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Research Article

Luminescence Characteristics of $LiCaAlF_6$:Eu TLD Phosphor

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Abstract. The material $LiCaAlF_6$:Eu (0.1 mol%) in microcrystalline form was prepared through water solution coprecipitation method followed by melting it at around 900 °C in a graphite crucible. The ingot was crushed and sieved through standard sieves to obtain powder approximate in the range 100-125 μm. The material was annealed at around 200-800 °C. The material was characterized by XRD. The materials were irradiated to different doses of γ-rays using ^{60}Co radioactive source and thermoluminescence (TL) glow curves were recorded. The powder material was found to be at least 10 times more sensitive than $CaSO_4$:Dy commercially available TLD pellets. However, as the dosimetry peak is at around 180 °C, there is fading around 20%. Considering these facts, the material could be considered as a highly sensitive and suitable TLD phosphor.

Keywords. $LiCaAlF_6$:Eu, Thermoluminescence (TL), High sensitivity, Dosimetry, TLD

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1. Introduction

Mixed fluorides, such as, $Li(AE)AlF_6$ (where, AE = Mg, Ca, Sr or Ba, alkaline earth elements) have very large band gaps and therefore their optical and luminescence properties could be tailored by doping with suitable impurities. Single crystals of such materials were also preferred as active media for solid state lasers due to their as the trivalent impurities could replace Al^{3+} easily, e.g., Cr^{3+} doped lithium-calcium-aluminum-hexafluoride (LCAF) over ruby red region and Ce^{3+} in UV region [2–5, 7–9, 13–17, 19, 25]. They are also found to be non-hygroscopic good scintillators [6, 20, 22, 24]. Fluorides are also found to exhibit good luminescence properties and sensitive to high energy radiations [1, 10, 21, 23]. For example, LiF:Mg,Ti, LiF:Mg,Cu,P and CaF_2:Mn are commercially available TLD phosphors. But there are some drawbacks of these materials. For example, LiF:Mg,Ti is not very sensitive and the later ones though highly sensitive lose their sensitivities if heated above 250 °C while recording TL. Therefore, there is always search for new phosphor materials. Mixed fluorides could be good choice due to reasons mentioned earlier. However, in case of lithium-based fluorides, both Li and F ions being highly reactive, they are not easy to prepare and there is a possibility of contamination. Also, there is also possibility of phase separation and formation of different phases if the materials are directly prepared by mixing and melting the constituent fluorides.

Recently, such materials have been prepared by wet-chemical coprecipitation method followed by melting the product in a graphite crucible at around 850 °C by Moharil *et al*. [11]. In the present study, this method has been used here to prepare europium (Eu) doped $LiCaAlF_6$. The material was characterized by XRD to confirm the formation of the material in a single phase. The TL properties were studied after irradiating the material to high-energy γ-radiation. The material was found to be highly sensitive for dosimetry of high-energy radiations using thermoluminescence (TL) and thus could be a good candidate for TL dosimetry.

Highlights

- Microcrystalline material was synthesized successfully by coprecipitation/melt method.
- The novelty of the method of preparation is phase separation in the mixed fluoride materials could be avoided.
- The material was characterized by XRD and found to be in a single phase.
- The material (100-125 μm particle size) found to be 5 times more sensitive than $CaSO_4$:Dy commercially available TLD pellets.
- The material is found to be highly sensitive TLD material useful for dosimetry of high-energy radiations.

