

Intrinsic UV-VUV luminescence and X-ray emission spectroscopy of BeO and multicomponent oxide dielectrics

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The experimental study of intrinsic UV-VUV luminescence and X-ray emission at the selective excitations near fundamental absorption edge as well as at the inner-shell excitations for binary BeO crystal and multicomponent oxide crystals Be_2SiO_4 , Y_2SiO_5 and $\text{La}_2\text{Be}_2\text{O}_5$ has been performed. The results show that relaxation during the time-scale of decay of short-living anion and cation excitations leads to creation of self-trapped excitons at the same low-symmetry local structural units of crystalline lattice. The applied experimental method gives an opportunity to clarify a participation of different crystalline units of complex oxides in the self-trapping of excitons.

Выполнено экспериментальное исследование собственной УФ-ВУФ люминесценции и рентгеновской эмиссии для бинарного BeO и комплексных Be_2SiO_4 , Y_2SiO_5 и $\text{La}_2\text{Be}_2\text{O}_5$ кристаллов при селективном возбуждении вблизи края фундаментального поглощения и в области поглощения остовных уровней. Результаты исследования показывают, что релаксационные процессы, происходящие в течение времени жизни короткоживущих как анионных, так и катионных возбуждений приводят к образованию автолокализованных экситонов в одних и тех же низко-симметричных локальных структурных фрагментах кристаллической решетки. Используемый экспериментальный метод позволяет установить степень участия различных фрагментов кристаллической решетки в процессах автолокализации экситонов в комплексных оксидах.

1. Introduction

The self-trapping of electronic excitations is an acknowledged mechanism of transformation of the absorbed energy in wide band gap crystals. Self-trapped excitons (STEs) in oxides were discovered thirty years ago. It was found that the discussed phenomenon was characteristic for oxide compounds with a low local symmetry of oxygen sites. However, the mechanisms responsible for the formation of excited states and models of STEs remain a subject of discussion to the present day. Some assump-

tions about space structure and possible model of STE are known solely for binary $\alpha\text{-SiO}_2$ and BeO [1, 2]. Additional interest in the case of the complex compounds consists of clarification how the different cation's sublattices participate in self-trapping of excitons.

At low temperatures anion self-trapped excitons (ASTE) in oxides may decay radiatively with luminescence or create defect-exciton complexes. In BeO crystal the ASTE luminescence at 4.9 eV and at 6.7 eV is a result of the decay of two different ASTEs, which are distinguished by symmetry of the

hole nucleus (O^- -ions either at the vertex or the bottom plane of the distorted oxygen tetrahedron around a central Be) [2]. ASTE luminescence has previously been observed in all complex crystals studied here [3–6]. The luminescence bands peaked at 3.5 eV and at 4.1 eV have earlier been interpreted as the radiative ASTE decay in Be_2SiO_4 crystals [3]. Later Zatsopin et al. considered that the creation of unrelaxed oxygen anion excitons result in formation of anion self-trapped excitons in both the silicon-oxygen and the beryllium-oxygen tetrahedra [4]. The luminescence at 3.5 eV is a result of the radiative decay of the ASTE formed in the silicon-oxygen tetrahedra, whereas the luminescence at 4.1 eV would be related to the ASTE decay within the beryllium-oxygen tetrahedra. Further, the observed 3.5 eV luminescence band is more intense than the 4.1 eV band, which indicates that the ASTE would be preferably formed within a silicon-oxygen tetrahedron. Simultaneously, the analysis of ASTE formation in Y_2SiO_5 crystals in [5] reaches a conclusion that only the polyhedra containing heavy cations are involved in the self-trapping process. Unlike the mentioned above materials for $La_2Be_2O_5$ crystals it was found a single band of ASTE peaked at 3.34 eV [6]. However, the role of the structural crystalline units in the self-trapping process has not been discussed in literature.

