Luminescence characteristics of LuAG:Pr and YAG:Pr single crystalline films

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ABSTRACT

Emission and excitation spectra and luminescence decay kinetics were studied for Pr³⁺-doped Lu₃Al₅O₁₂ and Y₃Al₅O₁₂ single crystalline films (SCF) grown by the liquid phase epitaxy method from a PbO-based flux. The influence of lead-induced centers on their scintillation characteristics was clarified. It was found that the influence of single Pb²⁺-based centers on the characteristics of Pr³⁺ centers due to the Pb²⁺ → Pr³⁺ energy transfer was weak. However, an overlap of the emission spectra of single and dimer lead-induced centers with the emission spectrum of Pr³⁺ ions, and especially a strong overlap of the 4f–5d₁ absorption band of Pr³⁺ ions with the slow emission of localized excitons in the 290 nm band had a considerable influence on the scintillation characteristics of the Pr³⁺-doped SCF.

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1. Introduction

Single crystals (SC) of Lu₃Al₅O₁₂ (LuAG) and Y₃Al₅O₁₂ (YAG) doped with Ce³⁺ or Pr³⁺ ions, having excellent mechanical and chemical stability and possessing an intense and fast emission, have been considered for fast scintillator applications (see, e.g. [1–5]). Under excitation in the band-to-band and exciton energy regions, an intense emission is present in the 280–350 nm range which arises at the Lu_{Al} or Y_{Al} antisite defects (ADs) [6]. This emission is overlapped with the Ce³⁺ and Pr³⁺ absorption bands and is responsible for slower decay components in the scintillation response of SC. The ADs are strongly suppressed in single crystalline films (SCF) grown by the liquid phase epitaxy (LPE) method [6]. However, lead ions are introduced into the crystal lattice during the SCF preparation with the use of a PbO-based flux [6–8]. In [8], the emission band at 344 nm in LuAG SCF and the corresponding excitation bands at 261 nm have been ascribed to single Pb²⁺-based centers. An effective energy transfer from the host lattice to Pb²⁺ and Ce³⁺ ions and from Pb²⁺ to Ce³⁺ ions has been observed, resulting in the appearance of slow decay components and reduction of the Ce³⁺ luminescence intensity. Under excitation in the exciton region, a slow emission in the band peaked at 290 nm

has been also found [6,8] which is overlapped with the absorption bands of Pr³⁺ and Ce³⁺ centers and can thus influence considerably the decay kinetics of the Ce³⁺ and Pr³⁺ emission. This emission has been assumed to arise from excitons localized near defects existing only in SCF (e.g. Pb or Pt ions, or their associates).

Luminescence of Pr³⁺ ions in LuAG and YAG has been studied in SC [4,5,9] and in SCF [10]. In LuAG:Pr SCF more intense slow emission components have been noted in comparison with LuAG:Ce SCF [10]. Due to such discrepancy, the influence of lead centers on the luminescent characteristics of Pr³⁺ ions in LuAG and YAG SCF is considered in more details in this paper.

2. Experimental procedure

The LuAG:Pr and YAG:Pr SCF were grown onto YAG SC substrates by the LPE method from a PbO–B₂O₃ flux in a Pt-crucible (see also [10]). Two SCF samples with different thickness (*h*) grown at different temperatures (*T_g*) were studied: LuAG:Pr (*h* = 38 μm, *T_g* = 1022 °C) and YAG:Pr (*h* = 27 μm, *T_g* = 995 °C).

The emission and excitation spectra in the 200–450 nm spectral range were measured at 4.2–300 K at the computer-controlled setup, consisting of a xenon lamp (Xe-150 W, Oriel), two monochromators (MDR-3 and Oriel Cornerstone 1/8 m) and an immersion helium cryostat. The emission was detected with the Hamamatsu (6240) photon counting system. The emission spectra were uncorrected,

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but the excitation spectra were corrected for the spectral distribution of the xenon lamp intensity and the transmission of the MDR-3 monochromator and cryostat windows. In the exciton absorption region (174–183 nm), the emission was excited at 11 K by the synchrotron radiation at the SUPERLUMI experimental station of HASY-LAB at DESY, Hamburg, Germany. The emission spectra were measured with an ARC monochromator and a Hamamatsu R6358P photomultiplier and were not corrected. The luminescence decay kinetics were measured at a modified 199S Spectrofluorometer (Edinburgh Instruments) under excitation with a nanosecond coaxial hydrogen-filled flashlamp (IBH Scotland) and using two single grating monochromators. The detection was performed by an IBH-04 photomultiplier module using the time-correlated single photon counting method. The deconvolution procedure (SpectraSolve software package) was applied to extract true decay times from the multiexponential approximation. The experiments at low temperatures were carried out with the use of an immersion helium cryostat or a vacuum nitrogen cryostat.

