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VUV excited emission pulse shapes of $LuAlO_3$:Ce

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Abstract

The scintillation mechanism in $LuAlO_3$:Ce is in the main based on radiative recombination of electron–hole pairs via Ce^{3+}. Although there are favorable conditions for a nonradiative energy transfer to Ce^{3+} from excitons responsible for host emission, in fact this process is insignificant. Results of spectroscopic experiments and detailed analysis of emission pulse shapes are presented to support this statement. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Scintillators; Scintillation; Energy transfer; $LuAlO_3$:Ce; (E.) luminescence; Synchrotron radiation

1. Introduction

The very promising scintillation properties of $LuAlO_3$:Ce (LuAP) crystals were first reported by Lempicki et al. [1]. The interest in this material is derived from the high light yield (>20,000 photons/MeV), high density (8.34 g/cm^3) and short decay time (~18 ns). These properties are crucial when fast timing, high counting rates, good stopping power, and energy resolution are of importance [1,2]. Taking into account that this material is not fully optimized yet, and there is evidence that its performance may be greatly improved [3,4], it becomes exceptionally desirable to understand the physics that govern its behavior.

2. Materials and experiments

LuAP samples were cut from boules grown by Litton Airtron by the Czochralski method. A detailed description of the growth process is presented in Ref. [1]. Crystals were optically clear and single phase. Ce-doped specimens were colorless with Ce concentrations of 0.035 and 0.11 mol% (as measured by spark source mass spectrometry). The level of Ce contamination in nominally undoped specimens was $<4\times10^{-5}$ mol%.

Excitation spectra were acquired using synchrotron radiation at the Brookhaven National Synchrotron Light Source. Emission spectra were recorded under optical (at BNSLS) and X-ray excitation. Emission pulse shapes were obtained under synchrotron excitation at BNSLS by the delayed coincidence single photon counting method.

3. Experimental results and discussion

3.1. Basic spectroscopy

Both Ce-doped and nominally undoped samples of $LuAlO_3$ have been studied in the UV and VUV under optical, γ and X-ray excitation [5,6]. For all kinds of excitation the luminescence of Ce-doped material is dominated by the well-known emission centered at about 360 nm and originating in fast 5d–4f transitions of Ce^{3+}. Trace (a) in Fig. 1 shows the X-ray excited room temperature emission spectrum of the Ce-doped sample. Nominally undoped material reveals the other emission. X-ray excited luminescence of the undoped sample (trace (b)) does not demonstrate distinguishable cerium emission, showing instead an intense, wide, asymmetrical band peaking at about 300 nm, the host emission. Selecting the right excitation wavelength we can observe the host as well as the Ce^{3+} emission of the Ce-doped specimen (trace (c)). The host emission is, however, highly distorted. The reason for this distortion is cerium absorption — one can observe dips in the host emission band at wavelengths clearly corresponding to bands in the Ce^{3+} luminescence excitation spectrum (trace (d), Fig. 1). These features indicate reabsorption of host emission photons by Ce ions, and at the same time the great possibility of Forster–Dexter-type nonradiative energy transfer from the trapped

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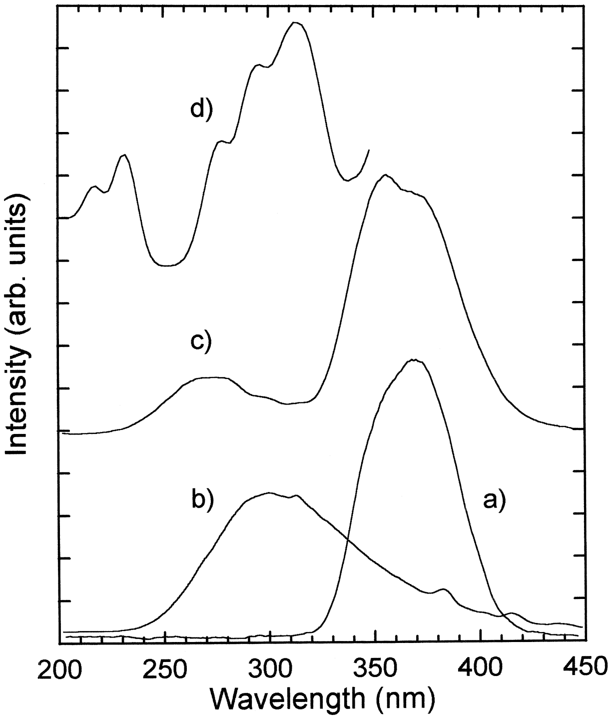

Fig. 1. Room temperature luminescence and excitation spectra of 0.11 mol% Ce-doped (a,c,d) and nominally undoped (b) $LuAlO_3$ crystals: X-ray excited emission spectra (a,b), emission under 160 nm synchrotron radiation excitation (c), excitation spectrum of 360 nm luminescence (d).

