Abstract

The positions of 4f–5d levels of cerium in K$_5$Li$_2$LaF$_{10}$ crystals were determined to be situated at: 33 145 cm$^{-1}$ (zero phonon line), 43 700, 45 900, 47 250 and 54 500 cm$^{-1}$. Thermoluminescence glow curves, depend on concentration of Ce$^{3+}$ and reveals occurrence of several traps with depths ranging from 0.3–0.84 eV; the low value of ratio TL/(TL+ssRL) for K$_5$Li$_2$CeF$_{10}$ (0.07) suggests that the trapping process is almost negligible in contrast to the K$_5$Li$_2$La$_{0.99}$Ce$_{0.01}$F$_{10}$ (0.44) one, where nearly half of the excitation energy is stored in traps.

Keywords: Thermoluminescence; VUV; Cerium; Fluoride crystal

1. Introduction

The scientific research on phosphors has a long history, it started more than 100 years ago. Recently, the investigation goes on three paths mainly: plasma displays and mercury-free efficient lamps [1–3]; scintillators for VUV–X-ray [4–6]; fast scintillators for gamma radiation using core-valence luminescence [7–10]. Besides these reasons the fundamental research is still attractive to give the possibility to predict theoretically the properties of new material, to reduce costs of investigations. Compounds doped with cerium, which can be used as scintillators, give information about behaviour of other lanthanide dopands, especially on f–d transition [11]. In this communication we present some results of our studies on spectroscopic and scintillation properties of K$_5$Li$_2$CeF$_{10}$ and K$_5$Li$_2$LaF$_{10}$:Ce single crystals. Crystals under study are uncommon in that the rare-earth ions do not share ligands between themselves, and are well spaced. Owing to this feature, the self-quenching of luminescence is strongly reduced, consequently the concentration of lanthanide ions can be maintained at a high-level without loss of emission efficiency.

2. Materials and experimental

Single crystals of K$_5$Li$_2$CeF$_{10}$ and K$_5$Li$_2$LaF$_{10}$:Ce were grown using the Bridgman process in graphite crucibles (IG-110). Excitation spectra, luminescence decay times, and the VUV-excited luminescence spectra were recorded using synchrotron radiation at the SUPERLUMI and HIGITI stations of the Synchrotronstrahlungslabor at DESY in Hamburg. Thermoluminescence spectra (TL) were recorded using a typical set-up consisting of an X-ray tube operated at 44 kV and 6 mA, a 0.5 m monochromator (Acton Research Corporation SpectraPro-500), a photomultiplier (Hamamatsu R928), and a closed-cycle helium cooler (APD Cryogenics, Inc.) with a programmable temperature controller (Lake Shore 330). Prior to the TL runs, the samples were exposed for 10 min to X-rays at a temperature of 10 K. The glow curves were recorded between 10 and 300 K at a heating rate of about 0.15 K/s.

3. Results and discussion

Although the luminescence, absorption and excitation spectra of Ce$^{3+}$ in K$_5$Li$_2$LaF$_{10}$ were presented elsewhere [12] for 3 and 100 at% of cerium, the detailed information about the 5d levels was not clear. Fig. 1 presents emission and excitation spectra of K$_5$Li$_2$LaF$_{10}$ doped with 0.1 at% of Ce$^{3+}$ at 8 K. The strong emission, with temperature...
Emission (dashed line) and excitation solid line of K₃Li₂La₀.₉₉₉Ce₀.₀₀₁F₁₀ recorded at 8 K. Inset presents the position of the zero-phonon line of f–d transition.

Indepenent life time ~32 ns, band is composed from transitions from the lowest 5d state to the excited ²F₇/₂ (29 610 cm⁻¹) and ground ²F₅/₂ (31 550 cm⁻¹) states, in good agreement with the data presented in Ref. [12]. An energy difference of about 1940 cm⁻¹, which is a typical value for the spin–orbit split of the states ²F₇/₂ and ²F₅/₂ of Ce⁢⁺ ion, confirms the Ce⁢⁺ d–f nature of this emission, excited at 54 500 cm⁻¹. X-ray excitation brings about the same emission band in K₃Li₂La₀.₉₇Ce₀.₀₃F₁₀.

Upon excitation at the band 70 000–80 000 cm⁻¹ self-trapped excitons (STE) luminescence can be observed, with maximum at ~23 000 cm⁻¹. This emission disappears at higher temperatures. For higher concentration of cerium the ratio of this STE emission to d–f one decreases. The decay, of this broad–band emission in the visible, is slower by orders of magnitude with respect to the d–f one. The intensity of the excitation spectrum slowly goes down, when the excitation energy is higher, and at near 81 080 cm⁻¹ (123 nm, 10 eV) rapidly goes to zero. This point is consistent with the absorption edge of the host.

