The role of Pb$^{2+}$ ions in the luminescence of LuAG:Ce single crystalline films

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Steady-state and time-resolved emission and excitation spectra and luminescence decay kinetics were studied at 4.2-350 K under excitation in the 2.5-15 eV energy range for the undoped and Ce$^{3+}$-doped Lu$_3$Al$_5$O$_{12}$ (LuAG) single crystalline films grown by Liquid Phase Epitaxy method. The spectral bands arising from the single Pb$^{2+}$-based centers were identified. Competition between Pb$^{2+}$ and Ce$^{3+}$ ions in the processes of energy transfer from the LuAG crystal lattice was evidenced. Due to overlap of the 3.61 eV emission band of Pb$^{2+}$ centers with the 3.6 eV absorption band of Ce$^{3+}$ centers, an effective energy transfer from Pb$^{2+}$ ions to Ce$^{3+}$ ions occurs, resulting in the appearance of slower component in the luminescence decay kinetics of Ce$^{3+}$ centers and decrease of the Ce$^{3+}$-related luminescence intensity.

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1 Introduction

Single crystals (SC) of Lu$_3$Al$_5$O$_{12}$ (LuAG) doped with Ce$^{3+}$ have found their applications as scintillating materials due to an intense and fast Ce$^{3+}$-related emission, high density and high mechanical and chemical stability [1–5]. The Ce-doped LuAG-based scintillators, prepared in the form of single crystalline films (SCF), can be employed for imaging screens with high spatial resolution [6–8].

Under excitation in the band-to-band and exciton energy range, an intense complex slow intrinsic luminescence was observed in the undoped LuAG SC in the UV spectral range and ascribed to the exciton localized near the Lu$_{Al}^{3+}$ antisite defect [9, 11] and emission of the Lu$_{Al}^{3+}$ antisite defect [10, 12]. The emission is overlapped with the Ce$^{3+}$ absorption bands, which influences timing characteristics of LuAG:Ce scintillators [9, 10]. It was found [9, 10, 12, 13] that the concentration of antisite defects is strongly suppressed in SCF grown by the Liquid Phase Epitaxy (LPE) method. However, at the preparation of SCF, lead ions are introduced into the crystal lattice due to the use of the PbO-based flux [7, 8, 14, 15]. The aim of this paper is to identify the spectral bands arising from the single Pb-related centers in LuAG SCF and to study the energy transfer processes from the host lattice to such centers.

2 Experimental

Single crystalline films of LuAG and LuAG:Ce were prepared by the LPE method from PbO-B$_2$O$_3$ flux in a platinum crucible and using the substrates of SC of LuAG or YAG (see [7–10, 14, 15]). The samples with different thickness of the layer, varying from 4.1 µm to 34.5 µm, were studied. For comparison, the undoped LuAG and YAG SC, LuAG:Ce SC with different Ce$^{3+}$ concentrations and LuAG:Pb ceramics were examined as well.

Emission and excitation spectra and temperature dependences of the emission intensity were measured at 80-350 K in the 1.5-6 eV energy range at the set-up with deuterium lamp and two monochromators

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(SF-4 and SPM-1). The spectra were corrected for the spectral distortions. Luminescence decay kinetics was measured at 4.2-300 K using the same set-up under excitation with the xenon flash lamp.

Time-resolved emission and excitation spectra (within 2-16 ns and the 30-99 ns time gates, further "fast" and "slow" components, respectively) were measured at 11 K under excitation in the 3.8-15 eV energy range using synchrotron radiation facility of HASYLAB at DESY, Hamburg, Germany, at SUPERLUMI experimental station. The emission spectra were measured with the monochromator ARC and PMT Hamamatsu R6358P, and were not corrected.

3 Experimental results and discussion

The study of luminescence characteristics of SCF of LuAG and LuAG:Ce and their comparison with the characteristics of the SC and ceramics allow us to conclude that the 3.61 eV band, observed in the emission spectra of LuAG SCF at 11 K, is connected with the single-Pb$^{2+}$-ion-based centres (Fig. 1a, curve 1). As the 3.61 eV emission band is overlapped with the 3.6 eV absorption band of Ce$^{3+}$ centres [3], in LuAG:Ce it appears like a "doublet" (Fig. 1a, curve 2). The 3.61 eV emission is absent in the undoped LuAG and YAG SC. Its intensity increases with the increasing thickness of the SCF layer and its dominant excitation band occurs around 4.75 eV (Fig. 2a, curve 1) coinciding with the absorption spectrum peak (curve 2). Luminescence characteristics of the 3.61 eV emission in LuAG:Ce SCF are the same as in the undoped LuAG and YAG SC. Under 7.12 eV excitation, the 3.61 eV emission band is overlapped with more intense broad 4.3 eV emission band (Fig. 1b, curve 1), excited only at $E_{\text{exc}}> 7.0$ eV. In LuAG:Ce SCF, this emission is strongly suppressed (curve 2).

The intensity of the main 4.75 eV excitation band (Fig. 2a, curve 1) increases with the increasing thickness of the SCF layer, e.g., with the total lead content.

The Ce$^{3+}$-doping reduces strongly relative intensity of the 3.61 eV emission, especially under excitation in the exciton region (Fig. 3a, compare curves 1 and 2).

