

Fast Exciton Relaxation in Oriented BeO Crystals after Pulse X-Ray and VUV Excitations¹

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This work presents the results of experimental complex study of electronic excitation dynamics for single BeO crystals. 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 10K for the oriented BeO crystals. The diversity among the channels of the radiative relaxation of the electronic excitations as well as the various multiplicity of the excited states of self-trapped excitons, depending on the crystal orientation and exciting photon energy are discussed.

1. Introduction

Self-trapped exciton (STE) manifestations in the broad band-gap oxides were revealed more than twenty years ago. However, all the suggested models for these STE as well as the channels of the STE formation remain yet to be widely debated topics. 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, α -Al₂O₃, 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 the fundamental absorption edge (FAE). To the contrary, the high-symmetry oxides (e.g. MgO, CaO) exhibit usually a well-resolved excitonic structure of the optical constant spectra, despite the fact that STE is not realized in these crystals. Therefore the analysis of pathways of STE formation and radiative relaxation is difficult in oxide because of low informativity of excitation spectra in the excitonic region. The efficiency of the same analysis was demonstrated in [2] for alkali halide crystals (AHC). The comparative research of both time-resolved luminescence spectra (LS) and luminescence excitation spectra (LES) has allowed to systematize in AHC three types of STE distinguished by a displacement of a two-halide hole kernel from regular position as well as to install for each type a multiplicity of excited states [2].

BeO crystals (the crystalline structure of wurtzite type, $E_g=10.63$ eV) have the expressed excitonic structure in reflection spectra, the edge luminescence is observed also. The local symmetry of oxygen ions (C_{3v}) occupies an intermediate situation between high-(MgO) and low-(Al₂O₃) symmetry matrixes. Wide bands 4.9 and 6.7 eV in luminescence spectra are interpreted as radiative relaxation of two types STE [5]. Moreover the anisotropy of the BeO crystalline structure enables to use an orientation spectroscopy methods.

In present work we researched channels of triplet and singlet STE formation by means of experimental studying of time-resolved LS and luminescence kinetics in UV- and VUV-ranges at a selective photoexcitation, and also LES of the oriented BeO crystals at T=10K.

2. Experimental details

All the examined BeO crystals were grown by V.A. Maslov through the use of the advanced flux method [4]. The content of impurities in the BeO samples was analysed using a laser mass-spectrography method. 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 [5]. 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). The investigation of an emission in VUV range was performed using a 0.5 m vacuum monochromator equipped with PM R1460 (Hamamatsu). Two in situ interchangeable gratings of the 2 m primary monochromator, Al and Pt coated, were applied in measurements of the LES over the 6-35 eV energy range. A typical spectral resolution was 0.25 nm. The LES were corrected for the equal number of the exciting photons for each energy region, but the emission spectra are presented as they are measured.

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Time-resolved spectra were recorded within a time window (length Δt) correlated with the arrival of SR pulses (delay δt). In the present experiments the delay and length were $\delta t_1=2.2$ ns, $\Delta t_1=8.2$ ns for a fast component, and $\delta t_2=23$ ns, $\Delta t_2=111$ ns for a slow component. Simultaneously with the excitation, the reflection spectra were recorded at an angle of incidence 17.5° by a XP2230B PM (Valvo) from a sodium salycylate coated window.

3. Experimental results

Time-resolved LS and LES in BeO find out the expressed orientation dependence. For example, the fast component of LS for BeO at $E \parallel C$ exhibits at least two emission bands at 4.0 eV and 5.0 eV with FWHM of ~ 1.0 eV (Fig.1). The emission spectrum of the fast component is shifted in its spectral position towards the long-wavelength side as the energy of the exciting photons increases from the range of FAE to the range of the interband transitions. From the LES spectrum for the fast component it follows that the 4.0 eV emission band is more effectively excited in the energy range around the $E_{n=2,3}$ maxima of the excitonic absorption, whereas the 5.0 eV emission band is effectively excited at the energy arranged much below than the first excitonic maximum (Fig.2). The fast component of the 4.0 eV emission band on photoexcitation around $E_{n=2}$ at 10 K demonstrates a decay time equal to 2.2 ns, whereas that for the 5.0 eV emission band at photoexcitation with energy 10.25 eV, i.e. below than $E_{n=1}$ exhibit $\tau=4.4$ ns (Fig.5). It should be noted that we have previously revealed the 4.0 eV emission band with $\tau=2$ ns on excitation by X-ray synchrotron radiation (XSR) [6], however the second fast component (5.0 eV) was not observed there because of its fairly narrow the effective excitation energy range.

