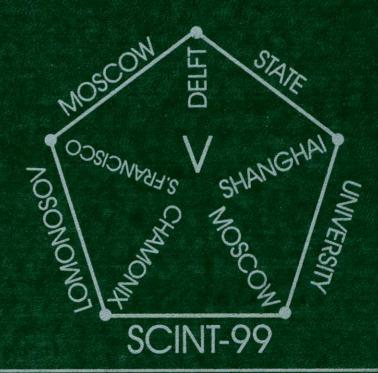


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Time-resolved spectroscopy of self-trapped excitons in oriented BeO crystals under X-ray and VUV excitations

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Abstract: The paper presents the results of a complex study of electronic excitation dynamics for single crystal BeO carried out by the use of the low-temperature optical and luminescent VUV spectroscopy with sub-nanosecond time-resolution under photoexcitation by synchrotron radiation. The decay kinetics (1 ns -500 ns) of the photoluminescence, reflectivity (8-35 eV), time-resolved emission (2.5-10.4 eV) and luminescence excitation (6-35 eV) spectra were measured at 9.6 K and 295 K for the oriented BeO crystals . A large variety of radiative relaxation channels of the electronic excitations, as well as the multiplicity of the excited states of self-trapped excitons, depending on the crystal orientation, exciting photon energy and temperature were revealed and are discussed.

Keywords: beryllium oxide (BeO), luminescence, self-trapped exciton time-resolved VUV - spectroscopy, synchrotron radiation

1. Introduction

It is known, that self-trapped excitons (STE) in broad band-gap oxides were discovered more than twenty years ago. However, all the suggested models for these STE as well as the channels of the STE formation are still under discussion. To date it was found that these STE are inherent in the oxides with a low local symmetry of the anion positions (e.g. SiO₂, Al₂O₁ YAlO₃, Y₃Al₅O₁₂) [1]. As a rule, these compounds demonstrate only slightly the typical excitonic structure of the optical constant spectra in the photon energy range around fundamental absorption edge (FAE). On the contrary, the high-symmetry oxides (e.g. MgO exhibit usually a well-resolved excitonic features in the optical constant spectra, despite the fact that STE is not realized in these crystals.

Hexagonal beryllium oxide crystal BeO (E_g =10.63 eV) is formed by the anion tetrahed distorted along the optical axis C. Because of this, the local symmetry of BeO is reduced C_{3v} , and there are both the 'base' and 'axial' configurations of the BeO lattice defects. In case of the trapped hole centres the 'base' configuration is associated either with a hole localized on the orbital of one of the three equivalent off-axis oxygens in the anion tetrahedron or with a hole, tunneling between these three equivalent positions. The anion configuration of the defect is usually attributed to a hole localized at the axial oxygen in the same tetrahedron [2-4].

Our first investigations of the photoluminescence (PL) excitation spectra over the 8-35 energy and 77-300K temperature regions for the BeO emission bands at 4.9 n 6.7 eV been made at the Nuclear Physics Institute in Novosibirsk by the use of the synchronic radiation (SR) of the VEPP-2M storage ring. For the energy ranges of both the excitonic interband transitions we have revealed not only the main features of the 4.9 eV and 6.7 eV

excitation spectra, but the principle differences between them as well. From these results we have developed a model of two kinds of STE in beryllium oxide crystal [2,3].

The next step in this field was made through the use of the time-resolved luminescent spectroscopy of BeO under excitation by the non-filtered X-ray synchrotron radiation (XSR) in the range from 3 eV to 62 keV ($\Phi = (0.1 \div 6) \times 10^{16} \text{ photons} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$) from the VEPP-3 storage ring. For the first time we revealed a premeditated population of some states not only for the optical centres in BeO, but for the excitonic states as well. The results of a study of both the luminescence decay kinetics and orientation effects allowed us to put forward a hypothesis about splitting of the multiplet excitonic states and radiative transitions from the singlet states in BeO [5].

The main goal of the present paper is not only a further investigation of the relaxation processes for the electronic excitations (EE) in BeO, but a study of the channels of a creation of the excited states of STE as well. The work was made by the use of the time-resolved luminescent spectroscopy with sub-nanosecond time-resolution over the UV- and VUV-emission ranges under selective photoexcitation of PL for the oriented BeO crystals at 9.6 and 295 K.

2. Experimental Details

All the examined BeO crystals were grown by V.A. Maslov through the use of the advanced flux method [6]. The content of impurities in the BeO samples was analysed using a laser mass-spectrography method [4,7]. The samples of the BeO single crystals were produced in the form of a prism or a plane-parallel plate with the naturally occurring facets oriented either parallel or perpendicular, regarding to the main optical C-axes.

