

PROCEEDINGS OF THE XIII FEOFILOV SYMPOSIUM
“SPECTROSCOPY OF CRYSTALS DOPED
BY RARE-EARTH AND TRANSITION-METAL IONS”

(Irkutsk, July 9–13, 2007)

Intrinsic Luminescence of Rare-Earth Oxyorthosilicates

V. Yu. Ivanov, E. S. Shlygin, V. A. Pustovarov, V. V. Mazurenko, and B. V. Shul'gin

Ural State Technical University, ul. Mira 19, Yekaterinburg, 620002 Russia

e-mail: ivy@dpt.ustu.ru

Abstract—The spectra and decay kinetics of luminescence and the excitation and reflection spectra of the luminescence of orthosilicates A_2SiO_5 ($A = Y, Lu, Sc, Gd$), both nominally pure and doped with cerium, are measured using time-resolved VUV spectroscopy in the ranges of energies $\hbar\nu = 1.5\text{--}16$ eV and temperatures $T = 8\text{--}300$ K. The band structure of the crystals is calculated in the local electron density approximation (LDA). The origin of the intrinsic luminescence in the crystals studied is established, and the assumption regarding the existence of self-trapped excitons and their structure is made.

PACS numbers: 78.55.-m, 71.35.-y, 71.20.-b

DOI: 10.1134/S1063783408090217

1. INTRODUCTION

Ions of rare-earth elements in crystals of oxyorthosilicates A_2SiO_5 ($A = Y, Lu, Sc, Gd$) form one of the cation sublattices. Crystals doped with cesium which substitutes for the rare-earth cation of the base exhibit remarkable scintillation properties. This accounts for the host of studies dealing primarily with the luminescence properties of doped $A_2SiO_5 : Ce$ crystals. The intrinsic luminescence of the matrices did not attract anything but scant attention. The latter are, however, of a certain interest from the standpoint of systematization of the relaxation of intrinsic electronic excitation in oxide compounds, in particular, of the processes involved in exciton self-trapping.

It is known that the existence in oxides of self-trapping of single carriers still awaits experimental confirmation. At the same time, some manifestations of self-trapped excitons, which originally had been observed in binary compounds with lowered symmetry of oxygen sites ($\alpha\text{-SiO}_2$ [1], $\alpha\text{-Al}_2O_3$ [2], Y_2O_3 [3], and BeO [4, 5]), were later found in a large number of composite crystals, such as $YAlO_3$, $Y_3Al_5O_{12}$ [2], Be_2AlO_4 , Be_2SiO_4 , $Be_3Al_2Si_6O_{18}$ [6], and many others. This prompted an idea that radiative decay of intrinsic relaxed electronic excitations in low-symmetry oxides occurs in most cases through the formation of self-trapped excitons. At the same time, systematic concepts on the spatial structure and models of self-trapped excitons in oxides are practically lacking, with some points having been discussed only in connection with the binary crystals $\alpha\text{-SiO}_2$ [7] and BeO [4]. In the case of composite compounds, of particular interest are attempts at revealing the part played by cation sublattices in exciton self-trapping.

The A_2SiO_5 isostructural oxyorthosilicates ($A = Y, Lu, Sc$) crystallize in space group symmetry $C2/c$ [8]. The rare-earth cation resides in the environment of six or seven oxygen ions, in contrast to binary rare-earth oxides, for which only sixfold coordination is typical. The gadolinium oxyorthosilicate Gd_2SiO_5 features a slightly different structure ($P2_1/c$) [8], and the rare-earth ion is here seven- or ninefold coordinated. The silicon cations are tetrahedrally coordinated in structures of both types, but, in contrast to one of the crystal-forming oxides, $\alpha\text{-SiO}_2$, the silicon–oxygen tetrahedra do not share anions.

We report here on a study of the intrinsic luminescence of A_2SiO_5 crystals ($A = Y, Lu, Sc, Gd$) by time-resolved luminescence spectroscopy and an ab initio calculation of the electronic structure for a number of objects of this study to establish the structure of relaxed excitations of intrinsic origin.

2. OBJECTS OF INVESTIGATION AND EXPERIMENTAL TECHNIQUE

The measurements were carried out on Y_2SiO_5 , Sc_2SiO_5 , $Y_2SiO_5 : Ce$ (0.1 mol %), Gd_2SiO_5 , and $Gd_2SiO_5 : Ce$ (0.5 mol %) crystals, Czochralski-grown by Korovkin at the Vavilov State Optical Institute [9], and on $Lu_2SiO_5 : Ce$ (0.5 mol %) grown by Melcher [8]. The samples used were optical-quality polished plane-parallel plates measuring $4 \times 4 \times 1$ mm.

