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Photo-transferred thermoluminescence of shallow traps in β-irradiated BeO ceramics

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ABSTRACT

Photo-transferred thermoluminescence signals from beryllium oxide (BeO) ceramics were measured in the low temperature range of 10–300 K. Samples irradiated at room temperature using a Sr^{90}/Y^{90} beta source were cooled down to 10 K and trapped charges were photo-transferred at this low temperature using the light from a high power blue LED emitting at ~470 nm (2.6 eV). Thermoluminescence glow curve recorded at 0.2 K/s heating rate exhibited three peaks around 90, 160 and 185 K. The analyses of the TL peaks of the glow curve were accomplished using curve fitting, differential and peak shape methods. Results obtained from these techniques are in good agreement about the presence of three trapping centers in BeO ceramics with activation energies of 0.24, 0.48 and 0.56 eV. Moreover, the analyses indicated that first-order kinetics (slow retrapping) is the dominant mechanism in the luminescence process. Heating rate dependence of the glow curves was also investigated between 0.2 and 0.8 K/s rates.

1. Introduction

Beryllium oxide (BeO) is a material of great interest in the personal dosimetry applications due to its near tissue-equivalence (Z_{eff}=7.1) and high sensitivity to radiation dose. Moreover, the availability in easily handled ceramic disc form, high thermal conductivity and low-cost made it very attractive to researchers. However, toxicity of the material in powder form and the light-induced fading of the thermoluminescence (TL) signal have prevented the usage of the BeO as a TL dosimeter in a broad application area. Recent studies on the optically stimulated luminescence (OSL) characteristics of BeO have revealed that OSL mode of the material has higher sensitivity than in the TL mode [1–3]. TL and OSL characteristics of the material have been reported in a large number of reports. Three and two TL peaks were revealed in BeO when excited by β particles (at 50, 90 and 280 °C) and ultraviolet light (at 90 and 280 °C), respectively [4]. Lakosi et al. observed two peaks at nearly 200 and 360 °C in the TL glow curve of the BeO [5]. In another study, TL glow curve measured at 1 K/s heating rate exhibited peaks around 180 and 287 °C [6]. Bulur et al. observed quite intense OSL signal using broad-band stimulation ranging from 420 to 550 nm [1]. From the analysis of data, thermal quenching energy and trap depth were found nearly as 0.5 and 1.7 eV, respectively. Bulur et al. have expanded their studies on the BeO ceramics by performing linearly modulated OSL experiments [7]. Analysis on the temperature dependence of the OSL signal resulted in that it originates from traps becoming unstable at around 340 °C and thermal quenching energies of the emission process were obtained as 0.55 and 0.59 eV. In another paper of Bulur et al., time resolved OSL studies on BeO ceramics resulted in thermal quenching and thermal assistance activation energies of 0.56 and 0.15 eV, respectively [8]. Recently, low temperature TL properties of X-ray irradiated BeO ceramics were investigated by Petrenko et al. [9] where the TL glow curve exhibited six peaks around 85, 150, 169, 187, 210 and 244 K. The peak shape method revealed the activation energy of the trap center at 85.2 K as 0.24 eV. In the same paper, authors have also reported the X-ray induced luminescence of the BeO ceramics. The observed spectra resulted in broad emission bands at 4.4 and 4.2 eV recorded at 6 and 293 K, respectively. Low temperature TL of BeO:Zn single crystals were also studied by Ogorodnikov et al. [10]. Four peaks at 20, 43, 145 and 307 K which are absent in the TL curve of BeO, were observed in the glow curve of BeO:Zn.

Photo-transferred TL (PTTL) is an observed phenomenon in many materials [11]. In PTTL process, TL emission is due to the charges localized at shallower traps which are filled by exciting the charges from deeper traps. Previously, Bulur has investigated the PTTL signals from BeO ceramics above room temperature [12]. Three peaks around 75, 220 and 340 °C were observed in the PTTL glow curve. In the present work, we investigate and report, for the first time, the PTTL characteristics of the BeO ceramics below room

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temperature (10 – 300 K). The observed peaks were analyzed using different methods to find the activation energies of the traps taking role in the PTTL emission. Heating rate dependence of the glow curve was also presented in the paper.

