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Luminescence and excited state dynamics in Bi^{3+}-doped $LiLaP_4O_{12}$ phosphates

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ABSTRACT

Photo- and X-ray-excited luminescence characteristics of Bi-doped $LiLaP_4O_{12}$ phosphates with different bismuth contents (from 1 to 25 at% in the melt) are investigated in the 4.2–300 K temperature range and compared with the characteristics of the undoped $LiLaP_4O_{12}$ phosphate. The broad 2.95 eV emission band of $LiLaP_4O_{12}$:Bi excited around 5.4 eV is found to arise from the bismuth dopant. Relatively large FWHM and Stokes shift of the emission band and especially the data on the low-temperature decay kinetics of the 2.95 eV emission and its temperature dependence, indicating a very small spin-orbit splitting energy of the corresponding excited state, allow the conclusion that this emission arises from the radiative decay of the triplet state of an exciton localized around a Bi^{3+} ion. No spectral bands are observed, arising from the electron transitions between the energy levels of Bi^{3+} ions. Phenomenological model is proposed for the description of the excited state dynamics of the Bi^{3+}-related localized exciton in $LiLaP_4O_{12}$:Bi and the parameters of the triplet localized exciton state are determined.

Keywords: Photoluminescence; Time-resolved spectroscopy; Excited states; Bi^{3+} centers; $LiLaP_4O_{12}$: Bi powders

1. Introduction

Luminescence of Bi^{3+}-related centers was systematically studied in various hosts starting from 1960s (see, e.g., literature reviews in [1–4]). In most of the Bi-doped compounds (e.g., alkali halides, alkaline-earth oxides and sulfates, aluminum perovskites, yttrium oxide, etc.), only the luminescence, arising from the radiative decay of the triplet relaxed excited state (RES) of Bi^{3+} centers, was detected. In this case, relatively narrow (with the full width at half maximum FWHM = 0.2–0.4 eV) emission band with the Stokes shift S = 0.3–1.2 eV was observed. At 4.2 K, the decay time of this emission was found to vary from hundreds of microseconds to milliseconds and be independent of temperature up to 30–100 K (see, e.g., [3,5–11]). However, in the luminescence spectra of Bi^{3+}-doped lutetium and yttrium aluminum garnets, the coexistence of the bands, arising from the triplet RES of a Bi^{3+} ion and from the states of an exciton localized around the Bi^{3+} ion, was found and the excited states model for the corresponding luminescence center proposed [3,5,6]. The same effect was detected in Bi^{3+}-doped oxyorthosilicates [7,8], but the luminescence of Bi^{3+}-related localized excitons in these systems appeared to be very weak as compared with the triplet emission of Bi^{3+} centers. Luminescence of excitons localized around Bi^{3+} ions was also reported in $CaWO_4$:Bi [12] and recently found in $PbWO_4$:Bi. It is of great interest to clarify whether analogous exciton-like emissions appear in the spectra of some other Bi^{3+}-doped materials. As the luminescence of an excitonic origin is usually fast, located in the visible spectral range and has a broad spectrum, these materials could find applications in X-ray screens, light sources (LED), scintillators and others. The aim of the present work is to investigate the origin and characteristics of the Bi^{3+}-related luminescence in the phosphates of the type of $LiLaP_4O_{12}$, which were studied earlier rather scarcely.

Indeed, the photoluminescence spectra of Bi-doped $LiLaP_4O_{12}$ glasses and powders were investigated only by Blasse et al. in [13,14]. Two luminescence bands were registered at LHeT: the 410 nm (3.02 eV) emission was observed under the 235 nm (5.28 eV) excitation and the 445 nm (2.79 eV) emission, under the 250 nm (4.96 eV) excitation. Both these emission bands were ascribed to the Bi^{3+} ions substituting for the La^{3+} ions in the

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crystal lattice of $LiLaP_4O_{12}$. To explain this fact, the presence of two crystallographic positions for a Bi^{3+} ion in the phosphate host was suggested. However, a later work [15] on the single crystal X-ray diffraction excluded this assumption.

In the present work, luminescence characteristics of $LiLaP_4O_{12}$: Bi powders with different Bi contents (1–25 at% in the melt) are investigated in the 4.2–400 K temperature range. For comparison, the characteristics of the undoped $LiLaP_4O_{12}$ powder are studied as well. Unlike [13,14], the luminescence characteristics of Bi-doped $LiLaP_4O_{12}$ observed in this work, especially the data on the luminescence decay kinetics and its temperature dependence, lead us to a conclusion that only the broad 2.95 eV emission band excited around 5.4 eV is connected with the bismuth dopant. We also conclude that this emission does not arise from the electron transitions between the energy levels of a Bi^{3+} ion. The 2.95 eV emission is suggested to arise from an exciton localized around a Bi^{3+} ion, which is produced as a result of the $Bi^{3+} \rightarrow La^{3+}$ charge-transfer process considered by Boutinaud [4] for many Bi^{3+}-doped oxide compounds.