The luminescence excitation spectra in the 4–16-eV region, luminescence spectra in the 1.5–6.0-eV region, and luminescence decay kinetics under selective excitation were measured by time-resolved VUV spectroscopy at the SUPERLUMI station (HASYLAB, DESY, Hamburg) [10]. The luminescence was excited by a

2-m vacuum monochromator with an Al grating (spectral resolution 3.2 \AA or $25 \times 10^{-3} \text{ eV}$ for the energy interval of $\sim 10 \text{ eV}$). The luminescence spectra were analyzed with a 0.3-m monochromator (ARC Spectro Pro380i) equipped with an R6358P PM tube (Hamamatsu). The luminescence and luminescence excitation spectra were measured in the time-integrated mode and in Δt_i -wide channels delayed by δt_i with respect to the pump synchrotron pulse. The VUV gate parameters: $\delta t_1 = 2.1 \text{ ns}$, $\Delta t_1 = 14.1 \text{ ns}$ and $\delta t_2 = 46 \text{ ns}$, $\Delta t_2 = 155 \text{ ns}$. The reflection spectra were measured synchronously with the luminescence spectra at a synchrotron beam incidence angle of 17.5° and recorded with XP2230B PM tube (Valvo). In order to prevent luminescence from contributing to the reflection spectra, the latter were measured, just as the luminescence excitation spectra, in a separate fast channel ($\Delta t = 22.5 \text{ ns}$, $\delta t = 2.0 \text{ ns}$), with detection of the signal from sodium salicylate. The luminescence excitation spectra were reduced to the same number of incident pump photons, while the luminescence spectra are presented without the corresponding correction. The parameters of the luminescence decay ns-kinetics were calculated by the convolution method.

The band structure of some objects was calculated in the local density approximation (LDA) by the linear muffin-tin orbital method in the atomic sphere approximation LMTO-ASA [11]. We chose the following atomic sphere radii for different elements of the Y_2SiO_5 and Lu_2SiO_5 compounds: $r(\text{Y}) = 1.53 \text{ \AA}$, $r(\text{Lu}) = 1.47 \text{ \AA}$, $r(\text{Si}) = 1.03 \text{ \AA}$, and $r(\text{O}) = 0.87 \text{ \AA}$. In order to fill completely the cell volume, empty spheres of different radii were added. The exchange correlation potential chosen was of the type described in [12]. 64 k points were used for discretization of the irreducible part of the Brillouin zone.

3. TIME-RESOLVED LUMINESCENCE SPECTROSCOPY OF OXYORTHOSILICATES

In nominally pure Y_2SiO_5 crystals photoexcited in the region of the long-wavelength fundamental absorption (LWFA) edge one detects at $T = 300 \text{ K}$ very weak luminescence originating from residual impurities. One could, in particular, isolate tentatively bands characteristic of the luminescence of Ce^{3+} and Gd^{3+} impurity ions. The situation at cryogenic temperatures is radically different. The distinct luminescence band peaking at 3.75 eV at 8 K is composite (Fig. 1a) and can be unfolded into Gaussians with maxima at 3.5 eV (FWHM $\approx 0.8 \text{ eV}$) and 3.8 eV (FWHM $\approx 0.6 \text{ eV}$). The luminescence spectrum measured in the fast channel at $E_{\text{exc}} = 6.8 \text{ eV}$ is slightly shifted toward higher energies. This fits the photoluminescence decay kinetics plotted in the inset in Fig. 1a. The kinetics of the higher-energy component at 3.8 eV is dominated by a fast component with $\tau_{\text{exp}} = 3 \text{ ns}$, whereas in the 3.5-eV luminescence the major part derives from the microsecond-compo-

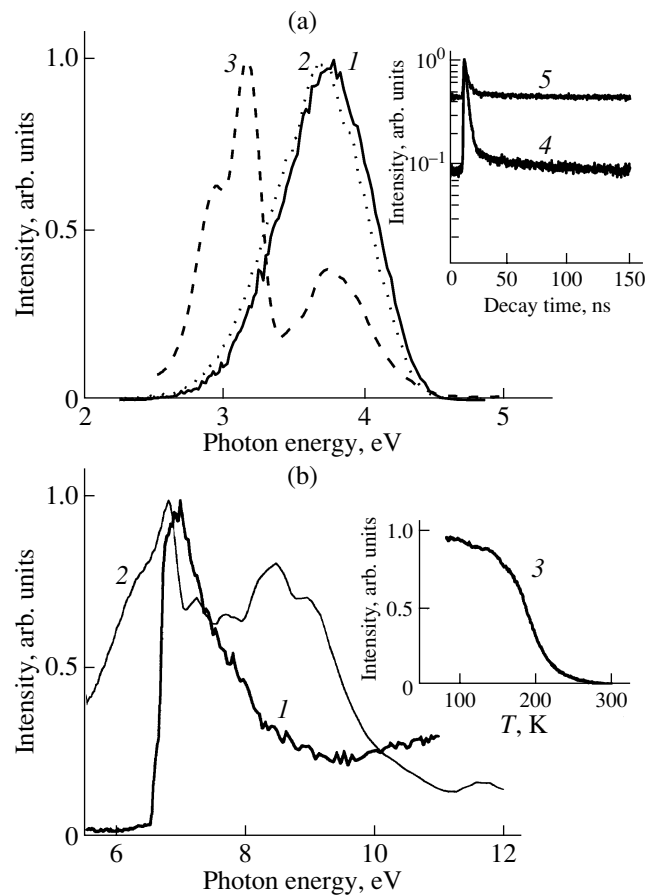


Fig. 1. (a) Luminescence spectra measured in the (1) fast and (2) slow channels and (3) in the integral mode and the decay kinetics recorded for spectral points of (4) 3.84 and (5) 3.45 eV for (1, 2, 4, 5) Y_2SiO_5 and (3) $\text{Y}_2\text{SiO}_5 : \text{Ce}$ under excitation with $E_{\text{exc}} = 6.9 \text{ eV}$. $T = 8 \text{ K}$. (b) (1) Excitation spectrum of luminescence at 3.75 eV for Y_2SiO_5 crystals measured in the fast channel at $T = 8 \text{ K}$ in comparison with (2) the reflection spectrum and (3) temperature dependence of the x-ray luminescence at 3.75 eV .