2. Experimental details

BeO ceramic samples used in the experiments were in the form of disks of diameter 4 mm and thickness of ~1 mm (Thermalox 995, Brush Wellman Inc.). Filling of the deeper traps were accomplished at room temperature by irradiating the samples with a Sr^{90}/Y^{90} beta source by Amersham (initial activity was about 40 mCi, bought in 1994). The source is mounted in an optical dating system (ELSEC. 9010) where a solenoid driven source holder was supplied as an attachment. Source to sample distance is a bit more than 2 cm, but colimated as it passes through a 10 mm hole in the lead shield. A sample of diameter 10 mm can be irradiated homogeneously using the system. The dose rate is approximately 27 mGy/s. The radiated sample was placed inside a closed cycle helium gas cryostat (Advanced Research Systems, Model CSW-202) and cooled to temperature of 10 K. Sample temperature between 10 and 300 K was adjusted using a LakeShore Model 331 temperature controller which can ramp the temperature linearly at a maximum rate of 1.0 K/s. A light tight measurement chamber which carries the detector, light source and the optics was connected to the optical access port of the cryostat (quartz window). The sample was placed to the focal plane of the optics for both measurement and illumination. Luminescence emitted from the sample was measured using a photomultiplier tube (Hamamatsu R928; spectral response: 185 to 900 nm) working in photon counting regime. Pulses from the photomultiplier were converted into TTL pulses using a fast amplifier/discriminator (Hamamatsu Photon Counting Unit C3866) and counted by the counter of the data acquisition module (National Instruments, NI-USB 6211). The sample was illuminated at low temperature using high power (3 W) blue LED emitting at ~ 470 nm (2.6 eV) and charges in the deeper traps were excited to shallower traps by this way. The flux at the sample position was about a few mW/cm^2. Software written in LabView™ graphical development environment was utilized to control the used devices by a computer. For a TL measurement, the sample was illuminated for 120 seconds at 10 K, after 60 seconds of waiting (to allow the unstable components to decay) the sample was heated linearly and the emitted luminescence is recorded as a function of temperature.

3. Results and discussion

TL spectra were recorded in the temperature range of 10–300 K in our measurements. However, TL glow curves throughout the paper are presented in the range in which TL peaks are observed. PTTL takes its name due to the transition of charge carriers from deep levels to shallower levels. These transferred charge carriers take role in the luminescence process. The physical explanation and experimental confirmation of calling our observed spectra as PTTL curve are given as: (i) Physically; BeO is a large band gap material (about 10 eV) it is not possible to induce direct TL using blue light with 2.6 eV photons. Irradiations were done at room temperature, and then the sample was cooled down for the experiments. Therefore one should expect that only charge trapping states that are stable at room temperature is populated by the beta irradiation. Using blue light illumination at low temperatures

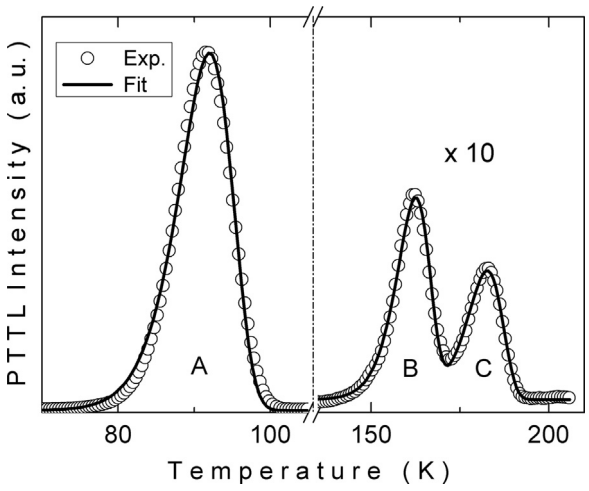

Fig. 1. Experimental TL glow curve (open circles) of BeO ceramics with heating rate $\beta = 0.2$ K/s. Solid curves show the fits to the experimental data.

charges at these states are supposed to be transferred to the shallower ones. (ii) Experimentally; the radiated sample at room temperature using beta source was cooled to temperature of 10 K. The cooled sample was not illuminated using LED and TL spectrum was measured in the 10–300 K range. The observed spectra did not exhibit any peak in this measurement. However, when the sample was illuminated using blue LED having energy smaller than band gap energy of the sample, the glow curve presented in Fig. 1 was observed. Under the light of these explanations, the observed curve is associated with PTTL signal. The experiments performed at a constant heating rate of 0.2 K/s resulted with the presence of three peaks around ~90, 160 and 185 K (see Fig. 1). Curve fitting, differential analysis and peak shape methods were applied to get information about the properties of the trapping centers associated with these peaks.