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 (Fig.1). First of them is more effectively excited in the 9.5-10.2 eV energy range, below $E_{n=1}$ (Fig.2). In this connection, the 4.2 eV emission band as well as fast emission 5.0 eV was attributed to a radiative relaxation of the electronic excitations (EE) localized on the impurity or lattice defects. Notably, on excitation by the 9.5 eV photons at 10 K, the initial stage of a decay kinetics of the 4.2 eV luminescence is characterized by two components with $\tau=2.7$ ns and 34 ns. At the same time, the 4.7 eV emission band is characterized by a decay kinetics with $\tau_1=54$ ns and $\tau_2=36$ ms. In doing so, the τ_2 component covers up to 95% of the total light yield. The LES of the slow component 4.7 eV testifies to that emission band is more effectively excited in the energy region adjacent to $E_{n=1}$ (Fig.2).

The fast component of the 4.0 eV luminescence in the opposite orientation of a BeO crystal ($E \perp C$) appears only slightly as well as fast emission 5.0 eV

(Fig.5). Almost the same result was obtained in our previous work by the use of the XSR-excitation [6]. The region of most effectively excitation of fast emission 4.0 eV in this orientation is the energy range around the $E_{n=2,3}$ maximal of the excitonic absorption. The slow component ($\tau=52$ ns) at this orientation is concentrated at the 4.5 eV emission band (Fig.3) and its LES differs from that for the fast component of the 4.0 eV emission band only by a more effective excitation around $E_{n=1}$ (Fig.4).

We have no observed fast components for the 6.7 eV emission band. In doing so, the main component of the VUV-luminescence decay kinetics is fitted by an exponent with $\tau=340$ μ s. This was in a full agreement with our previous results [3]. The VUV-luminescence of BeO at the $E \parallel C$ orientation is effectively excited around $E_{n=2,3}$ as well as in the region of a creation of the separated electron-hole pairs (Fig.6). However, this luminescence is more effectively excited in the range of the interband transitions ($E > E_g$) rather than in the excitonic area. It should be noted that the profile of the LES of 6.7 eV emission for $E \parallel C$ look like that for a fast component of the 4.0 eV emission band. At the $E \perp C$ orientation, the LES of VUV emission 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 (Fig.6).

4. Discussion

Time-resolved LS in BeO at a selective photoexcitation are characterized by several types of luminescences: fast emissions with maximums of bands at 4.0 and 5.0 eV and slow - with maximums of bands at 4.2-4.7 and 6.7 eV. It is principle to install a nature of observable luminescences - is they are stimulated by a EE radiative relaxation in a regular lattice (own luminescence) or are connected to defects of the crystal. At clearing up of this problem most informative represent time-resolved LES.

So from LES of a fast luminescence 5.0 eV (Fig.2 and 4) follows, what this emission has most effectively excitation in range 10.2-10.3 eV, laying below energy of the first excitonic peak of reflectance on 120-200 meV. This fact testifies that the EE radiative relaxation takes place around a defect of crystal. In case of a fast luminescence 4.0 eV a situation other. Though LES of this band in "fast" temporary window also contains a maximum in range 10.2-10.3 eV (Fig.2 and 4), this maximum is shaped by the contribution of slow components (certainly predominant in this range in LES), measured in "slow" temporary window. Fast luminescence 4.0 eV really has not excitation range 10.2-10.3 eV because the short component in kinetics of a luminescence is absents in case of excitation into 10.24 eV (Fig. 5). It allows to conclude, that the fast luminescence 4.0 eV provokes extremely

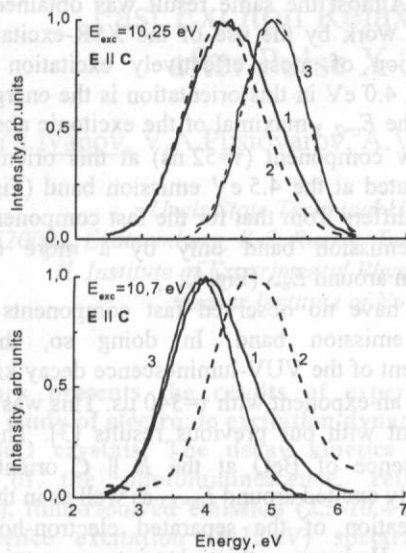


Fig. 1. Time-resolved luminescence spectra of BeO (T=10K) at different excitation energies: the spectra in "fast"(1) and "slow"(2) time windows, their difference and its fitting by Gaussian (3).

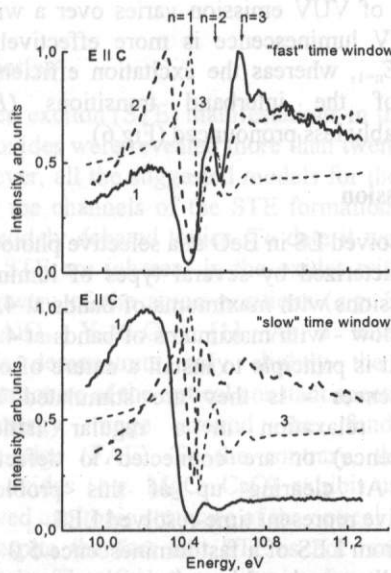


Fig. 2. The excitation spectra of luminescence 3.35 eV(1) and 4.75 eV (2) of BeO (T=10K) in comparison with reflection spectra (3).

in range of exciton states $E_{n=2,3}$ and in interband transitions range, i.e. has own character.

