Luminescence of Neutron-Irradiated Crystals Be_2SiO_4 and Be_2GeO_4[1]

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Abstract – Luminescence spectra of neutron-irradiated crystals Be_2SiO_4 and Be_2GeO_4 at selective excitation by synchrotron radiation pulses are studied. Parameters and probable models of radiation-induced centers are discussed.

1. Introduction

Beryllium ortosilicate Be_2SiO_4 and ortogermanate Be_2GeO_4 are crystal-chemical analogues, crystallize in phenakite structure and concern to a class of island silicates. The feature of crystal structure of island silicates is that silicate-oxygen tetrahedrons $[SiO]_4$ (in case of Be_2GeO_4 it is $[GeO]_4$) are isolated from each other. Crystals with phenakite structure have a higher radiating resistance than quartz and other network silicates since radiating defects in such crystals are formed mainly in silicon-oxygen sublattice [1].

Both crystals are dielectrics with wide area of the transparency. The width of forbidden gap for Be_2SiO_4 is 8.5 eV and for Be_2GeO_4 is 7.5 eV. The radiation defects arising in bulk and on surface of crystals Be_2SiO_4 are investigated in works [1–6]. It is established that after an irradiation with high-energy particles in crystals Be_2SiO_4 the oxygen vacancies are formed as paramagnetic E′-centers. These centers are characterized by EPR signal with $g_{||}$=2.0013 and $g_{\perp}$= 2.0020 and by optical absorption band at 215 nm [2,6]. At big dozes of an irradiation ($>6{\times}10^{17}$ cm^{-2}) in Be_2SiO_4 are found out oxygen-vacancy-associated complexes – double vacancies of oxygen (=Si or Si_2^0). They gave in optical absorption spectra a band with a maximum at 250 nm and X-ray-luminescence with λ = 430 nm [4]. Specified vacancy-associated defects are located in silicon-oxygen crystal sublattice and formed due to displacement of oxygen atoms.

In crystal Be_2GeO_4 radiation-induced defects were not studied earlier, however owing to crystal-chemical similarity of crystals Be_2GeO_4 and Be_2SiO_4 it is possible to believe that processes of the radiation defects formation and structure of radiation-induced defects will be identical.

Radiation-induced defects in crystals phenakite investigated earlier with the help of methods EPR, optical absorption spectroscopy [2,3,6], exoelectron emission spectroscopy [1,4,5]. Luminescence properties of radiation-induced defects in crystals Be_2SiO_4 and Be_2GeO_4 are investigated insufficiently. The luminescence is one of the most informative methods of study of defects in dielectric crystals. In the present work time-resolved spectra of selectively raised photoluminescence of irradiated by fast neutrons crystals Be_2SiO_4 and Be_2GeO_4 are investigated.

2. Samples and Experimental Methods

Single crystals Be_2SiO_4 and polycrystalline samples Be_2GeO_4 were investigated. Researched samples Be_2SiO_4 represented the polished flat parallel plates, which have cut out from single crystal perpendicularly of main crystal a C-axis. According to spectral analysis Al, Mn, Ti, Ge and Fe impurities (0.02–0.06 wt%) were presented in single crystals Be_2SiO_4.

Polycrystalline Be_2GeO_4 was received from oxide powders BeO and GeO_2 by high-temperature solid state reaction: $2BeO + GeO_2 = Be_2GeO_4$ with the subsequent check of homogeneity of phase composition.

The samples under study were irradiated in pulsed nuclear reactor IBR-30 by the fast neutrons fluences $4.5{\times}10^{17} \div 6.6{\times}10^{18}$ cm^{-2} with energy E ~ 1 MeV.

Time-resolved photoluminescence spectra in spectral region 1.5÷6.0 eV are studied at selective excitation by photons pulses with energy 4÷35 eV at temperature 10 K, and at temperatures 80 and 300 K – at excitation by a deuterium lamp. Measurements of spectra of photoluminescence at influence of pulses of synchrotron radiation and spectra of photoluminescence excitation were performed at the SUPERLUMI station (laboratory HASYLAB, DESY, Hamburg) [7].

