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Abstract

The work is aimed to study the nature of intrinsic luminescence in Lu_2SiO_5 (LSO) and Y_2SiO_5 (YSO) orthosilicates based on the results of luminescent spectroscopy under excitation by pulsed synchrotron radiation with the energy in the fundamental absorption range of their hosts. We confirm in this work that the intrinsic emission bands of LSO and YSO crystals, peaked correspondingly at 260 and 325 nm and 340 and 385 nm, can be caused by the luminescence of self-trapped excitons (STE) from the singlet and triplet radiative levels, respectively.

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Introduction

The crystals of Ce-doped Lu_2SiO_5 (LSO) and Y_2SiO_5 (YSO) orthosilicates are among the most efficient scintillators which are being widely used in Positron Emission Tomography (PET). Therefore, the luminescent and scintillation properties of LSO:Ce and YSO:Ce were the subject of intensive research in the last twenty years (see, for example [1-4] and references therein). At the same time, the intrinsic luminescence of LSO and YSO hosts is considered up to now only in a few publications [5-7]. Nevertheless, there are some significant ambiguities in the results and interpretations of the intrinsic luminescence of LSO and YSO compounds in the different crystalline forms obtained in these works. Thus, the nature of the intrinsic luminescence of LSO and YSO hosts is still unclear and needs the clarification. This pushes us to more detailed investigation of the intrinsic luminescence in orthosilicate compounds.

This work is aimed at investigation of the nature of the intrinsic luminescence of LSO and YSO orthosilicates on the basis of the results of time resolved luminescent spectroscopy at 8 K and 90 K under excitation by pulsed synchrotron radiation (SR) with the 3.7-25 eV energies at the Superlumi experimental station at HASYLAB, DESY (Hamburg, Germany).

LSO and YSO crystals were grown by the Czochralski method in the Institute for Scintillation Materials, Kharkiv, Ukraine from raw materials of 4N and 5N purity, respectively. For the luminescent investigation, the optically-graded samples with dimensions of 3*5*0.5 mm were prepared.

The emission and excitation spectra were measured both in the integral regime, and in time gates of 1.2-10 ns and 50-100 ns (called as the fast and slow components, respectively) in the limits of SR pulse with a repetition time of 100 ns and a duration of 0.127 ns. The excitation spectra were corrected for the spectral dependence of transmittance of Al-grating and intensity of SR beam; the emission spectra were not corrected. Using SR excitation, the decay kinetics of the luminescence was measured in the 1.2-100 ns time range.

Experimental results

The luminescence spectra of LSO and YSO crystal at 8 K and 90 K under excitation by SR in the fundamental absorption range of LSO and YSO hosts are shown in Fig.1. Two wide spectrally resolved emission bands peaked at 260 and 325 nm in LSO crystals, and at 340 and 385 nm in YSO crystal, are observed. Both emission bands in LSO and YSO crystals correspond to the intrinsic luminescence of LSO and YSO hosts. The sharp lines at 313 nm and in the 380-480 nm range in the spectra of LSO crystal are caused by the luminescence of Gd^{3+} and Tb^{3+} trace impurity coming into the crystal from the initial oxides of 4N purity, mainly from Lu_2O_3 oxide.

The excitation spectra of the intrinsic emission bands peaked at 260 and 325 nm in LSO crystal and at 340 and 385 nm in YSO crystal, are shown in Figs.2a and 2b, respectively. The luminescence in both