2. Experimental

Samples of $LiCaAlF_6$:Eu (0.05-2.0 mol%) in microcrystalline form were prepared by dissolving the analytical reagent grades of the chloride compounds of constituent metals (i.e., LiCl, $CaCl_2$ and $AlCl_3$ in triply distilled water in their stoichiometric ratios in a Polytetrafluoroethylene (PTFE, Teflon) beaker and stoichiometric amount of HF was added dropwise through a burette while stirring rigorously. Appropriate amount of $EuCl_3$ was added to the chloride solution of the ingredients before starting the coprecipitation reaction for preparing the Eu-doped samples, i.e., LiCaAlF$_6$:Eu (0.05-2.0 mol%). The maximum intensity for the doped material was found to be at 0.1 mol%. The precipitate was washed several times with distilled water/ethanol and dried in a vacuum oven at around 70 °C overnight. The details could be found in our earlier papers [12]. It was then rapidly heated in a graphite crucible in air till the powders completely melted (at around 900 °C). The melt was then quenched by pouring into another graphite crucible. The ingot thus obtained was crushed and sieved to obtain powders of different particle size ranges in the range of 100-120 μm. This material, i.e., LiCaAlF$_6$:Eu was further annealed and quenched at 400 °C for optimization of its dosimetry properties and used for further studies.

The Powder X-Ray Diffraction (PXRD) patterns were recorded at room temperature using a high-resolution D8 Discover X-ray diffractometer (Bruker, Germany) equipped with a point detector (scintillation counter). Cu-K$_{\alpha 1}$ radiation line (λ = 1.54056 Å) was used to obtain the XRD patterns. Thermoluminescence (TL) glow curves were on Harshaw TLD Reader (Model 3500) by taking approximate 5.0 mg every time and with heating rate 5 °C/s. Photoluminescence spectra were recorded on fluorescence spectrophotometer with spectral slit width of 1.5 nm. Approximately ~100 mg of the material was taken every time for these measurements.

3. Results and Discussion

3.1 X-Ray Diffraction (XRD)

Figure 1 shows the XRD patterns for the LiCaALF$_6$:Eu TLD phosphor material samples annealed at different temperatures to see that whether there is any phase/structural change(s) in the material on annealing. It could be seen in the figure that the XRD pattern of the pristine (as prepared by the coprecipitation method and melted in a carbon crucible) material matched well with the data available in the literature (PCPDS file no. ICDD 73-2441).

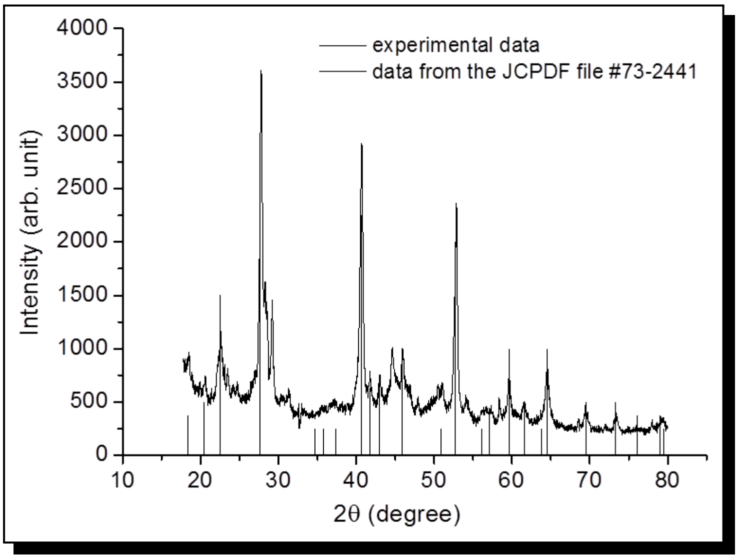

Figure 1. XRD patterns of LiCaAlF$_6$:Eu (0.1 mol%). Sticks graph using from the corresponding JCPDS file #73-2441 is also shown for ready reference

3.2 Glow Curves and Dose Response

Figure 2 shows the dose response of the material prepared by coprecipitation and melt-quenched method (without annealing). As mentioned earlier, it consists of three peaks at 180, 240 and 340 °C. The peak appearing at around 180 °C is of highest intensity called dosimetry peak and is of more interest for dosimetry as the peak height or area under the curve is used for estimation of the radiation doses. It could be seen in the figure that there is not much change in the peak temperatures. The glow curve of a standard phosphor $CaSO_4$:Dy (TLD 900) is also shown for comparison and the sensitivity of this phosphor is found to be at least 5 times more than that of the standard one. The Plot of TL intensity with that of doses given (dose response) is also shown in the figure and it could also be seen that it is very much linear in the dose range of (10-50 Gy).

