

Energy storage in Ce-doped LiCaAlF_6 and LiSrAlF_6 crystals

N. Shiran^{a,*}, A. Gektin^a, S. Neicheva^a, V. Voronova^a, V. Kornienko^a,
K. Shimamura^b, N. Ichinose^b

^a*Institute for Scintillation Materials, 60 Lenin Ave, Kharkov 61001, Ukraine*

^b*Kagami Memorial Laboratory of Mat. Sci. and Techn., Waseda University, 2-8-26 Nishiwaseda, Shinjuku, Tokyo 169-0051, Japan*

Received 26 November 2003; received in revised form 9 March 2004; accepted 13 March 2004

Abstract

Absorption, emission and thermoluminescence (TL) of as-grown and X-irradiated pure and Ce-doped LiCaAlF_6 (LiCAF) and LiSrAlF_6 (LiSAF) crystals have been analyzed. It is shown that the energy storage is defined by the dissimilarity of basic matrix properties, intrinsic defect structure, preferred Ce^{3+} ion disposition and charge compensation defect type. This is the reason of higher colorability and TL efficiency of as-grown Ce:LiSAF compared to Ce:LiCAF. Pre-filling of ultra-deep traps leads to enormous increases in the TL response. Due to these properties Ce:LiSAF and Ce:LiCAF are promising thermoluminescent dosimetric materials.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Ce:LiCaAlF₆; Ce:LiSrAlF₆; Colorability; Dosimeter

1. Introduction

LiCaAlF_6 (LiCAF) and LiSrAlF_6 (LiSAF) colquirite crystals offer many advantages. They are prospective VUV-transparent optical materials due to the possession of a large band gap (> 11 eV) (Shimamura et al., 2002). In optical lithography systems these window materials must withstand intense VUV-laser irradiation without transparency loss. Cr^{3+} -doped LiCAF and LiSAF are leading candidates for tunable solid state lasers in the near-IR region (Payne et al., 1989). Ce^{3+} -doped crystals are well known materials for UV solid-state lasers (Marshall et al., 1994). Ce-laser technology has been challenged, however, due to detrimental UV-induced coloring (“solarization” phenomenon) associated with the strong excited-state absorption. This effect is considerably stronger in LiSAF than in LiCAF.

As has been found out recently, Ce:LiCAF is a fast scintillator crystal (Gektin et al., 2002). This investigation is devoted to a study of the energy storage for irradiated (pure

and Ce^{3+} -doped) crystals. Thermoluminescence (TL) studies reveal the possibility of Ce:LiCAF dosimeter applications. Dosimetric properties of Ce:LiSAF crystals have not been studied so far.

Thus, it is evident that an investigation of the optical properties of as-grown and irradiated pure and Ce-doped LiCAF and LiSAF crystals is of considerable interest. In this paper attention is mainly focused upon a study of absorption, emission and energy storage of these materials.

2. Experimental

Pure and Ce-doped LiCAF and LiSAF crystals were grown by the Czochralski technique in a CF_4 atmosphere (Shimamura et al., 2002). The high purity of starting material and the effective elimination of water and oxygen traces enable us to obtain crystals without these contaminations.

Methods of excitation and emission spectrum measurements have been described elsewhere (Gektin et al., 2002). Absorption spectra were measured using a SPECORD 40 spectrophotometer (190–1100 nm) at room temperature (RT). Irradiation was performed using an X-ray tube (160 kV, 10 Gy/min). TL readings were carried out using

* Corresponding author. Tel.: +380-572-308-367; fax: +380-572-321-082.

E-mail address: shiran@isc.kharkov.com (N. Shiran).

a TL analyzer connected to a computer. TL curves were registered in the range from room temperature to 600°C at the constant heating rate of 0.2°C/s. UV filters were used at temperatures higher than 300°C for black-body emission elimination.

3. Results

Excitation and luminescence spectra of as-grown Ce-doped LiCAF and LiSAF crystals are shown in Fig. 1. The main bands are connected with f–d transitions in Ce³⁺ ions. They are slightly shifted and mostly washed out in Ce:LiSAF compared to Ce:LiCAF. The Stokes shift is equal to 0.3 and 0.22 eV for Ce:LiSAF and Ce:LiCAF, respectively.

