Luminescence and scintillation properties of the small band gap compound LaI₃:Ce³⁺

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Abstract

LaI₃:Ce³⁺ has the smallest band gap in the LaX₃:Ce³⁺ (X = F, Cl, Br, I) series and hence a potentially higher scintillation yield. The luminescence properties of LaI₃:Ce were investigated by means of optical, X-ray, and γ-ray excitation. Unexpectedly, the compound is a poor scintillator at room temperature but presents good scintillation properties for temperatures below 100 K where Ce³⁺ emission is observed peaking at 452 and 502 nm with a yield of ~16 000 photons/MeV. The drastic thermal quenching of luminescence is explained by the proximity of the Ce³⁺ lowest 5d excited state to the host conduction band. Autoionization of Ce³⁺ therefore prevents any scintillation effect at room temperature. The positions of Ce³⁺ levels relative to the host bands were estimated.
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1. Introduction

In the past five years the scintillation properties of the rare earth trihalides $LnX_3:Ce^{3+}$ were studied. First $LaF_3:Ce^{3+}$ demonstrated poor scintillation properties, i.e. a light yield of 2200 photons/MeV, a decay time of 26.5 ns and a density of 5.9 g/cm³ [1,2]. The low value for the scintillation yield was attributed to a too large energy gap between the lowest Ce³⁺ 4f level and the top of the host valence band [3,4]. The trapping of holes from the host valence band by Ce³⁺ is then a slow process. Instead Self-Trapped Excitons (STE) are created that quench thermally

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at room temperature. $LaCl_3:Ce^{3+}$ [5–7] and next $LaBr_3:Ce^{3+}$ [8,9] showed much more favorable features. They both combine a high light yield (respectively, 49 000 and 61 000 photons/MeV) with excellent energy resolution (around 3% for the 662 keV peak) and fast luminescence decay (respectively, 26 ns and 17–35 ns). They are the first choice candidates for scintillation crystals when good energy resolution and fast response are needed. We decided to look for improved performance based on the fact that the maximum attainable scintillation yield is directly proportional to the number of electron–holes pairs created when a γ quantum is absorbed. The number of electron–hole pairs is inversely proportional to the band gap. In order to increase the scintillation light yield we aim to study smaller band gap materials. In the sequence LaF_3, $LaCl_3$, $LaBr_3$ the gap decreases and light yield increases. The optical and scintillation properties of Ce-doped lanthanum halide $LaI_3:Ce$ with even smaller bandgap are the topic of this publication.

2. Results

$LaI_3:Ce$ was grown as a single crystal using the vertical Bridgman technique [10]. LaI_3 crystallizes in the $PuBr_3$-type structure with space group Cmcm [11]. The density is 5.614 g/cm^3. As $LaI_3:Ce$ is hygroscopic most experiments were performed on samples sealed in quartz ampoules.

X-ray excited optical luminescence spectra of $LaI_3:0.5\%Ce^{3+}$ were recorded at different temperatures between 85 and 350 K (see Fig. 1). At 85 K the spectrum is dominated by two very intense emission bands peaking at 452 and 502 nm assigned to Ce^{3+} 5d–4f transitions. The two Ce^{3+} transitions from the lowest 5d excited state to the $^2F_{5/2}$ and $^2F_{7/2}$ ground state levels are perfectly resolved. The spin–orbit splitting of the ^2F ground state of Ce^{3+} is $\sim2000\,cm^{-1}$. In addition a broad and low-intensity band can be distinguished between 560 and 660 nm. It is only visible from 85 K up to ~150 K and is attributed to STE luminescence. In contrast to $LaCl_3:Ce^{3+}$ [12] no STE emission was observed on the short wavelength side of the Ce^{3+} emission.
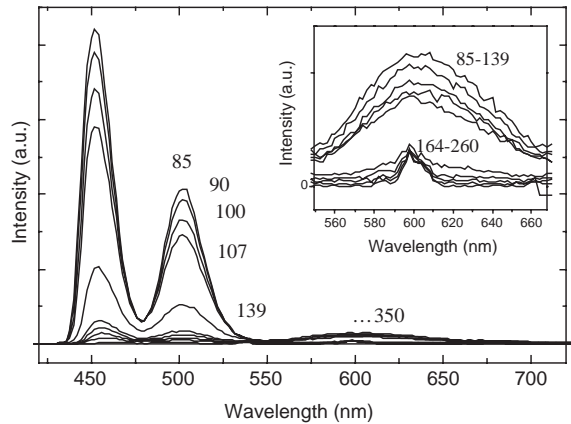