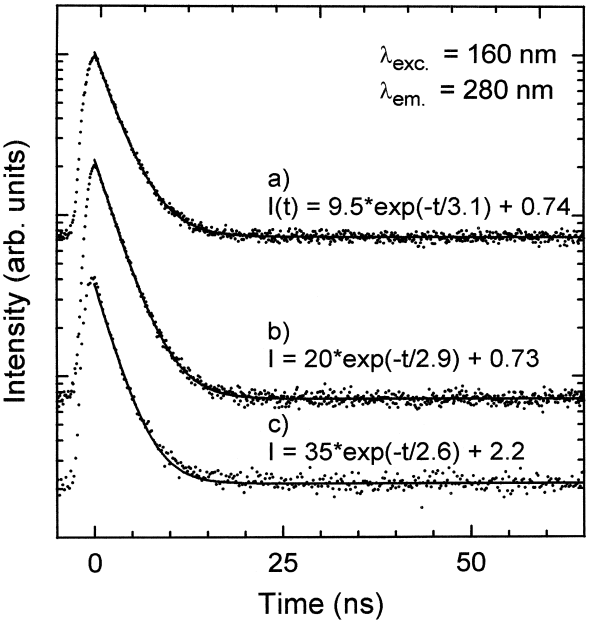

Fig. 2. Room temperature pulse shapes of host luminescence (280 nm) excited by 160 nm synchrotron radiation for undoped (a), and 0.035 (b) and 0.11 mol% Ce-doped $LuAlO_3$ (c).

excitons responsible for host emission to Ce^{3+}. This may be a scintillation mechanism in $LuAlO_3$:Ce. It has been established, however, that the scintillation mechanism in this material is, in principle, based on radiative recombination of electron–hole pairs via Ce^{3+} [7,5].

3.2. Pulse shape measurement

Examination of emission pulse shapes allows us to carry out quantitative estimations of possible energy transfers from trapped excitons to Ce^{3+}. Previous experiments with γ-excitation resulted in scintillation pulse shapes with an unmeasureable rise time (<1 ns) followed by the prompt decay with a main time constant of about 18 ns, typical for the excited Ce^{3+} lifetime in the $LuAlO_3$ lattice. The contribution of longer components was <5% of the zero-time amplitude. No faster components have been found. The decay curve for the Ce-doped sample has been published in Ref. [1]. Optical excitation in the Ce^{3+} d–f absorption bands gives a pulse shape with no rise time and a single exponential decay with time constant equal to that measured under γ-excitation. This remains true even for excitation in the band-to-band absorption region [3,6]. Fig. 2 shows selected pulse shapes of the host luminescence excited by 160 nm synchrotron radiation. Traces (a), (b) and (c) represent RT pulse shapes of the 280 nm luminescence in undoped, and 0.035 and 0.11 mol% Ce-doped samples, respectively. Results of fits of the analytic expression for one exponential decay plus the constant level are presented along with experimental data. In order to establish the background level, a separate measurement was made with the excitation beam turned off. A level of around 0.037 counts/s·ns was found, which is much less than in the case of all presented emission pulse shapes. This indicates that very slow components of decay are hidden in the background-looking constant level. Consequently, host emission pulses have two components — fast, with decay time constant around 3 ns, and very slow, the time constant of which cannot be determined because of the too high repetition rate of the excitation synchrotron pulses. The fast component decay time constant values indicate increasing quenching of the excitonic emission with increased level of cerium doping. This quenching most likely occurs by nonradiative energy transfer to Ce^{3+}. A comparison of these decay time constants allows an evaluation of the fraction of energy lost by excitons due to this process. At 0.035 mol% Ce doping, up to 5% of the excitons (which, in other cases, would decay radiatively within the fast component) could transfer energy to Ce^{3+}, and up to 14% at a Ce doping level of 0.11 mol%. But what happens to the slow components? We cannot determine their time constants, so we cannot compare them. In order to do this we have to analyze the pulse shape measurement in detail.

Emission pulse shapes were measured by the delayed coincidence single photon counting method. The sample was excited by pulses of synchrotron radiation at a repetition rate of 5.3 MHz. Delay times between excitation pulses and detection of emission single photons was measured by a time-to-amplitude converter and stored in a multichannel analyzer.