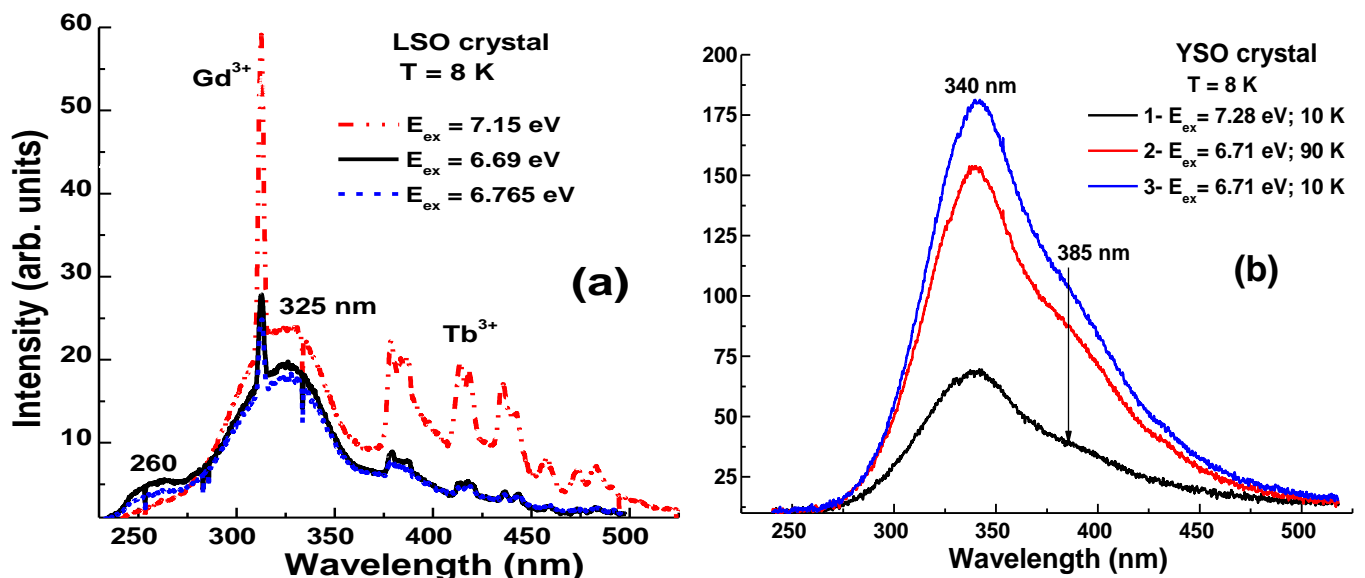


Fig.1. (a) - spectra of intrinsic luminescence of LSO (a) and YSO (b) crystals at 8 K and 90 K under excitation by SR with different wavelengths in the exciton range of LSO and YSO hosts.

