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White Light Emission from $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ Phosphor

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Abstract— *The photoluminescence (PL) and afterglow (AGL) characteristics of $Sr_xO/Ca_{1-x}O–Al_2O_3:Eu^{2+},Dy^{3+}$ phosphors are studied here. This phosphor was synthesized through solid-state route with two different precursor materials. At the synthesis/annealing temperature of 1200^0C and above, the phosphor prepared through either route exhibited similar PL and AGL emission. Substitution of strontium by calcium resulted in white afterglow emission at higher calcium concentration.*

1. INTRODUCTION

Long lasting phosphors find wide applications as displaymaterials in different fields such as road signs,emergencyexits, interior decoration, etc. These materials absorb lightenergy and gradually emit visible light in the absence of an excitation source for a long period of time. Among different afterglow(AGL) phosphors, europium-activated strontium aluminateslike $SrAl_2O_4:Eu^{2+},Dy^{3+}$,$SrAl_4O_7:Eu^{2+},Dy^{3+}$, $SrAl_{12}O_{19}:Eu^{2+}$, Dy^{3+}, and $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$are of special interestfor their efficient emission in the visible region. Different methods of phosphorsynthesis are currently an active area of research with an aim to enhance the duration and intensity of the afterglow. In this study, we have synthesized $(Sr_xCa_{1-x})_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$through solid-state reaction route. The objective of this study was to understand the effect of mixed aluminate matrices on the afterglow.

2. EXPERIMENTAL PROCEDURE

Stoichiometric and non-stoichiometric amounts of $SrCO_3$, H_3BO_3, Al_2O_3, $Eu(NO_3)_3.5H_2O$ and $Dy(NO_3)_3.5H_2O$ were taken to prepare the polycrystalline $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ through solid-state reaction. An appropriate amount of $BaCO_3$ or $CaCO_3$ or ZnO was added to substitute the strontium. All the reactants were of analytical grade and pulverized in agate mortar to obtain better homogeneity before making into pellets. The ratio of Eu^{3+} to Dy^{3+} was maintained at 1 mol% : 2 mol% in all samples. The optimum concentration of Ag^+ and Na^+ was 3 mol % and 1 mol % respectively with respect to Eu^{2+} photoluminescence emission intensity. About 2 mol % of boric acid was added as flux. The pellets were pre-fired under air atmosphere for 5 hrs. Subsequently, the pellets were annealed under reduced atmosphere (2% H_2) at 1300° C for 5 hours in alumina boats. The physical parameters such as heating rates, cooling rates and constant heating time were same for all samples.

3. RESULTS AND DISCUSSION

The excitation and emission spectra of $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$prepared at 1300^0C are shown in Fig. 1. For theexcitation at 396 nm, the emission maximum was observed at490 nm and agrees well with the reported spectral profiles.It isreported that a single-phase compound of $Sr_4Al_{14}O_{25}$ is verydifficult to obtain without flux. Addition of flux significantlyreduces the formation temperature to nearly 1300^0C. Further,the luminescence intensity of the phosphors prepared with flux issignificantly higher than the phosphors prepared without flux. Maximum luminescence was observed in the case of boric acid flux. Nag and Kutty[1] have concluded that the presence of rare earth ions (Eu^{2+},Dy^{3+}) and borate anions (BO_4 substitution to AlO_4) are required for the long persistent glow to be realized. Having identified boric acid as a better flux, the optimum concentration of flux was determined by taking various concentrations of boric acid.

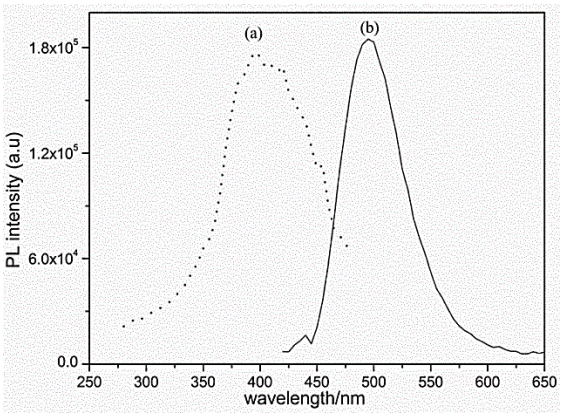

Fig. 1: PL excitation (a) (λ_{emi}= 490nm) and (b) emission spectra (λ_{exci} =396nm) of $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$.

Substitutions of strontium by different cations influence the optical properties of phosphors [2]. Therefore, in this

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study we have investigated $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ luminescence by substituting strontium with divalent and monovalent cations like Ca^{2+}, Ba^{2+}, Zn^{2+}, Ag^{+} and Na^{+}.The ionic radius of Ca^{2+},Sr^{2+},Ba^{2+},Zn^{2+},Ag^{+} and Na^{+} are 99,117,135,74,115, and 102 pmrespectively. Calcium, barium and zinc can occupy strontium site without causing charge imbalance due to isovalency. The atomic fraction was taken as X =A/B, where A=Sr, B=Ca/Ba/Zn). The ratio was varied from X = 0 to 1 in $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ host.

