Functional Materials 13, No.1 (2006)

Thermostimulated luminescence of $SrB_4O_7:Eu^{2+}$ single crystals

R.P.Yavetskiy, E.F.Dolzhenkova, A.V.Tolmachev, S.V.Parkhomenko, V.N.Baumer

STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

Received October 10, 2005

Thermallystimulated luminescence (TSL) of $SrB_4O_7:Eu^{2+}$ single crystals irradiated with γ and X-ray quanta has been studied for the first time and compared with that of SrB_4O_7 crystals. The induced optical absorption in the 400 to 700 nm region has been ascribed to $1s \rightarrow 2p$ transitions of F^+ centers. The Eu^{2+} ions have been shown to act simultaneously as traps and as radiative recombination of charge carriers. Basing on the TSL, optical absorption, and photoluminescence studies of $SrB_4O_7:Eu^{2+}$ single crystals, a TSL mechanism has been proposed associated with the decay of F^+ centers being in non-equivalent crystallographic positions followed by radiative recombination of charge carriers on europium ions. Possible positions of the localization of radiation-induced defects in the SrB_4O_7 crystal structure has been discussed.

Впервые изучена термостимулированная люминесценция монокристаллов $SrB_4O_7:Eu^{2+}$, облученных гамма и рентгеновскими квантами, в сравнении с монокристаллами SrB_4O_7. Наведенное оптическое поглощение в области λ = 400–700 нм приписано $1s \rightarrow 2p$ переходам F^+-центров. Показано, что ионы Eu^{2+} одновременно выступают ловушками, а также центрами излучательной рекомбинации носителей заряда. На основании изучения ТСЛ, оптического поглощения и фотолюминесценции монокристаллов $SrB_4O_7:Eu^{2+}$ предложен механизм ТСЛ, связанный с распадом F^+-центров, находящихся в неэквивалентных кристаллографических позициях, с последующей излучательной рекомбинацией носителей заряда на ионах европия. Обсуждаются возможные позиции локализации радиационных дефектов в кристаллической структуре SrB_4O_7.

Strontium tetraborate SrB_4O_7 (SBO) is known to be an highly suitable material in electron optics [1]. During last few year, SBO attracts a great attention researchers aimed at development and use of dosimetric materials. SBO belongs to rhombic system, space group $Pnm2_1$, a = 10.709(2) Å, b = 4.4255(7) Å, c = 4.2341(9) Å, V = 200.7 Å^3, d_{calc} = 4.011 g/cm^3, Z = 2 [1]. The SBO crystal structure is defined by the boron-oxygen framework. A specific feature of that compound is that the framework is formed by fourfold-coordinated boron atoms. The presence of an oxygen atom common for three tetrahedrons instead of two ones as in other borates is also a distinguishing feature. Anionic $(B_3O_9)^{9-}$ groups shaped as 6-membered opened rings are connected together by means of the common oxygen atoms and form chains extended along the [100] axis. The chains, being connected by oxygen atoms again, form layers parallel to the (100) plane and the layers are connected in turn into a three-dimensional network by bridge atoms. The Sr cations are coordinated by nine oxygen atoms. The metal cations stabilizing the framework are located in the framework voids parallel to [010] and [001] axes [2].

The presence of BO_4 tetrahedrons only in the framework (while in all borates belonging to that structure type, the polyanion is

formed by joining both boron-oxygen tetrahedrons and boron-oxygen triangles) provides the stabilization of rare-earth ions, e.g., Eu, Sm, Yb, in the bivalent state even if the compound is synthesized in air [3–5]. This makes it possible to obtain a wideband luminescence of Eu^{2+} and Yb^{2+} ions typical of interconfiguration $4f^{n-1}5d$–$4f^n$ transitions. The luminescence properties of SrB_4O_7:Eu^{2+} within a wide concentration range and the energy migration between Eu^{2+} ions have been studied in detail in [6, 7]. The presence of an intense luminescence of SrB_4O_7:Eu^{2+} peaked at $\lambda = 367$ nm allows to announce the material as an UV phospor of good promise [8].