The experiments were performed at the SUPERLUMI station of HASYLAB at DESY [8]. The luminescence in the 2.5-6.0 eV region was analyzed by a Czerny-Turner mounting monochromator equipped with a photomultiplier (PM) R2059 (Hamamatsu). For the emission in the VUV range was usd a 0.5 m vacuum monochromator equipped with PM R1460 (Hamamatsu). Two in situ interchangeble gratings of the 2 m primary monochromator, Al and Pt coated, were applied in measurements of the PL excitation spectra over the 6-35 eV energy range. A typical spectral resolution was 0.25 nm. The PL excitation spectra were corrected for the equal number of the exciting photons for each energy region, but the emission spectra are presented as they are measured. Time-resolved spectra were recorded within a time window (Δt) correlated with the arrival of SR pulses (delay Δt). In present experiments the delay and width were $\Delta t_1 = 2.2$ ns, $\Delta t_1 = 8.2$ ns for the fast component, and $\Delta t_2 = 23$ ns, $\Delta t_2 = 111$ ns for the slow component. Simultaneously with the excitation, the reflection spectra were recorded at the angle of incidence of 17.5° by a XP2230B PM (Valvo) with a help of a sodium salycylate coated window.

3. Experimental Results

We revealed that the crystallographic orientatation of BeO, relative to the electrical vector of the exciting radiation E, may have a dramatic effect on both the PL emission and PL excitation time-resolved spectra. For example, the fast component of PL for BeO at $E \parallel C$ exhibits at least two emission bands at $4.0 \, \text{eV}$ and $5.0 \, \text{eV}$ with FWHM of $\sim 1.0 \, \text{eV}$ (Figure 1a,b). The emission spectrum of the fast component is shifted in its spectral position lowerds the long-wavelength side as the energy of the exciting photons increases from the to the range of interband transitions. From the PL excitation spectrum for the fast component it follows that the $4.0 \, \text{eV}$ emission band is more effectively excited in the energy lange around the $E_{n=2, 3}$ maxima of the excitonic absorption, whereas the $5.0 \, \text{eV}$ emission length is effectively excited in the energy range adjacent to the first excitonic maximum

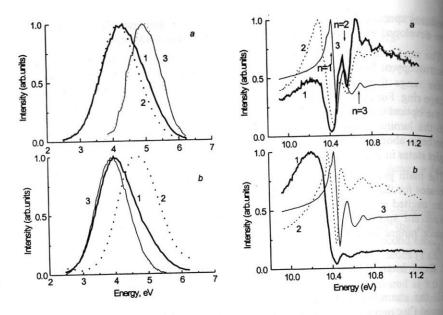


Figure 1. Time-resolved photoluminescence spectra of BeO (T=9,6K) at the orientation $E \parallel C$ and the excitation energies 10.25 eV (a) and 10.7 eV (b): 1- the spectrum in 'fast' time window; 2 - the spectrum in 'slow' time window; 3 - the spectrum of their difference and its fitting by Gaussian.

Figure 2. The excitation spectra of ultraviolet luminescence 3.35 eV (1) and 4.75 eV (2) of BeO (T=9.6K) measured in 'fast' (a) and 'slow' (b) time windows at the orientation $E \parallel C$ in comparison with reflection spectra (3).

The fast component of the 4.0 eV emission band on photoexcitation around $E_{n=2}$ at 9.6 K demonstrates a decay time equal to 2.2 ns, whereas that for the 5.0 eV emission band at photoexcitation around $E_{n=1}$ exhibit τ =4.4 ns (Figure 3). It should be noted that we have previously revealed the 4.0 eV emission band with τ=2 ns on excitation by XSR, however the second fast component (5.0 eV) was not observed there because of its fairly narrow the effective excitation energy range around $E_{\rm n}=1$. A slow stage of the decay kinetics in BeO at $E \parallel C$ is represented by two emission bands at 4.2 eV and 4.7 eV (Figure 1a,b). First of them is more effectively excited in the 9.5-10.2 eV energy range, below $E_{\rm n=1}$. In this connection the 4.2 eV emission band was attributed to a radiative relaxation of the electronic excitations localized on the impurity or lattice defects (Figure 2b). Notably, on excitation by the 9.5 cl photons at 9.6 K, the initial stage of a decay kinetics of the 4.2 eV luminescence characterized by two components with τ =2.7 ns and 34 ns. At the same time, the $4.7\,e^{-3}$ emission band is characterized by a decay kinetics with τ_1 =54 ns and τ_2 =36 ms. In doing so the τ_2 component covers up to 95% of the total light yield. The PL excitation spectrum of the slow component of the 4.7 eV emission band is comparable with that for the 'fast' component of the 5.0 eV emission band, namely, the 4.7 eV luminescence is more effectively excited the energy region adjacent to $E_{n=1}$ (Figure 2a,b).

