Photoluminescence and excited state structure in Bi³⁺-doped Lu₂SiO₅ single crystalline films

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Abstract Single crystalline films of Lu₂SiO₅:Bi, prepared by the liquid phase epitaxy method from the melt-solution based on Bi₂O₃ flux, are studied at 4.2-350 K by the time-resolved spectroscopy methods under excitation in the 2.4-6.2 eV energy range. An intense dominant ultraviolet (≈ 3.5 eV) luminescence of Lu₂SiO₅:Bi is shown to arise from the radiative decay of the metastable and radiative minima of the triplet relaxed excited state (RES) of Bi³⁺ centers which are related to the ³P₀ and ³P₁ levels of a free Bi³⁺ ion, respectively. At T<50 K, the radiative transitions from the metastable minima mainly take place. Thermally stimulated non-radiative transitions between the metastable and radiative minima of the triplet RES appear at T>50 K in the temperature evolution of the emission spectrum and decay kinetics. The excitation bands of the ultraviolet emission, located at 4.2 eV, 5.03 eV, and 5.95 eV, are assigned to the ¹S₀ → ³P₁, ¹S₀ → ³P₂, and ¹S₀ → ¹P₁ transitions of a free Bi³⁺ ion, respectively. The phenomenological model is proposed to describe the excited-state dynamics of Bi³⁺ centers in Lu₂SiO₅:Bi. Characteristic parameters of the triplet RES, in particular the energy separation between the excited states and the rates of the radiative and non-radiative transitions from these states, are determined. Much weaker ≈ 3.3 eV emission is ascribed to the Bi³⁺ ions located in the Lu₂ lattice sites. Weak broad ≈ 2.2 eV and ≈ 2.3 eV emission bands are assumed to arise from the Bi³⁺-related localized excitons.

Keywords Bi³⁺-doped Lu₂SiO₅ single crystalline films, time-resolved photoluminescence spectroscopy, triplet relaxed excited state, localized excitons

1. Introduction

Bi³⁺-doped rare-earth aluminate and gallate garnets, where a Bi³⁺ ion substitutes for a trivalent rare-earth ion, were considered as perspective materials for scintillators due to an intense and fast Bi³⁺-related emission [1-3]. In the single crystalline films (SCF) of Bi³⁺-doped aluminum garnets prepared by the liquid phase epitaxy (LPE) method, a large and variable concentration of Bi³⁺ ions was achieved [3]. In the emission spectrum of Y₃Ga₅O₁₂:Bi [1, 4], Gd₃Ga₅O₁₂:Bi [4], Y₃Al₅O₁₂:Bi [2-4], and Lu₃Al₅O₁₂:Bi [3-4], two main bands, located in the ultraviolet (UV) and visible (VIS) spectral ranges, were observed. The UV emission was assigned to the radiative decay of the triplet RES of Bi³⁺ centers, and the VIS emission, to the Bi³⁺-related bound excitons [5] or to complex Bi³⁺-based centers [2-4]. It was shown [6-8] that in Lu₃Al₅O₁₂:Bi and Y₃Al₅O₁₂:Bi, the properties of the Bi³⁺-related UV and VIS emissions are substantially different. The UV emission was ascribed to the radiative decay of the triplet RES

of a single Bi^{3+} center. The radiative decay of the excitons, localized near single Bi^{3+} and dimer $\text{Bi}^{3+}\text{-Bi}^{3+}$ centers, was shown to be responsible for two broad VIS emission bands.

The luminescence characteristics of Bi^{3+} -related centers in oxyorthosilicates have not been reported yet. Like in the case of Bi^{3+} -doped garnets, a large and variable concentration of Bi^{3+} ions can be achieved in the SCFs of Bi^{3+} -doped oxyorthosilicates. The aim of the present work was to study the luminescence characteristics of $\text{Lu}_2\text{SiO}_5\text{:Bi}$ SCF, to obtain information on the origin and structure of the corresponding RES, and to clarify the processes, taking place in the excited states.

2. Experimental details

Single crystalline film of $\text{Lu}_2\text{SiO}_5\text{:Bi}$ (LSO:Bi) with a thickness of 20 μm was grown by the LPE method from the melt-solution, based on a Bi_2O_3 oxide flux. An undoped single crystal of LSO was used as a substrate. The concentration of Bi^{3+} ions in the SCF was determined with a JEOL JXA-733 electron microprobe analyser and was found to be The luminescence characteristics of both the LSO:Bi SCF and the LSO substrate were studied and compared at the same experimental conditions.

The steady-state emission and excitation spectra and temperature dependences of the emission intensity were measured in the 4.2-350 K temperature range under selective excitation in the 2.4-6.2 eV energy range. A setup consisted of a deuterium DDS-400 lamp, two monochromators (SF-4 and SPM-1) and a photomultiplier (FEU-39 or FEU-79) with both amplifier and recorder. The 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.

Luminescence decay kinetics in the μs -ms time range was measured at 4.2-300 K at the same set-up but under excitation with a xenon flash lamp FX-1152 (EG&G) (the pulse duration of about 1 μs and maximum repetition frequency of 300 Hz). The decay curves $I(t)$ were measured at the same conditions for different emission (E_{em}) and (E_{exc}) excitation energies.

