



## Effect of Eu and Pb doping on the dosimetric properties of LiCAF

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### ABSTRACT

LiCaAlF<sub>6</sub> (LiCAF) crystals doped with two different ions (europium and lead) have been investigated as potential new dosimetric materials. The stability of thermally stimulated luminescence (TSL) glow peaks in LiCAF:Eu was evaluated by means of the initial rise technique. The decay times at room temperature of the traps related to the dosimetric glow peaks were found to range between 40 and  $2 \times 10^4$  years confirming the good dosimetric characteristics of this crystal. The glow curve of LiCAF:Pb is dominated by a peak at approximately 300 °C emitting in the UV region ( $^3P_{0,1} - ^1S_0$  transition of Pb<sup>2+</sup>) superimposed to a very broad structure at lower temperature (20–200 °C) featuring recombination at an intrinsic defect centre. The anomalous behavior of the low temperature structure during thermal cleaning procedures prevented any reliable numerical analysis of the TSL glow peak at 300 °C.

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## 1. Introduction

LiCaAlF<sub>6</sub> (LiCAF) colquirite crystal has been often investigated due to its wide range of applications, in particular as tuneable solid state laser host material and scintillator. Only recently its potential application as dosimeter material has been considered (Shiran et al., 2004; Di Martino et al., 2007). LiCAF effective atomic number, calculated for low energy photons, is  $Z_{\text{eff}} = 14.33$  (Rodnyi, 1997).

In a previous study LiCAF:Eu was shown to have a good linearity of the thermally stimulated luminescence (TSL) response versus dose in the range  $2 \times 10^{-1} - 1 \times 10^4$  mGy and a TSL sensitivity higher than LiF. The TSL spectrum was associated to the Eu<sup>2+</sup> emission (Di Martino et al., 2007).

In this work we further investigated the dosimetric properties of LiCAF:Eu 0.5 mol% by means of TSL. In particular, the thermal depth of the traps responsible for the glow peaks was evaluated by means of the initial rise technique and, in order to investigate the stability of the TSL peaks, the life-time at room temperature of the associated traps was estimated. Moreover, the effect of Pb doping on the dosimetric properties of LiCAF was also considered and the

correlation between the glow peaks and the luminescence centres was investigated by means of wavelength resolved TSL measurements.

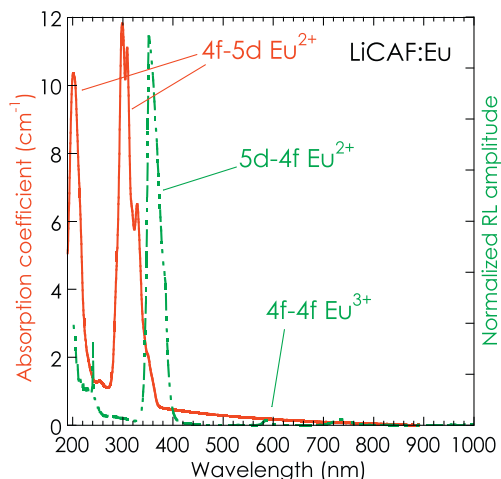
## 2. Experimental

LiCAF crystals were grown at Tohoku University (Japan) by different techniques. LiCAF:Eu 0.5 mol% crystals were grown by the Czochralski technique in a CF<sub>4</sub> atmosphere. The details of the process are described elsewhere (Di Martino et al., 2007). LiCAF:Pb 1 mol% crystals were grown by the micro-pulling down method from carbon crucible using Pt-wire as a seed. Applied pulling-down rate was 0.1 mm/min. An undoped sample was also considered as a reference.

UV–Vis optical absorption (OA) measurements were carried out in the 190–1100 nm range using a Cary 50 spectrophotometer.

TSL measurements above RT were performed and the glow curves were detected by a photomultiplier (EMI 9635QB) from 25 °C up to 450 °C, with a linear heating rate of 1 °C/s. Wavelength resolved TSL measurements were carried out using a home-made apparatus featuring a Hamamatsu IMD C-4560 detector coupled to a Jobin-Yvon CP 140-202 spectrograph. X-ray induced radio-luminescence (RL) spectra were collected using a home-made apparatus featuring a CCD (Jobin-Yvon Spectrum One 3000) coupled to a spectrograph (Jobin-Yvon Triax 180). The RL emission spectra were corrected for the instrumental response.