nent. The 3.75-eV luminescence of Y_2SiO_5 is not excited below the LWFA edge (Fig. 1b). The 3.75-eV luminescence excitation spectra measured under different gating conditions differ slightly. The maximum of the fast spectrum is shifted toward higher energies. Luminescence similar in spectral composition and excitation conditions is observed at cryogenic temperatures and in doped $\text{Y}_2\text{SiO}_5 : \text{Ce}$ crystals as well. Thus, Y_2SiO_5 crystals generate at low temperatures composite luminescence, which is typical both of binary and complex low-symmetry oxides [1–5] and by its features [7] can be assigned, by and large, to self-trapped exciton luminescence. Although the reflection spectrum of Y_2SiO_5 crystals does not reveal a clearly pronounced excitonic structure, the maximum of excitation of the composite band in the $3.0\text{--}4.5\text{-eV}$ region correlates with the falloff in the reflection spectrum. A study of the behavior with temperature of the 3.75-eV x-ray

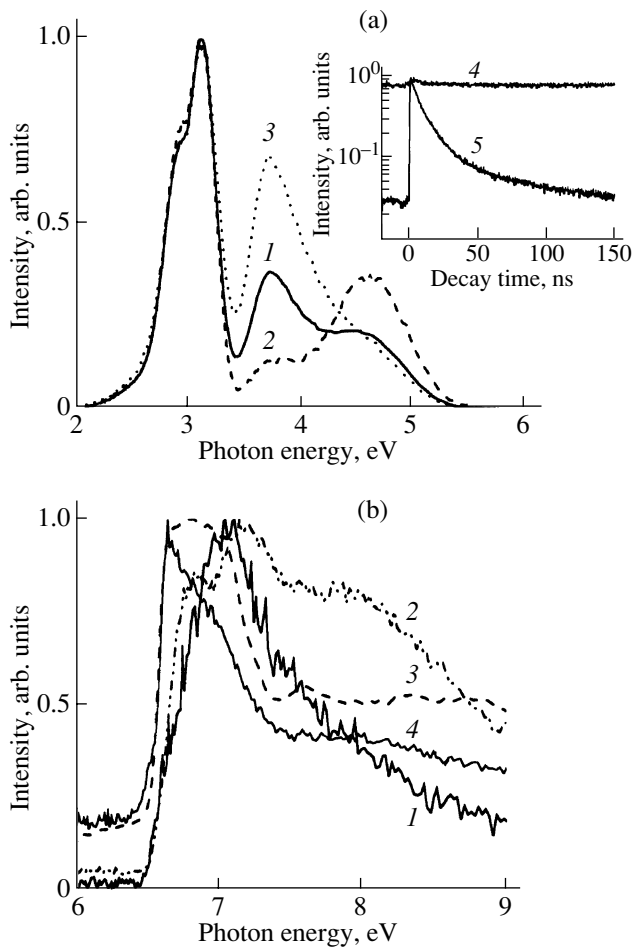


Fig. 2. (a) Luminescence spectra recorded (1) in the integral mode and in the (2) fast and (3) slow channels and (4, 5) the decay kinetics measured for the spectral points of (4) 3.75 and (5) 4.6 eV for the $\text{Lu}_2\text{SiO}_5 : \text{Ce}$ crystal excited at $E_{\text{exc}} = 7$ eV. $T = 8$ K. (b) (1) Luminescence excitation spectra measured in the fast channel at 4.6 eV and (2, 3) spectra measured in the slow channel at (2) 3.75 and (3) 3.1 eV in comparison with (4) the reflection spectrum of the $\text{Lu}_2\text{SiO}_5 : \text{Ce}$ crystal. $T = 8$ K.

luminescence of Y_2SiO_5 (inset to Fig. 1b) has established the Mott character of quenching with an activation energy $E_a = 180$ meV in the range $T = 150$ – 200 K characteristic of self-trapped exciton quenching in oxides. The complex composition of the luminescence at 3.0–4.5 eV can be due to the existence of self-trapped excitons of different types, a feature likewise typical of oxides. The fast luminescence at 3.8 eV, which by the character of its decay kinetics can be assigned to the singlet self-trapped exciton; its excitation spectrum peaks at energies higher than the maximum of excitation of the 3.5-eV slow luminescence (the small differences may be caused by pronounced band overlap). In some complex oxides, as well as in alkali halide crystals, it is at the relaxation from higher-lying states of large-radius excitons that the singlet self-trapped exciton luminescence is excited (see, e.g., [6]).

