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Luminescence characteristics of $LiCaAlF_6$:Eu phosphor

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A simple method for preparing $LiCaAlF_6:Eu^{2+}$ phosphor is reported. Photoluminescence (PL) and thermoluminescence (TL) studies were carried out. The TL sensitivity of the phosphor is nearly twice that of $CaSO_4$:Dy TLD phosphor. Several other properties required for TL dosimetry are superior as well. It is suggested that the phosphor can be a suitable replacement for $CaSO_4$:Dy.

1 Introduction

The Colquirite-type mixed metal fluorides $LiCaAlF_6$ and $LiSrAlF_6$ are being investigated for use in photonic devices because they are good hosts for optically active cations and can be grown easily [1]. Recent examples of applications include the use of $LiCaAlF_6:Nd^{3+}$ in photolithography [2] and $LiCaAlF_6:Ce^{3+}$ in ultraviolet (UV) chirped-pulse amplification [3]. In addition, both Ce^{3+}-doped $LiCaAlF_6$ and $LiSrAlF_6$ have been reported as leading candidates for tunable solid-state lasers in the UV region [4, 5]. $LiSr_{0.8}Ca_{0.2}AlF_6$ was first reported as a potential tunable laser in the visible region in 1992 [6]. Tunable ultraviolet laser oscillation and amplification have been demonstrated in $LiCaAlF_6:Ce^{3+}$ [7, 8] and $LiSrAlF_6:Ce^{3+}$ [8] crystals. $LiCaAlF_6$ is also a potential window material in the VUV region [9–11]. $LiCaAlF_6:Pr^{3+}$ exhibits photon cascade emission that can be useful for obtaining phosphors with quantum efficiency exceeding 100% [12].

Nikl et al. [13] reported for the first time the scintillation and thermoluminescence (TL) in $LiCaAlF_6:Ce^{3+}$. A TL glow peak was obtained around 230 °C and the emission spectrum was characteristic of Ce^{3+}. Gektin et al. [14] presented detailed results on scintillation properties and thermoluminescence of $LiCaAlF_6:Ce^{3+}$. They observed a glow peak at about 350 °C, while in undoped crystals glow peaks were observed around 190 and 260 °C. TL emission at 350 °C corresponded to Ce^{3+}. The role of Ce^{3+} in traps was also postulated as the glow-peak position was different in the Ce^{3+}-doped crystal. Gektin et al. [15] also suggested use of this material for neutron dosimetry. The sensitivity to X-rays was 100 times that of LiF-TLD100. The sensitivity of $LiSrAlF_6:Ce^{3+}$ was found to be still greater [16]. Sato et al. [17, 18], on the other hand, observed glow peaks around 180 °C and 250 °C, in Ce^{3+}-doped $LiCaAlF_6$ and observed that the emission spectrum was not related to Ce^{3+}emission. They also studied color centers in $LiCaAlF_6:Ce^{3+}$. They found that Mg^{2+} doping reduces the F centre formation significantly [9, 17]. Using time-resolved photoluminescence, Gektin et al. [19] studied energy transfer from self-trapped exciton (STE) to Ce^{3+} that is important for scintillation.

More recently, Shiran et al. [20] studied scintillation and thermoluminescence in $LiCaAlF_6:Eu^{2+}$. They observed glow peaks around 340, 420 and 490 K that are the same as those in the undoped material. However, TL intensities are much high in Eu^{2+}-doped material. Both RL and TL emission spectra re-

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vealed characteristic Eu^{2+} emission. LiCaAlF$_6$: Yb^{2+} was studied by Nikl et al. [21]. UV emission around 380 nm was observed. Bensalah et al. [22] studied low-temperature TL in this material. TL emission contained Yb^{2+} emission but some additional bands were also observed. Defects in LiCaAlF$_6$: RE^{3+} systems have been also studied theoretically [23, 24]. Theoretical calculations [23] show that in LiCaAlF$_6$, for La^{3+}, substitution at the Ca^{2+} site with Li$^+$ vacancy compensation is preferred, while for Ce^{3+}, substitution at the Li$^+$ site with Ca^{2+} vacancy compensation is favored. For the series from Pr to Tm, these two schemes give very similar energies. In the case of Gd^{3+}, substitution at the Ca^{2+} site with F$^-$ interstitial compensation is most likely. Another important prediction of the later work [24] is that doping with Ce^{3+} and Yb^{3+} may not have strong optical activity.