It has been shown [9] that SBO exhibits an intrinsic TSL comparable with that of TLD-700 in the order of magnitude. Due to its non-hygroscopicity combined with a high TSL yield, SBO can be considered as a prospective material for thermoluminescence dosimetry. The introduction of rare-earth activators is known to provide a substantial improvement of TSL yield for various materials. It has been shown before [10, 11] that the activation with Ce and Sm ions is inefficient while activation with Dy [12, 13] or Eu [12, 14] provides the TSL yield improved by several times. At the same time, the problems of radiation-induced defect formation in rare-earth activated SBO crystals do not find any sufficient attention in modern literature. Only recently, we have proposed a TSL mechanism for SBO:Eu^{2+} polycrystals associated with the decay of an F^+ center (oxygen vacancy having one captured electron) followed by radiative relaxation of a Eu^{2+} ion [14], but it cannot be considered to be a definitive one. The TSL of SBO:Eu^{2+} single crystals is not described at all, because borate single crystals are difficult to grow due to high melt viscosity and trend to considerable overcooling [15]. Thus, this work is aimed at study of the radiation-induced defect formation mechanisms in SrB_4O_7:Eu^{2+} single crystals.

The SBO:Eu^{2+} was synthesized by solid-phase method at temperatures of 973 to 1073 K. Strontium carbonate $SrCO_3$ (special purity grade) and boric acid H_3BO_3 (chemical purity grade) in stoichiometric ratio were used as the starting materials. Europium was introduced as oxide Eu_2O_3 (special purity grade). The final product phase composition was controlled by XPA. The SBO:Eu^{2+} single crystals were grown by Czochralski technique from platinum crucibles in air onto single crystal seeds oriented

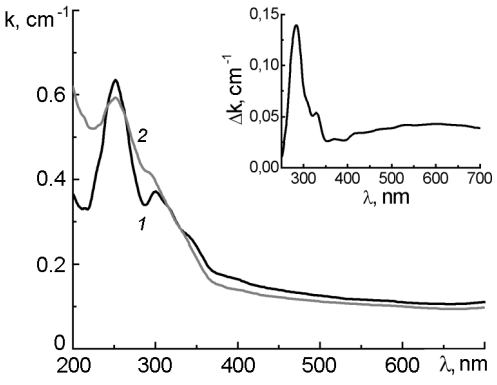

Fig. 1. Absorption spectra of a SrB_4O_7:Eu^{2+} single crystal prior to (*1*) and after (*2*) γ quanta irradiation (10^6 rad dose). Inset: differential absorption spectrum of unirradiated and irradiated SrB_4O_7:Eu^{2+} single crystal.

along the [001] direction. The rotation and pulling speeds were 20 rpm and 0.25 mm/h, respectively. The axial temperature gradient in the crystallization zone was 70 K/cm. Block type single crystals were obtained in the course of the growing experiments. Transparent polished samples of 5×5×2 mm3 size were cut out of homogeneous parts of the crystals and used in this work. The grown single crystals had the following crystallographic characteristics: a = 10.709(2) E, b = 4.4255(7) E, c = 4.2341(9) Å, V = 200.7 Å^3. The europium concentration in the crystals, as determined by chemical analysis, was 0.033 at. % .

Optical absorption spectra were measured using a Specord M40 UV-VIS double-beam spectrophotometer. The photoluminescence was studies on an automated SDL-2 setup (LOMO) under excitation with a Xe lamp. The samples were irradiated with γ or X-ray quanta at room temperature. A RUP-150/300-10-1X-ray unit (Cu anode, U = 160 kV, I = 9 mA) and ^{60}Co γ source (E_γ = 1.2 MeV) were used at the irradiation. The TSL curves were recorded using a home-made setup equipped with a FEU-79 PMT. The samples were heated using a RPM-2 heat controller at a rate of 5 K/min.

In Fig. 1, shown is the optical absorption spectrum of SBO:Eu^{2+} single crystals (curve *1*). The absorption is presented by two bands in the UV range peaked at 250 and 300 nm corresponding to the transitions from the ground $^8S_{7/2}$ state of Eu^{2+} ion to the excited states of mixed $4f^65d$ configuration. Strontium ion occupies one equivalent crystallographic position in the SBO crystal structure, the coordination number being 9

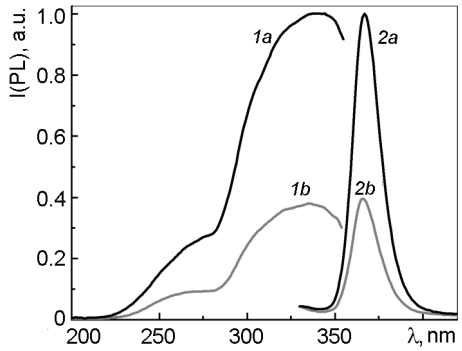

Fig. 2. Photoluminescence excitation spectra (λ_{em} = 367 nm, curves *1*) and photoluminescence spectra (λ_{ex} = 302 nm, curves *2*) of a SrB_4O_7:Eu^{2+} single crystal prior to (a) and after (b) X-ray irradiation (9000 R dose).