This allows obtaining time-resolved emission and excitation spectra at any moment of time (t) after the excitation pulse. The decay kinetics at 10-300 K was also measured with a modified Spectrofluorometer 199S (Edinburgh Instruments) under excitation with a nanosecond coaxial hydrogen-filled flashlamp (IBH Scotland) and using two single grating monochromators. The detection was performed with an IBH-04 photomultiplier module using the method of time-correlated single photon counting. A deconvolution procedure (SpectraSolve software package) was applied to extract true decay times using the multiexponential approximation.

The experiments at low temperatures were carried out with the use of an immersion helium cryostat, close-cycle refrigerator or vacuum nitrogen cryostat.

3. Experimental results

The absorption spectrum of LSO:Bi measured at 295 K is shown in Fig. 1a. The high optical density observed in the $E > 4.1$ eV energy range indicates a large Bi^{3+} content in the SCF studied. In the emission spectrum of LSO:Bi, a strong UV band (≈ 3.5 eV), much weaker 3.3

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eV band, and several visible bands are observed (Fig. 2). Their relative intensities depend on the excitation energy.

3.1. Ultraviolet luminescence

The characteristics of the UV emission of LSO:Bi are similar to those observed for the triplet emission of single Bi^{3+} centers in other Bi-containing oxide compounds (see, e.g., [1, 2, 4-11] and references therein). At 4.2 K, the UV emission band is located at about 3.47 eV (Fig. 3a). In the excitation spectrum of this emission, the bands peaking at 4.2 eV, 5.03 eV, and 5.95 eV are observed (Fig. 1b, see also Table 1). Under excitation in the lowest-energy absorption band, the emission band is peaking at 3.455 eV (FWHM=0.28 eV); thus, the Stokes shift is 0.745 eV (Fig. 3a, solid line). Under higher-energy excitation ($E_{\text{exc}} > 4.3$ eV), the emission band is shifted to higher energies (up to 3.485 eV) and is broader (FWHM=0.36 eV) (dashed line).

As the temperature increases, the maximum of the UV emission band is gradually shifting to higher energies from 3.455 eV at $T < 50$ K (Fig. 3b, solid line) up to 3.525 eV (FWHM=0.39 eV) at 130 K (dotted line). These data point to the presence of two components in the UV emission spectrum. The 3.525 eV emission band is the superposition of the low-energy component, arising from the lower excited level, and the high-energy component, arising from the upper excited level, which becomes thermally populated from the lower level at $T > 50$ K. Both the thermally stimulated redistribution of the intensities of the two emission components (Fig. 4a) and the largest shift of the UV emission band maximum (Fig. 4b, solid line) take place around 80 K. As the temperature increases, the FWHM of the emission band increases from 0.28 eV at 4.2 K up to 0.5 eV at 300 K (dashed line).

The maximum intensity of the total UV emission, measured under excitation in the maximum of the excitation band around 4.2 eV, remains constant up to 50 K and then decreases with the increasing temperature up to ≈ 120 K (Fig. 4c, solid line). This quenching stage well correlates with the temperature dependence of the maximum position of the UV emission band (Fig. 4b, solid line). It means that thermal quenching of the UV emission around 80 K arises from the non-radiative transitions from the upper level of the triplet RES. The second quenching stage of the UV emission is observed around 215 K.

In the decay kinetics of the UV emission, mainly the slow component (SC) is observed at 4.2 K with the decay time $\tau_{\text{SC}} = 292 \mu\text{s}$ (Fig. 5a). The higher-energy shift of the emission spectrum of the SC with the increasing temperature (Fig. 3c) is similar to that observed for the steady-state UV emission (Fig. 3b). Temperature dependence of the SC intensity (Fig. 4c, dashed line) is also similar to that obtained for the steady-state emission (solid line). A difference at $T > 100$ K is caused by the fact that for the SC, this dependence was measured at fixed values of E_{exc} and E_{em} . These data indicate that, like in the case of Bi^{3+} -doped garnets [6-8], the slow component strongly dominates in the decay kinetics of the triplet emission of Bi^{3+} centers in LSO:Bi.

As the temperature increases, the decay time value of the SC remains constant up to about 50 K. In the temperature range around 80 K τ_{SC} decreases, reaching the value of $10 \mu\text{s}$ at 120 K and $\approx 0.2 \mu\text{s}$ at 300 K (Fig. 6a). Similar temperature dependence of τ_{SC} was observed for the triplet emission of Bi^{3+} centers in some other hosts (see, e.g., [1, 6-11]). Thus, the decay kinetics data clearly indicate that the UV emission of LSO:Bi arises from the triplet RES of Bi^{3+} ions.