X-ray induced absorption spectra are similar for both crystal types, but the total coloration efficiency (integral of induced absorption) in Ce:LiSAF is about three times higher compared to Ce:LiCAF (Fig. 2). Simultaneously with the Ce³⁺-ion band decrease, intense UV absorption bands arise with maxima at 190, 235 and 300–320 nm. The intensities of bands induced in the visible (VIS) region (380–420 and 490 nm) and near-IR (NIR) region (~ 900 and 1080 nm) are well below those of the UV bands. The UV bands lead in the accumulation rate increase with the dose, whereas the increase in the VIS and NIR bands is far less (Fig. 2, inset).

Color center annealing occurs in two main stages. Centers absorbing in the VIS and NIR regions are destroyed at $T < 200\text{--}300^\circ\text{C}$, whereas Ce³⁺ centers are re-established. The disappearance of centers with bands situated in the UV range takes place at temperatures higher than 350°C. It should be noted that the UV bands are bleached easily by exposure to a Hg-lamp light (254 nm line) at RT.

The induced absorption spectrum contains a wide band with a maximum at 262 and 276 nm in undoped LiCAF and LiSAF, respectively. This band is presumably conditioned by F-centers. The TL response is very low. Energy storage of pure LiSAF was found to be several times higher than that of LiCAF for the same dose of X-ray irradiation.

The comparison of the induced absorption spectra obtained for pure and Ce-doped crystals shows that most types of color center in activated samples are connected with cerium.

Study of the glow curves revealed that the total light output of the recombination emission (area under the TL curve) is more than three times higher in Ce:LiSAF than in Ce:LiCAF (Fig. 3). The main TL peaks appear at 218°C and 285°C in Ce:LiSAF and Ce:LiCAF, accordingly. An additional intense peak at 450°C competes with the main one in Ce:LiSAF. TL emission shows a spectrum with characteristics similar to the 5d–4f Ce³⁺ emission (~ 300 nm).

Sensitization of both doped crystals was achieved by the pre-filling of deep traps by high-dose irradiation at RT and subsequent annealing at 350°C (Fig. 3, curves 1' and 2'). As a result, the main peak intensity reveals an enormous in-

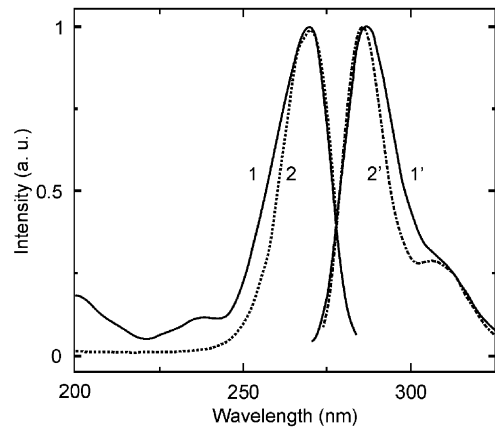


Fig. 1. Excitation (1, 2) and luminescence (1', 2') spectra of Ce-doped LiSAF (1, 1') and LiCAF (2, 2') crystals.

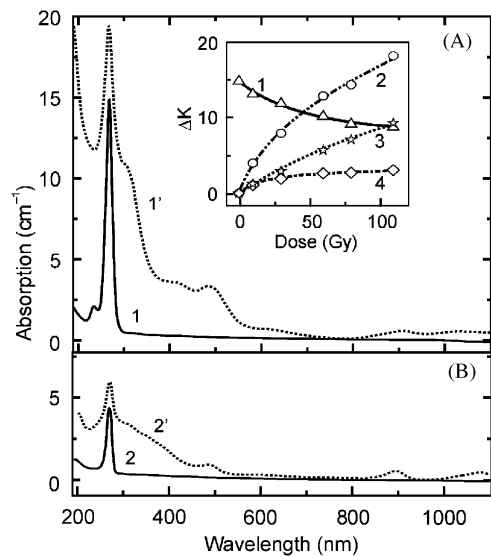


Fig. 2. Absorption spectra of as grown (1, 2) and irradiated (1', 2') Ce-doped LiSAF (A) and LiCAF (B) crystals. Dose 110 Gy. Inset: dose dependence of bands at (1) 268 nm, (2) 190 nm, (3) 320 nm and (4) 487 nm.

crease. In this way both Ce-containing LiSAF and LiCAF crystals became hypersensitive TLD materials with TL response several hundred times higher than that of TLD-100 (LiF:Mg,Ti).