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**Fig. 1.** Optical absorption (red solid line) and radio-luminescence (green dashed line) spectra of LiCAF:Eu 0.5 mol% crystal.

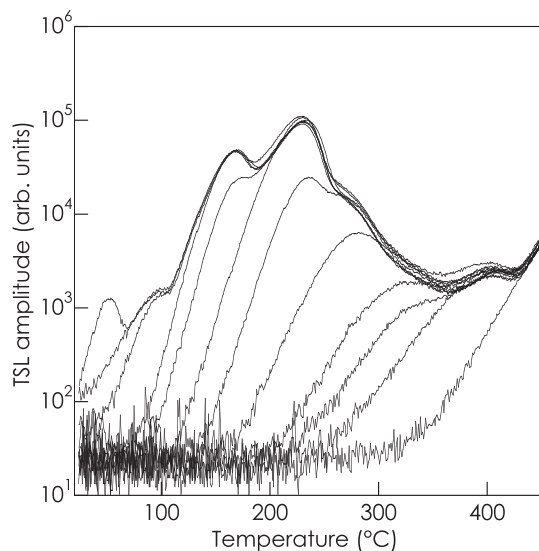
### 3. Results and discussion

#### 3.1. LiCAF:Eu

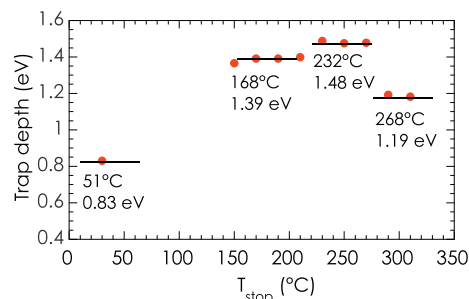
The OA spectrum of LiCAF:Eu 0.5 mol% crystal grown by Czochralsky technique is reported in Fig. 1 (red solid line). Two composite absorption bands are detected around 200 nm and 300 nm. These bands are assigned to the absorption from  $4f^7$  ground state into the crystal field split 5d states of the  $\text{Eu}^{2+}$  ion (Kirm et al., 2005).

The RL spectrum (Fig. 1, green dashed line) is dominated by the characteristic peak of  $\text{Eu}^{2+}$  around 360 nm ascribed to the 5d–4f transition. The presence of a weak emission around 590 nm assigned to a 4f–4f transition of  $\text{Eu}^{3+}$  reveals that a small amount of Eu was nevertheless incorporated in the matrix as trivalent ions.

The TSL glow curve of LiCAF:Eu (Fig. 2) reveals the presence of several peaks in the 50–400 °C temperature range. The trap thermal depth of these peaks was evaluated by means of the initial rise technique (McKeever, 1985). Being most of the peaks



**Fig. 2.** TSL glow curves of LiCAF:Eu 0.5 mol% crystal following room temperature X-ray irradiation (0.5 Gy) and heating up to different temperatures from 30 °C up to 400 °C. Only few selected glow curves are shown for better readability.



**Fig. 3.** Trap thermal depth versus partial cleaning temperature ( $T_{\text{stop}}$ ) in LiCAF:Eu crystal evaluated by the initial rise method.

overlapping with each other a partial cleaning of the glow curves was required. In Fig. 2 some of the glow curves obtained after RT X-ray irradiation and partial cleaning are shown.

Despite the pre-heating not all the TSL peaks could be effectively cleaned and investigated. Fig. 3 reports the trap depth values obtained only from reliable initial rise analysis.

