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Effect of Dy^{3+} on the thermoluminescence emission of potassium tetraborate

S. JIPA[a,b], T. ZAHARESCU[a], W. KAPPEL[a], L. M. GORGHIU[b], C. DUMITRESCU[b]
[a]*INCDIE, ICPE CA, 313 Splaiul Unirii, Bucharest 030138, Romania*
[b] *"Valachia" University of Târgovişte, 18-22 Unirii Av., Târgovişte 130082, Romania*

The general glow curve of the crystalline thermoluminescent materials exhibits one or more peaks when the charge carriers are released. The thermoluminescence glow curve provides information about the kinetic parameters, such as activation energy, order of kinetics and frequency factor. The main purpose of this thermoluminescence study is to investigate the trapping centers responsible for the thermoluminescence emission obtained for potassium tetraborate undoped and doped with Dy_2O_3 (3 moles%) samples. On the base of these curves the kinetic parameters were calculated using some of the methods described in the literature. In addition, a comparison of the results obtained by applying these methods for $K_2B_4O_7$ doped with Dy_2O_3 samples is presented.

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1. Introduction

Radiation-induced thermoluminescence (TL) is a phenomenon widely observed in inorganic substances. Most of the insulating solids have in their structure point defects, naturally occurring or artificially created, which induce electronic states in the forbidden band. The emission of light happens, when electrons (or holes) are released from traps by heating and return to stable states. These defects are strongly related to the thermoluminescence phenomenon. There are several models described in the literature, which explain the basic principles of the TL process using charge carrier traps induced by impurities named dopants. Many thermoluminescent materials, e. g. sulfate, borate, silicate, phosphate, aluminate, titanate, fluoride, carbonate and oxide have been investigated [1 – 24].

The development of new TL materials is still a goal in radiation dosimetry. Borate glasses are very useful materials for radiation dosimetry applications because of their nearly tissue equivalent response.

The basic purpose of the thermoluminescence study is the investigation on trapping centers responsible for the TL emission. The most important kinetic parameters for the characterization of TL properties are activation energy, E, the frequency factor, *s* and the order of kinetics, b.

In this paper the thermoluminescence characteristics of $K_2B_4O_7$:Dy were studied and the trapping parameters of this material are discussed.

2. Exprimental

The preparation of potassium borate was performed by mixing K_2CO_3 and H_3BO_3 in stoichiometric ratio. All the reagents were of analytical grade purity.

$K_2B_4O_7$ powder was mixed with Dy_2O_3 and the mixture was melted in air at 900°C in an electrically heated furnace. Vitrification was obtained by rapid cooling at room temperature. The resultant vitreous mass was ground and sieved to a size of 200 μm.

Gamma irradiation was performed at room temperature using ^{137}Cs GAMMATOR M-38-2 installation (USA) at a dose rate of 0.4 KGy/h.

For the thermoluminescence measurements (LTM Fimel, Harshaw apparatus), glass powders (~ 4 mg) were used. The linear heating rate was set at 5°/s and all measurements were taken in ambient atmosphere.

3. Results and discussion

The TL glow curves of undoped and Dy-doped $K_2B_4O_7$ samples are given in figure 1. The samples exhibit one TL glow peak placed at 112°C. The addition of Dy (3 mole %) to $K_2B_4O_7$ compound enhances the TL intensity by 700 times. It shows that Dy is a suitable dopant for potassium borate in respect of the enhancement in TL response.

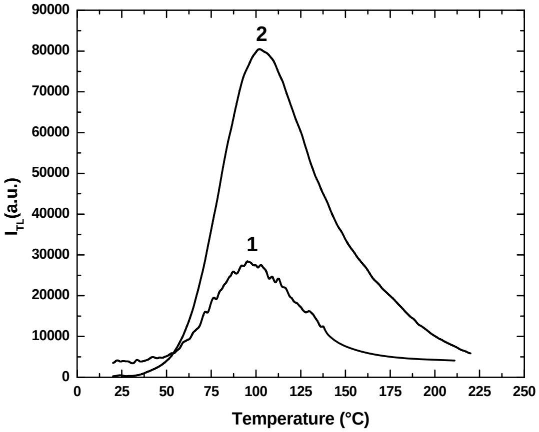

Fig. 1. The TL glow curves of pure (1) and Dy (2) doped (3 mole%) $K_2B_4O_7$ glass samples.