The fast component of the 4.0 eV luminescence at a different orientation of the Be crystal $(E \perp C)$ is only slightly pronounced (Figure 3). Almost the same result was obtain our previous work with the use of the XSR-excitation [5]. However, we have observed the fast component of the 5.0 eV luminescence at the $E \perp C$ orientation, though the energy of the exciting photons was varied over all the 6-40 eV energy range.

component (τ=52 ns) at this orientation is concentrated at the 4.6 eV emission band (Figure 4) and its PL excitation spectrum differs from that for the fast component of the $10 \, \text{eV}$ emission band only by a more effective excitation around $E_{n=1}$ (Figure 5). On photoexcitation at 9.6 K we have observed no fast components for the 6.7 eV emission band. The main component of the VUV-luminescence decay kinetics is fitted by an exponentian with τ=340 μs. This was in a full agreement with our previous results [2,5]. The VUVhuminescence of BeO at the $E \parallel C$ orientation is effectively excited around $E_{n=2,3}$ as well as in the region of creation of separated electron-hole pairs (Figure 6). However, this luminescence is more effectively excited in the range of interband transitions $(E > E_g)$ than in the excitonic region. It should be noted that the profile of the VUV PL excitation spectrum for $E \parallel C$ looks like that for a fast component of the 4.0 eV emission band. At the $E \perp C$ orientation, the VUV pl. excitation spectrum varies over a wide range. The VUV luminescence is more effectively excited around $E_{n=1}$, whereas the excitation efficiency in the range of the interband transitions $(E > E_g)$ is considerably less pronounced (Figure 6). Figure 7 demonstrates the steady-state pl excitation spectra for both the UV- and VUV-emission bands of BeO (E || C) at 9.6 K. One can see significant differences between these two PL excitation spectra not only in the exciton energy range, but in the range of the electronic excitation multiplication (EEM) at E >20 eV. The energy threshold for the EEM effect is equal to $2E_{n=1}$ for the 6.7 eV emission band, and $\sim 2E_g$ for the 4.8 eV emission band.

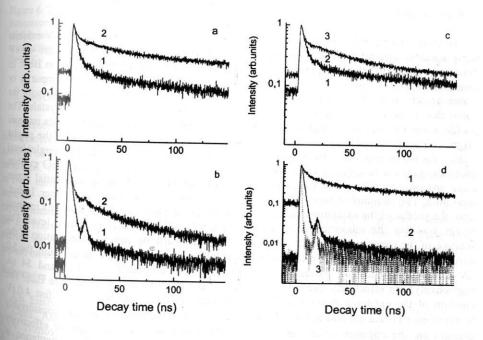
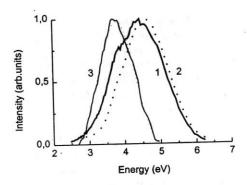


Figure 3. The PL decay kinetics for BeO at 9.6 K: (a) - $E_{\rm m}$ =5.0 eV, $E_{\rm ex}$ =10.24 eV, $E \parallel C$ (1), $E \perp C$ (2); (b) - $E_{\rm m}$ =3.35 eV, $E_{\rm ex}$ =10.67 eV, $E \parallel C$ (1), $E \perp C$ (2); (c) - $E \parallel C$, $E_{\rm m}$ =5.0 eV, $E_{\rm ex}$ =10.24 eV (1), 10.67 eV (2) and 11.27 eV (3); (d) - $E \parallel C$, $E_{\rm m}$ =3.35 eV, $E_{\rm ex}$ =10.24 eV (1), 10.67 eV (2); the excitation pulse recorded using the registration system (3).



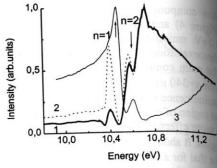


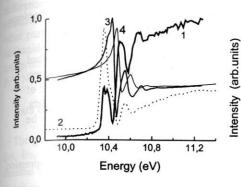
Figure 4. Time-resolved photoluminescence spectra of BeO (T=9,6K) at the orientation $\vec{E} \perp C$ and the excitation energy 10.25 eV: 1the spectrum in 'fast' time window; 2 - the spectrum in 'slow' time window; 3 -the spectrum of their difference and its fitting by Gaussian.

Figure 5. The excitation spectra of ultraviolet luminescence 3.35 eV (1) and 4.75 eV (2) of BeO (T=9.6K) measured in 'fast' (1) and 'fast' (2) time windows at the orientation $E \perp C$ in comparison with reflection spectra (3).