3. Experimental Results

Spectra of a photoluminescence and excitation for the neutron-irradiated crystals Be_2SiO_4 measured at T=10K are submitted in Fig. 1. At decomposition on gauss components in a spectrum of luminescence three bands with maxima at 3.93; 3.07 and 2.45 eV are were allocated (Fig. 1a). The excitation spectrum of luminescence at 3.93 and 3.07 eV consists of two bands: at 5.07 eV and 6.58 eV – for emission at 3.07 eV and at 5.1 and 6.68 eV – for emission at 3.93 eV (Fig. 1 b). The excitation bands located in the field of 6.5÷6.7 eV have a complex structure.

Excitation of a luminescence at 2.45 eV occurs in the range 5.1÷5.24 eV. This emission is raised also at 4.91 and 4.1 eV. At 80 and 300 K the luminescence band is registered at 2.2 eV. The specified band is most effectively exited at 5.23 eV and is less effectively at 4.91 and 4.1 eV.

At increase of a fluence from 2.1×10^{18} cm^{-2} up to 6.6×10^{18} cm^{-2} the intensity of a luminescence with a maximum at 3.93 eV grows approximately in two times. Intensity of emission at 3.07 and 2.45 eV practically do not vary.

Parameters of the basic bands of a luminescence and excitation and times of decay of a luminescence for crystal Be_2SiO_4 are given in Table 1.
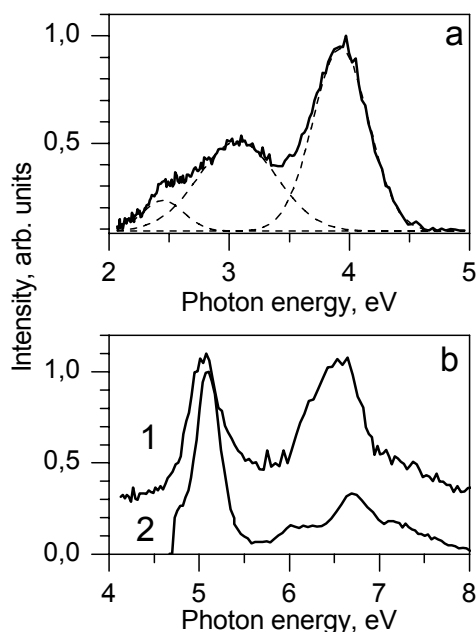

Fig. 1. Luminescence spectra at excitation energy 5.1 eV (a) and excitation spectra (b) of neutron-irradiated (2.5×10^{18}cm^{-2}) single crystal Be_2SiO_4. 1 – E_{emis} = 3.1 eV; 2 – E_{emis} = 4.0 eV. T=10K

A dotted line is Gauss decomposition

Spectra of luminescence and excitation of neutron-irradiated polycrystalline Be_2GeO_4 are submitted in Fig. 2. It is necessary to notice that a kind of luminescence spectra registered in Be_2GeO_4 at 10 K depends on energy of exciting photons. At excitation by photons with energy 6.56 eV the luminescence spectrum consisting of two overlapped bands with maxima at 2.2 and 2.4 eV (Fig. 2a) is observed. At excitation by photons with energy 7.35 and 27.5 eV the spectrum with two bands of emission at 3.1 and 3.6 eV is observed (Fig. 2b). At excitation in a band 5.2 eV the red luminescence described by a narrow line at 1.7 eV is observed (Fig. 3).