In Fig. 2, the variation of glow-peak temperature with heating rate for $K_2B_4O_7$:Dy is presented. As it is expected, glow-peak temperature increases with increasing heating rate. The straight line was fitted to an equation of the form (Fig. 3):

$$\ln T_m = A + B \cdot \ln\beta \tag{1}$$

where the constant A gives the value of T_m for the lower possible heating rate and B gives the variation rate of T_m according to Kitis et al [25]. The constant A and B are 5.875 and 0.03, respectively.

The kinetics parameters have been obtained using the initial rise method [26] as a first approximation, and then the peak shape methods [27].

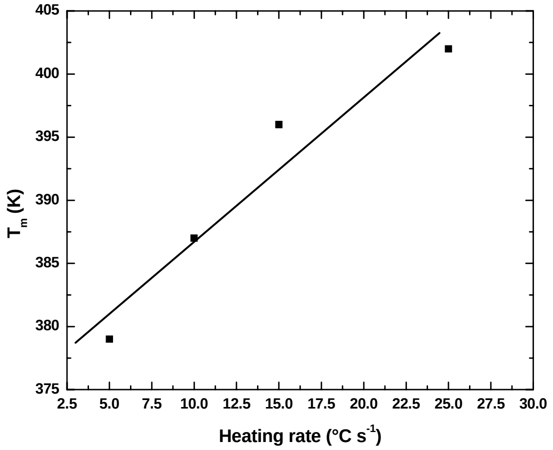

Fig. 2. Plot of glow-peak temperature from $K_2B_4O_7$:Dy against heating rate.

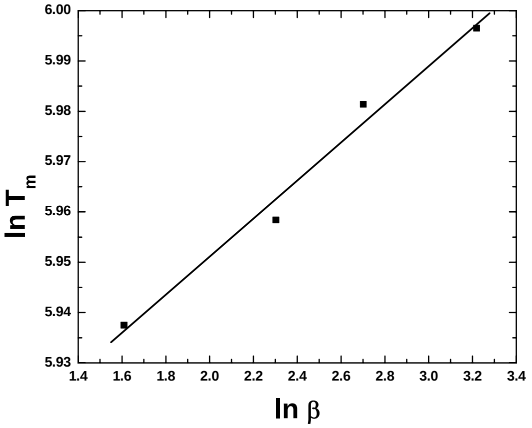

Fig. 3.Dependence of lnT_m vs. lnβ for glow peak from $K_2B_4O_7$:Dy

The initial rise method was formerly suggested by Garlick and Gibson [26] and it can be applied to any order of kinetics. If the ln I_{TL} is plotted against 1/kT, a straight line should be obtained and from the slope the activation energy (E) can be evaluated (I_{TL} is TL intensity). The plot is shown in Fig. 4.

The peak shape method is based on the geometrical characterization of a TL glow peak:

$$\mu_g = \frac{T_2 - T_m}{T_2 - T_1} \tag{2}$$

where T_1, T_m and T_2 represent the temperature of half-intensity at low temperature side, peak temperature and temperature of half-intensity at high temperature side of TL peak, respectively. In fig. 5, the T_1, T_m and T_2 are 349K, 385K and 416K, respectively. Inserting above values into eq. (2), the geometrical factor of 0.46 was obtained indicating that the recombination process obeys the first-order kinetics.

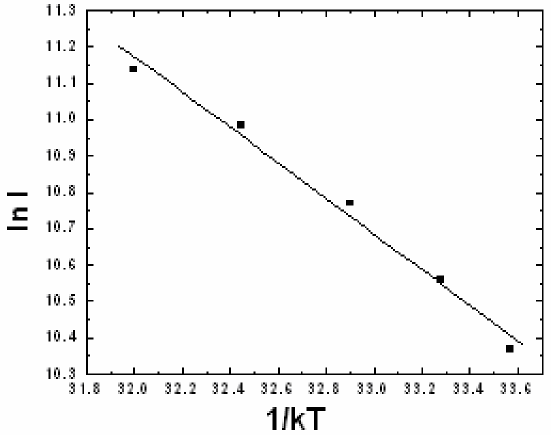

Fig. 4. Plot of lnI_{TL} vs 1/KT to evaluate the activation energy (initial rise method [26]).