4. Discussion

Table 1 summarizes the properties of LiSAF and LiCAF crystals. Lattice parameters of LiCAF are smaller than these LiSAF. The thermal expansion of LiSAF is highly

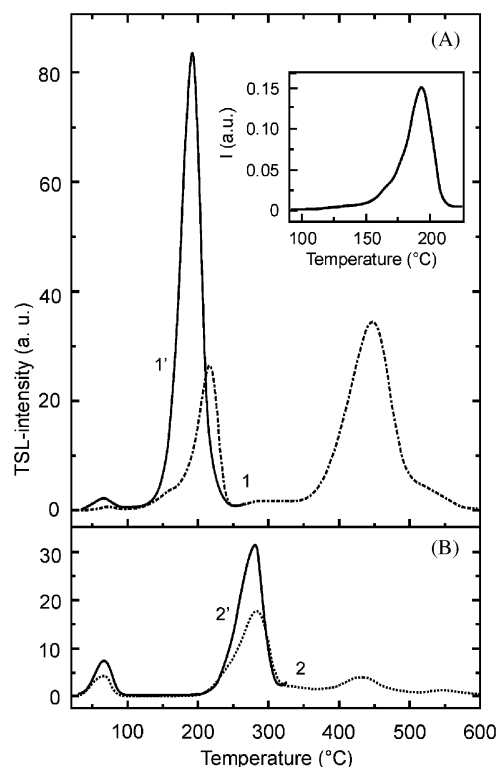


Fig. 3. TL curves of Ce-doped LiSAF (A) and LiCAF (B) crystals: as grown (1, 2) and preliminary treated (1', 2'). Inset: TL of LiF:Mg,Ti. Dose 0.5 Gy.

Table 1
Properties of LiCaAlF₆ and LiSrAlF₆ colquirite crystals

Parameter	Crystal	
	LiCaAlF ₆	LiSrAlF ₆
Lattice	Hexagonal	Hexagonal
Space group	P $\bar{3}1c$	P $\bar{3}1c$
Lattice parameter, Å	<i>a</i>	5.006
	<i>c</i>	9.636
Density, g/cm ³	2.94	3.45
Refractive index (290 nm)	1.41	1.42
Melting point, °C	825	750
Thermal expansion, 10 ⁻⁶ /K	<i>c</i>	22
	⊥ <i>c</i>	3.6
Thermal conductivity, W/(K m)	<i>c</i>	4.58
	⊥ <i>c</i>	5.14
Fracture toughness, MPa√m	0.18–0.37	0.4

anisotropic, i.e. the parameter *a* increases whereas *c* decreases with increase in temperature (Shimamura et al., 2002). Calculations of defects formation energies have

shown that F_i⁻ - v_F⁺ and Li_i⁺ - F_i⁻ Frenkel defects are the most probable in LiSAF whereas only Li_i⁺ and v_{Li}⁻ defects are likely in LiCAF (Amaral et al., 2003).

The higher X-ray sensitivity of LiSAF in comparison with that of LiCAF may be caused by higher concentrations and broader scale of the defects in the LiSAF crystals. Effective F-center formation may be particularly connected with the presence of additional fluoride vacancies to compensative the negative surplus charge of F_i⁻ ions.

Prediction of the sites occupied by Ce³⁺ ions in LiCAF and LiSAF is based on cationic radius values and lattice parameters, computer modeling and experimental results. Polarized luminescence and absorption spectroscopy as well as ESR data confirmed that Ce³⁺ ions occupy Me²⁺ sites (Me is Ca or Sr) (Marshall et al., 1994; Yamaga et al., 1998). The activator center is ascribed to a Ce³⁺v_{Li}⁻ defect in both crystal types while the theory predicts the possibility of additional Ce³⁺F_i⁻ centers in LiSAF only (Amaral et al., 2003). Note, Ce³⁺ and Ca²⁺ ion sizes are about the same (1.15 and 1.14 Å), whereas Ce³⁺ and Sr²⁺ ones are different (1.15 and 1.27 Å). Therefore, the octahedral CeF₆ cluster has to be extended in LiSAF. It is a well-known feature of the large Ce:LiSAF crystals that they are strongly strained (Shimamura et al., 2002). The lattice distortion may lead to washing out of typical absorption Ce³⁺, excitation and photoemission bands as well as to the Stokes shift increase. This effect takes place, as shown above.