It is clear from this brief survey that there has not been much work done on the development of LiCaAlF$_6$ as a TLD material. Most of the earlier work is related to the single crystals grown for scintillators, lasers or optical windows. In this paper we report a simple method for preparing LiCaAlF$_6$: Eu^{2+} powders that exhibit very intense thermoluminescence on exposure to gamma rays. The sensitivity of these powders is more than that of CaSO$_4$: Dy^{3+} TLD phosphor.

2 Experimental

– Fluorides are susceptible to hydrolysis. In preparing fluoride-based phosphors, it is important to have OH$^-$-free starting materials. Various approaches have been adopted to achieve this. Use of freshly synthesized powders from oxides with dry HF gas as fluorinating agent in an inert atmosphere is most effective in preparing OH$^-$-free phosphors. However, the preparation methods then become tedious and expensive. Modification of wet chemical processes have been earlier used successfully to prevent hydrolysis. Fresh fluoride powders may be prepared by neutralization of HF with metal carbonates. Precipitation in the presence of chlorine ions is also known to prevent hydrolysis [25, 26]. Various procedures were hence tried for preparation of LiCaAlF$_6$ powders.

– In the first method, the constituent fluorides were freshly prepared using metal carbonates as the starting materials and HF as the fluorinating agent. Weighed amounts of freshly prepared fluoride constituents in the stoichiometric ratio were thoroughly mixed along with the dopant EuF$_3$ and rapidly heated in a graphite crucible in air till the powders completely melted. The melt was then quenched by pouring into another graphite crucible. The molten mass was crushed to powder and particles in the range 72–210 μm were used for photoluminescence (PL) and TL measurements.

– Use of chlorides as starting materials helps prevent the hydrolysis [25, 26]. Hence, in the second method LiCaAlF$_6$ was prepared by dissolving the Analytical reagent grade chlorides of the constituent metals in the stoichiometric ratios in double distilled water in a PTFE container and a stoichiometric amount of HF was added drop wise. The precipitate was washed several times with distilled water and dried. It was then mixed with the dopants and the rest of the procedure was the same as that for the first method.

– The above-mentioned procedures involve several steps and experiments were carried out to determine whether these steps could be reduced in number. In the third method, LiCaAlF$_6$ along with dopants was obtained by coprecipitation. Subsequent XRD studies showed that LiCaAlF$_6$ was formed upon precipitation. However, the dopants were not dispersed, as indicated by the absence of PL. To achieve the dispersion of dopants, the powder obtained by precipitation was rapidly heated in a graphite crucible in air till the powder completely melted and the rest of the procedure described above was followed.

– Three different dopants (Eu, Dy or Mn) were tried. Compound formation was confirmed by recording powder diffraction pattern and matching with ICDD file 73-2441. An excellent match was obtained for all the samples.

Photoluminescence spectra were recorded on a Hitachi F-4000 spectrofluorimeter with a spectral slit width of 1.5 nm. A Theratron 780 E therapy machine employing a Co^{60} source was used for gamma exposures. The exposure rate was 2.32×10^{-2} C/kg/min. Thermoluminescence glow curves were recorded on Nucleonix, Hyderabad (India) TL Reader (Model no. TL 1009I) with a heating rate of 2 °C per second using a Hamamatsu R.6095 PMT that is sensitive over the region 300–650 nm with maximum sensitivity around 420 nm. For comparison, glow curves for $CaSO_4$:Dy powders were also recorded under identical conditions.

