Synthesis of Monophasic $SrAl_4O_7$ Compounds Doped with Europium and Dysprosium and Investigation of Luminescent Properties

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Introduction

The crystal structure of strontium aluminate $SrAl_4O_7$ is monoclinic with space group C2/c (No. 15) and having cell parameters $a = 13.04$, $b = 9.01$, $c = 5.55$ and β = 106.502° [1]. It also has a high-pressure form called β-$SrAl_4O_7$. Compared to other strontium aluminates ($SrAl_2O_4$, $Sr_3Al_2O_6$, $SrAl_{12}O_{19}$ and $Sr_4Al_{14}O_{25}$), it is less described in scientific literature. Capron and Douy suggested the synthesis of $SrAl_4O_7$ from a spray-dried amorphous precursor and specified its stability domains [2]. The results showed that kinetics of formation of this phase is very low, consequently the crystallization of $SrAl_4O_7$ is sensitive to the heating rate [2].

Luminescence of europium differ significantly depending on its species. Emission of Eu^{3+} is due to *f–f* transitions, thus emission spectra consist of sharp lines and usually such phosphors emits red light. On the other hand, emission of Eu^{2+} is determined by *d–f* transitions and emission spectra exhibit wide bands. This type of electron transitions are dependent on crystal field, so color of emission might vary from UV to red light. Furthermore, Eu^{2+} ions often exhibit persistent luminescence phenomenon and such materials are leaders in terms of afterglow times.

Experimental

Strontium aluminate samples were prepared by the conventional solid state reaction. Al_2O_3, $SrCO_3$, H_3BO_3, Eu_2O_3, and Dy_2O_3 were used as starting materials. The stoichiometric amounts of reagents were thoroughly ground in an agate mortar and then sintered in a furnace at $950\,^{\circ}\mathrm{C}$ for $4\,\mathrm{h}$ in reducing atmosphere (*formiergas*). Obtained powders were thoroughly ground in an agate mortar and used for characterization.

Powder X-ray diffraction (XRD) analysis has been carried out employing a Rigaku MiniFlexII diffractometer using $\Theta/2\Theta$ geometry and Cu_{K_α} radiation. All of the samples were phase pure, thus XRD diffractograms are not shown in this poster.

Photoluminescence (PL) characterizations were performed on Edinburgh Instruments FLS980 spectrometer equipped with double excitation and emission monochromators, $450\,\mathrm{W}$ Xe arc lamp, a cooled ($-20\,^{\circ}\mathrm{C}$) single-photon counting photomultiplier (Hamamatsu R928) and mirror optics for powder samples. The excitation spectra were corrected by a reference detector. In both cases step width was 0.5 nm and integration time was 0.4 s. Afterglow decay measurements were carried out on the same equipment. The samples were excited with $370\,\mathrm{nm}$ wavelength light for $60\,\mathrm{s}$, then shutter was shut-off and emission intensities at $475\,\mathrm{nm}$ were measured.

References

[1] A.J.Lindop, D.W.Goodwin. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1972, **8**, 2625–2626.

[2] M.L.Capron, A.Douy. J. Am. Ceram. Soc. 2002, **12**, 3036–3040.

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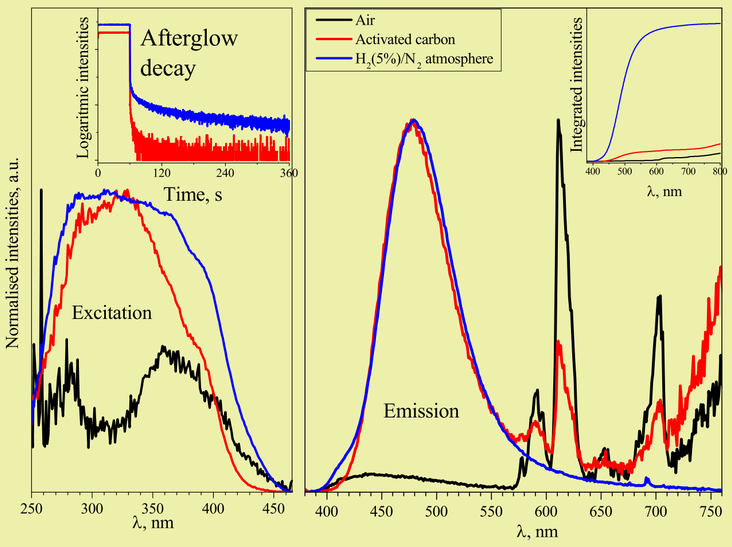
Reduction of Eu^{3+} to Eu^{2+}