The slow luminescences in BeO also find out a different nature. The luminescence 4.2 eV effectively provokes in range 10.2-10.3 eV (Fig.2) and, thus, corresponds to EE radiative annihilation around defect. In contrary, the luminescence with a maximum in range 4.4-4.7 eV (in dependence on orientation) finds out own character, as provokes extremely in range of excitonic peaks of reflectance, and also in interband transitions range ($E_{exc} > E_g$), Fig.2 and 4.

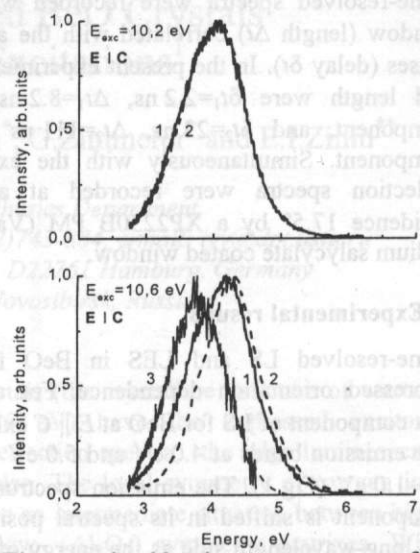


Fig.3. Time-resolved luminescence spectra of BeO (T=10K) at different excitation energies: the spectra in "fast"(1) and "slow"(2) time windows, their difference and its fitting by Gaussian (3).

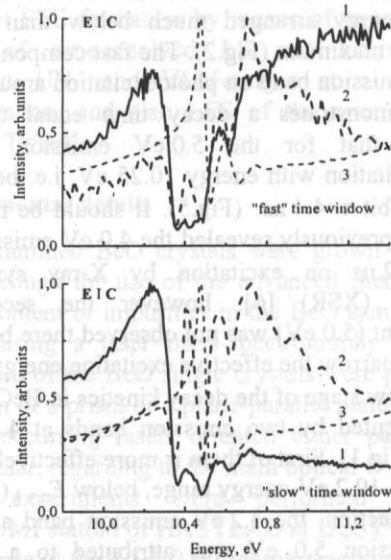


Fig.4. The excitation spectra of luminescence 3.35 eV(1) and 5.05 eV (2) of BeO (T=10K) in comparison with reflection spectra (3).

The VUV-emission band 6.7 eV is not blocked with other bands and is characterized by a single component of decay. LES of this luminescence (Fig.6) undoubtedly testify to its own character. It confirms the earlier made supposition that the 6.7 eV emission is connected to STE radiative annihilation [3].

Thus, in the oriented BeO crystals at T=10K with a method of selective time-resolved VUV-spectroscopy it is possible to observe the following luminescences of own character: fast - 4.0 eV ($t=2.2$ ns) and slow -

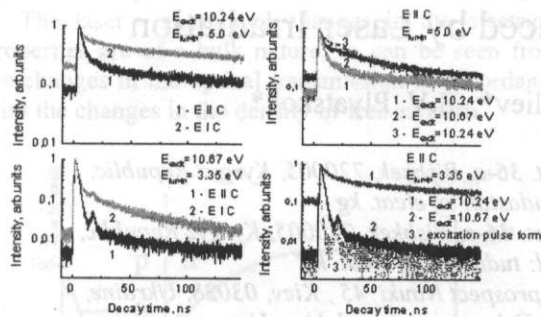
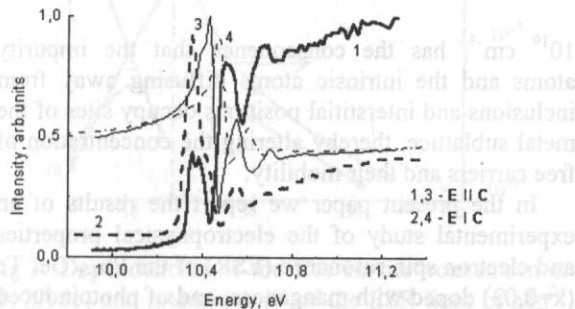


Fig.5. Luminescence decay kinetics of BeO at 10K.

Fig.6. Photoexcitation spectra (1,3) of VUV-luminescence and reflection spectra (2,4) of BeO at 10K. 4.4-4.7 eV ($t_1=54$ ns and $t_2=36$ ms) and 6.7 eV ($t=340$ ms). Another emission bands connect to crystal defects.