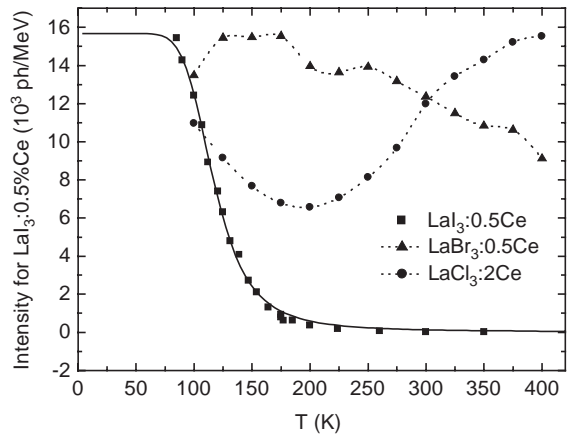Fig. 1. X-ray induced emission spectra of $LaI_3:0.5\%Ce$ recorded at temperatures between 85 and 350 K.

Fig. 2. Photon yields under X-ray excitation as a function of temperature for the $LaX_3:Ce$ (X = Cl, Br, I) compounds. Data for $LaCl_3:Ce$ and $LaBr_3:Ce$ were respectively taken from [9] and [12].

As the temperature increases the intensity of the Ce^{3+} doublet emission dramatically drops. At 350 K the Ce^{3+} emission bands are just above the noise level. The absolute light yields of Ce^{3+} emission for the different temperatures were evaluated by comparison to $YAlO_3:Ce$ emission under the same conditions. The evolution of the Ce^{3+} light yield as a function of temperature (T) is drawn in Fig. 2. For comparison the evolution of the light yields of $LaBr_3:0.5\%Ce$ and $LaCl_3:2\%Ce$

are shown as well in Fig. 2 as dotted lines. For LaCl$_3$:2%Ce the non monotonous trend exhibited was interpreted as a correlation between 100 and 225 K and then as an anti-correlation between 225 and 400 K with the STE emission intensity in the material [5,12]. A Ce emission mechanism by trapping part of the STEs by Ce^{3+} was therefore proposed. For LaBr$_3$:0.5%Ce the light yield decreases with temperature again correlating with the STE emission on the pure compound [9]. LaI$_3$:Ce exhibits a completely different T dependence than the other two materials Which is interpreted as a typical quenching behavior.

The solid curve through the LaI$_3$:Ce data represent a model calculation used to describe thermal quenching of luminescence. The light yield of the luminescence is given by

$$I(T) = \frac{I_0}{1 + \Gamma_0/\Gamma v \, \exp(-\Delta E_q/kT)} \quad (1)$$

where $I(T)$ is the light yield at temperature T, I_0 the light yield at $T = 0$, Γ_0 and Γ_v respectively, the thermal quenching rate at $T = \infty$ and the radiative transition rate. ΔE_q is the activation energy for thermal quenching and k the Boltzmann constant. From a fit to Eq. (1) values of $I_0 = 15700 \pm 300$ ph/MeV $\Gamma_0/\Gamma_v = 2500 \pm 700$ and $\Delta E_q = 79 \pm 4$ meV are obtained.

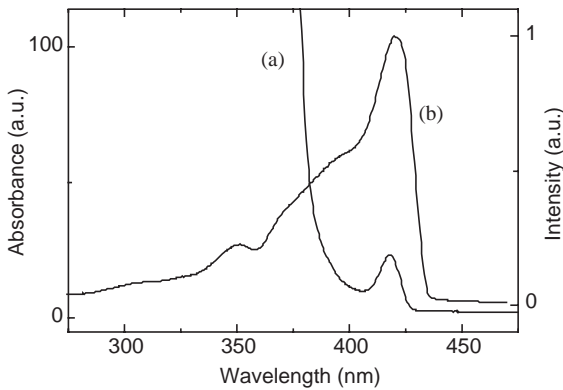The absorption spectrum recorded at 6 K is shown in Fig. 3 together with the optical excitation spectrum of Ce^{3+} emission at 500 nm recorded at 4 K. The absorption spectrum consists of a weak peak at $\sim$420 nm attributed to the Ce^{3+} 4f–5d transitions and it increases steeply below 380 nm. The optical band gap is estimated to be 3.3 eV (376 nm) at 6 K. The excitation spectrum monitoring the 500 nm emission is composed of an intense band peaking at 423 nm (2.93 eV) assigned to Ce^{3+} 4f–5d transitions and of a broad structured band spreading between 320 (3.88 eV) and 415 nm (2.99 eV).