3 Results and discussion

Figure 1 shows glow curves for $LiCaAlF_6$ samples with various activators (activator concentration 1000 ppm), exposed to 2.58×10^{-2} C/kg. The glow curves consist of a peak around 185 °C. A much weaker emission around 250 °C is also indicated, which becomes mixed up with heater emission at higher temperatures, and hence is not shown. There is no resolved peak beyond 250 °C. For Dy and Mn dopants a more complex structure is observed. For the Eu-doped sample the glow curve is simpler than that reported by Shiran et al. [20]. The difference may be attributed to the different preparation procedures. A glow peak in the vicinity of 185 °C has been observed without Eu doping in the earlier studies [14, 17, 18]. It is seen that the TL in Eu-doped samples is some two orders of magnitudes higher than that for Dy- or Mn-doped samples. If at all, Dy and Mn activators give intense TL, the emission is not in the range of the commonly available PMT (350–600 nm). $LiCaAlF_6$:Eu was thus chosen for further studies.

Figure 2 shows glow curves for $LiCaAlF_6$:Eu (1000 ppm) prepared by various methods. It is seen that the glow-curve shape remains the same for all three methods. The samples prepared by method 3 possess the highest sensitivity. The method is also quite simple to follow. Reproducibility was also found to be good. When three batches were prepared under identical conditions, the batch to batch variation in sensitivity was less than 10%.

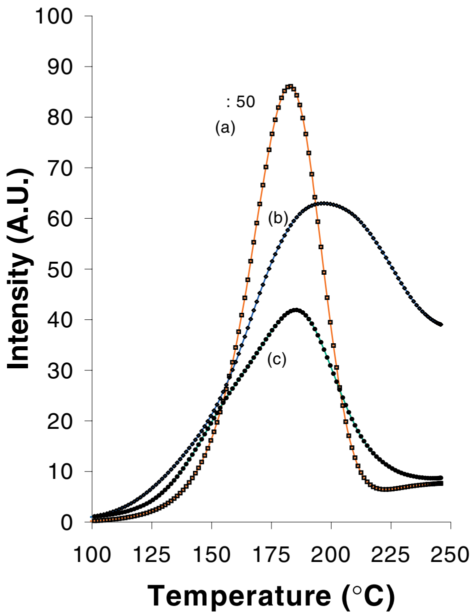

Fig. 1 (online colour at: www.pss-a.com) Typical glow curves for $LiCaAlF_6$ doped with 1000 ppm of various impurities exposed to 2.58×10^{-2} C/kg. (a) Eu, (b) Mn, (c) Dy. Curve (a) is divided by 50 to fit the ordinate scale.

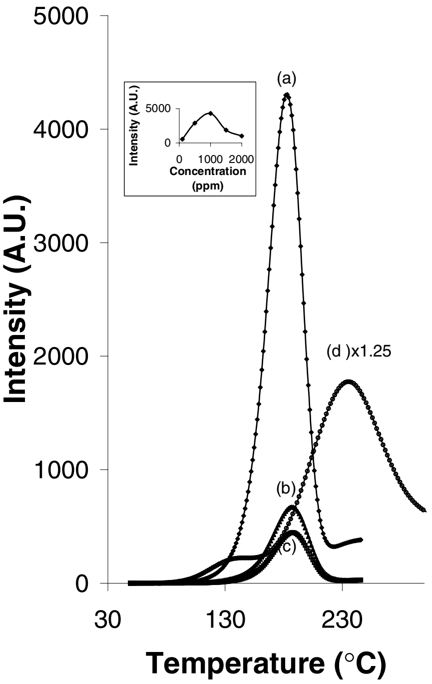

Fig. 2 Glow curves for $LiCaAlF_6$:Eu prepared by different methods exposed to 2.58×10^{-2} C/kg. (a) Method 3, (b) method 2, (c) method 1 (see text). Glow curve of $CaSO_4$:Dy is also given for the comparison (curve d). Curve (d) is multiplied by 1.25 to fit the ordinate scale. The inset shows the effect of Eu concentration on TL intensity.

