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## Energy transfer in pure and Ce-doped LiCaAlF<sub>6</sub> and LiSrAlF<sub>6</sub> crystals

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### Abstract

Intrinsic ultra-fast scintillations at pulsed X-ray excitation were found in LiCaAlF<sub>6</sub> and LiSrAlF<sub>6</sub>. Radiative recombination features of Ce-doped crystals are explained by differences of lattice properties, defect structure and Ce<sup>3+</sup> ion environment in these crystals. The role of exciton formation, electron and hole traps, and energy transfer to the activator centers are discussed.

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### 1. Introduction

Recently, Ce-doped LiCaAlF<sub>6</sub> (LiCAF) crystal was proposed as a new fast scintillator [1]. It was presumably supposed that the delayed rise time of the scintillation pulse might be connected with the transport and sequential capture of charge carriers

at or near the Ce<sup>3+</sup> ion. The overlapping self-trapped exciton emission and Ce<sup>3+</sup> ion absorption bands also makes radiative energy transfer possible. Studies of energy transfer processes have shown the presence of shallow and deep intrinsic as well as activator traps. Thermally stimulated luminescence (TSL) revealed the possibility to use Ce:LiCAF for dosimetric application [1]. The energy transfer mechanism of Ce:LiSrAlF<sub>6</sub> (LiSAF) crystals have not been studied so far. The paper is devoted to the study of VUV and pulsed

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X-ray excited charge transfer luminescence occurring in pure and Ce-doped LiCAF and LiSAF crystals.

## 2. Experimental

Crystals were grown by Czochralski technique in  $\text{CF}_4$  atmosphere [1]. High purity of raw material as well as water and oxygen traces effective elimination allowed to obtain crystals without irrelevant contaminations. The setups for recording absorption, excitation and emission spectra at steady-state conditions were described elsewhere [1]. The time-resolved spectroscopy using synchrotron radiation (SR) excitation in 4–30 eV range with time-resolution 300 ps (FWHM) was carried out at the SUPERLUMI station of HASYLAB [2]. Some luminescence studies were performed under soft X-ray excitation in the range of 80–330 eV at the undulator beam line BW3 [3]. The scintillation rise and decay times were studied using a pulsed X-ray (20 keV) system [4]. A response time of 35 ps FWHM was used to detect the scintillation photons in time bins of 3 ps.

## 3. Results

X-ray or VUV excitation results in luminescence with the maximum at 280 nm and a shoulder near 330 nm at 10 K in pure LiCAF (Fig. 1). The dominant luminescence band peaking at 335 nm is

typical for pure LiSAF. Excitation spectra of emission show an intense narrow excitonic peak at  $\sim 11.4$  eV [5]. Self-trapped exciton (STE) luminescence is thermally quenched above 160 K. Decay time of emission following excitation by 10.78 eV photons was estimated to be  $\sim 800$  ns at RT (Fig. 2, curve 1). The estimated energy gap ( $E_g$ ) is equal to  $\sim 12.65$  and 12.15 eV in LiCAF [5] and LiSAF [6], respectively. The additional fast emission covering 380–400 nm was revealed when the excitation energy becomes higher than  $E_g$ . Soft X-ray excitation of LiCAF crystal by 330 eV photons leads to the appearance of distinctive luminescence with spectrum composed of the main band at  $\sim 280$  nm and additional ones in blue region at RT (Fig. 3).

Prolonged irradiation caused redistribution of intensities of the bands: UV band decreases whereas blue one increases. The decay time of blue emission is considerably shorter ( $\sim 50$  ns) than that of UV luminescence (Fig. 2, curves 2, 3). Luminescence intensity increases with the lowering of temperature to 10 K. The decay curves of pure samples emission at the pulsed X-ray (20 keV) excitation are presented in Fig. 2 (curve 4). The rise time is ultra-fast ( $< 30$  ps) and beyond the measurement limit. The decay consists of the dominating fast ( $\sim 0.3$  ns) component.