First let us consider the simplest case of a single exponential pulse $I(t)$ with an amplitude A and a decay time constant τ:

$$I(t) = A \exp\left(-\frac{t}{\tau}\right) \tag{1}$$

An illustration of this kind of measurement is presented in Fig. 3. Each time the sample is excited it emits a pulse described by Eq. (1), but in fact at the same time it also emits portions of all pulses excited earlier. In practice, the detection system cannot distinguish photons originating in different pulses so it just adds up all detected photons. As a result, a pulse $I^{\mathrm{m}}(t_i)$ given by Eq. (2) is measured:

$$\begin{aligned} I^{\mathrm{m}}(t_i) &= I(t_i) + \sum_{k=0}^{1} I(t_i + k\,\Delta t) + \sum_{k=0}^{2} I(t_i + k\,\Delta t) + \cdots \\ &\quad + \sum_{k=0}^{N-1} I(t_i + k\,\Delta t) = A \cdot e^{ti/\tau} + \sum_{k=0}^{1} A \cdot e^{(t_i + k\,\Delta t)/\tau} \\ &\quad + \sum_{k=0}^{2} A \cdot e^{(t_i + k\,\Delta t)/\tau} + \cdots + \sum_{k=0}^{N-1} A \cdot e^{(t_i + k\,\Delta t)/\tau} \\ &= A \cdot e^{t_i/\tau} + A \cdot e^{t_i/\tau} \cdot \frac{1 - e^{-2\,\Delta t/\tau}}{1 - e^{-\Delta t/\tau}} + A \cdot e^{-t_i/\tau} \\ &\quad \cdot \frac{1 - e^{-3\,\Delta t/\tau}}{1 - e^{-\Delta t/\tau}} + \cdots + A \cdot e^{-t_i/\tau} \cdot \frac{1 - e^{-N(\Delta t/\tau)}}{1 - e^{-\Delta t/\tau}} \\ &= \frac{1}{1 - e^{-\Delta t/\tau}} \cdot A \cdot e^{-t_i/\tau} \sum_{k=1}^{N} (1 - e^{-k\,\Delta t/\tau}) \end{aligned}$$

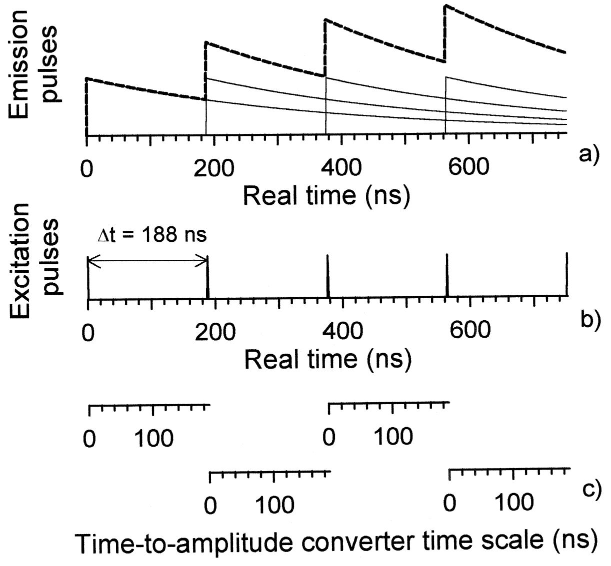

Fig. 3. Simulation of the measurement of a single exponential pulse: (a) (———) emission pulses; (- - -) aggregate of pulses − total intensity of emission; (b) excitation pulses; (c) time scale seen by the time-to-amplitude converter and multichannel analyzer.

$$\xrightarrow{\text{for large } N} \frac{N}{1 - e^{-\Delta t/\tau}} \cdot A \cdot e^{-t_i/\tau} \tag{2}$$

where N is the number of emission pulses, t_i is the time seen by the time-to-amplitude converter, and Δt is the time interval between excitation pulses. For a large number of pulses counted the time constant does not change, while the measured amplitude A^{m} is not only proportional to N, but also depends on the relation of τ to Δt:

$$I^{\mathrm{m}}(t_i) = A^{\mathrm{m}} \exp\left(-\frac{t_i}{\tau}\right), \text{ where } A^{\mathrm{m}} = \frac{N}{1 - \mathrm{e}^{-\Delta t/\tau}} \cdot A \tag{3}$$