Different glow curves were obtained by varying the dose over four orders of magnitude. Since no shift in the temperature of the TSL peaks was observed the occurrence of first order kinetic was assumed. It was thus possible to evaluate the frequency factor and the decay time at RT of the traps related to the TSL peaks. The values obtained are reported in Table 1 and they show that the stability of the peaks in the 160–270 °C temperature range is suitable for dosimetric applications. The trap depth of the 260 °C peak is smaller than that of the 232 °C one. Among the possible reasons for this somehow unusual value, we cannot rule out a distortion of the glow curve due to a possible thermal quenching of the luminescence centre. However, a monotonic increase of trap depth values of peaks at progressively higher temperature is not a general rule because of the contribution of the frequency factor to the determination of a peak position.

#### 3.2. LiCAF:Pb

Lead-doped LiCAF crystal is transparent and its OA spectrum shows only a sharp increase of the absorption close to 205 nm (Fig. 4 red solid line). It can be assigned to the A band ( $^1S_0$ – $^3P_1$ ) of  $\text{Pb}^{2+}$  ion (Pejchal et al., 2009). A strong optical absorption in the same UV region at 6.05 eV (205 nm) was observed in  $\text{BaF}_2:\text{Pb}$  crystals and was assigned to the A band of  $\text{Pb}^{2+}$  ion (Sastri and Kennedy, 1996).  $\text{Pb}^{2+}$  has two optically active electrons in the  $s^2$  configuration. The optical properties of  $s^2$  ions are known to be drastically influenced by the host lattice with the Stokes shift varying of one order of magnitude depending on the host (Blasse and Grabmaier, 1994).

The RL spectrum of LiCAF:Pb is dominated by a band in the UV region around 203 nm (Fig. 4, green dashed line) which reasonably coincides with the  $\text{Pb}^{2+}$  luminescence band excited by UV or X-rays (Pejchal et al., 2009). Moreover, a broad emission in the 800–1000 nm range and a weak composite emission between 250 and

**Table 1**

Trap depth, frequency factor and decay time at 293 K of the TSL peaks evaluated by the initial rise method.

Peak temp.	Trap depth	Freq. fact.	RT Decay time
51 °C	0.83 ± 0.01 eV	$10^{12} \text{ s}^{-1}$	260 ± 20 s
168 °C	1.39 ± 0.01 eV	$10^{15} \text{ s}^{-1}$	41 ± 5 years
232 °C	1.48 ± 0.01 eV	$10^{13} \text{ s}^{-1}$	$2.3 \pm 0.4 \times 10^4$ years
268 °C	1.19 ± 0.01 eV	$10^{10} \text{ s}^{-1}$	$1.6 \pm 0.3 \times 10^3$ years

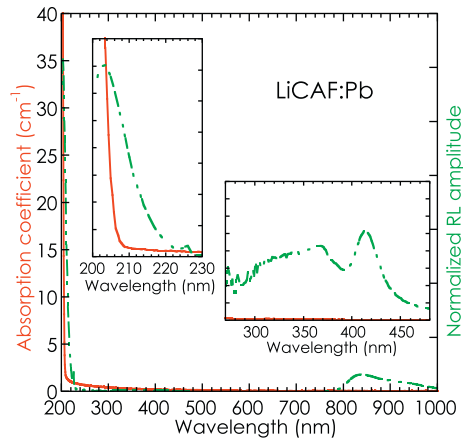


Fig. 4. Optical absorption (red solid line) and radio-luminescence (green dashed line) spectra of LiCAF:Pb 1 mol% crystal.

550 nm were also detected. The emission in the 250–550 nm range was the only one observed also in the undoped sample and it can thus be reasonably ascribed to intrinsic defect centres. Taking into account the previous considerations the emission band at 205 nm is assigned to the  $^3P_{1,0}-^1S_0$  transition of  $Pb^{2+}$ . The origin of the infrared band is not clear but could possibly be related to  $Pb^+$ .

The TSL glow curve of LiCAF:Pb 1 mol% is characterized by a peak at 300 °C and by a broad composite structure below 200 °C (Fig. 5). The broad peak below 200 °C is anomalous since, despite a partial cleaning performed pre-heating the sample up to 200 °C after irradiation, a strong TSL signal was nevertheless detected already at RT preventing any reliable evaluation of the trap thermal depth. This behavior can be due to a recombination occurring via tunnel effect between a trap and a luminescent centre nearby. The TSL sensitivity of the LiCAF:Pb sample proved to be approximately two orders of magnitude lower than that of LiCAF:Eu.