No intrinsic emission bands have been observed in luminescence spectra of $\text{Lu}_2\text{SiO}_5 : \text{Ce}$ crystals measured at 295 K either. When cooled down to 8 K, one can infer (Fig. 2a) at least two luminescence bands which are not excited in the crystal transparency region. Unlike Y_2SiO_5 , the luminescence bands in the 3.5–5.0-eV interval are well resolved, with one of the bands peaking at 3.75 eV (FWHM ≈ 0.8 eV), and the other, at 4.6 eV (FWHM ≈ 0.7 eV). The 3.75-eV luminescence exhibits a μs -range decay kinetics, whereas the kinetics of the 4.6-eV luminescence reveals exponential components with $\tau_1 = 7$ ns and $\tau_2 = 35$ ns superposed on a longer pedestal (see the inset to Fig. 2a). Intrinsic luminescence in Lu_2SiO_5 crystals is excited efficiently in the region where free excitons and electron–hole pairs are formed, but they differ slightly in their excitation spectra (Fig. 2b). Temperature quenching of the bands occurs in the interval from 40 to 100 K [13]; the band at 4.6 eV is quenched at the lowest temperature, the corresponding quenching activation energy by Mott being 13 meV. The well-known Ce^{3+} impurity luminescence characterized by distinct excitation bands in the crystal transparency region does not overlap in frequency the intrinsic luminescence bands. At cryogenic temperatures, the intrinsic and impurity bands compare in intensity. Thus, one observes in Lu_2SiO_5 crystals at least two bands of intrinsic luminescence typical of self-trapped exciton emission.

In Sc_2SiO_5 crystals one also detects two intrinsic luminescence bands, at 3.5 eV (FWHM ≈ 0.9 eV) and 4.3 eV (FWHM ≈ 0.5 eV), which are not excited below the LWFA edge (Fig. 3a). In contrast to the intrinsic luminescence of the yttrium and lutetium orthosilicates described above, these two emissions are stable at $T = 295$ K as well. Sc_2SiO_5 crystals exhibit a more pronounced difference between excitation spectra of the photoluminescence bands (Fig. 3b). The low-energy luminescence band at 3.5 eV is actually slowly decaying phosphorescence excited efficiently in the 6.2-eV region, i.e., about the LWFA edge, as well as in the formation region of electron–hole pairs. The 4.3-eV region luminescence is excited with a higher efficiency exactly in the region of electron–hole pairs. An analysis of the decay kinetics of intrinsic emission in Sc_2SiO_5 crystals (see inset in Fig. 3a) suggests that the short-lived component ($\tau = 1.3$ ns) is observed at $T = 8$ K only in the 4.3-eV luminescence when excited in the LWFA edge region. At $T = 295$ K, the decay kinetics of the emissions is dominated by μs -range components.

Unlike the isostructural A_2SiO_5 compounds ($A = \text{Y}, \text{Lu}$), the intrinsic luminescence in $\text{Gd}_2\text{SiO}_5 : \text{Ce}$ crystals overlaps heavily the Ce^{3+} emission, and, therefore, special techniques had to be devised to isolate it [14]. The low-temperature luminescence spectrum of an undoped crystal excited by 6.5-eV photons represents a broad composite band (Fig. 4a) with a dominant Gaussian component in the 2.7-eV region, whereas when excited at 7.3 eV, it is a narrow band at 3.95 eV. The latter

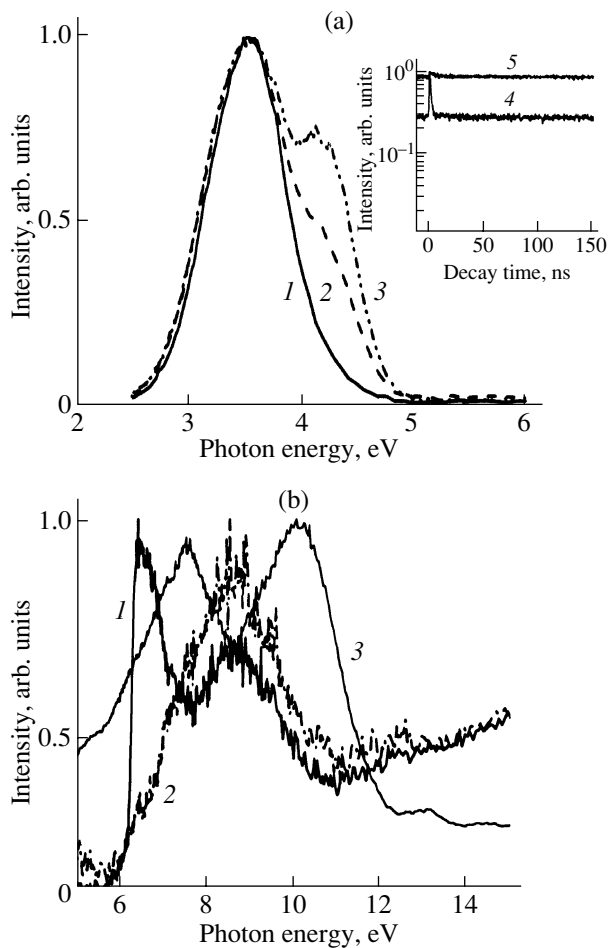


Fig. 3. (a) (1–3) Integrated luminescence spectra and decay kinetics at (4) 4.25 and (5) 3.26 eV for Sc_2SiO_5 crystals upon excitation at (1, 4, 5) 6.52, (2) 7.30, and (3) 24.70 eV. $T = 8$ K. (b) (1, 2) Luminescence excitation spectra measured for the spectral points of (1) 3.6 eV in the slow channel and (2) 4.6 eV in the fast channel and (3) the reflection spectrum for the Sc_2SiO_5 crystal. $T = 8$ K.