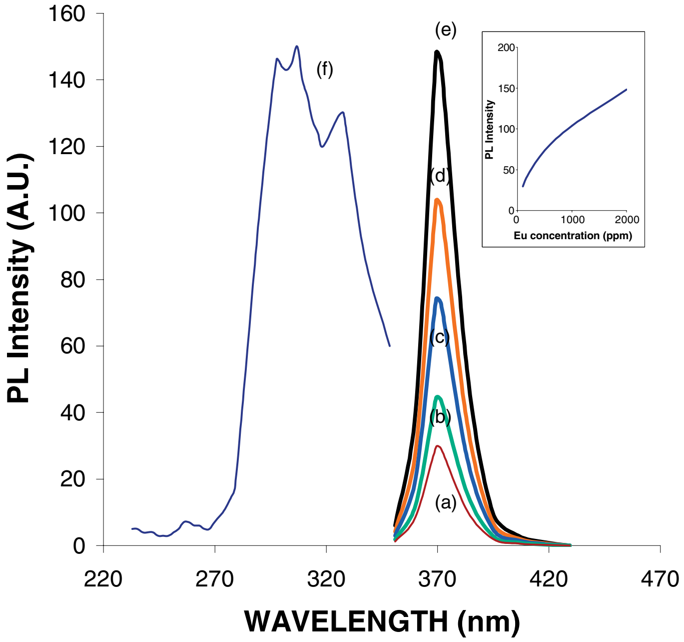

Fig. 3 (online colour at: www.pss-a.com) Effect of Eu concentration on the PL of $LiCaAlF_6$. (a)–(e) Emission spectra for 300 nm excitation. Eu concentration in ppm (a) – 100, (b) – 500, (c) – 1000, (d) – 1500 and (e) – 2000, (f) – typical excitation spectrum for 369 nm emission.

The glow curve of $CaSO_4$: Dy TLD phosphor is also given for comparison. The height of the 185 °C peak in $LiCaAlF_6$: Eu is almost twice that of the dosimetry peak of $CaSO_4$: Dy. It has to be noted that the comparison is only indicative. The relative heights of glow peaks for $LiCaAlF_6$: Eu and $CaSO_4$: Dy will depend on the PMT response. We have used a PMT Hamammatsu R6095 that has a maximum sensitivity around 420 nm. Though we have not recorded the detailed TL emission spectrum at this stage, it could be verified using filters that TL in $LiCaAlF_6$: Eu was around 375 nm, while that for $CaSO_4$: Dy is known to be in the form of narrow bands around 482 nm and 573 nm. PMT is much less effective for 573 nm emission of $CaSO_4$: Dy. The absolute sensitivities of $LiCaAlF_6$: Eu and $CaSO_4$: Dy are thus of the same order. However, in thermoluminescence dosimetry of ionizing radiations, PMT with response similar to that of R6095 are used. For practical purposes, $LiCaAlF_6$: Eu will be nearly twice as sensitive as $CaSO_4$: Dy. All subsequent studies were thus carried out using the $LiCaAlF_6$: Eu phosphor prepared by method 3.