4. Discussion

Presented experimental results demonstrate that fast BeO luminescence at 4.0 eV exhibits fairly specific spectral, kinetic, orientation and polarization features, which set the 4.0 eV emission band apart from the previously studied luminescence of the triplet STE in BeO. In addition, the 4.0 eV luminescence band can not be associated with any of the impurity or lattice defects in BeO. From the BeO electronic structure it can not be associated with the core-valence transitions, resulting usually in a typical fast emission in some crystals. The profile of the PL excitation spectra for the 4.0 eV emission band directly specifies its intrinsic origin and supports our previous hypothesis [2,3] concerning its association with the singlet STE. It should be noted that the relaxation of an exciton onto the lowest radiative singlet level proceeds from the $E_{n=2,3}$ excitonic states as in alkaline iodides [9]. However, BeO exhibits more pronounced red-shift of the singlet level, and this fact points on a substantial lattice relaxation. The fast luminescence at 5.0 eV should be considered in a similar manner. In fact, from the profile of the excitation spectrum of the 5.0 eV emission band it follows its intrinsic origin, however the relaxation of an exciton proceeds from the E_{n=1} excitonic level. The analysis of the experimental results allowed us to put forward the picture of relaxation of the intrinsic EE in BeO at 9.6 K. From this picture it follows that at the $E \parallel C$ orientation, the 50 eV and 4.7 eV emission bands (the characteristic time-constants of 4.4 ns and 54 ns. respectively) are effectively excited on creation of the excitons in a ground state E_{n=1}. The creation of the excitonic states $E_{n=2,3}$ results in more effective excitation of a fast 4.0 eV luminescence (τ =2.2 ns) and the 6.7 eV luminescence (τ = 340 μ s). The picture considerably changes for the opposite orientation $(E \perp C)$: the 6.7 eV luminescence can be effectively excited only around $E_{n=1}$, whereas the fast 4.0 eV luminescence at this orientation considerably suppressed even at excitation in the $E_{n=2,3}$ energy range. At the same time, the fast 5.0 eV luminescence is not observed, and a slow component (τ~52 ns) of a luminescence decay kinetics is represented by an intensive band at 4.6 eV. The UV- and VUV PL excitation spectra differ noticiably in profile over the photon energy range of creation of electron-hol pairs, starting above 11 eV. In terms of theory of hot scattering of electron-hole pairs, suggests that the UV and VUV emission bands differ also in respect to the migration energy losses. In fact, the formation of radiative state for the 6.7 eV emission band takes plant without energy losses, i.e. the place of self-trapping practically coincides with the birthpla

of the non-relaxed EE, but a creation of that for the 4.8 eV emission band occurs after a enflicient migration of the initial EE. The high value of $\sigma_0 = 0.60$ in the Urbach's rule for neO suggests a strong exciton-phonon interaction as well.



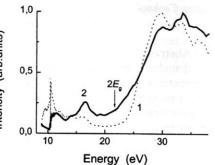


Figure 6. The excitation spectra of VUVluminescence 6.7 eV of BeO (1,2) in comparison with reflection spectra (3,4) at the orientation $E \parallel C(1,3)$ or $\mathbf{E} \perp \mathbf{C}(2,4)$, T=9.6K.

Figure 7. The excitation spectra of UVluminescence 4.8 eV (1) and VUVluminescence 6.7 eV (2) at the orientation $E \parallel C$, T=9,6K.

5. Conclusion

In present work the time-resolved PL spectra in the energy region from 2.5 eV to 10.4 eV, time-resolved PL excitation spectra over the broad energy range from 6 eV to 35 eV, decay kinetics of PL and reflectivity of the oriented single crystals of BeO at 9.6 K and 295 K were measured. We have revealed a number of the different channels of radiative relaxation of EE in BeO using a low-temperature VUV-spectroscopy. This method allowed us not only to separate with confidence the intrinsic and extrinsic emission bands, but to proof experimentally the various multipletisy of the relaxed excitonic states. A general picture of the EE relaxation in BeO looks fairly complicate. The EE relaxations from the basic and excited excitonic states result in creation of various emission centres. Their population depend on orientation and temperature of a crystal.

References

- Ch. Lushchik, In 'Excitons', E. Rashba and M. Sturge, Eds., p. 505, North-Holland, Publ. Conf., Amsterdam, 1982
- V. Ivanov, V. Pustovarov, S. Gorbunov, A. Kruzhalov, Fiz. tverd. Tela, 36(9) (1994) 2634
- V. Ivanov, V. Pustovarov, S. Gorbunov, et al., Fiz. tverd. Tela, 38(11) (1996) 3333
- I. Ogorodnikov, A. Kruzhalov, Material Science Forum, 239-241 (1997) 51
 - V. Pustovarov, V. Ivanov, A. Kruzhalov, É. Zinin, Fiz. tverd. Tela, 36(5) (1994) 1523
- V. Maslov et al., Proc. 6th Intern. Confer. On Cryst. Growth, p 268, Moscow, 1980
- S. Gorbunov, A. Kruzhalov, M. Springis, Phys. Stat. Solidi (b) 141 (1987) 293
- G. Zimmerer, Nucl. Instr. And Meth. A 308 (1991) 178
- T. Matsumoto, M. Shirai, K. Kan'no. J. Phys. Soc. Japan 64(3) (1995) 987