Besides the ≈ 3.5 eV emission of Bi^{3+} centers, much weaker ≈ 3.3 eV emission is observed under the 3.8 eV excitation (Fig. 2b, solid line and Fig. 7a). Due to the presence of this emission, the main UV emission band is shifting to lower energies with the decreasing excitation energy (down to 3.42 eV under $E_{\text{exc}}=3.9$ eV, Fig. 2b, dashed line). The excitation spectrum of the ≈ 3.3 eV emission (Fig. 1b, dashed line) is different from that of the 3.455 eV emission (solid line). Its shape suggests that in the excitation light absorption the center is competing with that responsible for the 3.455 eV emission. Consequently, the excitation spectrum of the ≈ 3.3 eV emission can be distorted due to an intense absorption arising from the Bi^{3+} centers (Fig. 1a). At 4.2 K, the main decay component of the ≈ 3.3 eV emission has the decay time of 298 μs (Fig. 5b). The uncorrected time-resolved emission spectrum of this component is shown in Fig. 7a, solid line. The temperature dependence of the decay time (Fig. 6b) is similar to that obtained for the 3.455 eV emission of Bi^{3+} centers (Fig. 6a). The ≈ 3.3 eV emission with the above-mentioned characteristics is not observed in the LSO substrate. The obtained data indicate that this emission can also arise from the triplet RES of Bi^{3+} ions, but the centers responsible for the 3.455 eV and ≈ 3.3 eV emissions are different. As this emission is overlapping with the 3.0-3.3 eV emission of the substrate and their intensities are comparable, its more detailed study is not feasible. The emission spectrum of the 19 μs -component, also appearing in the decay curve in Fig. 5b, consists of the bands located at 2.9 eV and 2.25 eV (Fig. 7a, dashed line), i.e., this component is not connected with the ≈ 3.3 eV emission.

3.2. Visible luminescence

The visible luminescence spectrum of LSO:Bi consists of many strongly overlapping bands. Unlike the Bi^{3+} -doped aluminum garnets studied in [6-8], the VIS emission of LSO:Bi is much weaker as compared with the UV emission (Fig. 2a). Detailed comparison of the characteristics of the LSO:Bi SCF and the LSO substrate used at the preparation of the SCF indicates that under excitation in the energy regions $E_{\text{exc}} > 4.5$ eV and $E_{\text{exc}} < 3.9$ eV, the VIS emission in LSO:Bi SCF is weaker than that in the substrate. Thus, some of the VIS bands of the SCF can arise from the substrate. However, under excitation around 4.2 eV, the VIS emission of LSO:Bi SCF is about two times more intense as compared with the substrate, i.e., in principle, it can arise from Bi-related centers. Therefore, we have studied the characteristics of the VIS emission only under this excitation. Our aim was to clarify whether the emission could not be associated with an exciton localized near a Bi^{3+} ion. Such emission was previously identified in Bi^{3+} -doped aluminum garnets [6-7].

Under excitation in the 4.2 ± 0.3 eV energy range, the steady-state VIS emission spectrum of LSO:Bi consists of the bands located at about 2.8 eV, 2.5 eV, 2.1 eV, and 1.85 eV (Fig. 2). Their FWHM are about two times smaller as compared with the VIS bands of exciton origin in Bi-doped garnets. The 2.8 eV emission is excited at 3.95 eV, while the 1.9-2.5 eV emissions, at 4.05 eV (see, e.g., Fig. 1c), i.e., their excitation spectra are shifted to lower energies with respect to those of the 3.455 eV emission (Fig. 1b, solid line), unlike Bi-doped aluminum garnets where the excitation spectra of the UV emission of Bi^{3+} centers and VIS emission of an exciton localized near a Bi^{3+} ion are close [6-7]. Besides, the shape of the excitation spectra indicates a competition between the main Bi^{3+} centers and the centers with the VIS emission in the excitation light absorption. As the temperature increases, the intensity of all the VIS emission bands measured under 4.07-4.15 eV excitation remains constant up to about 80 K and then decreases twice around 178 K (Fig. 4d). Unlike Bi^{3+} -doped aluminum garnets [6-7], no

intensity redistribution takes place between the UV and VIS bands. These data indicate that the emission of excitons localized near Bi^{3+} ions is too weak to appear in the steady-state luminescence spectra of LSO:Bi.

At 4.2 K, the decay curve of the VIS emission observed under 4.15 eV excitation consists of the components whose decay times are about 3 μs , 17 μs , 76 μs , and 384 μs (Fig. 5c). Their light sums ratio is 2.6 : 6.8 : 4.7 : 1.96. The study of the time-resolved emission spectra of the separate decay components (Fig. 7b) indicates that two slowest components arise from relatively narrow (FWHM $\approx$ 0.2 eV) emission bands located at 2.55 eV and 2.15 eV, respectively (solid line). However, the emission spectra of the $\approx$ 3 μs and $\approx$ 17 μs -components are broad (FWHM $\approx$ 1 eV) bands with the maxima at about 2.2 eV and 2.3 eV, respectively (dashed lines). The decay times of these two components decrease with the increasing temperature starting from 4.2 K (Fig. 6c), which points to a small spin-orbit splitting energy of the corresponding triplet RES. The temperature dependences of the decay times are similar to those observed in [6-8] for the visible luminescence in Bi^{3+} -doped aluminium garnets. By analogy with [6-8], these data allow us to suggest that both the $\approx$ 3 μs - and the $\approx$ 17 μs -component of the VIS emission of LSO:Bi can arise from the radiative decay of the triplet RES of excitons localized near Bi^{3+} -related centers. The light sum of these components is in, at least, two orders of magnitude smaller as compared with the light sum of the UV emission of the main Bi^{3+} centers.