The sub-nanoseconds emission was detected in a wide spectral range (from UV up to 380 nm). The decay kinetics of LiSAF was found to be similar.

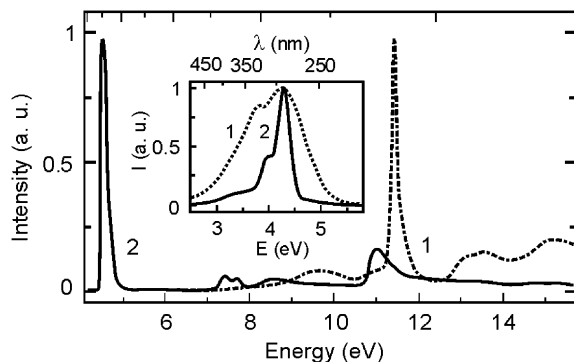


Fig. 1. Excitation spectra of pure (1) and Ce-doped (2) LiCAF crystals at 10 K. Inset: luminescence at  $E_{\text{exc}} = 11.4$  eV.

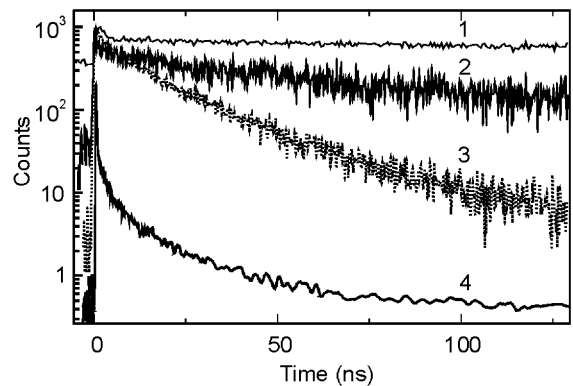


Fig. 2. Decay curves of pure LiCAF at RT:  $E_{\text{exc}} = 10.78$  eV ( $\lambda_{\text{em}} = 280$  nm)—1; 150 eV ( $\lambda_{\text{em}} = 300$  nm)—2; 150 eV ( $\lambda_{\text{em}} = 400$  nm)—3; X-ray (20 keV)—4.

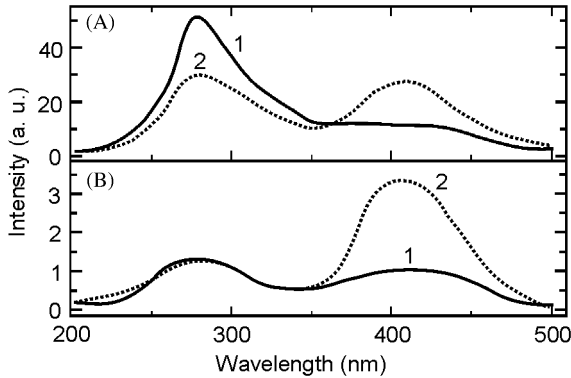


Fig. 3. Emission spectra at  $E_{\text{exc}} = 330 \text{ eV}$ , RT, with time gates: 150 ns (A) and 1.5 ns (B) for initial (1) and irradiated (2) pure LiCAF crystal.

High-dose X-ray irradiation of samples at RT leads to the color center formation. Induced absorption spectrum consists of a wide band with maxima at 262 and 275 nm in LiCAF and LiSAF, respectively, presumably assigned to the F-centers [1,7]. TSL response is very low. A rough estimate of energy storage was obtained from the integral of induced absorption and area under TSL curve. The radiation sensitivity of LiSAF is several times higher than that of LiCAF.

Excitation and luminescence spectra of Ce-doped samples measured at steady-state condition (RT) demonstrate typical 4f-5d transition in  $\text{Ce}^{3+}$  for both crystals (Fig. 4). Though, the features in excitation and emission spectra are smeared out and Stokes shift is larger for Ce:LiSAF. The STE emission has a strong overlap with the  $\text{Ce}^{3+}$  absorption band.