Table 1. The summary of parameters used in the model calculation related to Fig. 4, parameter K is a "zero temperature" rate related to k_{12} and k_{21} parameters, while g is the ratio of degeneracies of the levels 1 and 2.

k ₁	3.9e4 s	w _O	1e12 s
k ₂	3.7e5 s	Eo	200 meV
K	5e5 s	WED	1e9 s
D	0.45 meV	E _{ED}	100 meV
g	1(2)		12.11 String Dainy

References

- 1. M.Treadaway and R.C.Powell, J.Chem.Phys. 61 (1974) 4003.
- 2. W. van Loo, phys.stat.sol. (a) 27 (1975) 565 and 26 (1975) 227.
- 3. V.G. Baryshevski et al., NIM A322, 231 (1992).
- 4. M. Kobayashi, M.Ishii, Y.Usuki, H.Yahagi, NIM A333, 429 (1993).
- 5. K.Polak, M.Nikl, E.Mihokova, J.Lumin., 72-74 (1997) 781.
- 6. M.Martini et al, Chem. Phys. Lett., 260 (1996) 418.
- 7. V.Murk, M.Nikl, E.Mihokova, K.Nitsch, J.Phys.Cond.Mat. 9, (1997) 249.
- 8. Y. C. Zhang, N. A. W. Holzwarth, R. T. Williams, and M. Nikl, Electrochemical Soc. Proc. Series, Pennington, NJ (1998), PV 98-25, p. 420 (Proc. of EXCON98, Nov 1-5, 1998, Boston, USA).
- 9. V. Nagirnyi et. al., J.Phys. Cond.Mat. 7, (1995) 3637.
- 10. Y. Toyozawa and M.Inoue, J.Phys.Soc.Jap. 21 (1966) 1663.
- 11. M.Bacci, B.D. Bhattacharyya, A.Ranfagni, G.Viliani, Phys.Lett. 55A (1976) 489.
- 12. C.J.Balhausen and A.D. Liehr, J.Mol. Spectrosc. 2 (1958) 342.
- 13. A. Annenkov et. al. Phys.stat.sol. (a) 170 (1998) 47.
- 14. M.Nikl et. al., phys.stat.sol. 195 (1996) 311.
- 15. M.Nikl et. al., Chem.Phys.Lett. 291 (1998) 300.
- 16. M.Nikl et al., Appl.Phys.Lett. 71 (1997) 3755.

Optical and Luminescent VUV-Spectroscopy of La₂Be₂O₅ Single Crystals

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Abstract. The time-resolved emission spectra under excitation by synchrotron radiation of X-ray and VUV energy regions as well as by pulse electron beams, the time-resolved luminescence excitation spectra and reflection spectra, the decay kinetics of luminescence have been studied for pure and Ce-doped lanthanum beryllate crystals. The energy levels diagram and the energy gap was established. The excitonic states of the valence band are not displayed in spectra of the optical constants. The bifurcation of radiation relaxation of electron excitations is observed. The slow component in the luminescence spectra corresponds to emission of self-trapped excitons (STE), formed by a recombination pathways, the fast component can correspond to emission of relaxed metastable excitons from STE states.

Keywords: time-resolved spectroscopy, luminescence, excitonic states, oxide crystals, La₂Be₂O₅.

Introduction

The luminescence of triplet self-trapped excitons (STE) in the well-know alkali halide crystals is created by recombination pathway or directly through excitation of unrelaxed excitons [1]. At the same time for some complex oxide crystals, for oxides of metals of III group [2-4] the branching of radiative relaxation of electronic excitations (EE) takes place, in this case the direct optical creation of STE and their creation at recombination of electrons with holes give a different radiative states.

The lanthanum beryllate crystals used in laser and scintillation engineering. The significant interest to these crystals has occurred after observation in La₂Be₂O₅-Nd crystals of the effect of stimulation radiation [5]. The detailed spectroscopy researches of these doped crystals in the region $E < E_g$ were carried out in work [6]. In the fundamental absorption region the optical properties and efficiency of luminescence excitation were briefly investigated only in work [7]. At the same time the detailed research of EE structure and the processes of radiative relaxation permit to reveal in a considered context the characteristic features of EE in this class of oxides. On the one hand the motive of crystal structure of La₂Be₂O₅ crystals is similar with those of BeO crystals (deformed tetrahedrons BeO₄), for which in the optical spectra and in the processes of radiative relaxation of EE the excitonic states are expressed very brightly [8]. On the other hand for the compounds of transition d-metals (e. g., Sc₂O₃ [2,3], LaF₃ [9]) the manifestation of anion exciton states are completely away in optical spectra, that is determined by pd- genealogy of the top of the valence band (VB) and of the bottom of the conduction band (CB).