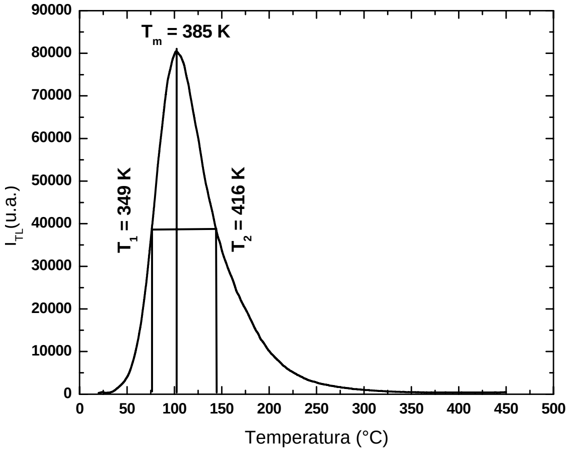

Fig. 5.Glow curve peak of $K_2B_4O_7$:Dy showing the geometrical parameters used in peak shape method.

Furthermore, Balarin [28] introduced the following parameter:

$$\gamma = \frac{T_2 - T_m}{T_m - T_1} \tag{3}$$

This parameter ranges from 0.7 to 0.8 for a first order kinetics and from 1.05 to 1.20 for a second order kinetics. Inserting values of T_1, T_m and T_2 into equation (2), the γ parameter was 0.86.

The kinetic order is obtained using the following expression given in ref. [28]:

$$b = 0.0563 \cdot 10^{2.95 \cdot \mu_g} \tag{4}$$

where μ_g is the geometrical factor. For $\mu_g = 0.46$, the value $b = 1.28$ is very close to first order kinetics.

The peak shape methods used in this study were proposed by Chen [29], Grossweiner [30] and Lushchik [31].

The activation energy (E) for the glow peak from $K_2B_4O_7$:Dy phosphor was calculated as follows:

Chen's method [29]:

$$E = 2.52 \cdot k \cdot \frac{T_m^2}{T_2 - T_1} - 2kT_m \tag{5}$$

Grossweiner's method [30]:

$$E = 1.51 \cdot k \cdot \frac{T_m \cdot T_1}{T_m - T_1} \tag{6}$$

Lushchik's method [31]:

$$E = 0.946 \cdot k \cdot \frac{T_m^2}{T_2 - T_m} \tag{7}$$

The results obtained applying the above mentioned methods are given in Table 1.

Table 1. Comparison of activation energies (eV) evaluated by different methods for $K_2B_4O_7$:Dy.

Method	E (eV)	Reference
Garlick-Gibson	0.48	[26]
Chen	0.41	[29]
Grossweiner	0.48	[30]
Lushchik	0.41	[31]
Mean	0.44	-

The frequency factor or attempt-to-escape factor is considered as a constant (not temperature dependent) which can be evaluated using the following equations:

Chen's equation [29]:

$$s = 2.67 \cdot \frac{\beta}{T_2 - T_1} \cdot 10^{\frac{T_m}{T_2 - T_1}} \tag{8}$$

Grossweiner's equation [30]:

$$s = \frac{3 \cdot T_1 \cdot \beta \cdot e^{\frac{E}{kT_m}}}{2 \cdot T_m \cdot (T_m - T_1)} \tag{9}$$

Chen and Weiner equation [32]:

$$\frac{\beta E}{kT_m^2} = s\left[1 + (b-1)\frac{2kT_m}{E}\right] e^{-\frac{E}{kT_m}} \tag{10}$$

where E is activation energy, b is kinetics order and β is heating rate. Table 2 summarizes the result obtained applying the above mentioned equations.

It can be noticed that there is a good agreement for the values of E and *s* calculated by different methods.

The evolution of the kinetics parameters as a function of the absorbed dose suggests continuous energy distribution for the trapping levels.

Table 2. Frequency factor (s) values obtained for $K_2B_4O_7$:Dy using different methods

Method	s (s^{-1})	Reference
Chen	$1.111 \cdot 10^5$	[29]
Grossweiner	$1.098 \cdot 10^5$	[30]
Chen and Weiner	$0.962 \cdot 10^5$	[32]
Mean	$1.057 \cdot 10^5$	-

Fig. 6 shows the variation of the activation energy (E) calculated by the initial-rise method as a function of the dose. Figure 7 shows the dependence of the temperature at the maximum (T_m) and the Balarin parameter (γ) as a function of the dose.

Fig. 8 shows the trend of both geometrical factor (μ_g) and kinetics order (b) as functions on dose. All these quantities are increasing as the irradiation dose increases.

This feature may be explained considering a complex structure for each trapping level, i. e. a continuous distribution of traps. Therefore, when the trapping levels with the lower activation energies are depleted, only the levels with higher values of energy remain filled and the E values increase as shown in figure 6. This result is in a good agreement to literature [33 – 36].