4. Discussion

The bulk single crystal of the lutetium oxyorthosilicate has a monoclinic X_2 type structure of the space group C2/c (see, e.g., [12-13]). There exist two crystallographically different Lu^{3+} ion sites, Lu1 and Lu2, with the same (C_1) point symmetry but with different coordination numbers (7 and 6) and Lu-O distances (2.32 Å and 2.22 Å), respectively [14]. A trivalent Bi^{3+} ion replaces a Lu^{3+} ion in the LSO crystal lattice. In principle, it can occupy both (Lu1 and Lu2) positions. By analogy with the Ce2 emission in LSO (see, e.g., [15]), the emission band of Bi2 centers should be located at lower energies as compared with the emission of Bi1 centers and excited at the lower-energy side of the A absorption band of Bi1 centers. In LSO:Bi, this emission is expected to appear in the 3.0-3.3 eV energy range and being excited around 3.8-4.1 eV. In principle, the weak $\approx$ 3.3 eV emission, which has the characteristics similar to those of the UV emission of the main Bi^{3+} centres, could arise from Bi2 centers. The larger Stokes shift and FWHM of this emission band as compared with the $\approx$ 3.5 eV band (Table 1) indicate to a stronger electron-phonon interaction in Bi2 centers, which is characteristic for a large Bi^{3+} ion in a small Lu2 site. As the ionic radius of Bi^{3+} is about 1.196 times larger than the ionic radius of Lu^{3+} [16], the location of a Bi^{3+} ion in the larger Lu1 site with the larger Lu-O distance seems to be much more preferable as compared with the Lu2 site. Therefore, we conclude that the intense $\approx$ 3.5 eV emission of Bi^{3+} centers arises mainly from the Bi^{3+} ions located in the Lu1 sites.

According to [17], the energies of electronic transitions from the ground 1S_0 level to the excited 3P_1 , 3P_2 and 1P_1 levels of a free Bi^{3+} ion (E_{free}) are 9.41 eV, 11.96 eV and 14.21 eV, respectively. In the crystal, the absorption bands, labelled as A, B and C, correspond to the electronic transitions to these levels. The lowest-energy A absorption band of LSO:Bi, corresponding to the $^1S_0 \rightarrow ^3P_1$ transition, is located at 4.2 eV, i.e. the transition energy in the

crystal (E_{crys}) is about 2.24 times smaller than that in a free Bi^{3+} ion. Taking into account the fact that the $E_{\text{free}}/E_{\text{crys}}$ ratio increases with the increasing E_{free} according to the approximate equation $E_{\text{free}}/E_{\text{crys}}=1+kE_{\text{free}}$, experimentally found in [18] and confirmed to be valid for all the ns^2 -ion-doped alkali halide crystals, the positions of the B and C bands of the Bi^{3+} center in LSO:Bi can be estimated. One can conclude that the ≈ 5.95 eV band arises from the allowed $^1\text{S}_0 \rightarrow ^1\text{P}_1$ transitions and the weak 5.03 eV band, from the $^1\text{S}_0 \rightarrow ^3\text{P}_2$ transitions. A small intensity of the 5.95 eV excitation band can be caused by the location of the corresponding excited level inside the conduction band.

Let us first consider the origin and structure of the energy levels responsible for the UV emission of Bi^{3+} center in LSO:Bi .

As shown above, the UV emission of LSO:Bi arises from the triplet RES of Bi^{3+} centers. The low-temperature 3.455 eV emission band arises mainly from the radiative decay of the lowest-energy metastable excited state, related to the $^3\text{P}_0$ level of a free Bi^{3+} ion. At $T > 130$ K, the radiative decay of the thermally populated higher-energy radiative excited state, related to the $^3\text{P}_1$ level of a free Bi^{3+} ion, also takes place, and the 3.525 eV emission appears. The $^1\text{S}_0 \rightarrow ^3\text{P}_1$ electronic transitions are partly allowed due to the mixing of the triplet $^3\text{P}_1$ state with the singlet $^1\text{P}_1$ state by the spin-orbit interaction. The radiative transitions from the $^3\text{P}_0$ -related state can occur due to the mixing of the $^3\text{P}_1$ - and $^3\text{P}_0$ -related states by the vibronic interaction with the non-totally symmetric vibrations or by the hyperfine interaction (see, e.g., [19] and references therein). As the only stable Bi isotope ^{209}Bi has a nuclear spin of $I=9/2$, in Bi^{3+} -doped or Bi^{3+} -containing compounds with a weak vibronic interaction, mainly the hyperfine interaction can be expected to be responsible for the radiative decay of the $^3\text{P}_0$ -related level. The influence of the hyperfine interaction on the probability of the radiative $^3\text{P}_0 \rightarrow ^1\text{S}_0$ transitions in Bi^{3+} -doped alkali-earth oxides was considered in [20].

The decay kinetics of the UV emission of LSO:Bi can be described within the phenomenological model used for Bi^{3+} centers in $\text{Y}_3\text{Ga}_5\text{O}_{12}$ [1] and in $\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Lu}_3\text{Al}_5\text{O}_{12}$ [8]. The model is sketched in Fig. 8a. The time evolution of the populations N_1 , N_2 of the excited levels 1 and 2, respectively, can be described by the following rate equations:

$$\begin{aligned} dN_1/dt &= -k_1N_1 - k_{12}N_1 + k_{21}N_2 \\ dN_2/dt &= -k_2N_2 - k_{21}N_2 + k_{12}N_1, \end{aligned} \quad (1)$$

where k_1 , k_2 , k_{12} , k_{21} , and $k_{1(2)x}$ are radiative transition rates from levels 1,2, non-radiative rates of phonon assisted transitions between the radiative level 2 and metastable level 1 and the quenching channel from the level 1(2), respectively. Non-radiative transitions between levels 1,2 can be written as:

$$k_{21} = K(n+1), k_{12} = Kn, \quad n = 1/[\exp(D/k_B T) - 1]. \quad (2)$$

Here K , n , D are the zero-temperature transition rate between the levels 1 and 2, the Bose-Einstein factor, and energy spacing between the levels, respectively.