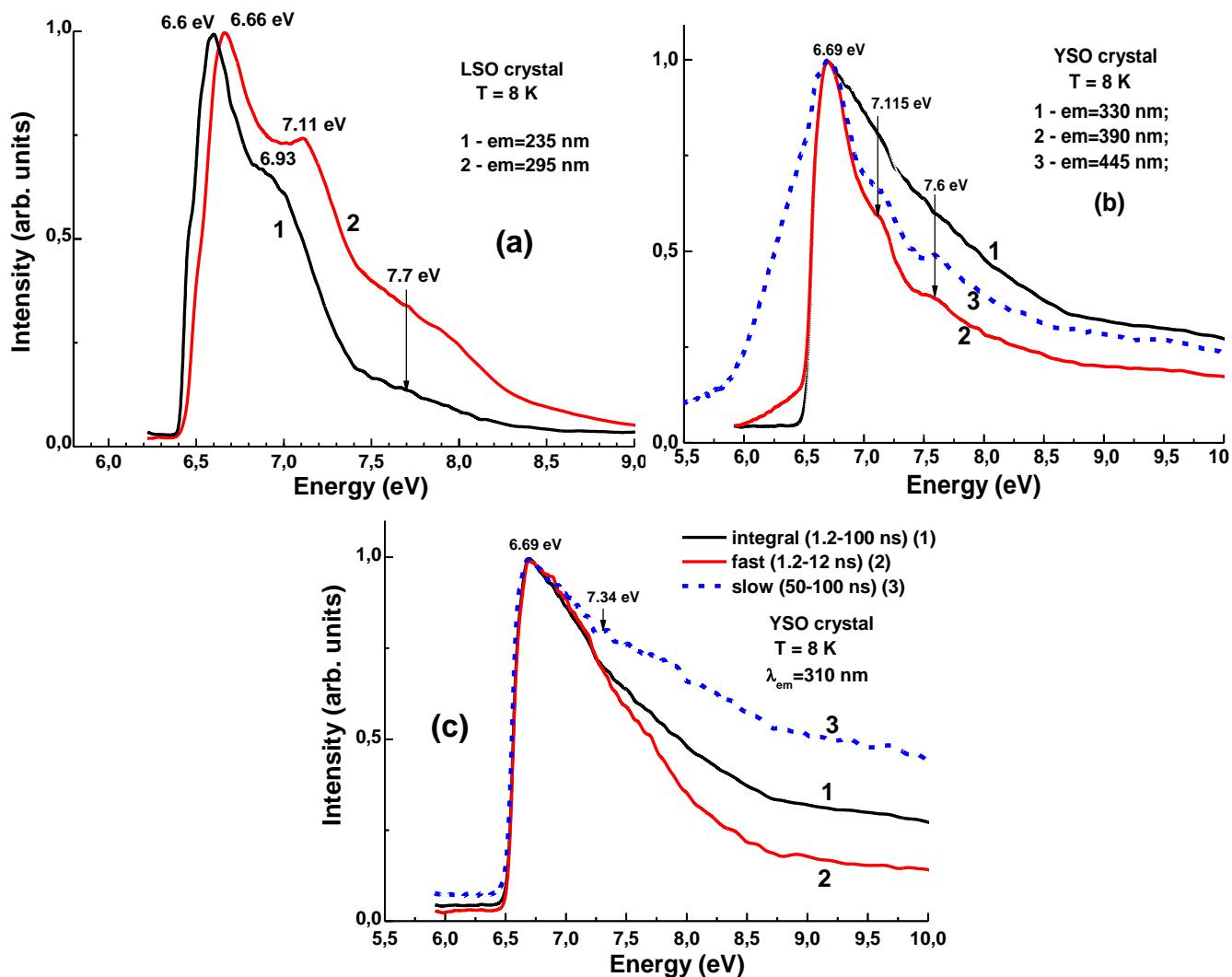


Fig.2. (a) - excitation spectra of exciton luminescence in 260 nm (1) and 325 nm (2) bands in LSO crystal, registered at 235 and 295 nm, respectively; (b) - excitation spectra of exciton luminescence in 340 nm (1) and 385 nm (2, 3) bands in YSO crystal, registered at 330 nm (1) and at 390 nm (2) and 445 nm (3), respectively; (c) – normalized excitation spectra of integral (1), fast (2) and slow (3) components of exciton luminescence in 340 nm band in YSO crystal, registered at 310 nm. T=8 K.

bands is excited only in the fundamental absorption range of the LSO and YSO crystals. For the LSO crystal, the excitation spectra of luminescence in the 260 nm and 325 nm bands have the similar structure, but their main maxima are spectrally shifted. Specifically, the luminescence in the band peaked at 260 nm, is excited in the doublet bands in the exciton range of LSO host peaked at 6.6 and 6.93 eV, while the similar doublet bands in the excitation spectrum of the 325 nm emission band are located at 6.66 and 7.11 eV.

From the comparison of the excitation spectra of the 260 and 325 nm emission bands in LSO crystal (Fig.2a, curves 1 and 2, respectively) it is clearly seen the dominant contribution of the 6.6 and 6.66 eV excitation bands to the total output of the luminescence in these bands. Taking into account this fact, the Stoke's shift for the excitation and emission in the 260 nm and 325 nm bands in the LSO crystal can be estimated as 1.84 eV and 2.85 eV, respectively (Table 1).

Due to strong overlapping of the intrinsic emission bands peaked at 340 and 385 nm in YSO crystal⁴ (Fig.1b), the main excitation maxima of the luminescence in these bands practically coincide and are located at 6.69 eV (Fig.2b, curve 1 and 2, respectively). Thus, the Stoke's shift for the excitation and emission in the 340 and 385 nm bands in the YSO crystal can be estimated as 3.05 and 3.475 eV, respectively (Table 1). The second excitation band peaked at 7.34 eV is also spectrally resolved in the excitation spectra of slow component of the luminescence in the 340 nm band (Fig.2c, curve 3). The second band at 7.115 eV is also registered in the excitation spectra of the luminescence in the 385 nm emission band (Fig.2b, curves 2 and 3). It is worth to note that position of the main excitation band at 6.69 eV is also the same in the excitation spectra of the 340 nm emission band, registered in the different time intervals (Fig.2c).

Apart from the main bands, other wide excitation bands peaked at about 7.7 eV and 7.6 eV, are observed in the excitation spectra of the intrinsic luminescence in the 260 nm and 324 nm bands in the LSO crystal, and in the 340 and 385 nm emission bands in the YSO crystal (Fig.2a and 2b, respectively). Most probably, these bands can correspond to the onset of inter-band transitions in the LSO and YSO hosts, respectively.

It is important to note here, that the both main excitation bands of the intrinsic luminescence in the LSO and YSO hosts are strongly overlapped; therefore for the spectral separation of the component of these bands, we need the additional consideration of the results, presented in Fig.1 and Fig.3. Specifically, the 260 nm luminescence band in LSO is better resolved in the emission spectra (Fig.1a) and decay kinetics of luminescence (Fig.3a) under excitation in the 6.6-6.7 eV range (Fig.2a, curve 1), while 325 nm luminescence band in the is better distinguished in the emission spectra (Fig.1a) and decay kinetics (Fig.3a) under excitation in the 7.115 eV band (Fig.2a, curve 2). For YSO crystal, the luminescence in the 340 nm band is better distinguished in the emission spectra (Fig.1b) under excitation in the 6.7 eV band, while the 390 nm band luminescence is better resolved under excitation in the 7.1-7.2 eV range (Fig.2b).