Fig.2 (A) shows the variation of photoluminescence as a function of X_{Ca}. Increase in calcium concentration (X_{Ca} = 0.1 to 0.3) decreased the emission intensity at 490 nm without any change in the spectral profile. However, for X_{Ca}> 0.5 the emission maximum started shifting towards blue region and at X_{Ca}=0.8, it was observed at 445 nm with no significant emission at 490 nm. XRD investigations revealed the signatures of new phase formation with increasing calcium concentration. The new phases identified were $CaAl_4O_7$ (JCPDS No.76-0706), $CaAl_2O_4$ and $SrAl_2O_4$.We have examined the excitation spectra of $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}(X_{Ca}=0.8)$, $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}(X_{Ca}=0)$ and $CaAl_4O_7:Eu^{2+},Dy^{3+}$. The excitation spectral profiles of $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}(X_{Ca}=0.8)$ and $CaAl_4O_7:Eu^{2+},Dy^{3+}$ recorded for 445 nm emission were similar (not shown here).The emission spectrum of calcium substituted $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (X_{Ca}=0.8) was also similar to the emission spectrum of $CaAl_4O_7:Eu^{2+},Dy^{3+}$. Both the emission profiles had maximum at 445 nm. Therefore, the shift in the emission maximum here can be attributed to the formation of the $CaAl_4O_7$ phase.The luminescence intensity of $CaAl_4O_7:Eu^{2+},Dy^{3+}$ is significantly less than that of $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ as shown in Fig 2 (A). This may be the reason for the fact that at low concentration of calcium substitution the emission at 490 nm was reduced and $CaAl_4O_7:Eu^{2+},Dy^{3+}$ emission was not observed though formation of this phase might have already started.

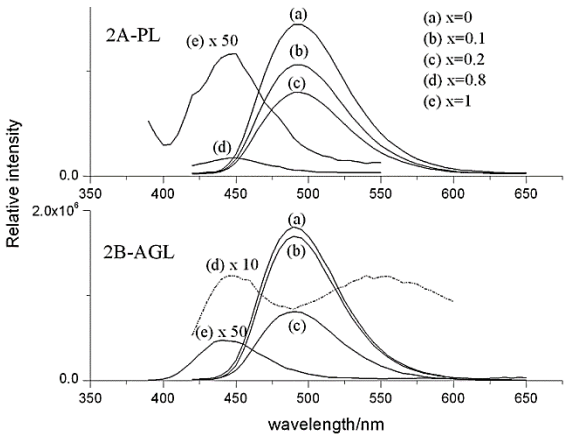

Fig. 2: Effect of calcium substitution on $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (A) PL emission; λ_{exci} = 396 nm for (a),(b),(c); λ_{exci} = 375 nm for (d), (e) (B) Afterglow; X_{Ca} = (a) 0, (b) 0.1, (c) 0.2, (d) 0.8 and (e) 1

The afterglow spectra of $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}(X_{Ca}=0.8)$,$Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}(X_{Ca}=0)$and $CaAl_4O_7:Eu^{2+},Dy^{3+}$ are shown in Fig.2 (B). The afterglow intensity decreased appreciably with increase in calcium concentration. Interestingly, we have visually observed a white emitting afterglow from the calcium-substituted host for X_{Ca}=0.7-0.8. The $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ or $CaAl_4O_7:Eu^{2+},Dy^{3+}$ did not exhibit white afterglow.The afterglow emission from $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (X_{Ca}=0.8) exhibited two peaks around 445 nm and 530 nm.

The AGL emission maxima of $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ and $CaAl_4O_7:Eu^{2+},Dy^{3+}$ in the present study were observed at 490 nm and 445 nm respectively. The observed white glow could be a simple mixture of emission from Eu^{2+} sitesin $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ and $CaAl_4O_7:Eu^{2+},Dy^{3+}$ phases as the $CaAl_4O_7$ phase was detected in $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (X_{Ca}=0.8) samples as mentioned above. To confirm it $CaAl_4O_7:Eu^{2+},Dy^{3+}$& $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ and $CaAl_4O_7:Eu^{2+},Dy^{3+}$& $SrAl_2O_4:Eu^{2+},Dy^{3+}$ powders prepared independently were mixed intimately before recording the emission. Irradiation of these mixtures by UV light did not yield any white afterglow visually and these mixtures did not exhibit emission peaks simultaneously at 445 and 530 nm on excitation. This indicates that the observed white afterglow was not a simple mixture of emission from $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ and $CaAl_4O_7:Eu^{2+},Dy^{3+}$ or $CaAl_4O_7:Eu^{2+},Dy^{3+}$& $SrAl_2O_4:Eu^{2+},Dy^{3+}$. The notable point here is that we observed two emission peaks in the AGL profile and one emission peak in the PL profile from $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (X_{Ca}=0.8) whereas Li-Te Chen et al [3]have observed no afterglow but two emission peaks at 445 and 530 nm in the PL profile from $Ca_xSr_{1-x}Al_2O_4:Eu^{2+}$ at room temperature. Appearance of two emission maxima was attributed by them to possible distribution of crystal field caused by the substituitonal disorder of divalent ions whereas we feel that probably this mixed host is very complicated and may be a minor change in the Sr/Ca ratio causes significant structural changes at micro level in the host affecting the optical properties of the activators.