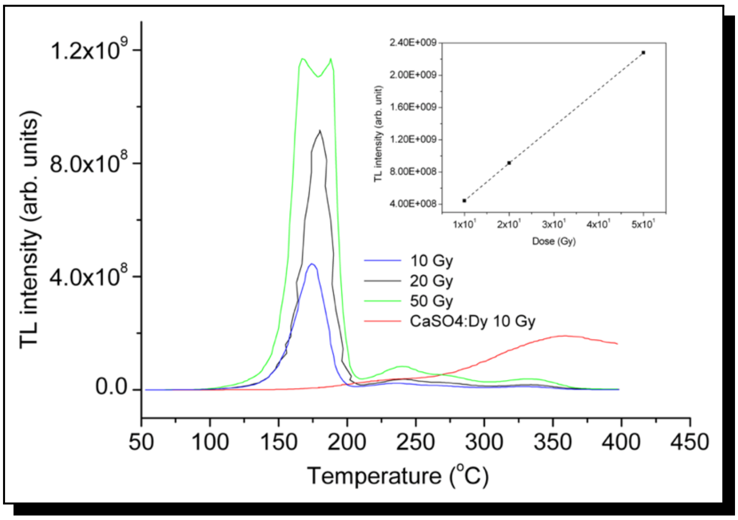

Figure 2. Dose response of LiCaAlF$_6$:Eu TLD phosphor material. The particle size of the material was in the range of 100-120 μm

3.3 Effect of Particle Size and Annealing

As mentioned earlier, the final material (LiCaAlF$_6$:Eu, obtained after melting in a graphite crucible) was crushed and sieved to obtain powders of different particle size ranges in the range of 45-210 μm. This material, i.e., LiCaAlF$_6$:Eu was further annealed and quenched at 400 °C for optimization of its dosimetry properties and used for further studies. It was irradiated to around 10 Gy of γ-rays from ^{60}Co source and TL glow curves were recorded. It was found that there is no change in the glow curve structure and the maximum TL intensity was found to be for the material having 100-120 μm particle size and annealed at 400 °C for 2 h.

3.4 Fading

The material (irradiated for 10 Gy) was stored in dark at room temperature and its TL was recorded at different intervals of time to study fading. Approximately, 16% fading was observed in one month, which is considered to be low for dosimetry purposes.

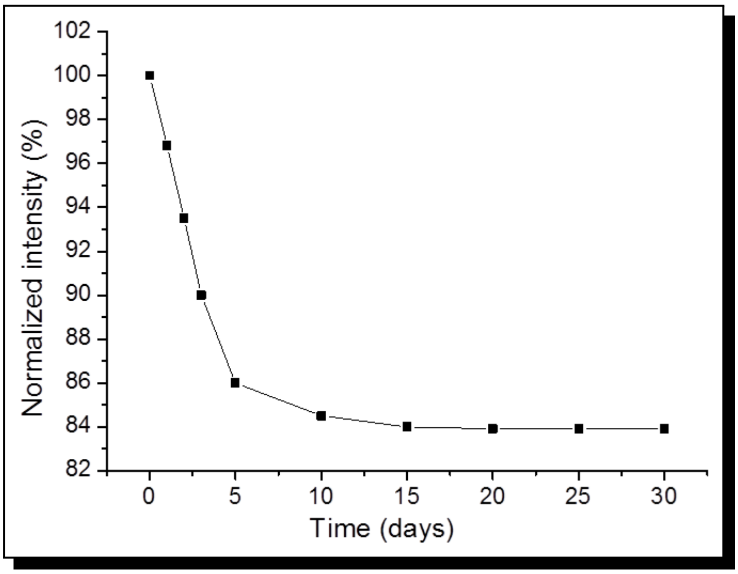

Figure 3. Fading of LiCaAlF$_6$:Eu.The material was irradiated for nominal dose of 10 Gy, stored in dark at room temperature and TL was recorded at different time intervals