The analysis of LES displays that the efficiency of own luminescences excitation in ranges of main ($E_{n=1}$) and excited ($E_{n=2,3}$) excitonic states depends on crystal orientation. For example, the LES of 6.7 eV luminescence (Fig.6) demonstrate the existence of orientation dependence of an exciton relaxation from main and excited states into self-trapped state. Earlier for low-symmetry oxides (α - Al_2O_3 , YAlO_3 , $\text{Y}_3\text{Al}_5\text{O}_{12}$) is established, that a relaxation of an exciton into self-trapped state and recombinative formation of STE reduce in creation of the different luminescence centers [7]. In present work for the first time for wide-gap crystals we observed an orientation dependence of the excitons relaxation leading to the different radiative centers.

The experimental data demonstrate that the fast own luminescence 4.0 eV in BeO has the spectral-kinetic, orientation, polarization characteristics essentially differs from the earlier studied STE luminescences in BeO [3,6]. Outgoing from BeO electronic structure, there are no also premises for connection it with core-valence transitions. LES of 4.0 eV emission confirms the supposition of early works [6] about its connection with a STE singlet luminescence. The preferred excitons relaxation on a singlet radiative STE level in BeO goes from $E_{n=2,3}$ exciton excited states.

It is known, that in AHC the STE triplet luminescence is polarized perpendicularly, and the STE singlet luminescence is collateral to axes of a

two-halide STE hole kernel [1]. Triplet character of a state, the transitions with which shape a VUV-emission in LS, now does not discuss doubt. The model of the luminescence center is offered by us [3], as STE with a hole kernel as a polaron of small radius as O^- ion in the axial configuration of a local crystalline tetrahedron. A main issue of interpretation of a fast 4.0 eV luminescence in BeO is its more low energy (than triplet STE) spectral position. The similar situation is implemented, in particular, in NaI, NaBr [8]. In model of an isoentropic potential energy curve the explanation of this fact is the minimum of a singlet STE potential energy has configurational coordinate Q_2 considerably major than coordinate of a triplet state Q_1 [8]. For BeO the observable difference of triplet and singlet states energies is much more. However, it is necessary to take into account that the BeO crystalline frame is characterized by low symmetry (C_{3v}). Self-trapping of an exciton leads to further local distortion of a crystal lattice. It can be the cause more essential, than in AHC, relative displacement of coordinates of triplet and singlet states.

In [2] for AHC is established that in case of STE radiative annihilation the shifts of a two-halide hole kernel from a regular position of ions to interstitial are different for different bands of a luminescence. The band of STE luminescence conforming to the greatest shift is characterized as well by the greatest Stokes displacement. In BeO the Stokes displacement is maximum for 4.0 eV luminescence. It is possible to assume that the conforming short-lived luminescence center forms at the most considerable local deformation of a crystal. If by analogy with AHC to assume that in BeO the tendency of anion shift into interstitial position also takes place, the originating luminescence center can be imagined as short-lived defect such as F^+ -center. It is interesting that stable F^+ -center in BeO is characterized by the 3.92 eV fast luminescence. Besides, the luminescence 4.0 eV forms at a excitons relaxation from excited states. In series AHC (NaCl, KI) the preferred excitons relaxation from excited states $n=2$ reduces in a situation of a c defect formation [9].

Thus, fast luminescence 4.0 eV should be really referred to singlet STE.

References

- [1] Ch. Lushchik, In 'Excitons', E. Rashba and M. Sturge, Eds., p. 505, North-Holland, Publ. Conf., Amsterdam, 1982.
- [2] T. Matsumoto, M. Shirai, K. Kan'no. J. Phys. Soc. Japan 64 (3) 987 (1995).
- [3] V. Ivanov, V. Pustovarov, S. Gorbunov, A. Kruzhalov. Fiz. tverd. Tela 36 (9) 2634 (1994).
- [4] V. Maslov et al., Proc. 6th Intern. Confer. On Cryst. Growth, p. 268, Moscow, 1980.
- [5] G. Zimmerer, Nucl. Instr. And Meth. In Phys. Res. A 308, 178 (1991).
- [6] V. Pustovarov, V. Ivanov, A. Kruzhalov, $\dot{\text{Y}}$. Zinin. Fiz. tverd. Tela, 36 (5) 1523 (1994).
- [7] A. Kuznetsov, V. Abramov, V. Murk, B. Namozov. Fiz. tverd. Tela, 33 (7) 2000 (1991).
- [8] T. Matsumoto, T. Kawata, A. Miyamoto, K. Kan'no. J. Phys. Soc. Japan 61 (11) 4229 (1992).
- [9] Ch. Lushchik, A. Lushchik. Nauka, Moscow (1989) 262 c.