In practice, for $\tau \ll \Delta t$ the measured amplitude A^{m} is almost exactly equal to $N \cdot A$, for $\tau = \Delta t$, $A^{\mathrm{m}} \cong 1.6 \cdot N \cdot A$, and for $\tau \gg \Delta t$ we obtain $A^{\mathrm{m}} \gg N \cdot A$. Now let us assume that the emitted pulse $I(t)$ has fast and slow components with amplitudes A_{f} and A_{s}, and time constants τ_{f} and τ_{s}, respectively:

$$I(t) = A_{\mathrm{f}} \exp\left(-\frac{t}{\tau_{\mathrm{f}}}\right) + A_{\mathrm{s}} \exp\left(-\frac{t}{\tau_{\mathrm{s}}}\right) \tag{4}$$

Consequently, the measured pulse $I^{\mathrm{m}}(t_i)$ can be described by

$$I^{\mathrm{m}}(t_i) = A_{\mathrm{f}}^{\mathrm{m}} \exp\left(-\frac{t_i}{\tau_{\mathrm{f}}}\right) + A_{\mathrm{s}}^{\mathrm{m}} \exp\left(-\frac{t_i}{\tau_{\mathrm{s}}}\right) \tag{5}$$

where

$$A_x^{\mathrm{m}} = \frac{N}{1 - \exp(-\Delta t/\tau_x)} \cdot A_x \tag{6}$$

In the case of multicomponent decay the measured amplitudes of particular components scale individually depending on the relation of τ_x and Δt. The ratio of the number of photons emitted in slow and fast components can be defined as:

$$R = \frac{A_{\mathrm{s}} \cdot \tau_{\mathrm{s}}}{A_{\mathrm{f}} \cdot \tau_{\mathrm{f}}} = \frac{A_{\mathrm{s}}^{\mathrm{m}} \cdot \tau_{\mathrm{s}}}{A_{\mathrm{f}}^{\mathrm{m}} \cdot \tau_{\mathrm{f}}} \cdot \frac{1 - \exp(-\Delta t/\tau_{\mathrm{s}})}{1 - \exp(-\Delta t/\tau_{\mathrm{f}})} \tag{7}$$

If all amplitudes and time constants can be taken from fits it is possible to compute real amplitudes and a coefficient R. In the case of the pulses presented in Fig. 2 the situation seems remediless, but in spite of the inability to fit $A_{\mathrm{s}}^{\mathrm{m}}$ and τ_{s}, it is still possible to find R. If we assume that the difference Δb of the real background and the background-looking level taken at time t_v is caused by the slow component with amplitude $A_{\mathrm{s}}^{\mathrm{m}}$ and time constant τ_{s}, it becomes possible to compute $A_{\mathrm{s}}^{\mathrm{m}}$:

$$A_{\mathrm{s}}^{\mathrm{m}} = \frac{\Delta b}{\exp(-t_v/\tau_{\mathrm{s}})} \tag{8}$$

Combining Eqs. (7) and (8) gives:

$$R(\tau_{\mathrm{s}}) = \frac{\Delta b \cdot \tau_{\mathrm{s}}}{A_{\mathrm{f}}^{\mathrm{m}} \cdot \tau_{\mathrm{f}} \exp(-t_v/\tau_{\mathrm{s}})} \cdot \frac{1 - \exp(-\Delta t/\tau_{\mathrm{s}})}{1 - \exp(-\Delta t/\tau_{\mathrm{f}})} \tag{9}$$

Then the percentage contribution of the slow component to the whole pulse can be computed as:

$$P(\tau_s) = \frac{R(\tau_s)}{R(\tau_s) + 1} \cdot 100\% \qquad (10)$$

Both $R(\tau_s)$ and $P(\tau_s)$ are functions of one variable, τ_s. Except for τ_s all other parameters can be determined from fits to the measured emission pulses (A_f^m, τ_f, Δb), are chosen arbitrary (t_v) or fixed by the experimental setup (Δt).

Fig. 4 presents results of the simulation of $P(\tau_s)$ for the pulses presented in Fig. 2 and τ_s values between 200 ns and 100 s. For all analyzed pulses for $\tau_s > 700$ ns, the values of $P(\tau_s)$ do not change more than 1%, and they are about 82, 69 and 79% for undoped, 0.035 and 011 mol% Ce-doped crystals, respectively. For τ_s between 700 and 200 ns, $P(\tau_s)$ increases an additional few percent, but τ_s in this range would probably result in a visible slope of the pulse curve. Large values of $P(\tau_s)$ indicate that the slow component is dominant in host emission pulses. Almost identical $P(\tau_s)$ values for undoped and 0.11 mol% Ce-doped specimens affirm that the proportion of the numbers of photons emitted in slow and fast components is similar for both undoped and Ce-doped material. Consequently, in doped material the slow component has to be quenched the same way as the fast component, and, finally, one can conclude that, at 0.11 mol% Ce doping, up to 14% of excitons can transfer energy to Ce^{3+}, regardless of the component these excitons would decay within.