3. Experimental results and discussion

Luminescence characteristics of Pr^{3+} -doped LuAG and YAG SCF in the UV range (200–400 nm) were found to be similar. Therefore, the results obtained for LuAG:Pr SCF are presented in more details in this paper.

The emission (Fig. 1a, curve 1) and excitation (Fig. 1b, curve 1) spectra of Pr^{3+} centers in LuAG:Pr SCF in the UV range were similar to those in SC [4,5,9]. The structured emission band was observed at 306, 325, 358 and 375 nm and could be interpreted as a radiative transition from a $5d_1$ excited state to $^3\text{H}_x$ ($x = 4, 5, 6$) and $^3\text{F}_{3(4)}$ multiplets in agreement with [5]. The presence of an additional emission band in the 320–380 nm range was evident in the latter

spectrum from a comparison of the emission spectra measured under excitation in the Pr^{3+} (Fig. 1a, curve 1) and Pb^{2+} (curve 2) related absorption bands. The excitation spectrum of the Pr^{3+} -related emission at 4.2 K consisted of complex bands located at 280–290 nm and around 240 nm (Fig. 1b, curve 1) which coincided with the $^3\text{H}_4\text{--}5d_{1,2}$ absorption bands of Pr^{3+} in a LuAG host [5]. The presence of an additional excitation band in the 250–270 nm range was evident in the latter spectrum from a comparison of the excitation spectra measured for the Pr^{3+} (curve 1) and Pb^{2+} (curve 2) related emissions. A comparison of these results with those reported in [8] indicated that the additional emission and excitation bands arose from single Pb^{2+} -based centers. The appearance of a Pb^{2+} -related band at about 260 nm in the excitation spectrum of the Pr^{3+} emission (curve 1) was caused not by the $\text{Pb}^{2+} \rightarrow \text{Pr}^{3+}$ energy transfer, but by the overlap of the emission spectra of the Pr^{3+} and Pb^{2+} centers. Unlike in the case of LuAG:Ce SCF, the overlap of the emission band at 344 nm of single Pb^{2+} -based centers with the absorption spectrum of Pr^{3+} in LuAG:Pr SCF was small, and therefore the efficiency of the $\text{Pb}^{2+} \rightarrow \text{Pr}^{3+}$ transfer in LuAG:Pr was small, as well.

In addition to the emission band at 344 nm belonging to single Pb^{2+} -based centers, a weak emission was observed at about 380 nm (Fig. 1a, curve 3) which was excited around 314 nm (curve 3'). This emission was assumed to arise from dimer lead centers [11]. Such a center could cause a decrease in the quantum efficiency of an Pr^{3+} emission due to an overlap of its excitation band with the Pr^{3+} emission resulting in the $\text{Pr}^{3+} \rightarrow$ (dimer Pb) energy transfer.

Like in LuAG:Pr SC, the intensity of the Pr^{3+} emission in LuAG:Pr SCF excited at 292 nm remained constant for temperatures up to 200 K (see the inset in Fig. 1, curve 1). However, a considerable decrease in the intensity of the Pb^{2+} -related emission band at 344 nm (curve 2) and emission intensity measured at 312 nm (maximum of the Pr^{3+} 5d–4f emission, curve 3) with the increasing temperature was observed in the same temperature range under excitation in the Pb^{2+} -related band. This effect was caused by the thermal quenching of the Pb^{2+} emission [8] and an overlap of the Pb^{2+} and Pr^{3+} emission bands.