In the present work the reflection spectra, the time-resolved luminescence spectra and decay kinetics of luminescence under X-ray and selective VUV excitations as well as the

time-resolved luminescence excitation spectra are investigated in the range 5-35 eV at $T \approx 295$ and 10 K in pure and Ce^{3+} -doped $La_2Be_2O_5$ crystals.

Experimental details

The samples were grown by Dr.V.Matrosov, the Czochralski method was used. The crystalline structure (space symmetry group C⁶_{2h} (C2/c), z=4, parameters of elementary cella=7,5356A, b=7,3436A, c=7,4387A, β =91 0 33') formed by deformed tetrahedrons BeO_{4, in} then inserted asymmetry the ions La³⁺ (the point group C₁), coordinated by ten oxygen ions [10]. The crystals were certificated by X-ray methods, the samples were produced in the form of polished plane-parallel plates (Ø10-15 mm, h=1 mm). The measurements were carried our on the storage ring VEPP-3 (excitation by X-ray photons) [11] and on the SUPERLIM station of HASYLAB (excitation by VUV photons) [12]. The excitation spectra were normalized to quantum intensities of synchrotron radiation (SR) falling into the crystal. The emission spectra in visible and UV region were analyzed by a B&M (Czerny-Turner sheme) secondary monochromator with a photomultiplier R2059 (Hamamatsu). The emission spectra were not corrected on spectral sensitivity of optical tract. The excitation spectra were measured for time-integrated (steady-state) luminescence as well as for the emission detected within time windows (length Δt_i) correlated with the excitation pulse of SR (delayed by δt.). The delay δt and length Δt were equal to 2,2 and 8,2 ns for fast component, 23,5 and 111 ns for slow component respectively. The reflection spectra were measured at SR incidence angle of 17.5°.

Results and discussion

The reflection spectrum (RS) in the energy region 5-35 eV has two groups of bands at energy of 7-12 and 17-27 eV, Fig. 1. The analysis of the photoelectron spectra and the accounts of the electron structure executed for La₂Be₂O₅ in work [13], as well as the observed essential analogy with RS of LaF₃ [9] allow us to connect the low energy bands 7,0 and 10.4 eV with the transition of electrons from VB, formed by the 2p-states of oxygen, to CB,

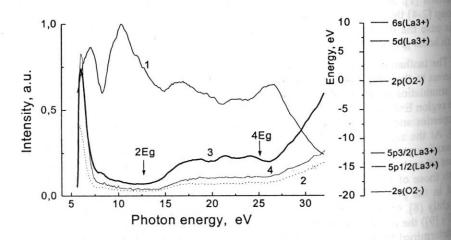


Figure 1. The reflection spectrum (1) and luminescence excitation spectra (E_{emission}=3,3 eV) of fast (2) and slow (3) components of decay kinetics of La₂Be₂O₅ crystals; the steady-state luminescence excitation spectra of Ce³⁺ centers (E_{emission}=2,7 eV) of La₂Be₂O₅-Ce (0,5 mol.%) crystals (4). T=10,8 K. To the right - the energy levels diagram of La₂Be₂O₅ crystals.

formed of 5d- and 6s-states of La^{3+} -ions. The manifestations of anion excitonic states in the region of longwavelength edge of fundamental absorption (LEFA) in RS do not take place. Therefore the band-gap energy E_g was determined on the basis of excitation spectra measurements, of low temperature thermostimulated luminescence and of the Urbach's rule $(E_0=6,3~{\rm eV},~\sigma_0=0,44,~\kappa_0=4x10^5~{\rm cm}^{-1})$ [7]: at T=80 K $E_g=6,2-6,5~{\rm eV}$. The bands in RS at energies higher more than 15 eV corresponds probablly to the transitions from 2p-states of oxygen to the higher states of CB. The structure at energies 19,4 and 20,3 eV corresponds to excitation of $5p_{3/2}$ μ $5p_{1/2}$ - levels of La^{3+} -ions (probablly it is a cation exciton). The transitions from 2s-levels of O^{2-} -ions form a peak 26,5 eV in RS. Fig.1 shows also the energy levels diagram.