Irradiation at RT leads to a decrease in the Ce³⁺ ions concentration and the simultaneous appearance of various color centers. The phenomenon is explained by the redox reaction typical for the Ce³⁺ ion. Bands at ~ 900 and 1080 nm are identical to those in Ce:CaF₂ (Alig and Kiss, 1969) and may be analogous ascribed to Ce²⁺ centers. The absorption in the VIS region is tentatively ascribed to F-type centers near Ce³⁺ (Pogatshnik and Hamilton, 1987). Electron color center destruction and Ce³⁺ reduction may be realized by annealing at 200–300°C. This process is accomplished by radiative recombination of a free electron with a hole trapped on (or near) Ce³⁺ and manifests itself as the main TL peak.

It was shown that color centers which absorb in the UV region (bands at 190 and 235 nm) may be bleached by light close to the F-band, from which allows we propose a hole nature of these centers. They are thermally stable up to 350°C and may be responsible for the additional high-temperature TL peak.

5. Conclusions

Lattice properties, Ce³⁺-ion environments and structure of defects influence the optical characteristics and energy storage peculiarities in Ce-doped LiSAF and LiCAF crystals. Comparison of X-ray induced absorption spectra and TSL of undoped crystals confirmed that the intrinsic defect concentration and scale are higher in LiSAF. Most of the color centers in activated crystals are related to cerium. It

is shown that the energy storage efficiency is conditioned by the dissimilarity of basic matrix properties: intrinsic and Ce-induced defects, preferred Ce^{3+} -ion disposition and charge compensating defects. These factors are the cause of the high colorability and higher TL response of Ce:LiSAF compared with Ce:LiCAF. Note, these features may be the cause of the strong UV-laser induced “solarization effect” observed in Ce-doped LiSAF, in contrast to LiCAF.

The nature of the color centers and the energy storage mechanism need further special inquiry. The high sensitivity, favorable temperatures of the TL peaks for both Ce-doped matrixes are demonstrated. These properties (as well as the possibility of an enormous increase of the TL response by the preliminary treatment of samples) denote the applicability of Ce:LiSAF and Ce:LiCAF crystals in TL dosimetry.

References

- Alig, R.C., Kiss, Z.J., 1969. Energy levels of Ce^{2+} in CaF_2 . *Phys. Rev.* 186, 276–284.
- Amaral, I.B., Plant, D.F., Valerio, M.E.G., Jackson, R.A., 2003. Computer modeling of defect structure and rare earth doping in $LiCaAlF_6$ and $LiSrAlF_6$. *J. Phys.: Condens. Matter* 15, 2523–2533.
- Gektin, A.V., Shiran, N.V., Neicheva, S.V., Shimamura, K., Fukuda, T., 2002. New scintillator $LiCaAlF_6(Ce)$ crystal. *Nucl. Instrum. Methods A* 486, 274–277.
- Marshall, C.D., Speth, J.A., Payne, S.A., Krupke, W.F., Guarles, G.J., Castillo, V., Chai, B.H.T., 1994. Ultraviolet laser emission properties of Ce^{3+} doped $LiSrAlF_6$ and $LiCaAlF_6$. *J. Opt. Soc. Am. B* 11, 2054–2071.
- Payne, S.A., Chase, L.L., Wilke, G.D., 1989. Optical spectroscopy of the new laser materials, $LiSrAlF_6:Cr^{3+}$ and $LiCaAlF_6:Cr^{3+}$. *J. Lumin.* 44, 167–176.
- Pogatshnik, G.I., Hamilton, D.S., 1987. Excited-state photoionization of Ce^{3+} ions in $Ce^{3+}:CaF_2$. *Phys. Rev.* 36 B, 8251–8257.
- Shimamura, K., Sato, H., Bensalah, A., Machida, H., Sakura, N., Fukuda, T., 2002. Growth of Ce-doped colquiriite and sheelite-type single crystals for UV laser application. *Opt. Mater.* 19, 109–116.
- Yamaga, M., Lee, D., Henderson, B., Han, T.P.J., Gallagher, H.G., Yosida, T., 1998. The magnetic and optical properties of Ce^{3+} in $LiCaAlF_6$. *J. Phys.: Condens. Matter* 10, 3223–3237.