SR excitation spectrum of  $\text{Ce}^{3+}$  luminescence in LiCAF at 10 K is shown in Fig. 1. The main intense f-d excitation band at 274 nm is narrow and coincides with that at steady-state conditions at RT. STE luminescence excited in the excitonic band (11.4 eV) is significantly suppressed in comparison with the pure crystal. It is noteworthy that the  $\text{Ce}^{3+}$  emission response distinctly decreases at prolonged soft X-rays irradiation.

Decay curves of Ce-emission at pulsed X-ray (20 keV) excitation are shown in Fig. 5. The presence of sub-nanosecond pulse identical to that of undoped crystal was detected. Contrary to pure

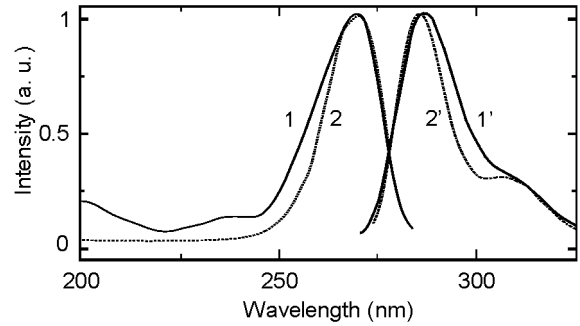


Fig. 4. Steady-state excitation and emission spectra of Ce-doped LiSAF (1, 1') and LiCAF (2, 2') crystals at RT.

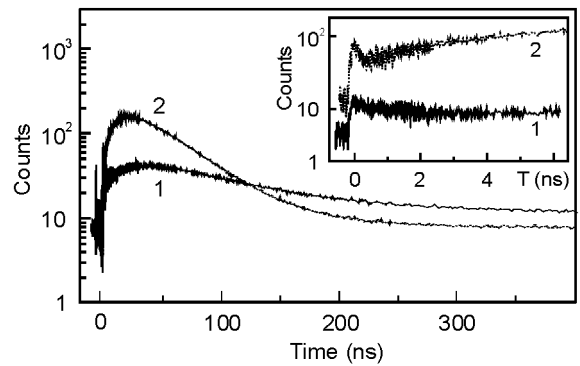


Fig. 5. Decay curves of Ce-doped LiSAF (1) and LiCAF (2).  $E_{\text{exc}} = 20 \text{ keV}$ , RT.

samples, a distinct initial stage with rise times of 20 and 43 ns were revealed in LiCAF and LiSAF, respectively. The decay time is equal to 53 ns in Ce:LiCAF whereas two components (160 and 617 ns) are observed in Ce:LiSAF. Notably, the decay time at direct excitation in spectral region of 4f-5d transition for  $\text{Ce}^{3+}$  does not exceed 25–28 ns [8]. X-ray induced absorption spectra are similar for both type of crystals but total coloration efficiency (integral of induced absorption) in Ce:LiSAF is several times higher compared to Ce:LiCAF. Features of Ce-color centers in LiCAF and LiSAF are reported in Ref. [7]. Simultaneously with the decrease of  $\text{Ce}^{3+}$  ion absorption band intense absorption bands in UV (at 190, 230 and 300–320 nm) as well as weak ones in visible and near IR regions arise. The TSL study revealed

that the total light output of recombination emission (area under glow curve) is more than three times higher in Ce:LiSAF than in Ce:LiCAF.

#### 4. Discussion

Theoretical calculation of defect formation energies has shown that  $F_i^-$  and  $Li_i^+$  Frenkel defects are the most probable in LiSAF whereas only  $Li_i^+$  defect is very likely in LiCAF crystal [9]. Higher X-ray sensitivity of undoped LiSAF emerged in induced absorption and TSL may be caused by higher concentration and broader variety of defects. Increased probability of F-center formation in LiSAF can be particularly related to the presence of fluoride vacancy, compensative the charge of  $F_i^-$ .