The decay kinetics of the luminescence in the 260 and 325 nm emission bands in LSO crystal at 8 K is shown in Fig.3a under excitation in the vicinity of main peaks of the excitation spectra at 6.665 and 7.115 eV (Fig.2a). The parameters of approximation of the corresponding decay curves are presented in Table 1. As one can see from Fig.3a and Table 1, the luminescence decay curves in both bands are substantially different. The fast components with decay times of 5.2-12.2 ns prevail in the decay kinetics of the 260 nm luminescence (Fig.3a, curve 1). At the same time, the main components of emission in the 324 nm band decays in the μ s-ms time range (Fig.3a, curve 2) and its decay can not be determined in conditions of our experiment due to very short time interval (100 ns) for registration of the luminescence.

In contrast to LSO, separation of the decay kinetics of the intrinsic luminescence from different emission bands in YSO is more complicated task due to the strong overlapping of the 340 and 385 nm bands. At the same time, we note that, by analogy with the LSO crystal, the decay kinetics of the luminescence

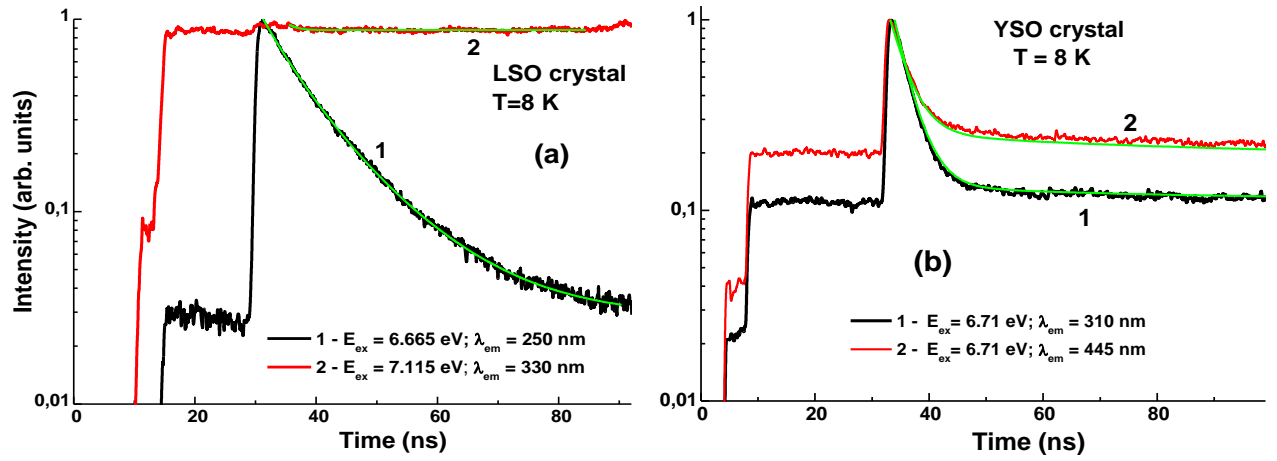


Fig.3. Decay kinetics of the different emission bands of exciton luminescence in LSO (a) and YSO (b) crystals under excitation by SR in the different bands in the exciton range of LSO and YSO hosts (see Figs.2a and 2b for details). $T=8$ K. The initial “pedestals” in all decay profiles are mainly caused by the short repetition time (100 ns) of the excitation synchrotron pulses.

Table 1. Parameters of approximation of the decay kinetics of the exciton luminescence in LSO (a) and YSO (b) crystals, presented in Fig.3a and 3b, respectively. The decay profiles are approximated by equation $I = \sum A_i \exp(-t/\tau_i)$; $i=3$.

Crystal	Excitation / emission	A_1	τ_1	A_2	τ_2	A_3	τ_3
LSO	$E_{ex}=7.115$ eV; $\lambda_{em}=330$ nm	0.06	1.4 ns	0.94	> 1 μ s		
	$E_{ex}=6.665$ eV; $\lambda_{em}=250$ nm	0.43	5.2 ns	0.55	12.2 ns	0.02	> 1 μ s
YSO	$E_{ex}=6.71$ eV; $\lambda_{em}=310$ nm	0.88	2.8 ns	0.02	47.5 ns	0.09	> 1 μ s
	$E_{ex}=6.71$ eV; $\lambda_{em}=445$ nm	0.77	3.0 ns	0.07	52.2 ns	0.16	> 1 μ s

in the 340 nm band in YSO crystal also possesses the dominant fast component with the decay time $\tau(1/e)=2.8-3.0$ ns (Fig.3b, curve 1 and Table 1), while the contribution of the slow components with decay times in the μ s-ms time range strongly increases in the decay kinetics of the luminescence in the 385 nm band (Fig.3b, curve 2).