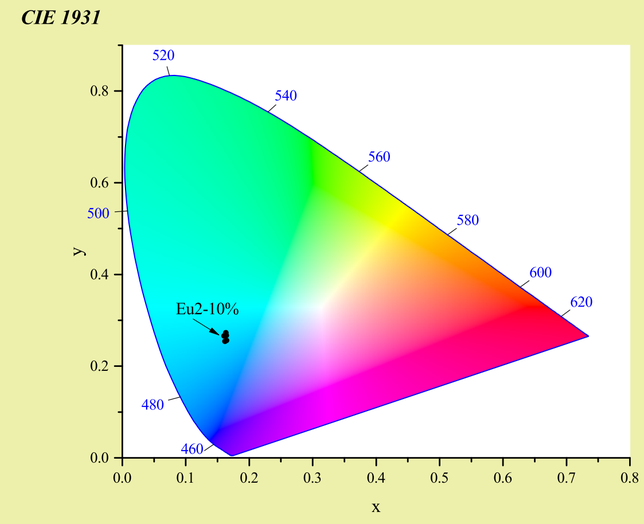
In order to reduce europium from Eu^{3+} to Eu^{2+}, three different samples were prepared – one by calcining simply in air atmosphere, second – in reducing atmosphere achieved by burning of activated carbon, and last – by using tube furnace and calcining in *formiergas* ($H_2(5\,\%)/N_2$) atmosphere. Results of PL measurements are presented in figures below. As one can see, PL of sample heated in air is typical to luminescence of Eu^{3+} and the sample obtained in H_2/N_2 atmosphere show only one wide emission band (λ_{max} at $475\,\mathrm{nm}$). The PL of sample prepared by heating with activated carbon show both – wide emission band and sharp lines (although of lower intensities), thus it contains a mixture of Eu^{3+} and Eu^{2+} ions. Moreover, stronger reducing atmosphere significantly increased afterglow decay times.



Excitation ($\lambda_{em} = 475\,\mathrm{nm}$) and emission ($\lambda_{ex} = 370\,\mathrm{nm}$) spectra of $Sr_{0.98}Al_4O_7{:}Eu_{0.02}$ samples prepared by annealing at different atmospheres. Right inset: integrated intensities of emission spectra. Left inset: afterglow decay curves.

Colors

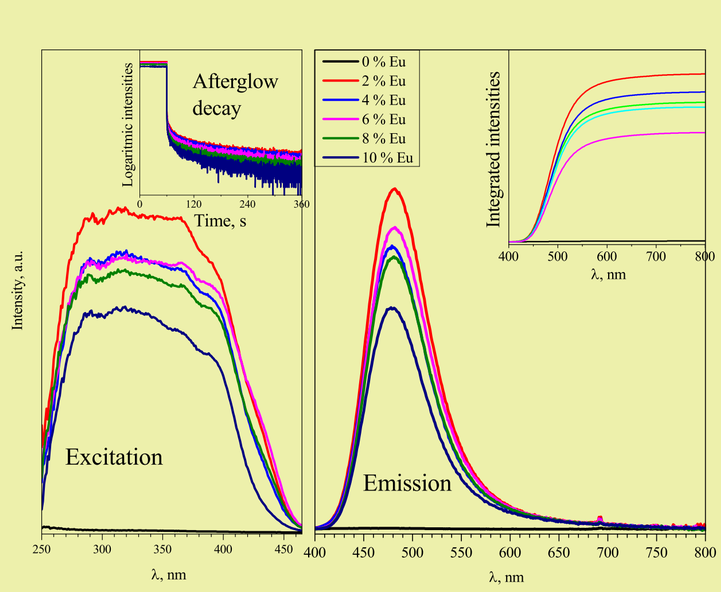
Color coordinates were calculated from emission spectra and plotted on CIE1931 diagram. All of the samples fall within greenish blue region.