Under excitation of both the LuAG and YAG SCF in the exciton absorption region (at $\lambda = 177$ nm), a wide band was observed at 11 K, consisting of a fast emission in the band at 260 nm of the

Fig. 1. (a) Emission spectra of LuAG:Pr SCF (uncorrected, normalized) at 4.2 K under excitation in the Pr^{3+} absorption band at 292 nm (curve 1), in the Pb^{2+} -related band at 266 nm (curve 2) and in the band at 314 nm of dimer lead centers (curve 3). Curve 3 is the excitation spectrum of the emission of dimer centers at 380 nm. In the inset: temperature dependences of intensities of the Pr^{3+} emission at 312 nm in LuAG:Pr SCF under excitation in the Pr^{3+} absorption band at 292 nm (curve 1); the Pb^{2+} -related emission at 344 nm (curve 2) and the Pr^{3+} emission at 312 nm (curve 3), both under excitation in the Pb^{2+} -related band at 266 nm. (b) Excitation spectra (corrected, normalized) at 4.2 K of the luminescence of Pr^{3+} ions at 306 nm (curve 1) and Pb^{2+} ions at 344 nm (curve 2) in LuAG:Pr SCF.

Fig. 2. Emission spectra (uncorrected) at 11 K of the undoped LuAG (a) and YAG (b) SCF under excitation in the exciton absorption region at 174 and 183 nm, respectively.

Fig. 3. Decay kinetics of the emission of single Pb^{2+} -based centers at 344 nm in LuAG:Pr SCF (a) and YAG:Pr SCF (b) at 80 K under excitation in the Pb^{2+} -related band. In the inset, the emission spectrum of single Pb^{2+} centers is shown measured at $\tau = 4 \mu\text{s}$ after the excitation pulse.

self-trapped exciton and a slow emission in the band at 290 nm of localized excitons (Fig. 2, see also [6,8]). The absorption and emission spectra of Pr^{3+} centers in LuAG and YAG were strongly overlapped with the band at 290 nm. A larger 290 nm/260 nm emission intensity ratio in LuAG SCF (Fig. 2a) as compared with YAG SCF (Fig. 2b) indicated that the concentration of the defects responsible for the emission band at 290 nm (e.g., Pb or Pt ions, or their associates [8]) was larger in LuAG SCF than in YAG SCF.

In the decay kinetics of the Pb^{2+} -related emission at 80 K, the fast component with $\tau = 14.2 \text{ ns}$ in LuAG:Pr and 19.8 ns in YAG:Pr arose from the Pr^{3+} emission (Fig. 3). A shorter decay time value of the Pr^{3+} emission in LuAG:Pr SCF with respect to that found in SC ($\approx 20 \text{ ns}$ [5]) could be caused by the energy transfer from Pr^{3+} to dimer lead centers [11] due to the overlap of the absorption band at 314 nm of dimers centers with the emission spectrum of Pr^{3+} ions. The decay time ($\approx 1.9 \mu\text{s}$ at 80 K) and the emission spectrum (shown in the inset) of the slowest component were similar to the single Pb^{2+} -based centers [8]. In LuAG:Pr SCF, the light sum of this component was about 32% of the total light sum, i.e. it was about 50% of that related to the 14.2 ns component belonging to the Pr^{3+} emission. In YAG:Pr SCF, the slow component contribution was considerably smaller (Fig. 3b). Due to the overlap of Pb^{2+} - and Pr^{3+} -related emission spectra the same slow component appeared also in the decay kinetics of the Pr^{3+} emission measured at 312 nm under excitation in the Pb^{2+} absorption band. At 295 K, no influence of Pb^{2+} -related centers on

the decay kinetics of the Pr^{3+} luminescence due to thermal quenching of the Pb^{2+} -related emission (see the inset in Fig. 1a, curve 2) was observed.

4. Conclusions

The absorption bands of Pr^{3+} centers in LuAG and YAG SCF were not overlapped with the emission bands of single and dimer lead centers. Therefore, the $\text{Pb}^{2+} \rightarrow \text{Pr}^{3+}$ energy transfer was absent and its influence on the characteristics of the Pr^{3+} centers was negligible with respect to the Ce^{3+} -doped LuAG and YAG SCF, where the $\text{Pb}^{2+} \rightarrow \text{Ce}^{3+}$ energy transfer was very effective. On the contrary, the overlap of the 314 nm excitation band of lead dimers with the $5d_1\text{--}4f$ emission band of Pr^{3+} ions was found. Consequently, a decrease in the Pr^{3+} quantum efficiency due to the energy transfer from the Pr^{3+} centers to the lead dimers became possible and was evidenced in shortening the decay time of the Pr^{3+} -related 312 nm emission band.

A strong overlap of the absorption bands of the Pr^{3+} centers with the emission band at 290 nm of localized excitons can result in a significantly larger content of slow components in the scintillation decay of LuAG:Pr and YAG:Pr SCF compared to LuAG:Ce and YAG:Ce SCF.

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