All the above mentioned parameters of the intrinsic exciton emission in LSO and YSO crystals at 8 K are summarized in Table 2.

Table 2. Parameters of intrinsic exciton emission in LSO and YSO crystals at 10 K. The σ/π ratio is the ratio between the intensity of σ - and π - STE emission components; S_{S-T} is the energy gap between the singlet and triplet STE radiative levels.

Crystal	Type of intrinsic emission	Emission, nm (eV)	σ/π ratio	Excitation, eV	Stoke's shift, eV	S_{S-T} , eV	Decay time
LSO	σ -STE	260 (4.76)	0.23	6.6; 6.93; 7.7	1.84	0.06	5.2-12.2 ns
LSO	π -STE	325 (3.81)		6.66; 7.11; 7.7	2.85		μ s-ms range
YSO	σ -STE	340 (3.64)	1.725	6.69; 7.34	3.05	> 0.01	2.8-3.0 ns
YSO	π -STE	385 (3.215)		6.69; 7.115; 7.6	3.475		μ s-ms range

Based on the results presented above, as well as the similar results on the nature of the intrinsic emission in other complex oxides (sapphire, garnets, perovskites) [8-10], we can confirm that the intrinsic luminescence of LSO in the 260 and 320 nm bands and YSO in the 330 and 385 nm bands (Fig.1a and 1b, respectively), which is excited only in the exciton range of LSO and YSO hosts (Fig.2b and 2b, respectively), is related to the radiation decay of self-trapped excitons (STE) [7]. Similarly to alkali-halide crystals [11, 12] and some oxides [13, 14], the 260 and 340 nm emission bands in LSO and YSO crystals, respectively, can be assigned to the singlet (σ) component of the STE luminescence, while the luminescence in the 325 nm and 385 nm bands in the same crystals can correspond to the triplet (π) component of STE emission. This assumption is strongly supported by the fast (in ns range) decay kinetics of the luminescence in the 260 and 340 nm bands and slow emission (in the μ s-ms range) in the 325 nm and 385 nm bands in LSO and YSO crystals, respectively (Fig.3a and 3b).

The notable difference in positions of the STE emission (Fig.1) and excitation (Fig.2) bands, as well as in the Stoke's shift values of the respective bands in LSO and YSO can be caused by different structure of the bottom of the conduction bands of LSO and YSO hosts formed by the Lu^{3+} ($5d^1 4f^{14} 6s^2$) and Y^{3+} ($4d^1 5s^2$) states, respectively. Specifically, on the basis of the excitation spectra of the luminescence in the both emission bands in LSO (Fig.2b) we can assume that the position of singlet radiative level of σ -STE at 6.6 eV in LSO host lies below the triplet radiative level at 6.66 eV of π -STE and is separated from its last level by the energy gap $S_{\sigma-T}=0.06$ eV (Table 2). From the excitation spectra of both intrinsic emission bands of YSO crystal (Fig.2b) we can conclude that separation of the singlet radiative level of σ -STE and triplet radiative level of π -STE in YSO crystal is significantly lower than in LSO crystal and is below the accuracy of our experiment (0.01 eV) (Table 2).

At the same time, several facts related to the nature of the intrinsic emission in the LSO and YSO host, still require additional investigation. First of all, unclear are the facts why the ratio between the intensity of the fast and slow components of the STE emission is substantially larger in YSO (1.725) than in LSO (0.23) (see Fig.1b and 1b, respectively, and Table 2) and the Stoke's shift value for σ -STE emission in YSO is significantly higher (3.05 eV) than respective value in LSO (1.84 eV) (see Table 2).

Conclusions

The parameters and nature of the Lu_2SiO_5 (LSO) and Y_2SiO_5 (YSO) intrinsic luminescence are studied under excitation by synchrotron radiation in the fundamental absorption range of YSO and YSO hosts. Fast emission in the nanosecond range in the bands peaked at 260 and 340 nm in LSO and YSO, correspondingly, can be assigned to the singlet (σ) component of the STE luminescence. Accordingly,

slow emission in the μs -ms range in the bands peaked at 325 nm in LSO and 385 nm in YSO can⁷ correspond to the triplet (π) components of STE emission.

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