derives from the well-known ${}^6P_{7/2} - {}^8S_{7/2}$ radiative transition in the gadolinium ion. The strongest among the 3.95-eV luminescence excitation spectrum bands is the one at 6.9 eV, which falls into the region of the high-energy $4f$ states of the gadolinium ion; one also observes a weaker group of bands at 4, 4.5, and 5 eV, which are assigned to 6P_J , 6I_J , and 6D_J transitions in the gadolinium ion, respectively. By contrast, the luminescence excitation spectrum of the 2.7-eV emission represents a band peaking at 6.1 eV which lies in the LWFA edge region (Fig. 4b). The luminescence excitation spectrum of intracenter luminescence of the Gd^{3+} ion (3.92 eV) features very low excitation efficiency in this region. The observed new wide-band (FWHM = 0.5 eV) luminescence exhibits a noticeable Stokes shift (over 3 eV). It is not excited at energies below the LWFA edge. The characteristics of the 2.7-eV emission permit its assignment to the intrinsic luminescence of

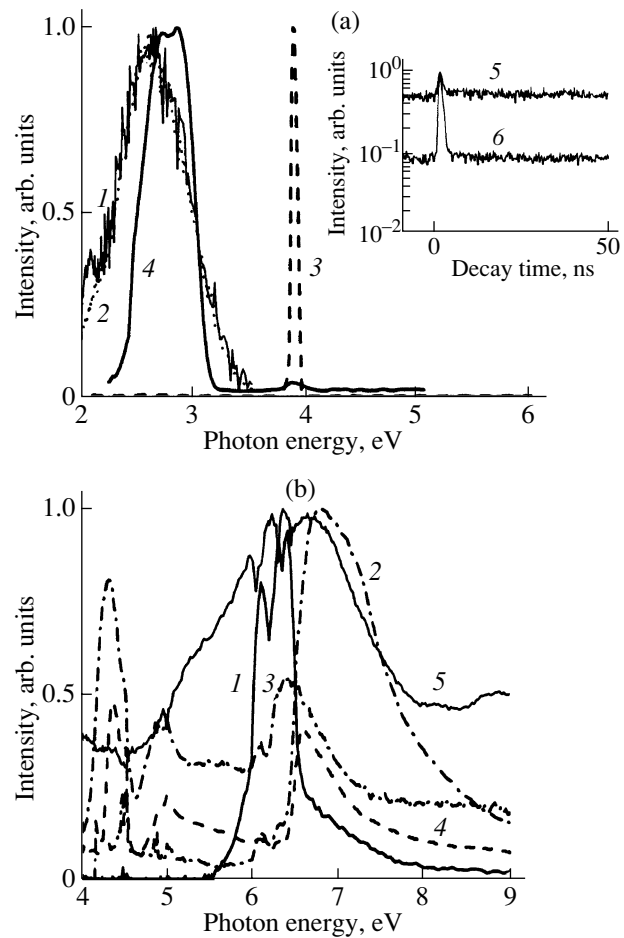


Fig. 4. (a) Luminescence spectra measured in the (1) fast and (2–4) slow channels and decay kinetics at the spectral points of (5) 2.0 and (6) 2.7 eV for (1–3, 5, 6) Gd_2SiO_5 and (4) $\text{Gd}_2\text{SiO}_5 : \text{Ce}$ crystals under excitation at (1, 2, 5, 6) 6.5 and (3, 4) 7.3 eV. $T = 8$ K. (b) Luminescence excitation spectra measured in the (1) fast and (2–4) slow channels for the emission at (1) 2.7, (2) 3.92, and (3, 4) 3.1 eV in comparison with (5) the reflection spectrum for (1, 2, 5) Gd_2SiO_5 and (3, 4) $\text{Gd}_2\text{SiO}_5 : \text{Ce}$ crystals. $T = (1, 2, 4, 5) 8$ and (3) 295 K.

the matrix. It was suggested [14] that the origin of the 2.7-eV luminescence stems from relaxation of the electronic excitation which is generated in the transition of the electron from the $2p$ oxygen states at the valence band top to the excitonic levels, i.e., actually from relaxation of the anion exciton. When excited above the LWFA edge, within the interband transition interval, the intracenter emission at 3.92 eV is excited again with a higher efficiency. Thus, in Gd_2SiO_5 crystals one also observes low-temperature luminescence of the intrinsic character. The decay time (inset to Fig. 4a) of the 2.7-eV luminescence in Gd_2SiO_5 crystals suggests the triplet character of the self-trapped exciton.