The curve fitting method was accomplished under the light of theoretical expressions giving the thermoluminescence intensity (I_{TL}) for first-order of kinetics as [11]

$$I_{TL} = n_0 \nu \exp\left\{-\frac{E_t}{kT} - \int_{T_0}^{T} \frac{\nu}{\beta}\exp(-E_t/kT)dT\right\} \quad (1)$$

where n_0 is the initial concentration of trapped charge carriers, ν is the attempt-to-escape frequency, E_t is the activation energy, β is the heating rate, T_0 is the starting temperature of heating process. The details of the curve fitting method were reported in our previous studies on the thermoluminescence [13,14]. In the TL experimental set-up, one of the important problems is the temperature lag effect which is known as the differences between the real temperature value of the sample and recorded temperature value. The possible reasons of these differences are thickness of the sample, non-ideal contact between the sample and heater element, temperature gradients in the heater element or through the sample. In the low temperature region, this problem is more efficient on the results of analyses method. Kitis and Tuyn introduced a method to minimize the effect of temperature gradient [15]. In the reported technique, experimental peak maximum temperature (T_m) values are corrected using the expression

$$T_{mj} = T_{mi} - c\ 1n\left(\frac{\beta_i}{\beta_j}\right), \quad (2)$$

Table 1
The peak maximum temperature (T_m), activation energy (E_t) and attempt-to-escape frequency (ν) of revealed trap (peak A) in BeO ceramics.

Rate (K/s)	Before temperature lag				After temperature lag			
	T_m (K)	E_t (eV) (Curve fit)	E_t (eV) (Peak shape)	ν (s^{-1})	T_m (K)	E_t (eV) (Curve fit)	E_t (eV) (Peak shape)	ν (s^{-1})
0.2	92.0	0.20 ± 0.01	0.22 ± 0.01	$(5.0 \pm 1.5) \times 10^9$	92.0	0.20 ± 0.01	0.22 ± 0.01	$(5.0 \pm 1.5) \times 10^9$
0.4	112.1	0.24 ± 0.01	0.24 ± 0.01	$(5.5 \pm 1.7) \times 10^9$	112.1	0.24 ± 0.01	0.24 ± 0.01	$(5.5 \pm 1.7) \times 10^9$
0.5	120.2	0.24 ± 0.01	0.23 ± 0.01	$(1.1 \pm 0.3) \times 10^9$	118.6	0.24 ± 0.01	0.23 ± 0.01	$(1.5 \pm 0.5) \times 10^9$
0.6	131.6	0.27 ± 0.01	0.27 ± 0.01	$(2.5 \pm 0.8) \times 10^9$	123.9	0.24 ± 0.01	0.23 ± 0.01	$(6.2 \pm 1.9) \times 10^8$
0.7	137.0	0.29 ± 0.02	0.29 ± 0.02	$(5.9 \pm 1.8) \times 10^9$	128.4	0.25 ± 0.01	0.25 ± 0.01	$(7.7 \pm 2.3) \times 10^8$
0.8	148.1	0.30 ± 0.02	0.30 ± 0.02	$(2.1 \pm 0.6) \times 10^9$	132.2	0.24 ± 0.01	0.24 ± 0.01	$(1.7 \pm 0.5) \times 10^8$
Meanvalue		0.26 ± 0.01	0.26 ± 0.01	$(3.7 \pm 1.1) \times 10^9$		0.24 ± 0.01	0.24 ± 0.01	$(2.3 \pm 0.7) \times 10^9$

where T_{mi} and T_{mj} are the peak maximum temperatures of glow curves obtained by heating the sample with different β_i and β_j, respectively, and c is a constant. Using the Eq. (2), the constant c is calculated using the two lower heating rates in which temperature lag can be considered as negligible. The usage of T_m values for rates of 0.2 and 0.4 K/s in Eq. (2) resulted in constant c for peak A as 29. Table 1 shows the experimental and corrected T_m values obtained under the light of determined c. The curve fitting method was applied for observed experimental and corrected/shifted glow curves separately. The fitting process successfully resulted under the light of Eq. (1) (solid line in Fig. 1). The results of curve fitting method are given in Table 1. As can be seen from the table, the activation energies obtained from glow curves with various heating rates are well-correlated with each other after applying the temperature lag method. The mean activation energy value was found as 0.24 eV for peak A. When the similar process is applied for peaks B and C, activation energies were obtained as 0.48 and 0.56 eV, respectively.