Temperature dependence of the 3.61 eV emission intensity obtained under 4.75 eV excitation is shown in Fig. 4, curve 1. The intensity is constant up to about 100 K and then decreases. Under 5.35 eV and 4.35 eV excitation, the emission intensity is constant up to ~180 K and then decreases gradually. This fact confirms the conclusion that the 5.35 eV and 4.35 eV excitation bands belong mainly to other emission bands strongly overlapped with the 3.61 eV band.

Decay kinetics of the 3.61 eV emission in LuAG SCF consists at 4.2 K of the fast submicrosecond component and the slow exponential component with the decay time of 97 µs. As the temperature increases, the decay time of the slow component remains constant up to about 20 K and then decreases...
In LuAG:Ce SCF, the slow component decay becomes accelerated and non-exponential (Fig. 5a, curves 2 and 3), in which the two-exponential fit was applied to get a description.

In the excitation spectrum of the 2.46 eV emission of Ce$^{3+}$ centres in LuAG:Ce SCF (Fig. 2b, curve 1), besides the main 5.8-5.5 eV, 3.61 eV and ~2.8 eV bands which exist also in LuAG:Ce SC (curve 2), an additional intense excitation band at 4.75 eV is observed, which coincides with the excitation band of the 3.61 eV emission (Fig. 2a, curve 1).

Temperature dependences of the 2.46 eV and 3.61 eV emission intensity in LuAG:Ce SCF, observed under 4.75 eV excitation, are different (Fig. 4, curves 1 and 2). The 4.75 eV band in the excitation spectrum of the 2.46 eV emission is intense even at room temperature, but the 3.61 eV emission is quenched. The temperature dependence of the 2.46 eV emission intensity (curve 2) is different from that observed under excitation in the Ce$^{3+}$-related 2.8 eV absorption band (curve 3).

Temperature dependences of the emission intensity measured under 4.75 eV excitation for the 3.61 eV emission of LuAG SCF (h = 12 µm) (curve 1) and for the 2.46 eV emission of LuAG:Ce SCF (h = 34.5 µm) under 4.75 eV (curve 2), and 2.8 eV (curve 3) excitations.

Temperature dependences of the slow component decay times of the 3.61 eV emission in LuAG SCF (h = 12 µm) (curve 1) and LuAG:Ce SCF (h = 34.5 µm) (curves 2 and 3). (b) Temperature dependence of the slow component decay time of the 2.46 eV emission in LuAG:Ce SCF (h = 34.5 µm).
In the decay kinetics of the 2.46 eV Ce\(^{3+}\) emission in LuAG:Ce SCF measured under 4.75 eV excitation, besides the fast (52 ns) component of Ce\(^{3+}\) center in LuAG SC [1], the slow component is observed with the decay time \(\sim 50\ \mu s\) at 4.2 K. Temperature dependence of the decay time of this component (Fig. 5b) is similar to that obtained for the 3.61 eV emission in LuAG:Ce SCF (Fig. 5a).

A wide 4.3 eV emission band, observed only in LuAG SCF [16] at low temperatures under excitation in the exciton absorption region, arises probably from an exciton localized near defect centers existing only in SCF (e.g., around Pb\(^{2+}\) ions). Strong suppression of this emission in LuAG:Ce SCF may be explained by the competition between the defects responsible for this emission and Ce\(^{3+}\) ions in the energy transfer processes from the host lattice or by the energy transfer from the 4.3 eV band to Ce\(^{3+}\) ions.

Strongly different excitation spectra observed in the host absorption region for the Pb\(^{2+}\)- and Ce\(^{3+}\)-related emissions of LuAG:Ce SCF (Figs. 3b and 3c) indicate the competition between Pb\(^{2+}\) and Ce\(^{3+}\) ions in the processes of energy transfer from the LuAG SCF lattice. Under the band-to-band excitation, the efficiency of energy transfer from the host lattice to Pb\(^{2+}\) ions is relatively much smaller than to Ce\(^{3+}\) ions. However, under excitation in the exciton region, the energy transfer to Pb\(^{2+}\) ions is effective.

Owing to a strong overlap of the emission band of Pb\(^{2+}\) centres with the 3.61 eV absorption band of Ce\(^{3+}\) centres, the energy transfer from the Pb\(^{2+}\) to Ce\(^{3+}\) ions is enabled. The experimental data obtained in this paper indicate that both radiative and non-radiative energy transfer processes are present.

4 Conclusions  In undoped and Ce-doped LuAG single crystalline films the 4.75 eV absorption and 3.61 eV emission peaks belong to the single-Pb\(^{2+}\)-ion-based center. An energy transfer from Pb\(^{2+}\)-based center towards Ce\(^{3+}\) is enabled due to the overlap of the 3.61 eV emission with 3.6 eV absorption peak of Ce\(^{3+}\) and is evidenced from the luminescence decay kinetics of both centers. Decreased efficiency and slowing-down of the Ce\(^{3+}\) luminescence response in the SCF was evidenced as due to the presence of Pb\(^{2+}\) ion especially under the excitation in the exciton absorption region of LuAG host.

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