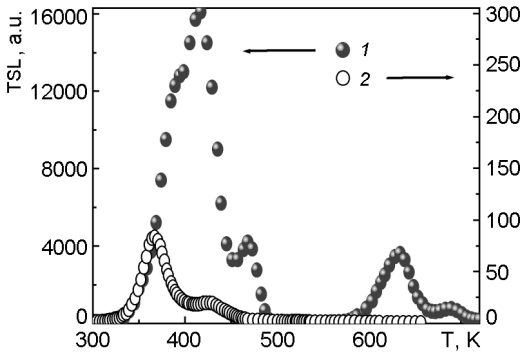

Fig. 3. TSL curves of SrB_4O_7:Eu^{2+} (*1*) and SrB_4O_7 (*2*) single crystals irradiated by X-ray quanta (9000 R dose).

and the point symmetry C_s. Similar ionic radii values of the elements ($r_{Sr^{2+}}(6)$ = 1.32 Å, $r_{Eu^{2+}}(6)$ = 1.31 Å) favor the substitution of Sr^{2+} by Eu^{2+} in the SBO crystal. Under the crystal field, the *d*-states of Eu^{2+} become split into two levels, t_{2g} and e_g. It is just the transitions to those levels that are observed in the absorption spectrum.

The photoluminescence spectrum of SBO:Eu^{2+} crystals consists of a wide band peaked at 367 nm that corresponds to the $4f^6 5d \rightarrow 4f^7$ ($^8S_{7/2}$) transitions in Eu^{2+} ion (Fig. 2). The photoluminescence excitation spectrum agrees with data from [4, 6] and contains wide bands in the 250–275 and 300–340 nm ranges that are observed also in the optical absorption spectra. The X-ray luminescence spectrum of SBO:Eu^{2+} crystals is similar to the photoluminescence one, thus evidencing the presence of an efficient channel of the energy transfer to the emission centers of Eu^{2+} according to a recombination mechanism.

Irradiation of SBO:Eu^{2+} crystals with X-ray or γ quanta results in a decreased intensity of the 250 and 300 nm absorption bands (Fig. 1, curve *2*) and in decreased photoluminescence intensity at 367 nm (Fig. 2, curve *2b*). This is due to the radiation-induced transition of a fraction of Eu^{2+} ions into trivalent charge state ($Eu^{2+} \rightarrow Eu^{3+}$). The excess charge may be compensated either due to formation of a radiation-induced strontium vacancy by impact mechanism or to local deformation of the boron-oxygen framework, since Eu^{3+} ionic radius is smaller than that of Eu^{2+} ion (1.09 Å and 1.31 Å, respectively). The fact that SBO:Eu^{2+} crystals show a TSL even after a UV irradiation [16] allows to suppose that the charge compensation occurs according to the second mechanism, since the UV energy is clearly insufficient to displace the strontium ion into an interstice. The experimental fact of the Eu ion charge state change is confirmed by simulation of the strontium tetraborate electron structure using the molecular orbital method. According to [16], the ground state of Eu^{2+} is about 3.9 eV higher than the valence band top. Taking into account the estimated band gap width for SBO (about 9 eV [16]), it is obvious that the Eu^{2+} ion act as an effective hole capturing center in SBO crystal.

Fig. 3 presents the TSL curve of SBO:Eu^{2+} single crystals irradiated with X-ray quanta in comparison to that of SBO ones. The SBO:Eu^{2+} single crystal TSL is presented by three main peaks in the 300–500 K range and by high-temperature peaks above 600 K (Fig. 3, curve *1*). The partial overlapped TSL peaks do not provide any correct evaluation of the charge carrier activation energy. To determine the parameters of the high-temperature TSL peak at 418 K being of the highest practical importance, the crystal was annealed at 378 K. The peak activation energy determined using the Chen's method after the annealing is 0.69 eV, first order kineticsr. It is seen from Fig. 3 that the SBO activation with Eu^{2+} ion does not result in any new TSL peaks but favors the intensity increase of the existing ones. The spectral composition of SBO:Eu^{2+} single crystal TSL corresponds to the Eu^{2+} ion emission. Thus, the TSL curves of SBO:Eu^{2+} can be supposed to be due to the decay of electron capturing centers.

