Radiative-optical Properties of Additively Colored BeO Crystals[1]

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Abstract – Thermally stimulated processes in additively colored berullium oxide (BeO) single crystals have been investigated. X-ray stimulated luminescence spectra were measured and the parameters of glow curves at the different heating rates were determined. A phenomenon of the integrated thermoluminescence reduction against the heating rate increase was found for main dosimetric peak of the anion-defective beryllium oxide. The character of the thermally stimulated processes in BeO crystals was compared with the same processes in α-Al$_2$O$_3$ crystals

1. Introduction

The radiation treatment results in modification of radiative-optical features of binary oxide crystals of MgO, BeO, α-Al$_2$O$_3$, et al [1]. Taking into account their excellent radiation stability, we could produce optically significant defects in these materials using solely corpuscular's irradiation (neutrons, electrons or ions). The photon's irradiation results in the changing of the charge states of the lattice or impurity defects.

Another method of the defect production in the mentioned materials is a thermo-chemical treatment at the different conditions resulting in the deficit of the components in the anion or cation sublattices [2]. The important feature of this method is the production of the significantly more thermally stable vacancy's defects in comparison with the radiation produced defects. Besides, anion vacancies are more thermally stable than vacancies of the cation sublattice. The mentioned preferences of thermo-chemical treatment have been used for the synthesis of anion-defective α-Al$_2$O$_3$ single crystals known as sensitivity detectors of ionizing irradiation for thermoluminescence dosimetry [3–5].

Thermo-chemical coloring of α-Al$_2$O$_3$ crystals were ensured the following rigid reduction conditions: high temperature and low partial pressure of oxygen. These conditions are an optimal for the diffusion of oxygen out of the crystal or its melt (substractive coloring). The yield of thermoluminescence of such anion-defective crystals was proportional to the concentration of the anion vacancies reached the value of 10^{17} cm^{-3} [5].

Single crystals of BeO and α-Al$_2$O$_3$ are wide-gap oxides with low symmetry of the crystal lattice. So, some manifestations of the electronic excitation's relaxation are similar for both materials. In particular, a phenomenon of the self-tapping of the excitons have been found in α-Al$_2$O$_3$ and BeO [6,7]. Therefore, we could wait a similarity of the thermally stimulated processes in both oxides, too, if we could produce the similar excess defect concentrations in anion or cation sublattices.

Some aspects of an application of beryllium oxide or BeO-containing materials in dosimetry were studied mainly for ceramic samples with different impurity compounds and regimes of the preparation. [8]. There were not special interest to control or to purposefully change the concentration of lattice defects in early works. This study deals with analysis of the thermally stimulated processes in the modified with thermo-chemical coloring anion-defective crystals of BeO and comparison of this processes with those investigated early for anion-defective crystals of α-Al$_2$O$_3$ [5].

2. Experimental

The subjects of study were nominally pure single crystals of BeO grown from a solution in a sodium or lithium tungstate melt by V.A.Maslov according technology described in [9]. Initial stoichiometric samples underwent thermal treatment in a metal beryllium vapour in the order to produce anion nonstoichiometry (additive coloring) [10]. During three hours process the temperature level was 1900°C and the beryllium vapour pressure value was 2.5 kPa. The concentration of anion vacancies (F-centers) were determined using an absorption spectrum of additively colored crystal in the band with the maximum at 6.6 eV and FWHM 0.82 eV. Using Smakula's formula, the concentration value was estimated in the order of $3 \cdot 10^{17}$ cm^{-3}.

Thermally stimulated luminescence (TL) of the samples were measured following ^{90}Sr/^{90}Y irradiation. TL at line and step heating, X-ray stimulated luminescence (XL) and thermally quenching of TL have been measured using standard methods.

3. Results

X-ray stimulated luminescence spectra of initial and additively colored BeO crystals at T=300K are presented in Figure 1.

Intrinsic luminescence band at 4.9 eV dominates in XL spectrum of initial crystal. This UV-luminescence

has been described early in terms of the self-trapping exciton's model [7]. Additive coloring results in the appearance of new band at 3.4 eV in XL spectrum (Fig. 1, curve 2). Blue luminescence was investigated in detail in [11] and has been described in terms of $^3A_1$ →$^1A_1$ transitions in F-centers. Everybody can see in Fig. 1 that blue luminescence of F-centers dominates in XL spectrum of additively colored crystals.
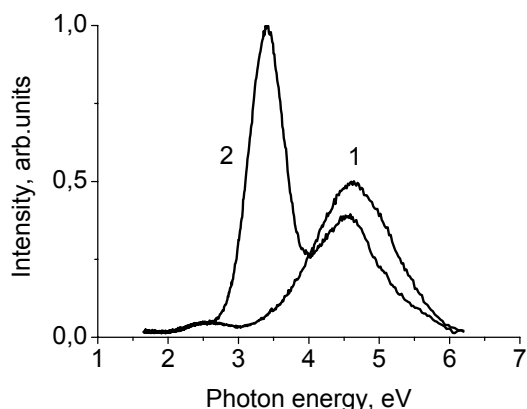