The best fit of the experimental $\tau(T)$ dependence is shown as a solid line in Fig. 6a. The parameters of the triplet RES corresponding to this fit are reported in Fig. 8a. The obtained data indicate that at $T < 50$ K, the contribution to the observed slow radiative decay comes mainly from the metastable minima (level 1) of the triplet RES of Bi^{3+} . At $T > 130$ K, the shortening of the UV emission decay time and the high-energy shift of the UV emission band with increasing temperature are both caused by thermally stimulated non-radiative transitions between the metastable (level 1) and radiative (level 2) minima of the triplet RES.

The same consideration is also valid for the ≈ 3.3 eV emission. The best fit of the experimental $\tau(T)$ dependence is shown as a solid line in Fig. 6b. The parameters of the triplet RES corresponding to this fit are reported in Fig. 8a.

The decay kinetics of both VIS emissions of LSO:Bi can be described within the phenomenological model used for Bi^{3+} -related localized excitons in $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Bi}$ and $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Bi}$ [8]. In this model, the excited state levels 1 and 2 would correspond to those of the localized exciton triplet states, and level 3 is the singlet level of the exciton state lying above the triplet levels of the RES. The model is sketched in Fig. 8b and the rate equations now read:

$$\begin{aligned} dN_1/dt &= -k_1N_1 - k_{12}N_1 - k_{13}N_1 + k_{21}N_2 + k_{31}N_3 \\ dN_2/dt &= -k_2N_2 - k_{21}N_2 - k_{23}N_2 + k_{12}N_1 + k_{32}N_3 \\ dN_3/dt &= -k_3N_3 - k_{31}N_3 - k_{32}N_3 + k_{13}N_1 + k_{23}N_2, \end{aligned} \quad (3)$$

where analogous parameters have the same meaning as in (1). In addition, k_3 is the radiative transition rate from the singlet level 3 and $k_{3(2)1}$, $k_{1(2)3}$ are non-radiative rates of transitions between the levels 3(2) and 1:

$$k_{31} = K_i(n'+1), k_{13} = K_i n', \quad n' = 1/[\exp(E/k_B T) - 1]. \quad (4)$$

Since $D \ll E$, we consider

$$k_{31} = k_{32}, \quad k_{13} = k_{23} \quad (5)$$

The best fits of the experimental $\tau(T)$ dependences obtained for the 2.2 eV and 2.3 eV emissions are displayed as solid lines in Fig. 6c. The parameters used to obtain the best fits are reported in Fig. 8b. The model described above successfully reproduces the data as well as the considered RES structure, and the parameters obtained are similar to those obtained for the localized exciton states in aluminum garnets [8]. Thus, the results of our decay kinetics modelling strongly support the hypothesis on the excitonic origin of both VIS emissions in LSO:Bi. At $T \leq 4.2$ K, the visible emissions are due to the radiative decay of the metastable minima of the triplet state of the localized exciton. The shortening of their decay time with increasing temperature in the 4.2-25 K range is caused by thermally stimulated non-radiative transitions between the metastable and radiative minima of the triplet RES. The energy distance between them is about 1.4-2 meV. Around 30 K, the thermal equilibrium between these minima is reached. The shortening of the decay time at further increase of the temperature is caused by thermally stimulated transitions between the triplet and singlet localized exciton states separated by the energy distance of about 80 meV. In Bi^{3+} -doped aluminum garnets, two visible emissions of exciton origin were ascribed to the excitons localized near single and dimer Bi^{3+} centers. In LSO:Bi, a more detailed study of the 2.2 eV and 2.3 eV emissions is not feasible due to their small intensity and strong overlap with other emission bands of unknown origin.

Two models have been proposed for the description of the ns^2 -ion-related RES in ionic crystals with strongly different electron-phonon and spin-orbit interactions. The systems with a *strong spin-orbit interaction and a very weak electron-phonon interaction* should be considered in the RES model, proposed by Seitz [21], which takes into account the spin-orbit interaction as the main one in the RES. In this model, the RES of the luminescence center originate from the 3P_0 , 3P_1 , 3P_2 and 1P_1 levels of a free ns^2 ion, which are split in the crystal field of the corresponding symmetry. For degenerate energy levels, the Jahn-Teller effect is taken into account as a perturbation. The totally symmetric 3P_0 state is non-degenerate, therefore it cannot be active in the Jahn-Teller effect. The configuration coordinates (q) of the 3P_0 and 1S_0 minima in this model should coincide.