The broad emission band (E_m =3,34 eV, FWHM=0,82 eV, quantum yield η =0,5 at 80K) is observed in pure crystals at low temperature in the steady-state luminescence spectra under

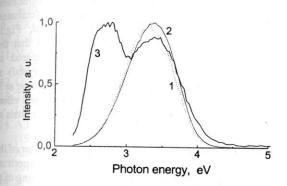


Figure 2. The fast (1), slow (2) and steady-state (3) luminescence spectra of $La_2Be_2O_5$ (1,2) and $La_2Be_2O_5$ -Ce (0,5 mol.Vo) (3) crystals. $E_{\text{excitation}}$ =6,2 eV, T=10,8 K.

the X-ray, electron beam or photons (E>5,8 eV) excitations, Fig.2. The decay kinetics of this luminescence under selective excitation by photons in the LEFA region or by photons with energy E>Eg contains the fast (\tau=1,7ns) and slow (microsecond time-range) components, Fig.3. The decay kinetics of slow component is nonexponential (under the electron beam pulse: τ_{1/2}=8 μs at 80 K). The steady-state and slow luminescence spectra are identical.

The maximum of the fast luminescence spectrum has

some shift to the low energy region (E_m=3,30 eV, FWHM=0,78 eV), Fig.2. The luminescence excitation spectra (LES) of the fast and slow components have no bands at the energy less than LEFA. Both emissions are excited exclusively only in the LEFA region as well as in the region of a creation of the separated electron-hole pairs, Fig1. The luminescence excitation spectra of fast and slow components are different in the LEFA region. The maximum of the fast component LES (E_m=5,94 eV, FWHM=0,78 eV) has a displacement to smaller energy with respect to a maximum of slow component LES (E_m=6,05 eV, FWHM=1,02 eV). At E>E_g the quantum yield of both emissions decreases. It is due to an increase of an absorption factor and losses of energy near the surface. The increase of both emissions is observed at the energy E>14 eV (E>2Eg). The region 19-21 eV corresponds to excitation of 5p levels of lanthanum ions, the RS and LES have an antibathic character. The second region of increase of quantum yield of fast, slow and steady-state emissions is observed in the energy E>4Eg, Fig.1. The effect of photon multiplication is displayed. The photoelectron spectral data [13] are specified, that the width of a valence band (E_v) is equal approximately 10 eV in La₂Be₂O₅ (as well as for the majority of oxide crystals E_v>E_g). This circumstance and availability of two thresholds of a quantum yield increase in the region (2-4)E_g according to modern representations of the photon multiplication theory [14] allow us to conclude that the electronhole mechanism of photon multiplication as a result of the nonelastic scattering of both hot Photoelectrons and hot photoholes is realized in La₂Be₂O₅.

The emission spectrum of Ce^{3+} -doped $La_2Be_2O_5$ crystals has a broad intense band ($E_{emiss}=2,66$ eV, FWHM=0,4 eV, $\eta=0,4$, $\tau=29$ ns at 300 K by direct selective 3,5-4,7 eV

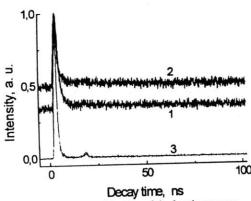


Figure 3. Decay kinetics of the luminescence $(E_{emission}=3,3 \text{ eV})$ of $La_2Be_2O_5$ crystals, $E_{excitation}=6,2 \text{ eV}$ (1) and 21,4 eV (2), T=10,8 K. The exciting pulse of synchrotron radiation - (3).

photoexcitation (4f -5d transitions in Ce³⁺-ions) and τ =38-45 ns, τ_{rise} =4-6 ns by pulse electron beam or X-ray excitations). The thermoactivation spectroscopy data of irradiated and thermochemical reduced crystals [7] show, that the excitation of Ce3+ centers is due to the electronic mechanism under recombination excitation in the LEFA region or in E>E_g energy region: $(Ce^{3+} + h^{+} \rightarrow Ce^{4+})$ $Ce^{4+} + e^{-} \rightarrow (Ce^{3+})^{*} \rightarrow Ce^{3+} + hv$). All peculiarities in the LES of Ce3+- centers (including the photon multiplication effect) correspond to the LES (emission 3.34 eV) of a pure crystal, Fig.1 However, it should be noted that the migration losses [15] (compared to emission 3,34 eV in pure crystal) at

energy transfer to impurity centers are higher, and a narrow dip in LES of Ce³⁺- emission at 7-14 eV confirms this fact. These parameters of Ce-emission and the brightly expressed effect of photon multiplication at energy E>2E_g allows us to offer and use La₂Be₂O₅-Ce crystals as scintillation materials [16].