Low-temperature emission of the intrinsic origin which is characteristic of the self-trapped exciton in low-symmetry binary and complex oxides is observed

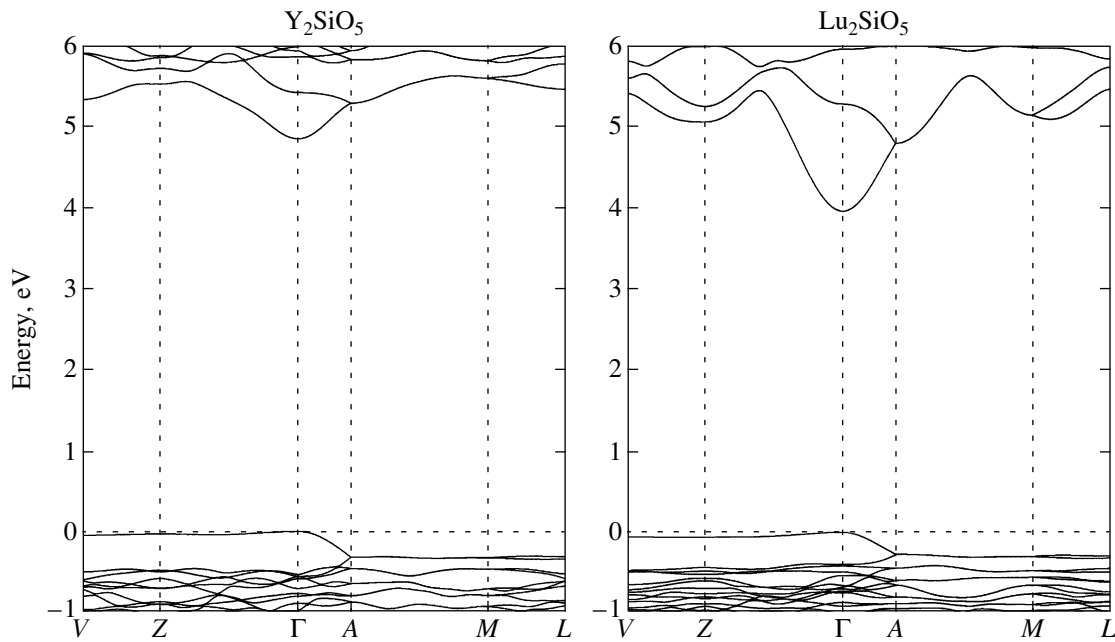


Fig. 5. Band structures of Y_2SiO_5 and Lu_2SiO_5 derived from the LDA calculations.

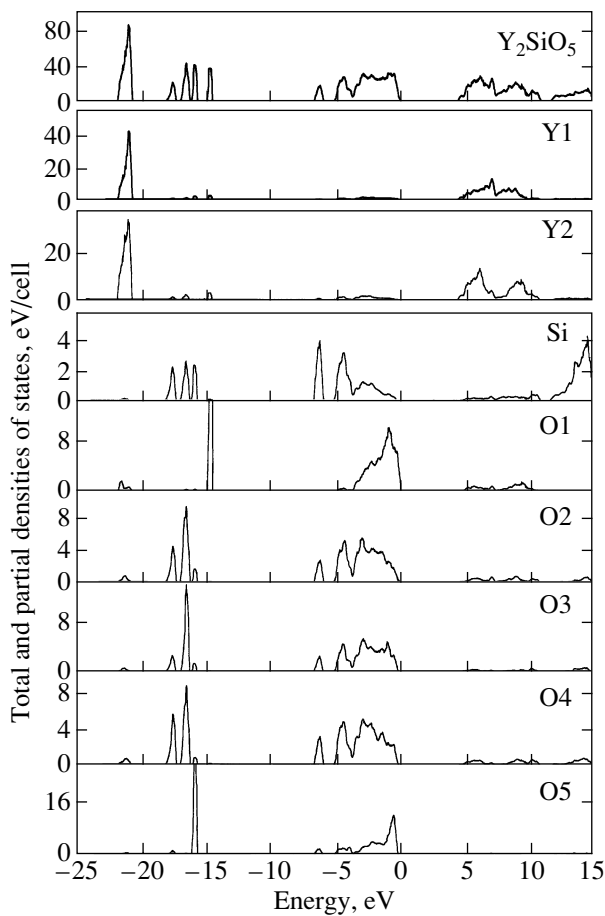


Fig. 6. Total and partial densities of states for Y_2SiO_5 derived from the LDA calculations.

in Y_2SiO_5 , Lu_2SiO_5 and Gd_2SiO_5 . This suggests that existence of the self-trapped exciton is a phenomenon common to the family of the rare-earth oxyorthosilicates. In Sc_2SiO_5 crystals, intrinsic luminescence is stable under temperature variation and displays features of ms-range phosphorescence.