For the systems with a *strong electron-phonon interaction*, the RES theory was developed in [22]. In this theory, the interaction of impurity optical electrons with non-totally symmetric vibrations is considered as the main one in the RES, while the spin-orbit, hyperfine and other interactions are taken as small perturbations. As a result, the Jahn-Teller minima of different symmetries can be formed on the adiabatic potential energy surface of the singlet (1P) and triplet (3P) excited states. Due to the spin-orbit interaction, each Jahn-Teller minimum of the triplet RES is split into the upper radiative level and the lower metastable level. The applicability of this model was confirmed by the systematic experimental study of luminescence characteristics of ns^2 -ion-doped alkali halide crystals (see, e.g., review [19]). It was also found that in the Tl^+ , Pb^{2+} , Bi^{3+} centers with a strong spin-orbit interaction, each metastable minimum of the triplet RES can lie not exactly under the corresponding radiative minimum, like in the Ga^+ , In^+ , Ge^{2+} , Sn^{2+} centers with a weak spin-orbit interaction, but it can be shifted towards smaller configuration coordinate (q) values with respect to the emitting minimum (see, e.g., Fig. 8b). Due to that, the energy barriers for thermally stimulated transitions between the metastable minima of various orientations can be much lower than those between various emitting minima (see, e.g., [10, 19, 23] and references therein).

A free Bi^{3+} ion is characterized by the largest spin-orbit interaction energy (ξ) among all ns^2 ions ($\xi=1.074$ eV [24]). The luminescence characteristics of two Bi^{3+} -doped crystals with strongly different electron-phonon interaction (KCl:Bi and CaO:Bi) were compared in [10]. It was concluded that the theoretical model [22] is valid in the case of KCl:Bi but it is not valid in the case of CaO:Bi due to a very weak electron-phonon interaction in the latter system. The comparison of the values of the FWHM and Stokes shift of the UV emission band in LSO:Bi obtained in this paper with the corresponding characteristics of Bi^{3+} centers in KCl:Bi and CaO:Bi (see Table 2) indicates that Bi^{3+} centers in LSO can be characterized by a relatively weak electron-phonon interaction and considered as an intermediate case between Bi^{3+} -doped CaO and KCl.

The comparison of the Stokes shifts and FWHM of the UV emission bands (Table 2) and the parameters of the triplet RES of Bi^{3+} centers in aluminum garnets [6-8] and in LSO (Fig. 8a) allows us to conclude that the electron-phonon interaction in LSO:Bi is noticeably stronger than in the garnets. For example, the smaller value of the spin-orbit splitting energy of the triplet RES of Bi^{3+} center in LSO:Bi ($D=65$ meV) as compared with $Lu_3Al_5O_{12}:Bi$ ($D=103$ meV) and $Y_3Al_5O_{12}:Bi$ ($D=110$ meV) can be just due to the stronger suppression of the spin-orbit interaction by the electron-phonon interaction.

A schematic configuration coordinate diagram of the triplet excited state of a Bi^{3+} ion in a cubic crystal field of the system with a relatively weak electron-phonon interaction is presented in Fig. 8b together with the approximate position of the Bi^{3+} -related localized exciton state. Due to the low (C_1) symmetry of the nearest neighbourhood of a Bi^{3+} ion in the crystal lattice of Lu_2SiO_5 , the energies of different Jahn-Teller minima of the triplet RES of Bi^{3+} center can be different. This explains the dependence of the UV emission band position on the excitation energy shown in Fig. 3a.

5. Conclusions

The strong ultraviolet luminescence of $Lu_2SiO_5:Bi$ arises from the radiative decay of the metastable and radiative minima of the triplet RES of Bi^{3+} centers, which are related to the 3P_0 and 3P_1 levels of a free Bi^{3+} ion, respectively. Both the high-energy shift of the emission

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spectrum (from 3.455 eV at 4.2 K to 3.525 eV at 130 K) and the shortening of the decay time with the increasing temperature observed at $T > 50$ K are caused by thermally stimulated non-radiative transitions between the metastable and radiative minima of the triplet RES. The excitation bands of the UV emission, located at 4.2 eV, 5.03 eV, and 5.95 eV, are assigned to the $^1S_0 \rightarrow ^3P_1$, $^1S_0 \rightarrow ^3P_2$, and $^1S_0 \rightarrow ^1P_1$ transitions of a free Bi^{3+} ion, respectively. The phenomenological model is proposed to describe the excited-state dynamics of Bi^{3+} centers. Application of the two-excited-level model on the temperature evolution of the UV luminescence decay times has allowed determination of characteristic parameters of the triplet RES of Bi^{3+} centers: the energy separation between the excited states and the rates of the radiative and non-radiative transitions from these states.

The dominant ≈ 3.5 eV emission of Bi^{3+} centers arises mainly from the Bi^{3+} ions located in the Lu1 sites of the Lu_2SiO_5 crystal lattice (Bi1 centers). The weak ≈ 3.3 eV emission is assumed to arise from Bi2 centers, and weak ≈ 2.2 eV and ≈ 2.3 eV emissions, from the excitons, localized near Bi^{3+} ions. Unlike Bi^{3+} -doped aluminum garnets, the emission of the Bi^{3+} -related localized excitons in $\text{Lu}_2\text{SiO}_5\text{:Bi}$ is very weak.

Owing to the presence of an intense and relatively fast (200 ns at RT) luminescence in the UV spectral range, the Bi^{3+} -doped oxyorthosilicates can be perspective for their applications in scintillation detectors.