It is just the F-like centers (anionic vacancies with one or two captured electrons) that are the typical electron capturing cen-

ters in the framework type borate crystals, including SBO. The Coulomb repulsion forces cause a lower stability of the F center (oxygen vacancy with two captured electrons) as compared to that of the F^+ one (oxygen vacancy with one captured electron). According to [16], the F center formation in the O4 position results in three energy levels appearing in the crystal band gap, namely, those lying 0.1 eV above the valence band top, 0.1 eV under the conductivity band bottom and 3.1 eV above the valence band top. The captured electrons are supposed to occupy the first mentioned level. Such traps are obviously unstable at room temperature. Thus, in our opinion, it is just the F^+ centers that are the electron capturing centers in SBO:Eu^{2+} crystals. This statement is confirmed by data on the induced optical absorption in SBO:Eu^{2+} single crystals (inset in Fig. 1). The wide band in long-wavelength spectral region (400 to 700 nm) is typical of $1s \rightarrow 2p$ absorption of F^+ centers [17].

The main radiation-induced processes in SBO:Eu^{2+} crystals are the charge state change of Eu ions ($Eu^{2+} \rightarrow Eu^{3+}$) and the F^+ center formation by the impact mechanism or due to recharging of intrinsic oxygen vacancies. Let various possible mechanisms be considered resulting in a radiative recombination of charge carriers in the course of TSL. The tunneling or direct recombination of an electron (released under thermal decay of an F^+ center) with a hole captured at an Eu^{3+} ion results in appearance of an excited state $(Eu^{2+})^*$ that relaxes emitting a characteristic light quantum: $Eu^{3+} + e^- \rightarrow (Eu^{2+})^* \rightarrow Eu^{2+} + h\upsilon$. Then the three peaks in the TSL curve in the 350 to 500 K range are connected most likely with the decay of F^+ centers located in non-equivalent crystallographic positions and differing in the activation energy values. The deep traps responsible for the high-temperature TSL peak at 634 K may be associated with the presence of uncontrollable impurities in the single crystal which are not detected by XPA [18]. The high-temperature annealing restores the initial Eu^{2+} photoluminescence intensity and the absorption coefficient near 250 and 300 nm.

To determine the crystallographic positions of atoms instead of which the radiation-induced vacancies may appear, we have considered the SBO crystal structure (Fig. 4). Oxygen atoms occupy four independent positions in the structure. O1 and

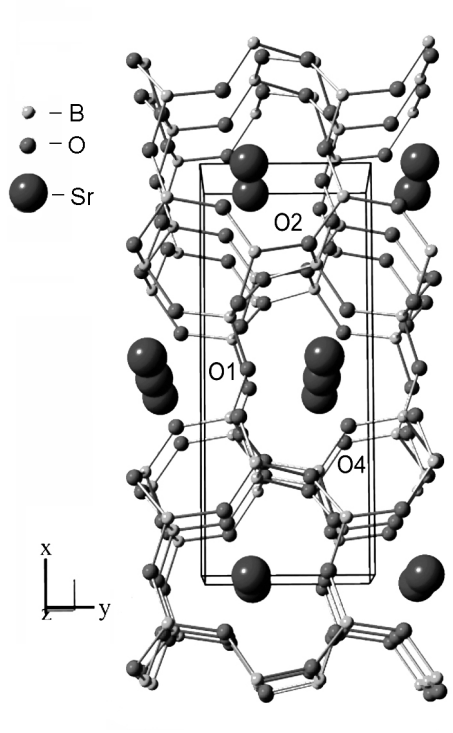

Fig. 4. SrB_4O_7 single crystal structure. A unit cell is shown by lines.

O2 atoms are the bridge ones, O2 connecting the boron-oxygen chains extended along the [100] direction into a boron-oxygen layer parallel to (100) while O1 cross-linking the adjacent layers into a three-dimensional framework. The bridge bindings in any crystal structure are known to be the weakest ones [19]. Therefore, the oxygen vacancies are formed under radiation most probably in the crystallographic positions of O1 and O2. The interatomic bindings within the chains forming the basic elements of the boron-oxygen link are much more difficult to break down. However, a peculiar oxygen atom O4 is present in the chains that is common for three boron-oxygen tetrahedrons (Fig. 4). It is characterized by considerably elongated bindings, thus, those are much weaker (average B–O4 distance is 1.55 Å while the B–O distances for other oxygen atoms are 1.36 to 1.47 Å long). Therefore, the O4 atom is also a potential precursor of a radiation-induced vacancy. Thus, the three peaks in the TSL curve of SBO:Eu^{2+} single crystals are associated with thermal decay of electron capturing centers, namely, F^+ centers localized at the sites of O1, O2, and O4 oxygen atoms.