4. QUANTUM-CHEMICAL MODELING

In order to provide a basis for development of models of intrinsic electronic excitations in A_2SiO_5 oxyorthosilicates, the band structure of Y_2SiO_5 and Lu_2SiO_5 crystals was calculated by LMTO-LDA method in the formalism of density functional theory. The results of the calculations are presented in graphical form in Figs. 5 and 6. The positions of yttrium (Y1, Y2), silicon (Si) and oxygen (O1–O5) ions in the Y_2SiO_5 lattice in Fig. 6 were chosen as in the study [15] of the structure of this crystal. As seen from Figs. 5 and 6, the band structure is typical of dielectrics with a comparatively wide band of forbidden states (BFSs) and a flat valence-band top. The BFS was calculated to be 4.8 eV for Y_2SiO_5 and 3.95 eV for Lu_2SiO_5 . The experimental values of the BFS which can be roughly derived from intrinsic luminescence excitation spectra exceed the calculated values by 1–2 eV. This is a consequence of the well-known general underestimation of the dielectric BFS width typical of LDA theory.

The calculated width of the upper valence band (UVB) in Y_2SiO_5 is 6 eV. The UVB has a multiplet structure and consists of two subbands separated by an energy gap. The top of the UVB is formed by oxygen $2p$ states with a small addition of lower-lying silicon $3p$

states. The lower UVB subband derives from mixed orbitals of the $2p$ states of oxygen and $3s$ states of silicon. The $2s$ oxygen states and the $4p$ yttrium states are separated from the UVB top by more than 14 eV. The bottom of the conduction band is formed primarily by the $4d$ and $5s$ orbitals of yttrium with a small contribution of the silicon $3s$ states. The main difference found from this pattern in Lu_2SiO_5 is the presence in the UVB of lutetium $4f$ states whose maximum of density lies 2.5 eV below the top of UVB and provides certainly a dominant contribution to the total valence-band density of states. Interestingly, as follows from the calculations, in both crystals the top of the UVB derives directly from $2p$ orbitals of the oxygen ion which provides sixfold coordinated environment for the cation but not enters the silicon–oxygen tetrahedron (O1 in Fig. 6). This point is significant for the hypothesis on the self-trapped exciton structure in oxyorthosilicates to be formulated below.

5. DISCUSSION OF THE RESULTS OF THE EXPERIMENT AND THE CALCULATION

The intrinsic luminescence bands observed by us in Y_2SiO_5 and Lu_2SiO_5 crystals resemble very much in spectral positions and structure those observed in Y_2O_3 [3] and Lu_2O_3 [13]. One may thus suggest that the formation of the exciton and its subsequent relaxation develop in simple rare-earth oxides and the oxyorthosilicates under study here in a similar pattern. This conclusion is not in conflict with the analysis of the partial composition of the energy bands in rare-earth oxyorthosilicates, whose results also argue for the dominant part played by the rare-earth cation sublattice in the processes involving localization of intrinsic electronic excitations. It is well known that wide-gap oxides featuring self-trapping excitons have typically strong exciton–phonon interaction. Also, migration of intrinsic electronic excitation after the generation is brought to a minimum. It may be safely assumed that in the limiting case the generation and localization of the exciton occur in the same local structural fragment of the lattice. A local fragment of the crystal structure which is closely common in the crystal-forming oxides (Y_2O_3 , Lu_2O_3) and the silicates under consideration (Y_2SiO_5 and Lu_2SiO_5) is the sixfold-coordinated rare-earth ion. It is in this structural polyhedron that one can identify the oxygen ion which is not a part of the silicon–oxygen tetrahedron. Calculations of the partial densities of states suggest that it is the orbitals of this anion that dominate in the top of the UVB. And it is highly probable that it is this fragment that is responsible for the existence of self-trapped excitons in Y_2SiO_5 and Lu_2SiO_5 crystals.

The crystal structure of Gd_2SiO_5 , just as that of Y_2SiO_5 and Lu_2SiO_5 , likewise contains oxygen ions which, while being present in the gadolinium polyhedra, do not have a silicon ion in their nearest environ-

ment. Therefore, we may have here a similar situation with exciton self-trapping. The lack of any literature information on the intrinsic luminescence in binary Gd_2O_3 and on quantum-chemical calculations of Gd_2SiO_5 does not permit one, however, to develop a viable substantiation for a mechanism of the formation of self-trapped excitons in the gadolinium silicate.

In contrast to Y_2O_3 , exciton self-trapping in Sc_2O_3 crystals has not been observed [16]. A possible reason for this could be [16] the dominant contribution of $3d$ states of the cation to formation of the conduction band bottom. In this connection, we have performed a rough estimation of the partial band composition in Sc_2SiO_5 . With precise experimental crystallographic data on this crystal lacking, we used in the calculation the lattice parameters of Y_2SiO_5 . The calculations showed that, in contrast to the yttrium and lutetium oxyorthosilicates, the lowest-lying states responsible for the flat character of the conduction band bottom in Sc_2SiO_5 are the $3d$ states of scandium. Therefore, the pattern of the 3.5-eV luminescence in scandium oxide and scandium orthosilicate is the same, and its ms-range suggests that the emitting state can form as a result of tunneling recombination of carriers. In this case, the weak deformation potential of d states, just as in the binary oxide, does not bring about the formation of self-trapped excitons. At the same time, the 4.3-eV luminescence, observed by us and existing only in Sc_2SiO_5 , is excited efficiently at energies 2 eV above the LWFA edge. Rough estimates seem to indicate that the s states of the cations lie energywise higher than the $3d$ states of scandium. Because the luminescence is seen in the complex oxide only, it is conceivable that the formation of the excited state of the emission center involves silicon ion orbitals. The short-lived ($\tau = 1.3$ ns) component of the decay kinetics (Fig. 3) is characteristic in this case of the center lifetime, and the long-lived component, of the recombination-based formation of this state, which, similar to the case of the 3.5-eV luminescence, is of the tunneling character.