Fig. 1. X-ray stimulated luminescence spectra of initial (1) and additively colored (2) BeO crystals at T=300K

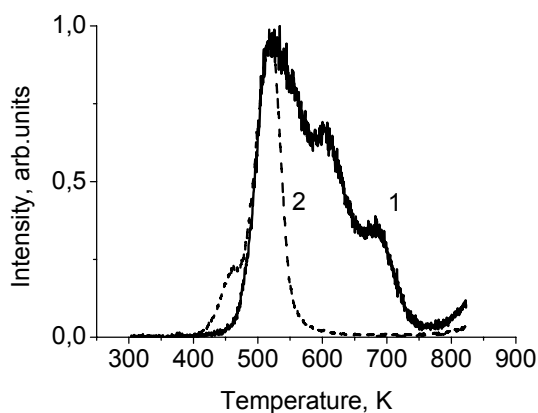Glow curves of initial and additively colored crystals following ^{90}Sr/^{90}Y irradiation are shown in Fig. 2.

Fig. 2. Glow curves of initial (1) and additively colored (2) BeO crystals following ^{90}Sr/^{90}Y irradiation. The doze level was 130 mGy and the heating rate was 0.5 K·s^{-1}

Glow curve of initial sample is a sum at least of three peaks in the temperature region of 450–750 K (Fig. 2, curve 1). The complex character of glow curve was observed early in [12] and its dominated peak has been connected with release of electrons from impurity cation traps. Additive coloring simplifies a shape of glow curve significantly (Fig. 2, curve 2). We see in Fig. 2 a single dominated peak at T=520K and a weak shoulder in its low temperature range.

Observed in Figures 1 and 2 transformations of XL spectrum and glow curve following an additive coloring of BeO crystal are analogous to those observed in α-Al$_2$O$_3$ following F-center creation as a result of the substractive coloring [5]. The suitable position of dominated peak as well as the simple sharp of glow curve is attractive to use additively colored crystals of BeO for the purpose of thermoluminescence dosimetry.

From this point of view some peculiarities of thermoluminescence (TL) of additively colored crystals of BeO were investigated more attentively. Usually, the intensity and temperature of TL peak increase with heating rate. Simultaneously the anomalous reduction of integrated TL has been recorded. The results of the measurements of TL parameters of anion-defective BeO crystals are presented in Table 1.

Table I. TL parameters at the different heating rate

Heating rate, K·c^{-1}	TL intensity	Integrated TL	Temperature of maximum, K
0.5	0.21	1.00	526
1	0.30	0.78	536
2	0.49	0.71	556
4	0.62	0.46	574
6	0.76	0.38	599
8	0.90	0.34	625
10	1.00	0.32	644

The similar dependence of the changing of TL parameters against heating rate was observed for substractively colored crystals of α-Al$_2$O$_3$ [5]. In the last case the reduction of integrated TL against heating rate is connected with nonradiative relaxation of uncaptured carriers, including repeated capture on the thermally more deep traps. Really, the measurement of RL temperature behavior in the band of F-centers luminescence of additively colored BeO crystals demonstrates the temperature decay of XL in the range at 400–500K (Figure 3).

The measured curve of the temperature decay of F-centers XL is easily described using a Mott-Seitz formalism [13]:

$$\eta(T) = \frac{I(T)}{I_0} = \frac{1}{1 + \omega \cdot \exp(-\frac{W}{kT})}, \qquad (1)$$