To conclude, it has been shown that the induced optical absorption of the irradiated SBO:Eu^{2+} single crystals in the 400 to

700 nm range may be due to $1s \rightarrow 2p$ transitions of F^+ centers. The TSL of SBO:Eu^{2+} single crystals in the 300 to 500 K range is associated with decay of electron capturing centers (F^+ centers) localized in non-equivalent positions. Europium ions in the SBO:Eu^{2+} single crystals are the capturing centers and those of the charge carrier radiative recombination. Proceeding from the SBO crystal structure, the positions of O1 and O2 bridge oxygen atoms as well as that of O4 one coordinated by three boron atoms are most probable precursors for the electron capturing centers.

Authors are thankful to A.Raevskiy for assistance in experimental work.

References

1. Yu.S.Oseledchik, A.L.Prosvirin, V.V.Starshenko et al., *J. Cryst. Growth*, **135**, 373 (1994).
2. F.Pan', G.Shen, R.Wang et al., *J. Cryst. Growth*, **241**, 108 (2002).
3. Z.Pei, Q.Su, *J. Alloys and Compounds*, **198**, 51 (1993).
4. Z.Pei, Q.Zeng, Q.Su, *J. Phys. Chem. Solids*, **61**, 9 (2000).
5. Q.Su, H.Liang, T.Hu et al., *J. Alloys and Compounds*, **344**, 132 (2002).
6. K.Machida, G.Adachi, J.Shiokawa, *J. Luminescence.*, **21**, 101 (1979).
7. A.Meijerink, J.Nuyten, G.Blasse, *J. Luminescence.*, **44**, 19 (1989).
8. D.S.Thakare, S.K.Omanwar, P.L.Muthal et al., *Phys. Stat. Sol. (a)*, **201**, 574 (2004).
9. M.Santiago, A.Lavat, E.Caselli et al., *Phys. Stat. Sol. (a)*, **167**, 233 (1998).
10. J.Paun, A.Iozsa, S.Jipa, *Radiochem. Radioanal. Lett.*, **28**, 411 (1977).
11. H.M.Diab, *Rad. Effects and Def. Solids*, **160**, 137 (2005).
12. A.Lavat, C.Graselli, M.Santiago et al., *Crys. Res. Technol.*, **39**, 840 (2004).
13. J.Li, J.Q.Hao, C.Y.Li et al., *Radiat. Meas.*, **39**, 229 (2005).
14. M.F.Dubovik, T.I.Korshikova, S.V.Parkhomenko, A.V.Tolmachev, *Crystallography Reports*, **50**, S141 (2005).
15. N.I.Leonyuk, *J. Cryst. Growth*, **174**, 301 (1997).
16. K.C.Mishra, J.K.Berkowitz, B.G.DeBoer, E.A.Dale, *Phys. Rev. B*, **37**, 7230 (1988).
17. V.Yu.Ivanov, V.A.Pustovarov, E.S.Shlygin et al., *Phys. Solid State*, **47**, 466 (2005).
18. R.H.Bube, Photoconductivity of Solids, Tohm Viley Inc., NY-London, (1960).
19. G.B.Bokiy, Introduction to Crystal Chemistry, MGU Publ., Moscow (1954) [in Russian].

Термостимульована люмінесценція монокристалів SrB_4O_7:Eu^{2+}

Р.П.Явецький, О.Ф.Долженкова, О.В.Толмачов, С.В.Пархоменко, В.М.Баумер

Вперше вивчено термостимульовану люмінесценцію монокристалів SrB_4O_7:Eu^{2+}, опромінених гама та рентгенівськими квантами, у порівнянні з монокристалами SrB_4O_7. Наведене оптичне поглинання в області $\lambda = 400–700$ нм приписано $1s \rightarrow 2p$ переходам F^+-центрів. Показано, що іони Eu^{2+} одночасно виступають пастками, а також центрами випромінювальної рекомбінації носіїв заряду. На основі вивчення ТСЛ, оптичного поглинання і фотолюмінесценції монокристалів SrB_4O_7:Eu^{2+} запропоновано механізм ТСЛ, пов'язаний з розпадом F^+-центрів, що знаходяться у нееквівалентних кристалографічних позиціях, з наступною випромінювальною рекомбінацією носіїв заряду на іонах європію. Обговорюються можливі позиції локалізації радіаційних дефектів у кристалічній структурі SrB_4O_7.