All set of the experimental data confirms the assumption [7] about intrinsic character of the 3,34 eV emission in the pure crystals La₂Be₂O₅. Availability of this emission in the spectrum of thermostimulated luminescence directly points to its recombination origin. A splitting of p-states of a valence band in a field of a low symmetry occurs in oxide crystals, therefore one of p-orbital appears as a nonbinding one [2]. The hole mass for a nonbinding p-orbital can be more higher than that for the other valence band, and because of this, there are prerequisitions for self-trapping of this hole. At the present time on the basis of a similarity between La₂Be₂O₅ and the binary or complex oxides (for example, CaWO₄ [4]) one can envisage that the 3,34 eV emission band in pure La₂Be₂O₅ is a result of recombination of electrons with self-trapped holes in the form of the O type polarons of a small radius.

The absence of excitonic manifestation in RS of La₂Be₂O₅ in the LEFA region as well as this for compounds of transition d-metals is determined by pd- genealogy of the valence band top and the conduction band bottom. In addition, the availability of the vacant 4f-levels can significantly shorten a life time of the 5d-states of La³⁺-ions, as it was suggested in Ref.[9] for LaF3, therefore the excitonic states should be metastable. At the same time, the value of the parameter σ_0 =0,44 in the Urbach's rule for La₂Be₂O₅ points out on the strong exciton-phonon interaction and on the opportunity of self-trapping for excitons. The effective excitation of the fast 3,30 eV component in the LEFA region at lower energy than that for the maximum of LES for the 3,34 eV slow component points out on the bifurcation of an electronic excitation relaxation on different pathways, which is typical for various oxides [2-4]. On the basis of this, we believe, that the anion excitons in La₂Be₂O₅ are metastable. In this connection, they have no manifestations in RS, however, they manifest temselves in processes of the radiative relaxation. The radiative transitions from the relaxed STE's states can determine a spectrum of the fast 3,30 eV emission band. The allowed type of these transitions points out on the singlet character of STE. Though the LES (3,30 eV emission) does not correspond absolutly to the general tendency of formation of singlet STE in the well-know alkali halide crystals (primary excitation from the n=2 excitonic states [17]), it reflects a specific character of electronic excitation relaxation in La2Be2O5 crystals.

References

- 1. Ch.Lushchik. Excitons. Nauka, Moskow, 1985.
- A.I.Kuznetsov, V.N.Abramov, V.V.Murk and B.R.Namozov, Sov. Phys. Solid State 33 (1991) 2000.
- V.Murk, O.Svinarenkov. Inorganic scintillators and their applications. Delft University Press, Delft, The Nitherlands. (1995). P.227.
- 4. V.Murk, B.Namozov and N.Yaroshevich, Radiation Measurements 24 (1995) 371.
- 5. H.P.Jenssen, R.F.Begley, R.Webb, R.C.Moris, J. Appl. Phys. 47 (1976) 1496.
- A.A.Kaminskii, Ngoc Tran, S.E.Sarkisov, V.N.Matrosov, M.I.Timoshechkin, Physica status solidi (a) 59 (1980) 121.
- 7. A.V.Kruzhalov, V.A.Pustovarov, A.A.Maslakov, V.L.Petrov and B.V.Shulgin, Optika i spektroskopiia 63 (1987) 457.
- V.Yu. Ivanov, V.A. Pustovarov, A.V. Kruzhalov and B.V. Shulgin, Nucl. Instr. and Meth. in Phys. Res. A282 (1989) 559.
- 9. C.G.Olson, D.W.Lynch and M.Piacentini, Phys. Rev. B18 (1978) 5740.
- 10. L.A. Harris, R. Yakel, Acta Cryst. B24 (1968) 672.
- 11. V.A.Pustovarov, E.I.Zinin, A.L.Krymov, B.V.Shulgin, Review of Scientific Instrum. 63 (1992) 3521.
- 12. G.Zimmerer, Nucl. Instr. and Methods in Phys. Res. A308 (1991) 178.
- 13. T.A.Betenekova, A.V.Kruzhalov, N.M.Osipova, V.P.Palvanov, V.L.Petrov, I.N.Shabanova, Sov. Phys. Solid State 25 (1983) 175.
- A.Lushchik, E.Feldbach, R.Kink, Ch.Lushchik, M.Kirm and I.Martinson. Phys. Rev. B53 (1996) 5379.
- A.N.Vasil'ev, V.V.Mikhailin and I.V.Ovchinnikova, Izvestia Akademii Nauk USSR, ser. fiz. 49 (1985) 2044.
- L.V.Viktorov, A.V.Kruzhalov, A.A.Maslakov, V.L.Petrov, B.V.Shulgin and V.N.Matrosov, Copyright certificate USSR N921328. Bull. Izobretenii 14 (1982).
- 17. T.Matsumoto, M.Shirai and K. Kanno, J. Phys. Soc. Japan 64 (1995) 987.