

Low temperature delayed recombination decay in scintillating garnets



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ABSTRACT

We study the temperature dependence of delayed recombination decay intensity in a variety of scintillating crystals based on garnet hosts in a wide temperature range 8–500 K. Previous work on several scintillating materials based on silicate hosts showed nonzero constant signal from very low temperatures up to about 120 K. This observation supported a previously suggested hypothesis on low temperature losses of fast scintillation light due to quantum tunneling between the activator and nearby traps. In garnets, the subject of the present article, we observe practically constant signal in the entire monitored temperature range. We thus further test and confirm the quantum tunneling hypothesis in a different class of scintillating materials. We also show that there is no thermal ionization of the activator's excited state in all materials studied, well above room temperature.

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1. Introduction

In applications of scintillators where fast response is required any losses of fast scintillation light are highly undesired and need to be prevented. They are usually associated with thermal effects such as classical thermal quenching of the activator's luminescence or thermal ionization of its excited state. Recently, however, using the delayed recombination decay technique, it has been observed that the losses of fast scintillation light can occur at very low temperatures where none of the above thermal effects apply [1].

Delayed recombination measurement has been developed to study thermal ionization of the luminescence center excited state [2] as an alternative to other techniques, such as photoconductivity using blocking electrodes [3], the microwave resonator technique [4] or thermoluminescence after UV excitation [5–7]. It consists in the observation of slow tails in luminescence decay under UV excitation. When the luminescence center is thermally ionized, charge carriers that do not decay promptly can migrate through conduction or valence bands. After being trapped and released they return to the luminescence center and recombine producing delayed (slow) light.

As addressed above, a nonzero delayed recombination signal was also observed at very low temperatures. These low temperature losses of fast scintillation light have been associated with quantum tunneling from the activator to a nearby trap and back,

as in the scheme in Fig. 1. A similar mechanism of excitation energy or electron transfer is in the usual donor–acceptor situation also referred to as Dexter transfer, or transfer due to the exchange interaction depending on the overlap between the wave functions of the activator and the trap.

The hypothesis was supported both experimentally and theoretically. Experimentally, in a variety of Ce and Pr-doped scintillating silicates, constant delayed recombination decay intensity was measured at least up to about 120 K, a result consistent with the temperature independence of quantum tunneling [8]. Theoretical support was first provided by a simple one-dimensional model [9] that attained several orders of magnitude delay of the activator's luminescence decay due to quantum tunneling. Extending the numerical calculation to two dimensions allowed a finer check of the tunneling hypothesis, and indeed the correct orders of magnitude were again obtained. Furthermore, analytic estimates on a relation between a trap's depth and its distance from the activator have also been made [10] and are expected to allow estimates of significant properties of the traps. Unlike many calculations based on tunneling between traps and recombination centers in various materials [11–17] this approach is independent of any assumptions about “attempt frequency”.

In this work we study the temperature dependence of delayed recombination decay intensity in a variety of scintillating Ce³⁺ and Pr³⁺-doped simple garnets. These materials are considered to have significant potential in the family of fast and high light yield oxide scintillators. For this reason, experimental and theoretical aspects have been addressed by many groups in last two decades

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[18–27]. The present work is intended to help understand unexplained features previously observed in a novel, more complex material, multicomponent garnet $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}:\text{Ce}^{3+}$ (GGAG:Ce) [8]. Ultraefficient GGAG:Ce single crystal scintillator was discovered in 2011 [28] and immediately became a hot topic in the scintillator community [28–32]. We now monitor simple garnets in a broad temperature region 8–500 K and observe practically constant signal throughout. These results show that quantum tunneling between activator and nearby trap(s) is at work in another wide class of scintillating materials. Previously observed features in GGAG:Ce delayed decay are discussed in the light of results currently obtained for simple garnets.

2. Samples and experimental details

Pr^{3+} -doped $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG) and $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) single crystals with Pr concentration in the crystal of 0.19 wt% and 0.16 wt%, respectively, were grown by the Czochralski technique from 5N Lu_2O_3 and 5N Pr_2O_3 raw powders by CRYTUR, Ltd. (Turnov, Czech Republic).

Two LuAG:Ce single crystals were grown by the Czochralski technique in a molybdenum crucible under a reducing atmosphere by CRYTUR, Ltd. (Turnov, Czech Republic). The samples with Ce concentration 0.03, and 0.12 wt% were grown from 5N Lu_2O_3 and 4N Al_2O_3 raw powders.

LuAG:Ce nanopowder was prepared by UV-irradiation of aqueous solutions containing soluble metal salts. The details of preparation can be found in [33]. Ce(III) nitrate hexahydrate was added to the solutions according to the stoichiometry $\text{Lu}_{3-x}\text{Ce}_x\text{Al}_5\text{O}_{12}$, where $x=0.5\%$. Photochemically prepared powder was calcined at 1200 °C.

Single crystalline LuAG:Ce thin film was grown by liquid phase epitaxy from a $\text{BaO}-\text{Ba}_2\text{O}_3-\text{BaF}_2$ flux on (1 1 1) oriented LuAG substrate; the growth process is described elsewhere [34,35]. The thickness of the film was 12.3 μm and the Ce concentration 0.28%.