CIE 1931 chromaticity diagram of the $Sr_{1-x}Al_4O_7{:}Eu_x$ samples.

Influece of Eu^{2+} concentration

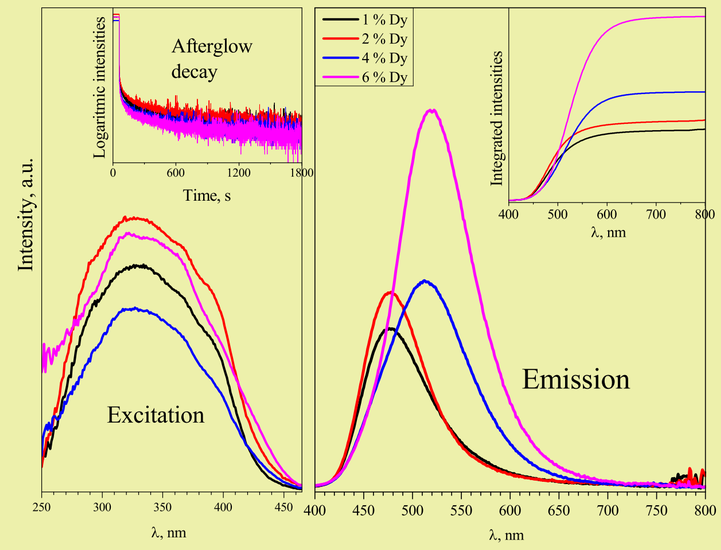
All of the samples (except undoped one) exhibit broad emission peaking at $475\,\mathrm{nm}$. The sample doped with $2\,\%$ Eu^{2+} exhibited highest intensities and strongest persistent luminescence.



Excitation ($\lambda_{em} = 475\,\mathrm{nm}$) and emission ($\lambda_{ex} = 370\,\mathrm{nm}$) spectra of $Sr_{1-x}Al_4O_7{:}Eu_x$ samples. Right inset: integrated intensities of emission spectra. Left inset: afterglow decay curves.

Co-doping with Dy^{3+}

Different concentrations of dysprosium was co-doped in $Sr_{0.98}Al_4O_7{:}Eu_{0.02}$ samples. Interestingly, higher Dy^{3+} concentrations shifted emission maxima towards higher wavelength. Highest co-dopant concentration yielded highest PL intensities, while strongest persistent luminescence was observed in $2\,\%$ Dy sample.



Excitation ($\lambda_{em} = 475\,\mathrm{nm}$) and emission ($\lambda_{ex} = 370\,\mathrm{nm}$) spectra of $Sr_{0.98-x}Al_4O_7{:}Eu_{0.02}, Dy_x$ samples. Right inset: integrated intensities of emission spectra. Left inset: afterglow decay curves.

Conclusions

Solid state synthesis is a suitable way for the preparation of monophasic $SrAl_4O_7$ doped with Eu and co-doped with Dy. Reducing atmosphere achieved by using $5\,\%$ H_2/N_2 gas mixture is sufficient for the reduction of Eu^{3+} to Eu^{2+}. Greenish blue emission maxima of europium doped samples is at $475\,\mathrm{nm}$ and $2\,\%$ doped sample exhibit highest intensity and persistent luminescence with afterglow lasting up to 5 minutes. Co-doping with Dy^{3+} significantly increase afterglow duration up to 30 min. Moreover, high concentrations of dysprosium shifts emission maxima to $512\,\mathrm{nm}$.