Parameters of the basic bands of a luminescence and excitation and decay times of a luminescence for crystal Be_2GeO_4 are given in Table 2.
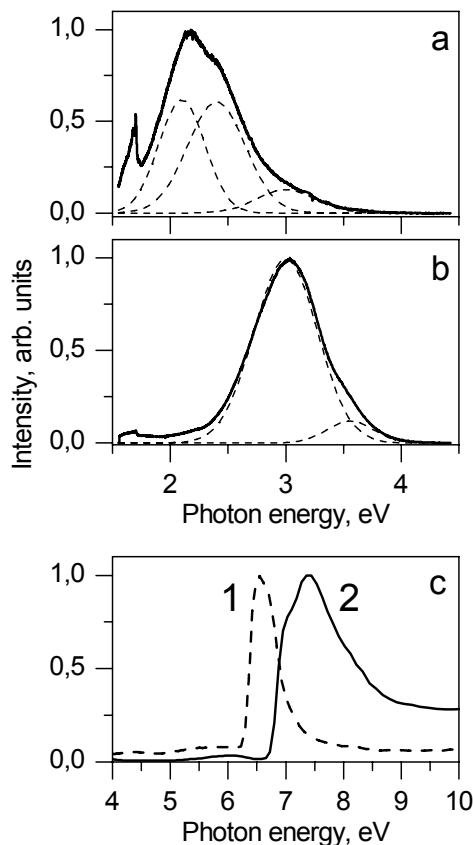

Fig. 2. Luminescence spectra of neutron-irradiated polycrystalline Be_2GeO_4: (a) E_{exc} = 6.56 eV; (b) E_{exc} = 7.35 eV. Excitation spectra (c): 1 – E_{emis} = 2.15 eV; 2 – E_{emis} = 3.1 eV. T = 10K
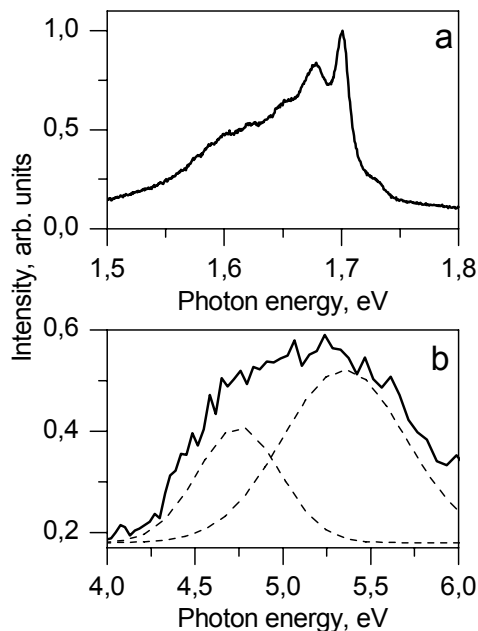

Fig. 3. Photoluminescence spectrum (a) and excitation spectrum (b) of neutron-irradiated ($\Phi=4.7 \times 10^{17}$cm^{-2}) polycrystalline Be_2GeO_4. T=10K.

A dotted line is Gauss decomposition

4. Discussion

The observably in researched crystals bands of a luminescence raised in the range of a transparency of a crystal are connected with intra-center radiating transitions. The luminescence centers of such type are impurities or own initial defects. In crystal Be_2SiO_4 with these defects there are necessary to connect all observably bands of a luminescence since they are excited in the range of transparency of crystal.

In polycrystalline Be_2GeO_4 the bands of radiation at 2.2; 2.4 and 1.7 eV excited in spectral area 6.56 and 5.2 eV are connected with intra-center transitions. The luminescence 3.0 eV in Be_2GeO_4 excited in a band 7.35 eV is caused most likely by radiative relaxation exciton since the corresponding excitation band is close to width of the forbidden zone.

In Be_2SiO_4 intensity of luminescence at 3.07 and 2.45 eV does not depend on a doze of an irradiation. This fact allows to attribute the specified bands to the defects present in structure of an initial non-irradiated crystal. The luminescence at 2.45 eV can be caused by impurity ions Mn^{2+}, replacing ions Be^{2+} or Si^{4+} in Be_2SiO_4 crystal lattice. Impurity ions of divalent manganese Mn^{2+} were found out in researched single crystals Be_2SiO_4 by methods of EPR and spectral analysis [2]. A similar band of luminescence Mn^{2+} with a maximum ~2.4 eV and FWHM = 0.20÷0.25 eV observed in structural analog of beryllium ortosilicate, willemite Zn_2SiO_4, activated by manganese [8].