Once the TL glow curve has been fitted and E_t and T_m are determined, then we can calculate the attempt-to-escape frequency (ν) and capture cross section (S_t) of the traps according to the following expressions [11]

$$\nu = \frac{\beta E_t}{kT_m^2}\exp\left(\frac{E_t}{kT_m}\right) \text{ and } S_t = \frac{\nu}{N_c \upsilon_{th}},$$

where $N_c = 2(2\pi\, m_e^* kT/h^2)^{3/2}$ is the effective density of states in the conduction band and υ_{th} is thermal velocity of a free electron. The capture cross sections of the trap levels were calculated using the effective mass $m_e^* = 0.73 m_0$ [16]. The ν and S_t values were found as 2.3×10^9, 3.3×10^{12} and 1.1×10^{13} s^{-1} and 1.2×10^{-16}, 5.2×10^{-13} and 1.4×10^{-12} cm^2, respectively (Table 2).

The derivative of the natural logarithm of thermoluminescence intensity (Eq. 1), under the assumption of that ν is independent of T, is obtained as [17],

$$\frac{d(\ln I_{TL})}{dT} = \frac{E_t}{kT^2} - \frac{\nu}{\beta}\exp(-E_t/kT). \quad (3)$$

Since the intensity is highest at $T = T_m$, the Eq. (3) results in

$$\frac{E_t}{kT_m^2} = \frac{\nu}{\beta}\exp(-E_t/kT_m). \quad (4)$$

Using the Eq.(4), the second derivative of the $\ln(I_{TL})$ can be written at temperature of T_m as

$$\left[\frac{d^2(\ln I_{TL})}{dT^2}\right]_m = -\frac{E_t}{kT_m^3}\left(2 + \frac{E_t}{kT_m}\right) = \alpha_m \quad (5)$$

Activation energy of the observed trap can be calculated from the slope of the tangent (α_m) at $T = T_m$ of the first derivative of the thermoluminescence curve. Fig. 2 presents the graphs of the first derivative of the intensity for glow curve observed with $\beta = 0.2$ K/s. The derivatives are equal to zero at $T_m = 91.7$, 162.3 and 182.8 K with a tangential slopes of $\alpha_m = -8.86 \times 10^{-2}$, -4.85×10^{-2} and -3.87×10^{-2} for peaks A, B and C, respectively. The activation energies of the traps are calculated from Eq. (4) as $E_t = 0.21$, 0.49 and 0.55 eV using α_m values. When the differential analyses method were applied for the other curves obtained at various heating rates, the mean activation energies were found as 0.23, 0.50 and 0.56 for peaks A, B and C, respectively.

The other analysis method we have used is the peak shape method in which E_t is associated by $\omega = T_h - T_l$, where T_l and T_h are the low and high half-intensity temperatures, respectively [11]. The activation energy is obtained from

$$E_t = \frac{2.52 kT_m^2}{w} - 2kT_m.$$

The activation energy values for the observed peaks were found as 0.22, 0.47 and 0.57 eV (Tables 1 and 2). The characteristic parameter $\mu_g = (T_h - T_m)/(T_h - T_l)$ values for the traps in BeO ceramics were found between 0.42 and 0.45. These values are close to the 0.42 suggested for the slow retrapping process [11].

Heating rate dependence of the PTTL glow curves was also investigated. Fig. 3 and its insets show the glow curves obtained at the rates between 0.2 and 0.8 K/s. According to Chen and McKeever [11], T_m shifts to higher temperatures with increasing heating rate. The increase of the T_m values with increasing β was observed to be realized in our PTTL glow curves. Fig. 4 presents the dependencies of peak maximum temperatures of observed peaks on heating rates. Following Chen and McKeever, the heating rate β is related to the maximum peak temperature T_m by expression

$$\beta = \frac{\nu k}{E_t} T_m^2 \exp\left(-\frac{E_t}{kT_m}\right).$$

Table 2
The activation energy (E_t), capture cross section (S_t) and attempt-to-escape frequency (ν) of revealed traps in BeO ceramics.