Decay time measurements of LaI$_3$:0.5%Ce from 10 to 185 K under 406 nm (3.05 eV) laser excitation were recorded. Decay curves for three temperatures are shown in the inset of Fig. 4. All curves are composed of a single exponential component. The decay time τ of the Ce^{3+} luminescence is reported as a function of T in Fig. 4. For $T < 125$ K the characteristic decay time is $\sim$19 ns which is typical for the allowed 5d–4f Ce^{3+} transitions. It remains stable from 10 K to 125 K and then drops.

The solid curve in Fig. 4 shows model calculations according to the quenching process:

$$\tau(T) = \frac{1/\Gamma_v}{1 + \Gamma_0/\Gamma_v \, \exp(-\Delta E_q/kT)} \quad (2)$$

where Γ_0, Γ_v and ΔE_q have the same meaning as in Eq. (1). From a fit to Eq. (2) values of $1/\Gamma_v = 18.9 \pm 0.3$ ns and $\Delta E_q = 200 \pm 20$ meV were calculated. Different values of
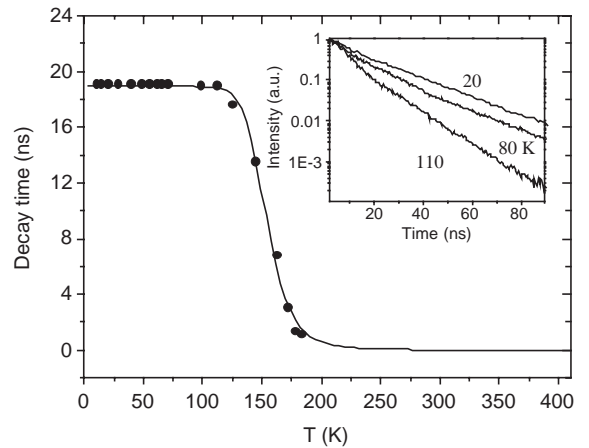

Fig. 3. (a) Absorption spectrum recorded at 6 K and (b) optical excitation spectrum monitoring emission at 500 nm recorded at 4 K for LaI$_3$:0.5% Ce.

Fig. 4. Decay times of LaI$_3$:0.5%Ce as a function of temperature. The solid line is a fitting following Eq. (2). Inset: decay curves at three different temperatures.

$\Gamma_0 = 1.3 \times 10^{11} \pm 0.4 \times 10^{11}$ Hz   or $\Gamma_0 = 1.6 \times 10^{14}$ $\pm 0.2 \times 10^{14}$ Hz can be deduced from the values of Γ_0/Γ_v found resp. in Eq. (1) or Eq. (2).

3. Discussion and conclusions

The scintillation properties of LaI$_3$:Ce are peculiar. At $T < 70$ K the scintillation output consists of an intense ($\sim$16 000 ph/MeV) doublet emission arising from the Ce^{3+} 5d–4f transition. Furthermore, it seems that luminescence is produced solely by a fast process ($\sim$20 ns) showing no evidence of STE intervention. However these interesting scintillation properties totally collapse as the temperature rises. At 200 K the light yield amounts only to some hundred of photons/MeV and the lifetime of the Ce^{3+} luminescence is around 1–2 ns. Experiments monitoring the light yield and the decay time under X-ray or optical excitation showed thermal quenching behavior for the Ce^{3+} luminescence. Considering that LaI$_3$ was initially chosen as the ultimate host in the LaX$_3$ series due to its smallest band gap we propose an explanation of the quenching based on the position of the Ce^{3+} levels relative to the host bands, see Fig. 5. At low temperature the lowest Ce^{3+} 5d level is below the conduction band and enables a fast transfer of free electrons and holes to Ce^{3+}. The material then presents fast and efficient scintillation properties. When the temperature increases thermal energy is provided to the electron of the Ce^{3+} excited configuration. As the Ce^{3+} 5d level is close in energy to the