The inset of Fig. 2 shows the effect of europium concentration on the TL intensity. The concentration refers to the amount of Eu relative to Ca added in the solution. The samples were exposed to 2.58×10^{-2} C/kg. It is seen that the highest TL intensity is obtained for Eu concentration of 1000 ppm. The dependence of PL on Eu^{2+} concentration was also studied (Fig. 3). PL of Eu^{2+} was observed in form a narrow band around 369 nm (Fig. 3a–e) arising from a transition from the lowest level of the $4f^65d^1$ configuration to the $^8S_{7/2}$ level of the $4f^7$ configuration. This is in excellent agreement with the literature value [27]. The excitation (curve f) consists of several overlapping bands between 290–325 nm. These are characteristic of transitions from the $^8S_{7/2}$ level of the $4f^7$ configuration to the levels of the $4f^65d^1$ configuration. The PL intensity increases monotonously, though in a sublinear manner, with Eu concentration. The TL intensity, on the other hand, shows a different behavior (Fig. 2 inset). The curve passes through a maximum that corresponds to Eu concentration of 1000 ppm and the intensity falls for higher concentrations. The difference can be understood on the basis of a suggestion of Shiran et al. [20]. Eu is assumed to play a dual role. It stabilizes the traps and it also acts as a luminescence center. Thus, beyond

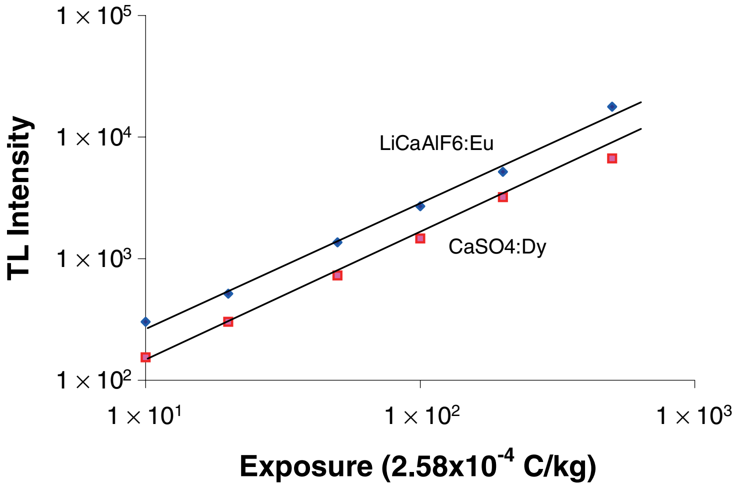

Fig. 4 (online colour at: www.pss-a.com) Response curve for $LiCaAlF_6$: Eu and $CaSO_4$: Dy Dy in the exposure range 2.58 × 10^{-3} – 1.26 × 10^{-1} C/kg. Peak heights are plotted as a function of exposure.

a certain concentration further increase does not result in an increase in TL yield. On the contrary the process is hampered possibly due to pair formation. Alternatively, the results might be explained also by postulating an independently driven concentration of electron traps (F centers most probably). As the intensity of the TSL glow curve is determined by the smaller concentration from those of the hole and electron traps, and Eu^{2+} must act as the hole trap, it is easy to understand the increase of TSL intensity with increasing Eu concentration and its later saturation (due to constant concentration of electron traps, which becomes smaller with respect to the Eu one). Though we have not recorded the detailed TL emission spectrum at this stage, it could be verified using filters that the TL emission is in the same region as the Eu^{2+} emission.

Though the PL emission spectra were scanned between 320–700 nm, only the relevant portion is shown in Fig. 3. In contrast to the observations of Shiran et al. [20], we did not observe any Eu^{3+} emission in our samples. Glow curves for $LiCaAlF_6$: Eu and $CaSO_4$: Dy in the exposure range 2.58 × 10^{-3} – 1.26 × 10^{-1} C/kg were recorded. The glow curve for $LiCaAlF_6$: Eu remains essentially the same in shape in this exposure range. Figure 4 shows the response curves for $LiCaAlF_6$: Eu and $CaSO_4$: Dy in the range 2.58 × 10^{-3} – 0.126 C/kg. Peak height was used to plot the curves. The two curves are almost parallel.

4 Conclusions

A simple method to prepare $LiCaAlF_6$: Eu^{2+} is described. The phosphor has a high TL sensitivity, almost twice that of $CaSO_4$: Dy, a simple glow-curve structure that does not change in shape with the exposure, and linear response. These properties make it a strong candidate for consideration as a TLD phosphor that can replace $CaSO_4$: Dy.

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