Peak	T_m (K)	E_t (eV) Curve fitting method	E_t (eV) Differential analysis method	E_t (eV) Peak shape method	S_t (cm^2)	ν (s^{-1})
A	92.0	0.24 ± 0.01	0.21 ± 0.01	0.22 ± 0.01	$(1.2 \pm 0.4) \times 10^{-16}$	$(2.3 \pm 0.7) \times 10^9$
B	162.5	0.48 ± 0.02	0.49 ± 0.02	0.47 ± 0.02	$(5.2 \pm 1.6) \times 10^{-13}$	$(3.3 \pm 1.0) \times 10^{12}$
C	182.7	0.56 ± 0.03	0.55 ± 0.03	0.57 ± 0.03	$(1.4 \pm 0.4) \times 10^{-12}$	$(1.1 \pm 0.3) \times 10^{13}$

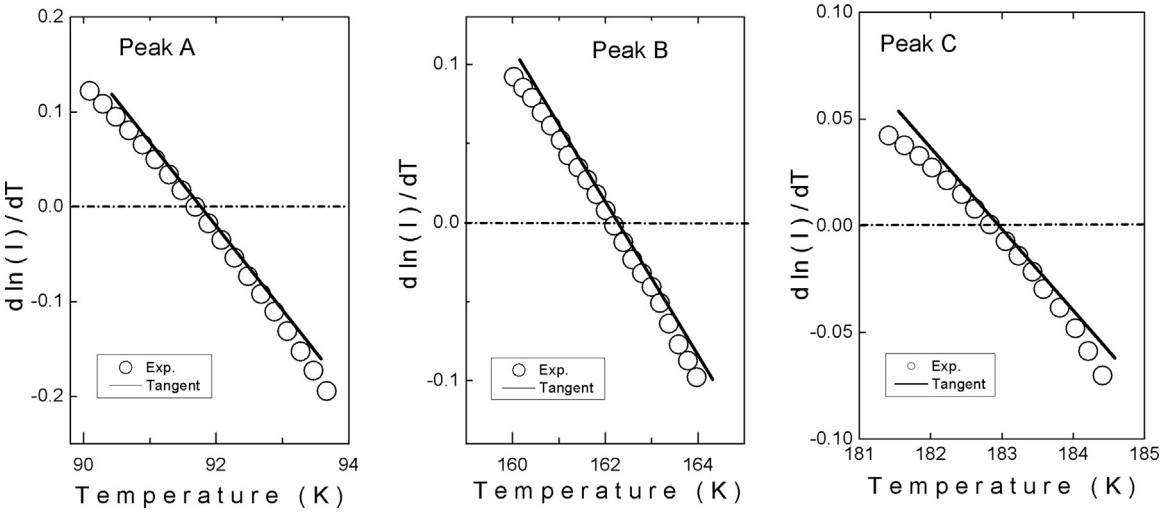

Fig. 2. Derivatives of the TL curve of BeO ceramics with heating rate β=0.2 K/s. Open circles are experimental data and the lines are the tangents at T_m=91.7, 162.3 and 182.8 K for peaks A, B and C, respectively.

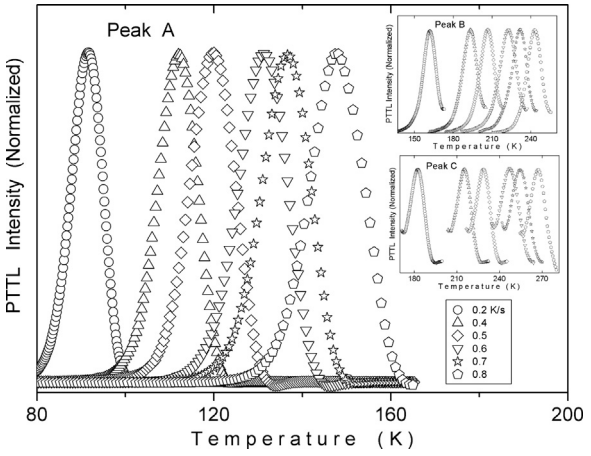

Fig. 3. Experimental normalized TL curves of BeO ceramics with various heating rates.