conduction band the electron can escape into the conduction band of the host. A non-radiative process may occur and scintillation light is lost. In this interpretation the activation energies calculated above may be closely related to the energy difference ΔE between the host conduction band and the Ce^{3+} excited state [13]. Two slightly different values were found for the activation energies depending on the set-up used for the experiment (light yield under X-ray excitation or decay time under laser excitation). The difference may arise from a temperature offset between the two types of temperature control devices. It is not possible to reduce the uncertainty on that point. Thus considering the picture described in Fig. 5 the lowest 5d state of Ce^{3+} would be situated at $\sim$0.1–0.2 eV from the bottom of the conduction band (see Fig. 5).

Photoconductivity measurements are envisaged to confirm this model. In any case LaI$_3$:Ce demonstrated its failure as a scintillator due to a too small band gap compared with the energy difference between the 4f and 5d Ce levels. One would expect to return to good scintillation properties with a slight increase of the bandgap. This is likely to be obtained with the replacement of the lanthanum by lutetium. Thus LuI$_3$:Ce is currently under study to verify this hypothesis and test its scintillation properties.

Acknowledgments

Fig. 5. Scheme of Ce^{3+} 4f and lowest 5d levels positions relative to the host bands in LaI$_3$:Ce. VB : valence band. CB: conduction band.

References

[1] W.W. Moses, S.E. Derenzo, Nucl. Instr. and Meth. A 299 (1990) 51.

[2] A.J. Wojtowicz, M. Balcerzyk, E. Berman, A. Lempicki, Phys. Rev. B 49 (21) (1994) 14880.

[3] D. Bouttet, C. Dujardin, C. Pedrini, W. Brunat, D. Tran Minh Duc, J.Y. Gesland, Proceedings of International Conference On Inorganic Scintillators and Their Applications, SCINT95 (1996) Delft University Press, 111.
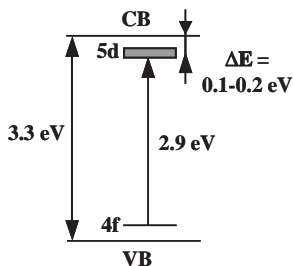
[4] C. Pedrini, A.N. Belsky, A.N. Vasilev, D. Bouttet, C. Dujardin, B. Moine, P. Martin, M.J. Weber, Mat. Res. Soc. Symp. Proc. 348 (1994) 225.

[5] O. Guillot-Noël, J.T.M. de Haas, P. Dorenbos, C.W.E. van Eijk, K. Krämer, H.U. Güdel, J. Lumin. 85 (1999) 21.

[6] E.V.D. van Loef, P. Dorenbos, C.W.E. van Eijk, K. Krämer, H.U. Güdel, Appl. Phys. Lett. 77 (10) (2000) 1467.

[7] E.V.D. van Loef, P. Dorenbos, C.W.E. van Eijk, K. Krämer, H.U. Güdel, IEEE Trans. Nucl. Sci. NS-48 (3) (2001) 341.

[8] E.V.D. van Loef, P. Dorenbos, C.W.E. van Eijk, K. Krämer, H.U. Güdel, Appl. Phys. Lett. 79 (2001) 1573.

[9] E.V.D. van Loef, P. Dorenbos, C.W.E. van Eijk, K.W. Krämer, H.U. Güdel, Nucl. Instr. and Meth. A 486 (2002) 254.

[10] L.B. Asprey, T.K. Keenan, F.H. Kruse, Inor. Chem. 3 (1964) 1137.

[11] K.W. Kramer, H.U. Gudel, P. Fischer, L. Keller, Appl. Phys. A 74 (Suppl.) (2002) S595.

[12] E.V.D. van Loef, P. Dorenbos, C.W.E. van Eijk, J. Phys.: Condens. Mat 15 (2003) 1367.

[13] Li-Ji Lyu, D.S. Hamilton, J. Lumin. 48–49 (1991) 251.