Table I. Spectroscopic parameters of luminescence bands for the neutron-irradiated crystal Be_2SiO_4

Luminescence band, eV	FWHM, eV	Excitation energy, eV	Time decay, ns
3.93	0.46	5.10	t_1=7.56; t_2=3.02
		6.10	t_1=8.02; t_2=2.35
		6.68	t_1=9.80; t_2=1.60
		7.2	-
3.07	0.65	5.07	t_1=13; t_2=2.78
		6.6	-
		7.35	-
2.45	0.39	4.95 7.3	-

Luminescence bands in the field of 3.0÷3.1 eV for quartz and silicate crystals are connect to the hole centers on oxygen in a vicinity defective silicate-oxygen tetrahedrons formed due to replacement of silicon by impurities ions (Ge^{4+}, Al^{3+}) [9]. However in researched single crystal Be_2SiO_4 we did not observe the paramagnetic centers $[AlO_4]^{4-}$ and $[GeO_4]^{5-}$, charac-

teristic for these impurities. At the same time the band at 3.1 eV was registered at 10 K in a spectrum of a luminescence of non-radiated Be_2SiO_4. This band is excited by synchrotron radiation with energy both in the range of a transparency of a crystal (6.0 eV) and around the fundamental absorption edge (8.2 eV). It allows also to related the band of luminescence 3.1 eV to initial defects present in crystal lattice of non-irradiated sample Be_2SiO_4.

Table II. Spectroscopic parameters of luminescence for the neutron-irradiated polycrystalline Be_2GeO_4

Luminescence band, eV	FWHM, eV	Excitation energy, eV	Time decay, ns
3.6	0.4	5.10 7.35 27.5	-
3.0	0.55	5.10	
		7.35	t_1=8.02; t_2=2.35
		27.5	t_1=9.80; t_2=1.60
2.2	0.4	5.07	t_1=13; t_2=2.78
		6.56	-
2.4	0.5	5.07 6.56	-
1.7		4.7 and 5.2	-

The similar band of an intensive luminescence at 3.1 eV is observed in Be_2GeO_4 (Fig. 2). The paramagnetic centres $[AlO_4]^{4-}$ and $[GeO4]^{5-}$ are observed earlier in this samples Be_2GeO_4. They are connected with uncontrollable impurities Al and Ge. Luminescence bands at 3.0 and 3.6 eV in Be_2GeO_4 are excited by photons with energy around the fundamental absorption edge and more high-energy photons. These facts are allowed to consider that luminescence bands at 3.0 and 3.6 eV arise by radiative relaxation of excitons localized on impurities defects.

From above-stated follows that in neutron-irradiated crystals Be_2SiO_4 and Be_2GeO_4 the luminescence band in the region of 3.0 eV can be connected to different defects.

A band of a luminescence at 3.93 eV in a spectrum of Be_2SiO_4 it is possible to relate to the defects connected to radiating damage of structure, since its intensity grows with increase of a dose of a neutron irradiation. It was earlier established for Be_2SiO_4 that neutron irradiation fluence is higher 10^{18} cm^{-2} to formed not only single oxygen vacancies, but also more complex oxygen-vacancy-associated defects [4,5]. At these dozes in a spectrum of optical absorption Be_2SiO_4 there are a number of new bands [6]. One of them has maximum at 5.0 eV that is close to a

band of excitation 5.1 eV of luminescence at 3.93 eV. Because of the given band can be connected with the oxygen-deficient centers (ODC) [10].

The spectrum of luminescence with a maximum at 1.7 eV has oscillatory structure characteristic for molecular ion-radicals weakly connected with a crystal lattice. We assume that the luminescence at 1.7 eV is related to the interstitial molecular ion O^{2-} that is formed during neutron irradiation at displacement of atoms of oxygen.

Thus, the received results have shown that a point defects responsible for the observed luminescence in neutron-irradiated crystals Be_2SiO_4 and Be_2GeO_4 are formed both due to atoms displacement and the impurities defects present in lattice of non-irradiated samples. In case of Be_2SiO_4 the radiation-induced luminescence is connected with neutral oxygen-vacancy defects (ODC), whereas for Be_2GeO_4 the luminescence centers are displaced interstitial oxygen atoms.

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