Two single crystals of YAG:Ce were grown by the Czochralski technique from 6N Y_2O_3 and 5N Al_2O_3 raw powders in a molybdenum crucible by CRYTUR, Ltd. (Turnov, Czech Republic). The Ce concentration in these crystals was about 0.32 wt% of CeO_2 in the melt (later designated as low Ce) and 1000 ppm of Ce in the high quality industrial single crystal (later designated as high Ce).

Absorption spectra were measured by the Shimadzu 3101PC spectrometer in the 190–1200 nm range. Photoluminescence emission (PL) and excitation (PLE) spectra were measured by using a custom made 5000M Horiba Jobin Yvon spectrofluorometer. Excitation was realized with a deuterium steady state lamp. Temperature between 8 and 497 K was controlled by a Janis Instruments closed cycle refrigerator. PL delayed recombination decays were excited by a microsecond xenon flashlamp and measured using the multichannel scaling method. The decay data were fit by three-exponential function used the *Spectra-Solve* program package. From the fit three delayed decay times were determined.

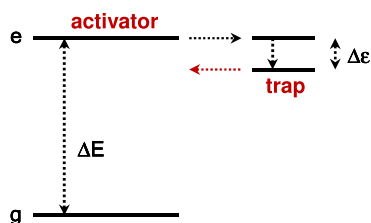


Fig. 1. Simple scheme for a tunneling process between the activator, with ground state g and excited state e, and the trap located nearby. The energy separation of the ground and excited state of the activator is ΔE while that of the excited state of the activator and the trap is $\Delta \epsilon$.

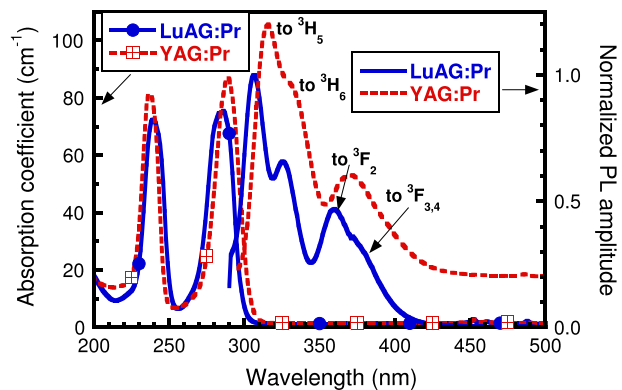


Fig. 2. Absorption spectra at RT and normalized PL spectra at 8 K of LuAG:Pr $^{3+}$ and YAG:Pr $^{3+}$ single crystals, excitation wavelength is 285 nm. Emission spectrum of YAG:Pr $^{3+}$ is vertically shifted by 0.2.

The errors on decay times from the shortest to the longest were estimated from statistical error of the number of counts in each channel to be up to 1%, 2–3% and 4–5%, respectively. Based on these estimates the error on delayed recombination intensities obtained by integration of the decay curves is estimated to be up to 5%.

3. Results and discussion

3.1. Pr $^{3+}$ -doped aluminum garnets

Absorption spectra at room temperature (RT) and PL emission spectra of LuAG:Pr $^{3+}$ and YAG:Pr $^{3+}$ measured at 8 K are displayed in Fig. 2. The lowest absorption band, at about 280 nm, corresponds to a transition from the $^3\text{H}_4$ ground state to the lowest $^5\text{d}_1$ state of Pr $^{3+}$, while the band at about 240 nm corresponds to a $^3\text{H}_4 \rightarrow 5\text{d}_2$ transition [36]. The PL emission between 280 and 420 nm contains several bands corresponding to $5\text{d}_1 \rightarrow 4\text{f}$ transitions of Pr $^{3+}$ (final $^3\text{H}_x$ and $^3\text{F}_x$ multiplet 4f states are well resolved as shown in Fig. 2). The same transitions in a YAG host are shifted to lower energies with respect to the LuAG host.

In Fig. 3a we display the delayed recombination intensity of LuAG:Pr $^{3+}$ and YAG:Pr $^{3+}$ measured under UV excitation into the $4\text{f} \rightarrow 5\text{d}$ transition of the Pr ion within the 8–500 K temperature interval. An almost perfectly constant signal is observed in the whole temperature range. Such temperature independence of the delayed recombination intensity manifests two important features. First, it supports the hypothesis of quantum tunneling between the activator and nearby trap(s) as suggested in [1,9]. Second, it also shows no signs of thermally induced ionization of the Pr $^{3+}$ excited state and therefore confirms the known temperature stability of Pr $^{3+}$ -doped aluminum garnets well above RT [2]. Fig. 3b shows an example of delayed recombination decay at 8 K for both Pr $^{3+}$ -doped LuAG and YAG. The decay is approximated by a three-exponential function indicated in the figure. Such complex decay represents a tunneling between an activator and several traps: either traps of a different kind or traps of the same kind distributed at various distances from the activator.

3.2. Ce $^{3+}$ -doped lutetium aluminum garnet

The results for two Ce $^{3+}$ -doped LuAG single crystals are displayed in Figs. 4 and 5. We compare two samples with different concentrations of Ce $^{3+}$ in the crystal, *low* and *high* (cf. Section 2). The Ce concentration difference can be assessed from absorption spectra shown in Fig. 4, namely from the Ce $^{3+}$ absorption band

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