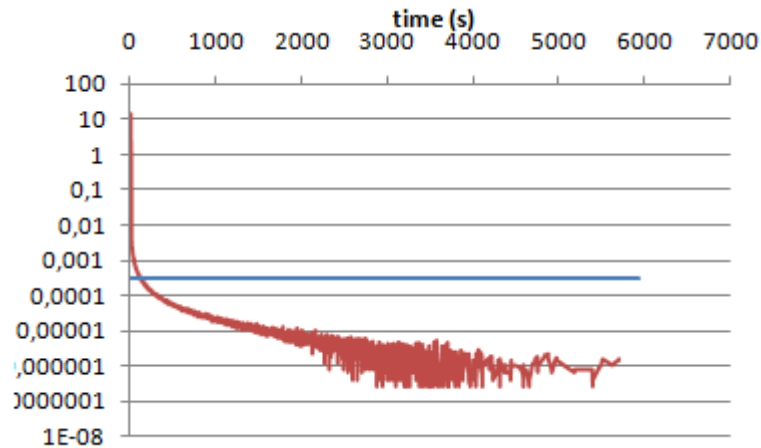


Fig. 6. Decay time of afterglow of SrAl₂O₄:Eu(1%).

CONCLUSION

We synthesized SrAl₂O₄:Eu²⁺ by combustion method and measured PL properties at different temperatures. In contrast to the room temperature, at low temperatures (77, 150K) the second band arises. This material gives us 2 minute afterglow. It is a very

interesting result because in most phosphors it is given in microseconds.

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