The lowest energy 5d state maximum is situated at 33 670 cm⁻¹ with a well-resolved zero phonon line presented in inset of Fig. 1 placed at 33 145 cm⁻¹. The energy of this zero phonon line gives the possibility to predict the position of the lowest f–d transitions for other lanthanides (Pr-Gd) in K₃Li₂LnF₁₀ crystal [11]. It should be 30 600 cm⁻¹ (220 nm) for praseodymium, 55 800 cm⁻¹ (179 nm) for neodymium, 59 645 cm⁻¹ (168 nm) for samarium, 69 045 cm⁻¹ (145 nm) for europium and 78 945 cm⁻¹ (127 nm) for gadolinium, which is in agreement with observation [13].

In addition to the first crystal field level of the 5d state at 33 145 cm⁻¹, all four remaining levels were observed at energies 43 700, 45 900, 47 250 and 54 500 cm⁻¹. This gives crystal field splitting, defined as the difference between the lowest and highest 5d level, equal to 21 355 cm⁻¹, which makes it possible to determine the red shift and calculate the so-called spectroscopic polarizability of ligands in the crystal host [14–16].

Fig. 2 presents the thermoluminescence glow curves of K₃Li₂CeF₁₀ (A) and K₃Li₂La₀.₉₇Ce₀.₀₃F₁₀ (B), recorded at heating rate 0.15 K/s following a 10 min, X-ray irradiation. As a steady-state radioluminescence intensity during the irradiation prior to the TL runs has also been recorded it is possible to evaluate a ratio, defined as TL/(TL + ssRL), the trap depth, \( E \), the heating rate, \( n₀ \)—the initial concentration of traps, \( T \)—the trap depth, \( s \)—the frequency factor, and \( k_B \)—the Boltzmann constant. Preliminary input values of \( n_0, E_i \), and \( s \) have been chosen by trial and error. The effect of the non-ideal heat transfer [18] has been neglected due to a very low heating rate. The results of the fitting procedure are summarized in Table 1.

As a steady-state radioluminescence intensity during the irradiation prior to the TL runs has also been recorded it is possible to evaluate a ratio, defined as TL/(TL + ssRL), indicating the fraction of the total excitation energy that has been accumulated in traps, see Fig. 2.

### 4. Conclusions

The detail information about the 5d levels structure and energies were given. The zero-phonon line was determined...
at 33 145 cm\(^{-1}\) (301.70 nm). Recorded TL spectra inform about the frozen energy stored in traps and defects. The low-value of ratio TL/(TL + ssRL) for K\(_5\)Li\(_2\)CeF\(_{10}\) (0.07) suggests that the trapping process is almost negligible. On the contrary, in case of K\(_5\)Li\(_2\)La\(_{0.99}\)Ce\(_{0.03}\)F\(_{10}\) (0.44) nearly half of the excitation energy is stored in traps.

Acknowledgements

This work was supported by the European Community—Research Infrastructure Action under the FP6 “Structuring the European Research Area” Programme (through the Integrated Infrastructure Initiative “Integrating Activity on Synchrotron and Free Electron Laser Science”. We are grateful to Toyo Tanso Co., Ltd., Osaka, Japan for providing high quality IG-110 purified graphite.

The Committee for Scientific Research supported this work as research project in 2005–2007.

References


Table 1

Parameters of traps detected in K\(_5\)Li\(_2\)CeF\(_{10}\) and K\(_5\)Li\(_2\)La\(_{0.97}\)Ce\(_{0.03}\)F\(_{10}\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak no.</th>
<th>T(_{\text{max}}) (K)</th>
<th>(n_0)</th>
<th>E (eV)</th>
<th>ln s</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(_5)Li(<em>2)CeF(</em>{10})</td>
<td>1</td>
<td>152</td>
<td>159 300</td>
<td>0.4063</td>
<td>27.61</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>256</td>
<td>38 290</td>
<td>0.6236</td>
<td>24.14</td>
</tr>
<tr>
<td>K(<em>5)Li(<em>2)La(</em>{0.97})Ce(</em>{0.03})F(_{10})</td>
<td>1</td>
<td>167</td>
<td>2 668 000</td>
<td>0.4615</td>
<td>28.52</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>211</td>
<td>142 700</td>
<td>0.296</td>
<td>11.89</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>230</td>
<td>167 900</td>
<td>0.8435</td>
<td>39.05</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>247</td>
<td>206 000</td>
<td>0.8245</td>
<td>34.88</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>274</td>
<td>86 170</td>
<td>0.384</td>
<td>11.55</td>
</tr>
</tbody>
</table>

\(T_{\text{max}}\) is the temperature (at which the glow curve peaks were observed), E the trap depth, \(s\) the frequency factor, \(n_0\) is in the same units as TL intensity and \(s\) is in s\(^{-1}\).