In contrast to the data of a few reports of ASTE investigations, just singular works by resonant inelastic X-ray scattering (RIXS) method were devoted to the formation of cation self-trapped excitons (CSTEs) in wide-gap compounds [7, 8]. Resonant inelastic scattering of X-ray photons in the region of the absorption edges for elements from the region of ultra soft X-ray allowed us to reveal the specificity of atomic symmetry and symmetry of orbital shells. The method is bulk sensitive and thus is more preferable for our investigation instead of traditional electron spectroscopy. First Ma et al. [7] observed a distinguishable side-band adjacent to the elastic scattering peak in the RIXS spectra for excitations in the vicinity of the C 1s core exciton resonance, while the absorption spectrum only showed a single sharp excitonic peak (without any side-band). The authors suggested that the origin of this RIXS side-band is related to the strong vibronic coupling that would lead to a local lattice distortion, and to the corresponding shifts in the excited elec-

tronic state. The appearance of the energy loss wing in the electronically elastic part of the RIXS spectra indicates that such distortion must have occurred already during the lifetime of the inner-shell hole. In oxide compounds a similar energy loss wing has been observed in the RIXS spectra of powder $LiNO_3$ [8], where it was attributed to the dynamics of X-ray emission, accompanying the distortion of NO_3 -species.

The present work is devoted to combined research of the UV-VUV-luminescence and X-ray emission at the selective XUV excitation in several oxide crystals: BeO , Be_2SiO_4 , Y_2SiO_5 and $La_2Be_2O_5$ with the purpose to understand a role of different crystalline units in the process of self-trapping.

2. Experimental procedure

The crystals BeO and Be_2SiO_4 have been grown from a solution in sodium tungstate melt by V.A.Maslov, G.V.Bukin and L.I.Isaenko method and $La_2Be_2O_5$ crystals have been grown using at Czohralski method by V.N.Matrosov at the Design and Technological Institute of Monocrystals in Novosibirsk (Russia) and the crystal of Y_2SiO_5 was grown by A.M.Korovkin using Czokhralski method at the Vavilov State Optical Institute in St. Petersburg (Russia).

The luminescence spectra (2.5–8 eV), the luminescence excitation spectra (7–24 eV and 50–200 eV) at $T = 10$ K and at 300 K were measured at the SUPERLUMI station [9] and at the BW3 beamline using the luminescence installation described in [10], both at HASYLAB, Hamburg, Germany.

The RIXS spectra with the excitations in the vicinity of Be 1s and Si 2p photoabsorption spectra were measured at $T = 300$ K at beamline I511-3 at MAX-lab, Lund, Sweden [11]. The resolution of the beamline monochromator (a modified SX700 by Zeiss) was set to 0.1 eV and the resolution of X-ray spectrometer on the end station was set to 0.2 eV.

3. Results and discussion

The luminescence spectra and the luminescence excitation spectra in the vicinity of the fundamental absorption edge (for ASTE creation) and near Be 1s photoabsorption thresholds (for CSTE creation) for BeO are presented in Fig. 1. The values of the Stokes shifts of the intrinsic luminescence bands give a measure of the energy loss during ASTE formation. The RIXS spectra of BeO crystals at the selective excitation

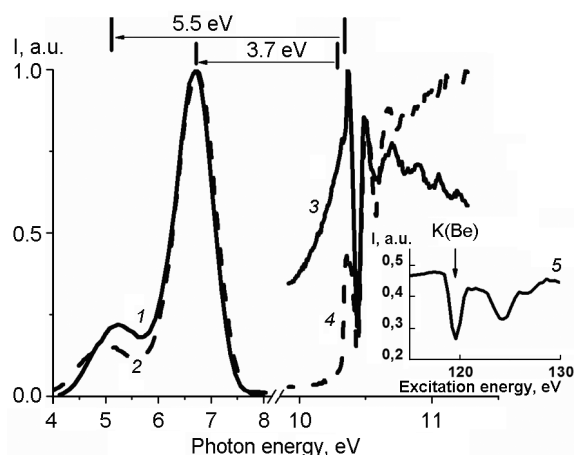


Fig. 1. The photoluminescence (1, 2) and luminescence excitation (3, 4, 5) spectra of BeO crystals at $T = 10$ K. Excitation energy: 10.8 eV (curve 1) and 119.5 eV (curve 2). Emission energy: 4.9 eV (3, 5) and 6.7 eV (4).

with the photons of different energies near Be 1s photoabsorption edge are presented in Fig. 2. One can see the elastic peak of the RIXS spectra has an unusually strong energy loss wing at its low energy side. In our earlier works [12–15] this observed peculiarity of the RIXS spectra was attributed to the CSTE formation. The spectral width of the energy loss wing is shown in Fig. 2 to estimate the energy loss for the CSTE formation. The comparison of respective values shown in Fig. 1 and 2 leads us to a conclusion that the energy loss for both the ASTE and the CSTE formation is approximately equal (near 5.5–6 eV in the case of BeO). The results presented in Fig. 1 and 2 and as we have earlier discussed in detail in [14].