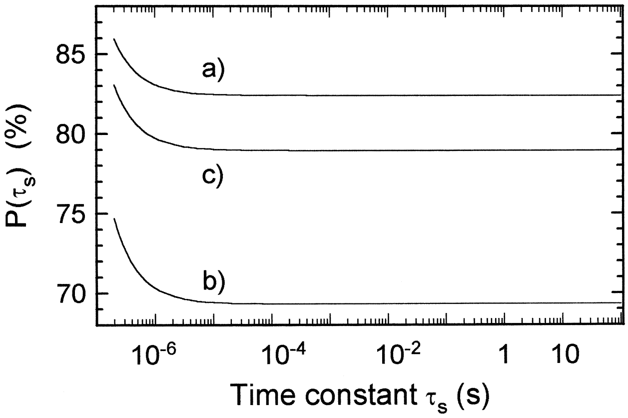

Fig. 4. Simulation of results of $P(\tau_s)$ for undoped (a), and 0.035 (b) and 0.11 mol% Ce-doped (c) $LuAlO_3$.

3.3. Host emission excitation spectra

Host emission excitation spectra of undoped and 0.11 mol% Ce-doped $LuAlO_3$ crystals are compared in Fig. 5. Both spectra consist of the same bands, but ratios of their intensities are different. In general, the intensities of the higher energy bands are decreased in comparison with the 160 nm band. Since absorption of 160 nm radiation creates excitons, and the 153 nm radiation generates free e–h pairs, it is evident that the presence of Ce in the lattice does not affect the direct creation of excitons, but to some extent prevents their formation from free band charge carriers [5,6]. The mechanism of this “prevention” is most probably competition for holes and electrons by Ce^{3+}, which strongly supports the scintillation model based on consecutive carrier trapping. Because there is no reason that the presence of Ce should increase the probability of the direct creation of excitons, it is reasonable to scale the presented spectra so that the intensities of the 160 nm band are equal. Consequently, comparison of the shorter wavelength band intensities allows us to state that the presence of Ce in $LuAlO_3$ decreases the number of excitons generated by high-energy radiation at least by 50%.

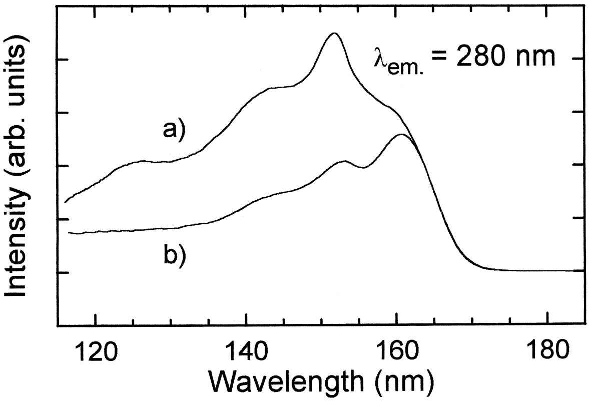

Fig. 5. Host emission excitation spectra of undoped (a) and 0.11 mol% Ce-doped (b) $LuAlO_3$.

4. Summary

In Section 3.1 it was stated that, at first sight in the γ excited $LuAlO_3$:Ce the very favorable conditions exist for nonradiative energy transfer from the excitons (responsible for host emission) to Ce^{3+}. Analysis of host emission pulse shapes demonstrates, however, that actually no more than about 14% of excitons transfer their energy to Ce ions. Since for 1 MeV deposited energy in undoped $LuAlO_3$, radiative decay of about 12 500 excitons is observed, and in 0.11 mol% Ce-doped material about 17 000 photons of Ce luminescence are emitted [6], only about 10% of Ce ions could gain excitation energy from excitons preceding host emission. Apart from this, in Section 3.3 it was established that the presence of Ce^{3+} reduces the number of excitons generated by high-energy radiation by at least 50%. Taking this into account one can finally estimate that no more than 5% of scintillating Ce ions are excited by nonradiative energy transfer from excitons.

All the presented estimations lead to the conclusion that scintillation of $LuAlO_3$:Ce as previously stated is generally accomplished by the radiative recombination of electron–

hole pairs via Ce^{3+}, while other mechanisms are insignificant.

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