where η(T) – luminescence efficiency, I$_0$ – RL initial intensity of the luminescence, k – Boltzmann constant, T – sample temperature, ω and W – selective parameters with the value of ω=10^6 и W=0.55 eV. More detail comparison of the integrated TL against temperature position of TL peak depends on heating rate and the temperature decay of XL in the band at 3.4 eV for additively colored BeO crystals are presented in Figure 4.
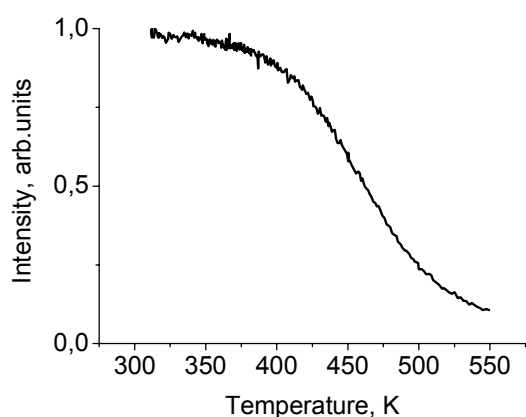
Fig. 3. Temperature behavior of X-ray stimulated luminescence of additively colored BeO crystals measured in the band at 3.4 eV and in the crystal's cooling regime
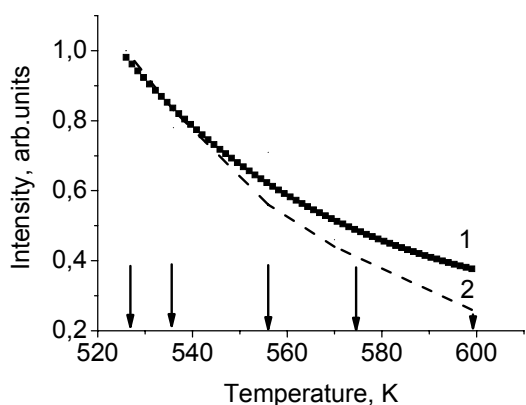

Fig. 4. Integrated thermoluminescence of additively colored BeO crystals (curve 1) against the temperature position of TL peak (vertical arrows) and the temperature decay of the radioluminescence in the band at 3.4 eV (curve 2)

The similar behavior of curves 1 and 2 (Figure 4) gives evidence of influence of temperature decay of F-centers luminescence on the changing of TL parameters following heating rate increase. (Table 1).

To find additional evidences of the supposed influence the computer modeling of glow curves were made according to algorithm described in [13]. The best coincidence of model and experimental glow curves was received if the model equation includes the component calculated temperature decay:

$$I(T) = \eta(T) S n_0 \exp\left[-\frac{E}{kT}\right] \cdot \left[1 + \frac{(b-1)S}{\beta} \int_{T_0}^{T} \exp\left[-\frac{E}{kT'}\right] dT'\right]^{\frac{b}{b-1}}$$

where $I(T)$ – TL intensity, $\eta(T)$ – luminescence efficiency, S – frequency factor, n_0 – initial concentration of the captured carriers, E – activation energy of TL process, T_0 – initial temperature of heating, β – heat-

ing rate, b – order of kinetic, k – Boltzmann constant. The parameters of two traps corresponded to two peaks of the glow curves (Figure 2, curve 2) were found during process of modeling: $E_1=1.442$ eV, $n_{01}=2.0 \cdot 10^2$ cm^{-3}, $E_2=1.448$ eV, $n_{02}=8.5 \cdot 10^3$ cm^{-3}. Parameters b and S reached the values of $b_1=2$, $b_2=1$ и $S=5.0 \cdot 10^{11}$, consequently. In search of best satisfactory value of the activation energy of more intensive TL peak (E_2) the result of step heating experiment was taken into account. The measurement of glow curve following fractional glow technique was done accordingly the method described in [14] and results in experimental determination of the average activation energy value (Figure 5). The presence of the weak TL peak does more difficult to use fractional glow technique. At the same time, if we measure the glow curve following UV-irradiation from mercury lamp (DRT-200 type) a weak TL peak is absence. The parameters of the main TL peak didn't change after UV-irradiation and the average activation energy can be estimated using fractional glow method.
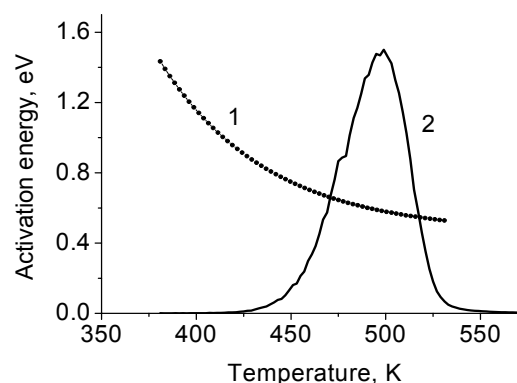

Fig. 5. Average activation energy of thermoluminescence (1) of additively measured BeO crystals calculated from experimentally measured glow curve (2) following fractional glow technique

4. Conclusions

The results discussed above show that a lot of peculiarities of thermally stimulated processes discovered in additively colored BeO crystals don't follow from known models described the kinetic of thermoluminescence in solids. More detail, the integrated TL decrease against heating rate increase and the average activation energy of themoluminescence decrease in the temperature range of the main TL peak. The investigation of the temperature behavior of radioluminescence permits to connect the mentioned peculiariries with TL temperature decay. The similar peculiarities were early obtained in anion defective crystals of α-Al$_2$O$_3$ [5]. Consequently, the mechanisms of TL formation have similar character in both materials. This conclusion permits to use anion defective crystals of BeO in TL dosimetry, especially taking into account body equivalent character of beryllium oxide.

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