6. CONCLUSIONS

Our time-resolved spectroscopic study suggests that intrinsic luminescence is characteristic of the family of the $A_2\text{SiO}_5$ oxyorthosilicate family ($A = \text{Y, Lu, Sc, Gd}$) investigated. Intrinsic luminescence is a low-temperature phenomenon observed in crystals with large-radius rare-earth cations, in which, as follows from an analysis of experimental results and calculations, combined with crystal chemical data, exciton self-trapping involves a rare-earth cation and an anion that is not bound to the silicon ion. Only Sc_2SiO_5 reveals indications that silicon sublattice is involved in the relaxation of intrinsic electronic excitations.

ACKNOWLEDGMENTS

We are grateful to G. Zimmerer (Hamburg University) and M. Kirm (Institute of Physics, Academy of Sciences of Estonia, Tartu) for their assistance in performing the experiments, A.M. Korovkin and Ch. Mel'cher for providing samples for this study, and A.V. Kruzhalov for support of this work.

This study was supported by the Russian Foundation for Basic Research (project no. 08-02-00843) and the Council on Grants from the President of the Russian Federation (grant no. MK-1041.2007.2).

REFERENCES

1. A. R. Silin' and A. N. Trukhin, *Point Defects and Elementary Excitations in Crystalline and Vitreous SiO₂* (Zinatne, Riga, 1985) [in Russian].
2. A. I. Kuznetsov, B. R. Namozov, and V. V. Myurk, *Fiz. Tverd. Tela (Leningrad)* **27** (10), 3030 (1985) [*Sov. Phys. Solid State* **27** (10), 1819 (1985)].
3. V. N. Abramov, A. N. Ermoshkin, A. I. Kuznetsov, and V. V. Muerk, *Phys. Status Solidi B* **121**, K59 (1984).
4. V. Yu. Ivanov, V. A. Pustovarov, S. V. Gorbunov, and A. V. Kruzhalov, *Fiz. Tverd. Tela (St. Petersburg)* **36** (9), 2634 (1994) [*Phys. Solid State* **36** (9), 1436 (1994)].
5. V. A. Pustovarov, V. Yu. Ivanov, M. Kirm, A. V. Korotaev, A. V. Kruzhalov, and G. Tsimmerer, *Fiz. Tverd. Tela (St. Petersburg)* **43** (7), 1189 (2001) [*Phys. Solid State* **43** (7), 1233 (2001)].
6. V. Yu. Ivanov, V. A. Pustovarov, E. S. Shlygin, A. V. Korotaev, and A. V. Kruzhalov, *Fiz. Tverd. Tela (St. Petersburg)* **47** (3), 452 (2005) [*Phys. Solid State* **47** (3), 466 (2005)].
7. N. Itoh and A. M. Stoneham, *Material Modification by Electronic Excitation* (Cambridge University Press, Cambridge, 2001).
8. C. L. Melcher, J. S. Schweitzer, C. A. Peterson, R. A. Manente, and H. Suzuki, in *Proceedings of the Conference on Inorganic Scintillators and Their Applications (SCINT-95), Delft, The Netherlands, 1995* (Delft University Press, Delft, The Netherlands, 1995), p. 309.
9. G. V. Anan'eva, A. M. Korovkin, and O. I. Merkulaeva, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **17**, 1037 (1981).
10. G. Zimmerer, *Nucl. Instrum. Methods Phys. Res., Sect. A* **308**, 178 (1991).
11. O. K. Andersen, *Phys. Rev. B: Solid State* **12**, 3060 (1975).
12. U. von Barth and L. Hedin, *J. Phys. C: Solid State Phys.* **5**, 1629 (1972).
13. D. W. Cooke, B. L. Bennett, R. E. Muenchausen, J.-K. Lee, and M. A. Nastasi, *J. Lumin.* **106**, 125 (2004).
14. V. Yu. Ivanov, K. I. Shirinskiĭ, E. S. Shlygin, and V. A. Pustovarov, *Izv. Vyssh. Uchebn. Zaved., Fiz., No. 4 (Suppl.)*, 53 (2006).
15. N. I. Leonyuk, E. L. Belokoneva, G. Bocelli, L. Righi, E. V. Shvanskii, R. V. Henrykhson, N. V. Kulman, and D. E. Kozhbakhteeva, *Cryst. Res. Technol.* **34**, 1175 (1999).
16. A. Lushchik, M. Kirm, Ch. Lushchik, I. Martinson, and G. Zimmerer, *J. Lumin.* **87-89**, 232 (2000).

Translated by G. Skrebtsov