Two intrinsic luminescence bands with maxima at 3.5 eV and at 4.1 eV shape the luminescence spectra of the crystalline Be_2SiO_4 with excitations near the fundamental absorption edge as well as in the vicinity of core level thresholds (Fig. 3). The crystalline lattice of Be_2SiO_4 contains distorted silicon-oxygen and beryllium-oxygen tetrahedra. According to the reasoning presented in Ref. 4 the higher relative intensity of the 3.5 eV luminescence indicates that the probability of ASTE formation rate is higher in the silicon-oxygen tetrahedra. The RIXS spectra of Be_2SiO_4 excited in the vicinity of Si 2p and Be 1s photoabsorption edges are shown in Fig. 4, respectively. In both cases we were able to distinguish an energy loss wing adjacent to the elastic scattering peak. We interpret this as an indication that the CSTE can be created at both Be- and Si-centered tetrahedra. It can

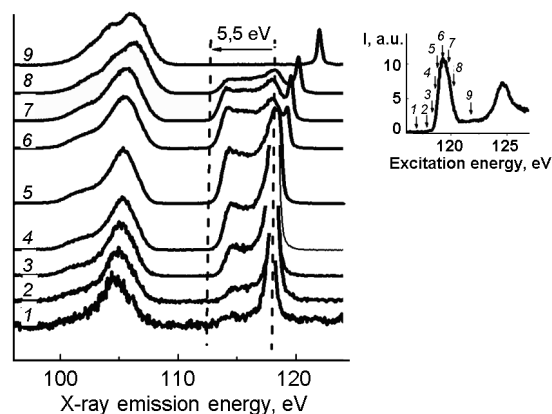


Fig. 2. The X-ray emission spectra of BeO crystals excited in the vicinity of Be 1s photoabsorption edge. The numbers at the curves denote different excitation energies (see insert).

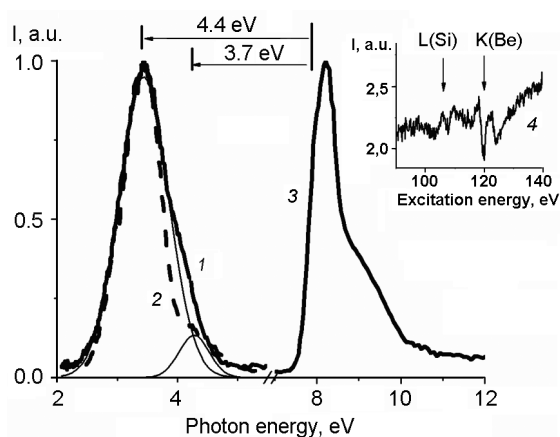


Fig. 3. The photoluminescence (1, 2) and 3.5 eV luminescence band excitation (3, 4) spectra of crystalline Be_2SiO_4 at $T = 10$ K. The excitation energy is 8.2 eV (curve 1) and 130 eV (curve 2). The decomposition of curve 1 into Gaussian components is shown by narrow lines.

well be seen from the comparison of left and right parts of Fig. 4 that for the excitations near the 2p absorption edge of Be_2SiO_4 Si the sub-bandgap energy loss wing is more pronounced than for excitations near Be 1s edge. This result of our present study obtained for CSTE in their creation region provides a further support for the suggestion made in Ref. 4 on the dominating role of the silicon-oxygen tetrahedra in the self-trapping processes. Additionally, we can see from the comparison of the luminescence of Be_2SiO_4 (in Fig. 3) and the X-ray emission spectra (in Fig. 4 and 5) that the energy loss values for the ASTE