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Table 1. Emission peak positions (E_{em}), full widths at half maxima (FWHM), and the Stokes shifts (S) at 4.2 K and 130 K, as well as excitation peak positions (E_{exc}) and decay times of the slow (τ_{SC}) decay component at 4.2 K of some emission bands of Bi^{3+} -related centers in $\text{Lu}_2\text{SiO}_5\text{:Bi}$.

E_{em} (4.2 K) eV	FWHM eV	S eV	E_{em} (130 K) eV	FWHM eV	S eV	E_{exc} (4.2 K) eV	τ_{SC} (4.2 K) μs
3.455	0.28	0.745	3.525	0.39	0.675	5.95; 5.03; 4.2	292
3.3	0.4	0.80				>5.9; 5.05; 4.4; 4.1	298
2.2	1.0	1.85				4.35; 4.05	2.7
2.3	1.0	1.75				4.35; 4.05	16.8

Table 2. A comparison of the characteristics of the two (lower-temperature and higher-temperature) spectral components of the triplet luminescence of Bi^{3+} centers in single crystalline films of Lu_2SiO_5 and $\text{Lu}_3\text{Al}_5\text{O}_{12}$, and in single crystals of KCl and CaO. The notations are the same as in Table 1. E_{exc} is the position of the lowest-energy excitation band.

Crystal	E_{em} eV	FWHM eV	S eV	E_{exc} (4.2 K) eV	τ_{SC} (4.2 K) μs	References
$\text{Lu}_2\text{SiO}_5\text{:Bi}$	3.455	0.28	0.745	4.20	292	this work
	3.525	0.39	0.675			
$\text{Lu}_3\text{Al}_5\text{O}_{12}\text{:Bi}$	4.08	0.24	0.55	4.63	1100	[6]
	4.19	0.27	0.44			
KCl:Bi	2.68	0.38	1.13	3.81	2800	[10]
	2.46	0.41	1.35			
CaO:Bi	3.10	0.14	0.4	3.50	3250	[10]
	3.30	0.20	0.2			

Figure captions

Fig. 1. (a) Absorption spectrum measured at 295 K. Normalized excitation spectra of (b) the UV emission measured at $E_{em}=3.5$ eV (solid line) and 3.15 eV (dashed line), and (c) the VIS emission measured at $E_{em}=2.8$ eV (solid line) and $E_{em}=2.3$ eV (dashed line). $T=4.2$ K.

Fig. 2. Emission spectra measured at 4.2 K under excitation with (a) $E_{exc}=4.15$ eV, (b) $E_{exc}=3.8$ eV (solid line) and $E_{exc}=3.9$ eV (dashed line).

Fig. 3. Normalized steady-state emission spectra (a) $T=4.2$ K, $E_{exc}=4.15$ eV (solid line), $E_{exc}=4.6$ eV (dashed line); (b) different temperatures indicated in the legend, $E_{exc}=4.15$ -4.07 eV; (c) normalized uncorrected time-resolved emission spectra of the slow decay component of the UV emission at 4.2 K (solid line) and 140 K (dashed line), $E_{exc}=4.15$ eV.

Fig. 4. Temperature dependences of (a) the emission intensities measured under $E_{exc}=4.15$ eV for two opposite sides of the UV emission band: at $E_{em}=3.2$ eV (solid line) and $E_{em}=3.7$ eV (dashed line); (b) the peak position (solid line) and FWHM (dashed line) of the UV emission band; (c, d) the maximum intensity of the UV emission (c) and the VIS emissions (d) under excitation in the A band maximum (4.15-4.07 eV). Dashed curve in Fig. 4c is obtained for the light sum of the slow decay component of the UV emission measured for $E_{em}=3.45$ eV under $E_{exc}=4.15$ eV.

Fig. 5. Decay curves of the (a) ≈ 3.5 eV, (b) 3.3 eV, and (c) 2.3 eV emissions measured at 4.2 K under $E_{exc}=4.15$ eV (a, c) and $E_{exc}=3.85$ eV (b).

Fig. 6. Temperature dependences of the slow component decay times of the (a) ≈ 3.5 eV, (b) 3.3 eV, and (c) 2.2 eV, 2.3 eV emissions. $E_{exc}=4.15$ eV (a, c) and $E_{exc}=3.9$ eV (b). Solid and empty circles are experimental data. Solid lines are the best fits to the experimental data of the two or three excited-state level models shown in Figs. 8a, b respectively (for details, see the text). The parameters of the fits are reported in Figs. 8a,b.

Fig. 7. Normalized uncorrected time-resolved emission spectra measured at 4.2 K at different time instants (t) after the excitation pulse. In (a) $E_{exc}=3.85$ eV, in (b) $E_{exc}=4.15$ eV.

Fig. 8. (a,b) The energy level diagrams used to describe the excited states dynamics of Bi^{3+} centers in Lu_2SiO_5 . The values of the parameters obtained from the best fits to the experimental $\tau(T)$ data shown in Fig. 6 are reported. For details, see the text. (c) Schematic configuration coordinate diagram of the Bi^{3+} -related triplet excited state. The electronic transitions between the ground state, corresponding to the 1S_0 level, and the excited states, corresponding to the 3P_1 and 3P_0 levels of a free Bi^{3+} ion and the triplet Bi^{3+} -related localized exciton state, are indicated by arrows.