It was shown that the intrinsic low-temperature emission of LiCAF is connected with self-trapped exciton (STE) [1,5]. The decay kinetics of STE emission under photoexcitation with energy  $\sim 11.4\text{ eV}$  ( $E < E_g$ ) contains only slow component with  $\tau \leq \mu\text{s}$ . Irradiation by  $E \gg E_g$  creates electron–hole pairs with high kinetic energy. Therefore, carriers in the pair become well separated and can be captured by some intrinsic traps. The excitation by energy  $\sim 330\text{ eV}$  leads to appearance of fast (50 ns) emission in blue region. Increase of this component in a sequence of recorded emission spectra relates it with defects induced by irradiation.

The presence of ultra-fast pulse ( $\tau_r < 30\text{ ps}$ ,  $\tau_d \cong 0.3\text{ ns}$ ) in a wide spectral range of 280–380 nm was found at X-ray excitation (20 keV) in pure and in doped samples as well. This luminescence may be attributed to excitonic emission or to intraband transitions of hot carriers reported earlier for several materials [4].

It is possible to predict the  $Ce^{3+}$  ion environment in LiCAF and LiSAF based on value of cationic radius and lattice parameters, computer modeling [9] and experimental results [1,5,7,8,10]. Activator center is ascribed to  $Ce_M^{3+}v_{Li}^-$  defect ( $M = Ca^{2+}$  or  $Sr^{2+}$ ) in both type crystals while the theory predicts the possibility of additional  $Ce_{Sr}^{3+}F_i^-$  centers in LiSAF. Note that the sizes of  $Ce^{3+}$  and  $Ca^{2+}$  ions are similar whereas  $Ce^{3+}$  and

$Sr^{2+}$  ones are different. Therefore, octahedral  $CeF_6$  cluster has to be extended in LiSAF. The lattice distortion may lead to smearing out of features in absorption, excitation and photoluminescence  $Ce^{3+}$  bands as well as to the increase Stokes shifts shown for Ce:LiSAF. The rise time of scintillation pulse in both Ce-contained crystals may be connected with the sequential electron–hole recombination of carriers, captured directly at  $Ce^{3+}$  ion or at the adjacent defect. In addition, the overlap of the STE emission and the  $Ce^{3+}$  absorption bands points to probable existence of resonant exciton energy transfer. Delay in the energy transfer from host to the  $Ce^{3+}$  ion is controlled by thermal release of carriers from the shallow traps.

$Ce^{3+}$  concentration decreases and color centers appearance at irradiation is explained by the typical for  $Ce^{3+}$  redox reactions. Destruction of electron color center ( $Ce^{2+}$  and F-center near  $Ce^{3+}$ ) and  $Ce^{3+}$  ion reduction can be achieved by annealing at 200–300 °C. This process is accomplished with radiative recombination of free electron with the hole trapped at (or near)  $Ce^{3+}$  and manifests as a main TSL peak. Hole color centers are thermally stable up to 350 °C and can be responsible for the additional high-temperature TSL peak.

#### 5. Conclusions

The presence of intrinsic ultra-fast scintillation was found in LiCAF and LiSAF. This effect may tentatively be attributed to exciton emission and/or radiative intraband transitions of hot carriers.

Radiative recombination features of Ce-doped crystals are explained by differences of lattice properties, defect structure and  $Ce^{3+}$  ion environment in LiCAF and LiSAF crystals. The initial stage of scintillation pulse can be connected with the sequential electron–hole recombination of carriers, captured directly at  $Ce^{3+}$  ion or at adjacent point defect. The STE emission and the  $Ce^{3+}$  absorption bands overlap allows the resonant exciton energy transfer. The shallow traps are responsible for delayed charge transfer to the  $Ce^{3+}$  ion. Deep and ultra-deep activator traps

affect the effective coloration and TSL in samples irradiated at RT.

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