2. Experimental procedure

Rare-earth based inorganic phosphates can be synthesized by various techniques, such as the solid-state reaction [16,17], melt-solution [18,19], Pechini sol–gel [20], and co-precipitation methods [21,22]. Onoda et al. [23,24] has shown that the solid-state reaction technique has an advantage to easily form the condensed phosphate and to control the molar ratio of cation/phosphorus. On the other hand, the main problem of this technique is keeping the homogenity of materials. A synthesis of rare-earth based phosphates via the Pechini sol–gel and co-precipitation methods allows to avoid a problem [21,22]. However, the products of the reactions are nanoparticles, in which case a surface significantly influences physical processes in rare-earth based phosphate compounds. A good homogeneity of the starting components under lower temperatures as compared to solid-state reaction could be obtained via the melt-solution reaction [18,19], which has been used in this work to prepare $LiLa_{1-x}Bi_xP_4O_{12}$ with different Bi contents in the melt (x=0.01, 0.02, 0.05, 0.10, and 0.25). The starting materials Li_2CO_3, $NH_4H_2PO_4$, Bi_2O_3, and La_2O_3 in the stoichiometric ratio were mixed and melted in quarts crucibles at 700 °C for 2 h under air atmosphere. After the reaction at 700 °C, the products were slowly cooled down to room temperature and removed from the quartz crucible. The size of the obtained Bi-doped $LiLaP_4O_{12}$ microcrystals was in the range of 5–10 μm.

The purity of the samples and the crystal structure of $LiLaP_4O_{12}$: Bi were checked using X-ray powder diffraction (XRPD). The data were collected in the transmission mode on a STOE STADI P diffractometer (Stoe WinXPOW version 3.03, Stoe & Cie GmbH) with the following setup: Cu $K\alpha_1$-radiation, curved Ge (111) monochromator on primary beam, $2\theta/\omega$-scan, angular range for data collection 5.000–100.505° 2θ with increment 0.015, linear position sensitive detector with step of recording 0.480° 2θ and time per step 320 s, U=40 kV, I=40 mA, T=24 °C. The crystal structure was refined by the Rietveld method with the program FullProf.2k (version 5.30) [25,26], applying a pseudo-Voigt profile function and isotropic approximation for the atomic displacement parameters.

The steady-state emission and excitation spectra in the 80–400 K temperature range were measured using a setup, consisting of a deuterium DDS-400 lamp and two monochromators (SF-4 and SPM-1). The luminescence was detected by a photomultiplier (FEU-39 or FEU-79) with an amplifier and recorder. In the 4.2–300 K temperature range, the spectra were measured with the use of the computer-controlled setup consisting of the LOT-ORIEL xenon lamp (150 W), two monochromators (MDR-3 and ORIEL Corner Stone 1/8 m), and Hamamatsu 6240 photon counting system.

Luminescence decay curves in the μs – ms time range were measured at the latter set up but under excitation with a xenon flash lamp FX-1152 (EG&G) with the pulse duration of about 1 μs and maximum repetition frequency of 300 Hz. The detection of the signal and the registration of decay curves were performed with a photon counting head and a multichannel analyzer with the time gate up to 10 s and the resolution up to 2 μs. In decay curves, data averaging with different numbers of points in different time scales was used to increase the signal-to-noise ratio. In the ns – μs time range, the decay kinetics was measured with a custom made 5000 M model of Horiba Jobin Yvon spectrofluorometer under excitation with a nanosecond coaxial hydrogen-filled flashlamp (IBH Scotland) or nanoLED sources. The detection was performed with an IBH-04 photomultiplier module using the method of time-correlated single photon counting. The decay curves I(t) were measured at the same conditions for different emission (E_{em}) or excitation (E_{exc}) energies. This allows the reconstruction of the time-resolved emission and excitation spectra at any time moment (t) after the excitation pulse. A convolution procedure (SpectraSolve software package, Ames photonics) was applied to the decay curves to extract true decay times (τ) using the multi-exponential approximation.

The X-ray-excited emission spectrum was measured at the same Horiba Jobin-Yvon setup under an X-ray (anode voltage 40 kV, current intensity 10 mA) tube (Seifert Gmbh) excitation source. The dependences of the X-ray-excited emission spectra on Bi content were measured using a laboratory X-ray source (anode voltage 40 kV, current intensity 15 mA), monochromator MDR-2 and photomultiplier FEU-100.

All spectra were corrected for the spectral distribution of the excitation light, the transmission and dispersion of the monochromators, and the spectral sensitivity of the detectors. The experiments were carried out with the use of an immersion helium cryostat, a close-cycle refrigerator (Janis Research) or a vacuum nitrogen cryostat.

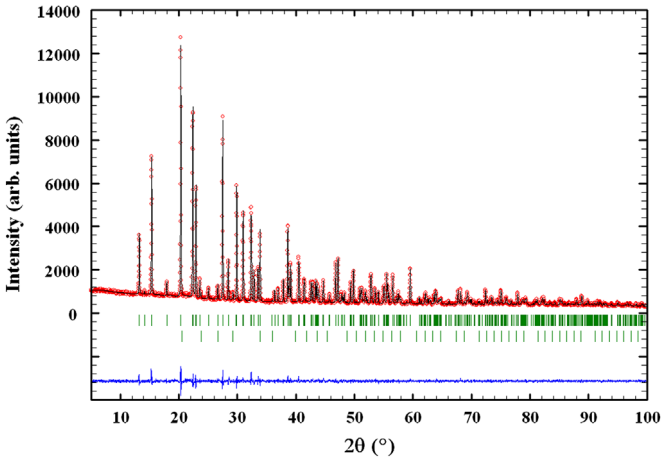

Fig. 1. XRPD profiles for the $LiLa_{0.98}Bi_{0.02}P_4O_{12}$ sample (Cu $K\alpha_1$-radiation). Experimental data (circles) and calculated profile (solid line running through the circles) are presented together with the calculated Bragg positions (vertical ticks) and difference curve (solid line at the bottom). The upper vertical ticks correspond to the main phase of Bi-doped $LiLaP_4O_{12}$ and the lower ticks, to additional SiP_2O_7 phase in the sample studied.