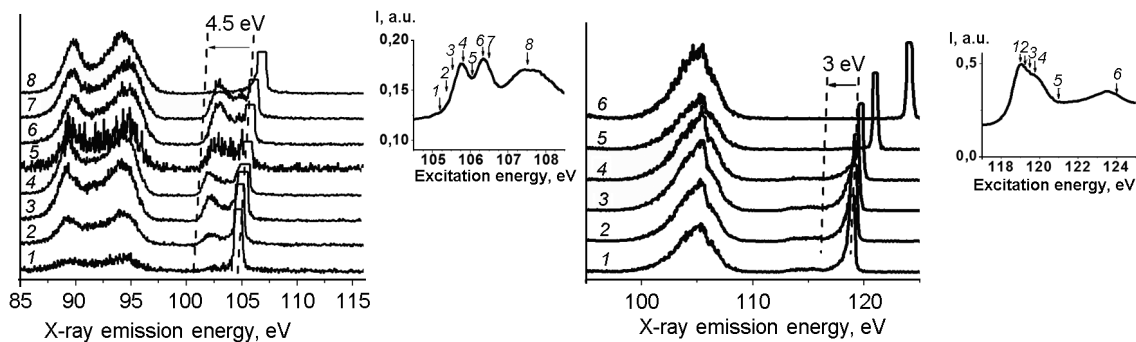


Fig. 4. The X-ray emission spectra of crystalline Be_2SiO_4 excited in the vicinity of the Si $2p$ photoabsorption threshold (left part) or in the vicinity of the Be $1s$ photoabsorption threshold (right part). The numbers at the curves denote excitation energies as shown at the fluorescence yield curves in the inserts in the both cases.

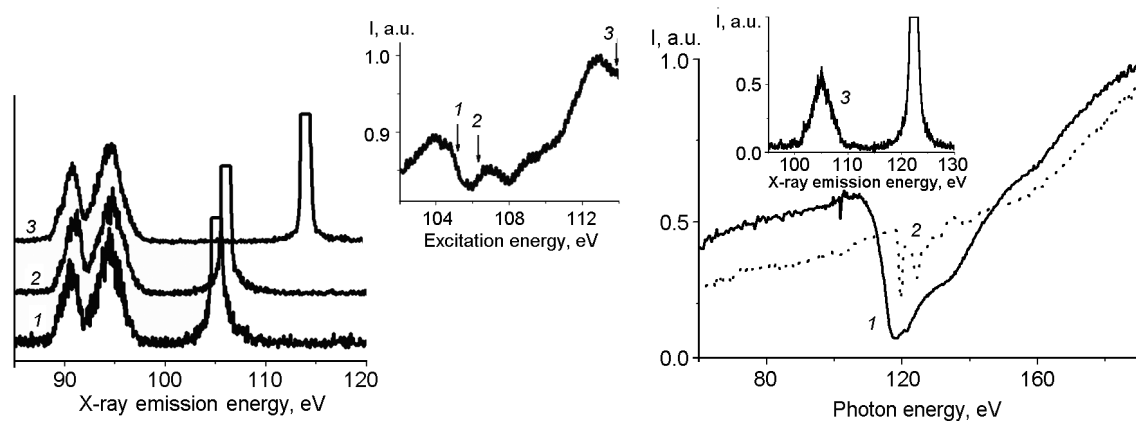


Fig. 5. The X-ray emission spectra of Y_2SiO_5 crystals measured in the vicinity of Si $2p$ photoabsorption edge (left part). Numbers of curves denote different excitation energies of excited photons (shown at the fluorescence excitation spectrum in the insert of left part). At the right part: the excitation spectra of 3.34 eV intrinsic luminescence of $\text{Be}_2\text{La}_2\text{O}_5$ crystal (curve 1) and intrinsic luminescence peaked at 4.9 eV of BeO crystal (curve 2) in the vicinity of La $4d$ and Be $1s$ photoabsorption thresholds, respectively. At the insert of right part: The X-ray emission spectra of crystalline $\text{Be}_2\text{La}_2\text{O}_5$ at the excitation energy of 120 eV.

and the CSTE formation are again approximately equal like in BeO.

In contrast to the situation observed for Be_2SiO_4 , the RIXS spectra of Y_2SiO_5 in the vicinity of Si $2p$ photoabsorption edge (shown in left part of Fig. 5) do not contain any detectable sub-bandgap energy loss features. This result is in a good agreement with the conclusion made in Ref. 5 which stated that silicon-oxygen tetrahedra did not play a significant role in the process of the self-trapped exciton's formation in Y_2SiO_5 .

The situation with co-existence of ASTE and CSTE in Be_2SiO_4 and Y_2SiO_5 crystals earlier discussed in [16,17] allows to propose that the self-trapping of anion and cation excitons occurs in the same local units of the crystalline lattice in oxides and that it may be caused by the predisposition of

such local units to short-term transient distortion. In current work we more carefully considered the results of joint analysis of intrinsic UV-luminescence and RIXS spectra of $\text{La}_2\text{Be}_2\text{O}_5$ crystals. As opposed to other objects of the investigation $\text{La}_2\text{Be}_2\text{O}_5$ crystals are characterized by only one band of intrinsic luminescence. In the luminescence excitation spectra there were no features in the vicinity of Be $1s$ photoabsorption edge thresholds (Fig. 5, insert of right part). At once the decreasing of luminescence light yield in the vicinity of La $4d$ photoabsorption edge thresholds is well-outlined. It allows to suppose that beryllium sublattice probably does not participate in the process of CSTE formation. The confirmation of this can be found in studying of the RIXS spectra in the vicinity of Be $1s$ photoabsorption edges. The RIXS spectrum (Fig. 5,