3.5 Reusability

The material (in the pellet form) was irradiated to approximate 10 Gy doses of γ-rays from ^{60}Co source and TL was taken several times. No appreciable change either in the glow curve structure or in the intensity was observed. Thus, the material was found to be reusable and economic for the dosimetry purposes.

3.6 PL Emission Spectrum of LiCaAlF$_6$:Eu

For studying the ionic state of the impurity in the material PL emission spectra were recorded on excitation with 350 nm wavelength. A typical PL emission spectrum is as shown in Figure 4.

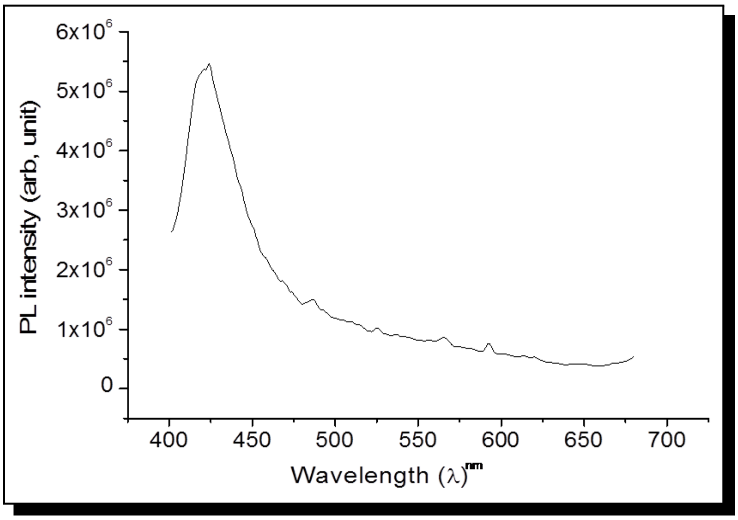

Figure 4. Photoluminescence (PL) of LiCaAlF$_6$:Eu. The material was excitation by 350 nm wavelength

An emission peak could be observed at around 420 nm in the spectrum and could be attributed to Eu^{2+}. The emission Eu^{2+} emission arises from the lowest band of $4f^6 5d^1$ configuration to $^8S_{7/2}$ state of $^4f_7$ configuration. The ground-state electronic configuration of Eu^{2+} is $^4f_7$. This results in an $^8S_{7/2}$ level for the ground state. The next f_7 manifold (^6P_J) lies approximately 28,000 cm^{-1} higher. The lowest lying $4f^6 5d$ levels begin near 34,000 cm^{-1} and are labeled ^8H_J for the free ion. The $4f^6 5d$ levels experience much more crystal field splitting than the $^4f_7$ levels due to the increased spatial extent of the 5d orbitals and often are the metastable states or the lowest excited states, when the Eu^{2+} ions are incorporated in a crystalline host [18].

4. Conclusion

The TLD phosphor material $LiCaAlF_6$:Eu was successfully prepared in a single phase by a two-stage method, firstly, through coprecipitation and by quickly melting in a carbon crucible. Thus, formation of different possible phases like Li_3AlF_6 (further existing in orthorhombic, monoclinic and cubic phases), $CaAlF_5$ could be avoided.

An isolated single dosimetry peak at around 180 °C, high sensitivity (approximately 5 times more than that of commercially available $CaSO_4$:Dy TLD phosphor, low fading and excellent reusability makes this phosphor a good candidate for dosimetry of high energy radiations. High sensitivity may be attributed the incorporation of the Eu impurity in the 2+ ionic state having emission in the 420 nm wavelength range, where most of the common PMTs (used as photodetectors) are also sensitive.

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Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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