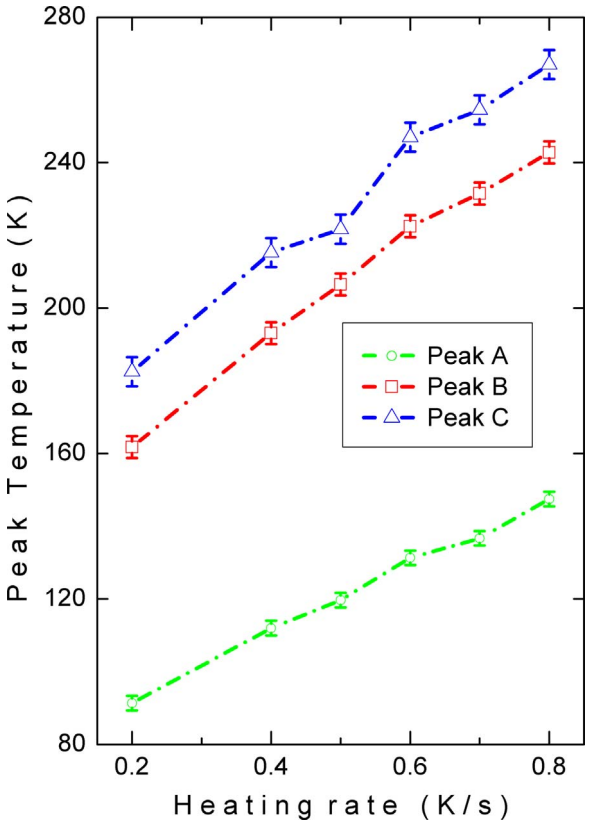

Fig. 4. Dependencies of peak maximum temperatures of observed peaks on heating rates. Dash-dotted lines are only the guides for the eyes.

The increase of β would necessarily result in an increase in the right-hand side. Because $T_m^2 \exp\left(-\frac{E_t}{kT_m}\right)$ is an always increasing function of T_m, a growth in the value of the function necessarily implies an increase in the argument T_m. In the literature, there are two analyses methods to calculate activation energy using the heating rate dependent T_m values. In these methods, E_t values are found using the slopes of $\ln\left(T_m^2/\beta\right)$ – $1/T$ and $\ln(\beta)$ – $1/T$ plots [11]. When we applied these techniques, E_t values were found much smaller than those obtained from above-given techniques. We have faced with this problem in most of our previously reported papers on thermoluminescence and thermally stimulated current in low temperature region. At this moment, there is no any evidence and/or report addressing/explaining this problem. However, we think that this problem may be due to the strong dependency of escape frequency on temperature in low temperature region.

Taking into account the revealed energies, we prepared Fig. 5 showing the energy band diagram and transitions taking role in PTTL process. The used samples were irradiated with Sr^{90}/Y^{90} beta source at room temperature to excite the electrons from valence band to conduction band. When the excited electrons return to their initial delocalized band, some of them are captured by trap centers. Since electrons in shallow centers have big probability to be excited to conduction band, these levels cannot be filled at room temperature. To fill these levels and investigate their properties, experiments are performed in low temperature region. The electrons in deep levels are excited to conduction band via a possible illumination source (blue LED in our experiment) and

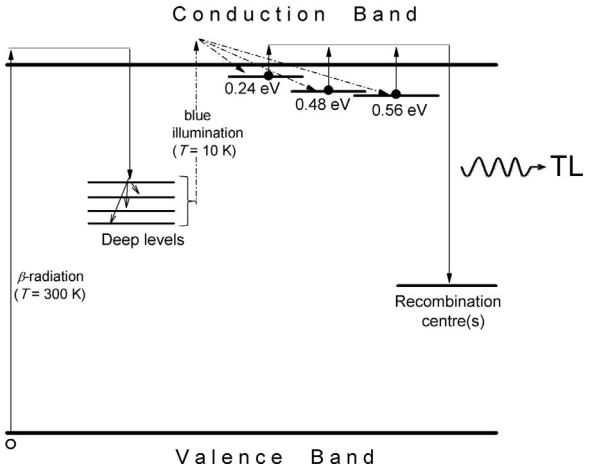

Fig. 5. Energy level diagram showing transitions in PTTL process and revealed shallow trap centers.

then trapped in shallow levels. Fig. 5 presents a simple diagram of obtained shallow traps and transitions in PTTL.

4. Conclusion

Shallow trapping centers giving luminescence below room temperature in BeO ceramics were revealed using photo-transferred thermoluminescence measurements in the temperature range of 10–300 K. The analysis of the observed PTTL glow curve using different methods resulted with the presence of three centers with activation energies of 0.24, 0.48 and 0.56 eV. The curve fitting method and peak shape analyses showed that retrapping is negligible in the luminescence process. Moreover, heating rate dependence of the peak maximum temperature of observed peaks were also investigated. The shift of the T_m values to higher values with increasing heating rate as suggested by theoretical approach was observed in the PTTL glow curves.

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