Fig. 1. (a) Absorption spectrum measured at 295 K. Normalized excitation spectra of (b) the UV emission measured at $E_{em}=3.5$ eV (solid line) and 3.15 eV (dashed line), and (c) the VIS emission measured at $E_{em}=2.8$ eV (solid line) and $E_{em}=2.3$ eV (dashed line). $T=4.2$ K.

Fig. 2. Emission spectra measured at 4.2 K under excitation with (a) $E_{\text{exc}}=4.15$ eV, (b) $E_{\text{exc}}=3.8$ eV (solid line) and $E_{\text{exc}}=3.9$ eV (dashed line).

Fig. 3. Normalized steady-state emission spectra (a) $T=4.2\text{ K}$, $E_{exc}=4.15\text{ eV}$ (solid line), $E_{exc}=4.6\text{ eV}$ (dashed line); (b) different temperatures indicated in the legend, $E_{exc}=4.15\text{-}4.07\text{ eV}$; (c) normalized uncorrected time-resolved emission spectra of the slow decay component of the UV emission at 4.2 K (solid line) and 140 K (dashed line), $E_{exc}=4.15\text{ eV}$.

Fig. 4. Temperature dependences of (a) the emission intensities measured under $E_{\text{exc}}=4.15$ eV for two opposite sides of the UV emission band: at $E_{\text{em}}=3.2$ eV (solid line) and $E_{\text{em}}=3.7$ eV (dashed line); (b) the peak position (solid line) and FWHM (dashed line) of the UV emission band; (c, d) the maximum intensities of the UV emission (c) and the VIS emissions (d) under excitation in the A band maximum (4.15-4.07 eV). Dashed curve in Fig. 4c is obtained for the light sum of the slow decay component of the UV emission measured for $E_{\text{em}}=3.45$ eV under $E_{\text{exc}}=4.15$ eV.

Fig. 5. Decay curves of the (a) ≈ 3.5 eV, (b) ≈ 3.3 eV, and (c) ≈ 2.3 eV emissions measured at 4.2 K under $E_{\text{exc}} = 4.15$ eV (a, c) and $E_{\text{exc}} = 3.85$ eV (b).

Fig. 6. Temperature dependences of the slow component decay times of the (a) ≈ 3.5 eV, (b) ≈ 3.3 eV, and (c) 2.2 eV, 2.3 eV emissions. $E_{\text{exc}}=4.15$ eV (a, c) and $E_{\text{exc}}=3.9$ eV (b). Solid and empty circles are experimental data. Solid lines are the best fits to the experimental data of the two or three excited-state level models shown in Figs. 8 a,b, respectively (for details, see the text). The parameters of the fits are reported in Figs. 8 a,b.

Fig. 7. Normalized uncorrected time-resolved emission spectra measured at 4.2 K at different time instants (t) after the excitation pulse. In (a) $E_{\text{exc}} = 3.85 \text{ eV}$, in (b) $E_{\text{exc}} = 4.15 \text{ eV}$.

a)

$$E_{em} \approx 3.5 \text{ eV} \quad E_{em} \approx 3.3 \text{ eV}$$

$$k_1 = 3.51 \times 10^3 \text{ s}^{-1} \quad k_1 = 3.36 \times 10^3 \text{ s}^{-1}$$

$$k_2 = 10^8 \text{ s}^{-1} \quad k_2 = 6 \times 10^7 \text{ s}^{-1}$$

$$K = 10^8 \text{ s}^{-1} \quad K = 5 \times 10^7 \text{ s}^{-1}$$

$$D = 65 \text{ meV} \quad D = 55 \text{ meV}$$

b)

$$E_{em} \approx 2.3 \text{ eV} \quad E_{em} \approx 2.2 \text{ eV}$$

$$k_1 = 6.1 \times 10^4 \text{ s}^{-1} \quad k_1 = 3.3 \times 10^5 \text{ s}^{-1}$$

$$k_2 = 7.5 \times 10^5 \text{ s}^{-1} \quad k_2 = 3.3 \times 10^6 \text{ s}^{-1}$$

$$k_3 = 10^9 \text{ s}^{-1} \quad k_3 = 5 \times 10^9 \text{ s}^{-1}$$

$$K = 5 \times 10^5 \text{ s}^{-1} \quad K = 9 \times 10^5 \text{ s}^{-1}$$

$$K_i = 2 \times 10^9 \text{ s}^{-1} \quad K_i = 8 \times 10^9 \text{ s}^{-1}$$

$$D = 2 \text{ meV} \quad D = 1.4 \text{ meV}$$

$$E = 80 \text{ meV} \quad E = 80 \text{ meV}$$

c)

Fig. 8. (a,b) The energy level diagrams used to describe the excited states dynamics of Bi^{3+} centers in Lu_2SiO_5 . The values of the parameters obtained from the best fits to the experimental $\tau(T)$ data shown in Fig. 6 are reported. For details, see the text. (c) Schematic configuration coordinate diagram of the Bi^{3+} -related triplet excited state. The electronic transitions between the ground state, corresponding to the 1S_0 level, and the excited states, corresponding to the 3P_1 and 3P_0 levels of a free Bi^{3+} ion and the triplet Bi^{3+} -related localized exciton state, are indicated by arrows.