inset) shows the absence of energy loss wing of the elastic scattering peak of exciting photons. From the point of view of systematic suppositions of present work it experimentally confirms that the self-trapping of cation excitons on near Be ion does not occur in $\text{La}_2\text{Be}_2\text{O}_5$. So, the situation with anion and cation excitons self-trapping is similar for Y_2SiO_5 and $\text{La}_2\text{Be}_2\text{O}_5$ crystals and it considerably differs in the case of Be_2SiO_4 crystal where both cation sublattices participate in the excitons self-trapping.

From structural point of view these two groups of crystals differ in the main. In Be_2SiO_4 cations of both types have small differences in sizes and similar tetrahedral environment. In crystals with rare earth elements as structural elements the last are considerably larger than the cations of light elements. Consequently, they are differ by a high coordination number and by weaker bonds with anions. According to [17] the bond length between yttrium and oxygen ions (from 2.199 to 2.604 Å) in Y_2SiO_5 is about two times more than one of silicon-oxygen bond (from 1.602 to 1.636 Å). The similar situation is for $\text{La}_2\text{Be}_2\text{O}_5$ crystal. In accordance with [18] the La–O bond length is at the range of 2.415–2.999 Å, while Be–O bond length is significantly shorter (from 1.602 to 1.678 Å). At once, two bands of intrinsic luminescence are observed for Y_2SiO_5 crystals [5] and only one band — for $\text{La}_2\text{Be}_2\text{O}_5$ crystals [6]. To explain the reason of this it is necessary to analyze in detail the structural features of the both crystals. In yttrium oxyorthosilicate the rare earth element can occupy one of two positions with coordination number 6 and 7 respectively. Therefore, there are two types of various structural lattice fragments bound to heavy cation and each of them can be the local fragment for realization of self-trapping process. In $\text{La}_2\text{Be}_2\text{O}_5$ crystal the coordination number of heavy cation is 10 and, therefore, there is only one type of polyhedron.

Thereby, the results of the present work logically develop the conclusions of previous investigation [16,17] concerning the fact that if excitons self-trapping process in oxide binary and complex crystals occurs then it realizes for anion and cation excitons in the same local fragments of the crystal lattice. Such fragments are more predisposed to lattice deformation accompanied the self-trapping process. The results of the investigation indicate that in the case

of considerable differences in cation sizes the sublattice of light (smaller in size) cation does not participate in self-trapping processes.

4. Conclusions

RIXS and luminescence spectroscopic study of intrinsic UV-VUV luminescence and X-ray emission at the selective excitations near fundamental absorption edge as well as at the inner-shell excitations for binary BeO crystal and complex oxide crystals Be_2SiO_4 , Y_2SiO_5 and $\text{La}_2\text{Be}_2\text{O}_5$ has been carried out. The results show that the relaxation during the time-scale of decay of short-living anion and cation excitations leads to creation of self-trapped excitons at the corresponding local structural units of crystalline lattice. This can be caused by increase of dynamical instability of such low symmetry local structural units (in comparison with high symmetry ones), which facilitate the self-trapping processes in these systems. In the case when cation sizes are differ considerably the sublattice of light cation does not participate in the self-trapping processes.

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Спектроскопія власної УФ-ВУФ люмінесценції і рентгенівської емісії у ВеО і комплексних оксидних діелектриків

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Виконано експериментальне дослідження власної УФ-ВУФ люмінесценції і рентгенівської емісії для бінарного ВеО і комплексних Ве₂SiO₄, Y₂SiO₅ й La₂Ве₂O₅ кристалів при селективному збудженні поблизу краю фундаментального поглинання і в області поглинання остовних рівнів. Результати дослідження показують, що релаксаційні процеси, що відбуваються протягом часу життя короткоживучих як аніонних, так і катіонних збуджень приводять до утворення автолокалізованих екситонів у тих самих низьких-симетричних локальних структурних фрагментах кристалічної ґратки. Використаний експериментальний метод дозволяє встановити ступінь участі різних фрагментів кристалічної ґратки у процесах автолокалізації екситонів у комплексних оксидах.