The PL emission spectra of $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (X_{Ca}=0.8),$Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (X_{Ca}=0) and $CaAl_4O_7:Eu^{2+},Dy^{3+}$ recorded at 77K are shown in Fig.4. The PL emission at 490 nm from $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ is enhanced nearly 10 times at 77 K but this phosphor did not emit at 530 nm either at room temperature or at 77 K. $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (X_{Ca}=0.8) exhibited PL emission at 445 nm and 530 nm at 77 K and only 445 nm emission at RT (Fig. 3 b, d). The PL emission profile of $CaAl_4O_7:Eu^{2+},Dy^{3+}$ had two peaks at 445 and 530 nm at 77.

K and only 445 nm emission at RT (Fig.3 c, e). These observations suggest that the 530 nm emission in case of $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (X_{Ca}=0.8) at 77 K is probably due to

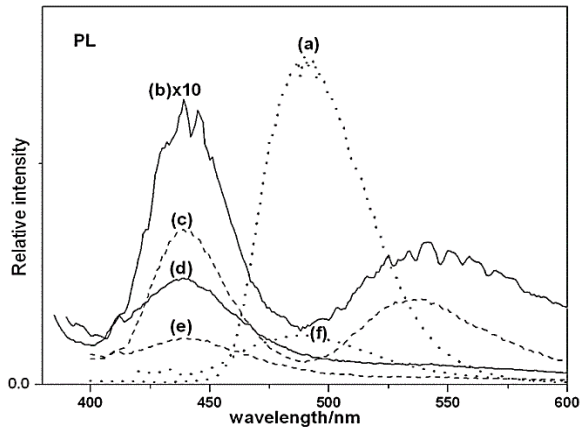

Fig. 3: PL emission spectra of $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (X_{Ca}=0) λ_{exci} = 396 nm (a) at 77 K, (f) at RT $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (X_{Ca}=0.8) λ_{exci} = 375 nm (b) at 77 K, (d) at RT $CaAl_4O_7:Eu^{2+},Dy^{3+}\lambda_{exci}$ = 375 nm (c) at 77 K, (e) at RT.

the presence of calcium since $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (X_{Ca}=0) or $SrAl_2O_4:Eu^{2+},Dy^{3+}$ (X_{Ca}=0) did not exhibit this emission even at that temperature. It is to be noted that the 530 nm broad PL emission was not observed at room temperature for $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$($X_{Ca}$=0.8) but the AGL spectrum exhibits this emission prominently at this temperature. This indicates that the presence of calcium in $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ helps in inducing AGL but not PL at room temperature. This means calcium takes part in the trapping and detrapping dynamics though the exact process is yet to be understood. In the earlier section, we have noted that in case of non-stoichiometric strontium aluminate samples the PL maxima were shifted but not the AGL maxima and now we have seen that presence of calcium in this host induces AGL emitting at two widely different wavelengths (445 and 530 nm) with PL emission only at 445 nm at room temperature. These two important interesting observations led us to believe that the PL and AGL are not due to the same europium sites though at this juncture the experimental observations are not sufficient to propose a suitable mechanism explaining the observed phenomena. The trap dynamics in case of persistent luminescence is very complex and probably a minor change in the host composition is reflected considerably in its luminescence characteristics. Based ontheClaube's [4] proposed mechanism to explain persistent luminescence involving oxidation ofEu^{2+} to Eu^{3+} upon UV irradiation we tried to trace the signature of Eu^{3+} if any in $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$. However, we did not see the Eu^{3+} emission either before the irradiation of UV light or after in case of $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (X_{Ca}=0.8) or $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (X_{Ca}=0) either at room temperature or at 77 K. The observations made here clearly require further studies to understand the mechanism of persistent luminescence. The white afterglow observed here from $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (X_{Ca}=0.8) persisted for 30 min. To the best of our knowledge this is the first report of white afterglow observation from europium, dysprosium doped calcium/strontium aluminate host though $CaAl_2O_4:Dy^{3+}$ is said to emit white afterglow [5].

4. CONCLUSION

Non-stoichiometric $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ phosphors exhibited enhanced photoluminescence intensity. The maximum PL enhancement was seen in strontium rich samples. The photoluminescence emission maximum was influenced by the non-stoichiometry whereas the emission maximum in case of afterglow luminescence was not. Strontium deficit phosphors have shown enhanced afterglow intensity. Calcium substituted $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$exhibited white afterglow. However, its photoluminescence and afterglow emission characteristics were different. Barium substitution resulted in enhanced photoluminescence but the afterglow was decreased significantly. Substitution by silver ions enhanced the trap density and hence the afterglow emission significantly.

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