Wavelength resolved TSL measurements (Fig. 6) revealed that different recombination centers are involved in the glow peaks. The trap responsible for the 300 °C peak recombines via the  $^3P_{1,0}-^1S_0$  transition of  $Pb^{2+}$ , on the other hand, the emission of the TSL structure at lower temperature is centred at around 410 nm and is probably of intrinsic nature as suggested by RL spectra. Finally, a weak TSL peak at 450 °C whose emission occurs at  $Pb^{2+}$  ions was also detected.

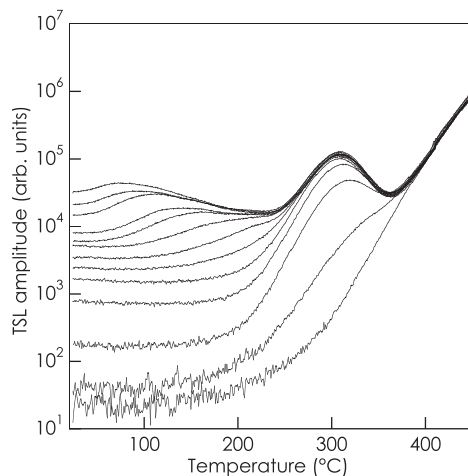


Fig. 5. TSL glow curves of LiCAF:Pb 1 mol% crystal following room temperature X-ray irradiation (1.5 Gy) and heating up to different temperatures from 30 °C up to 400 °C. Only few selected glow curves are shown for better readability.

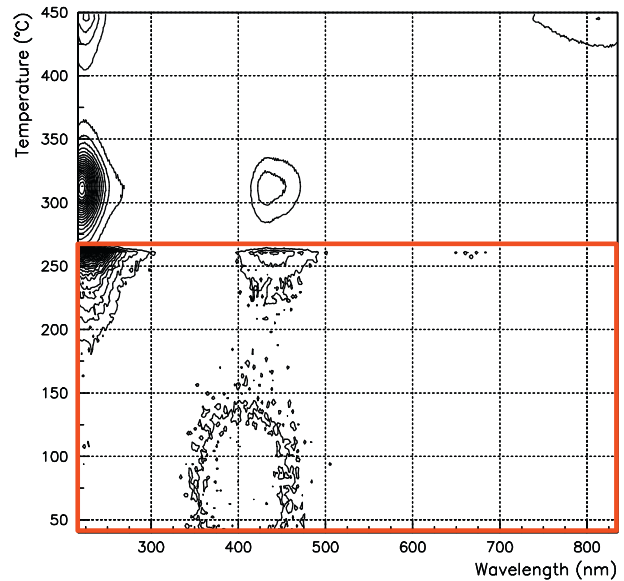


Fig. 6. Contour plot of a wavelength-resolved TSL measurement performed on LiCAF:Pb 1 mol% crystal following RT X-ray irradiation (heating rate = 1 °C/s, dose = 9 Gy). The lower temperature range of the measurement (40–250 °C) enclosed in the red box was obtained after 17.5 Gy X-ray irradiation in order to detect the weaker emission at 100 °C.

#### 4. Conclusions

TSL results above room temperature showed that LiCAF:Eu has potential application as a dosimeter since it features very stable traps (three traps centered at 168 °C, 232 °C and 268 °C with a lifetime ranging from 40 years up to  $2 \times 10^4$  years). The long life-times of the traps evaluated in this work coupled with the excellent linearity of the TSL response vs. dose and the high sensitivity, previously demonstrated, reinforce the utility of LiCAF:Eu as a dosimeter. Its dosimetric characteristics have been found to be better than those of a standard TLD-100 LiF dosimeter (Di Martino et al., 2007).

TSL glow curves LiCAF:Pb were characterized by a very broad TSL structure below 200 °C, followed by a single peak at 300 °C; its trap depth could not be determined precisely due to the influence of the lower temperature components.

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