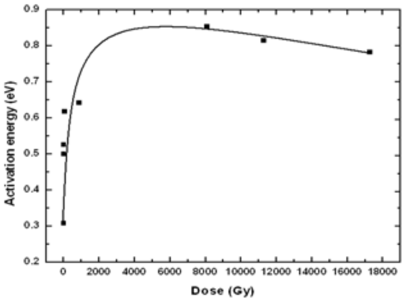

Fig. 6. Variation of the activation energy (E) as a function of the dose for $K_2B_4O_7$:Dy.

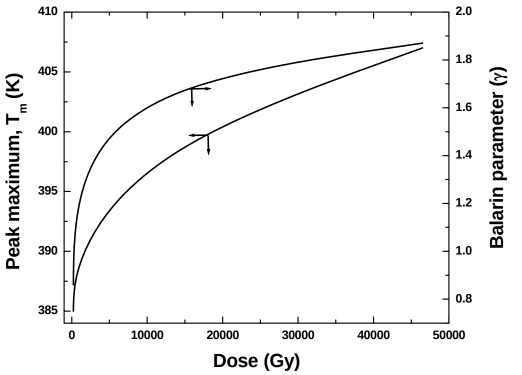

Fig. 7. Dependence of both peak maximum temperature (T_m) and Balarin parameter (γ) as a function of the dose for $K_2B_4O_7$:Dy.

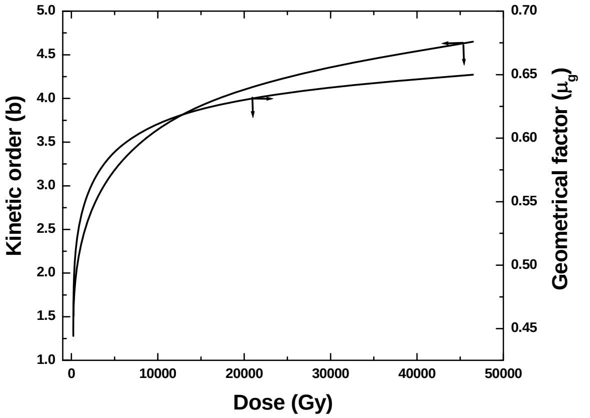

Fig. 8. Behavior of both kinetic order (b) and geometrical factor (μ_g) as functions on dose for $K_2B_4O_7$:Dy

The TL output of the $K_2B_4O_7$:Dy glassy phosphor exposed with different doses of ^{137}Cs gamma radiation is shown in figure 9. The samples have been responded linearly up to 20 KGy. Beyond 20 KGy phosphor reaches in sub-linearity region due to the filling of most of the electron traps by radiation produced free electrons.

The TL response was found to reach saturation beyond 40 KGy, as all TL centers seem to be filled by the free electrons produced by radiation.

Fading may be due to several causes. Thermal fading originates from the fact that even at room temperature there is a certain probability that charge carriers escape from their trapping centers. The probability per unit time of release of an electron from the traps is assumed to be described by the Arrhenius equation:

$$p = s \cdot e^{-\frac{E}{kT}} \tag{11}$$

where p is the probability per unit time, s is frequency factor, E is activation energy, k is Boltzmann's constant and T is absolute temperature at which the sample is stored after the irradiation.

The half-life for thermal fading is defined like:

$$t_{1/2} = \frac{\ln 2}{p} = \frac{0.693}{s \cdot e^{-\frac{E}{kT}}} \tag{12}$$

for 298 K, s = $1.057 \cdot 10^5$ s^{-1}, E = 0.44 eV and $t_{1/2}$ is 187 s.

This phosphor is a near tissue equivalent material with an effective atomic number for photoelectric absorption equal to 8.8 compared to 7.4 for water and soft biological tissue.

The mechanism leading to TL process in $K_2B_4O_7$:Dy could be related to the relaxation of the excited Dy^{3+} ions, $(Dy^{3+})^*$, as follows:

$$Dy^{3+} + e^- \xrightarrow{\gamma-irradiation} Dy^{2+}$$

$$Dy^{2+} \xrightarrow{e^-} \left(Dy^{3+}\right)^* \longrightarrow Dy^{3+} + (h\nu)_{TL}$$

The trapped charges are thermally released from the traps and transferred to the activator. $K_2B_4O_7$:Dy captures energy from the incident γ-ray and the energy is released from the traps by thermal vibration and then transferred to Dy^{3+} ion whose characteristic transition is thus resulted [37].

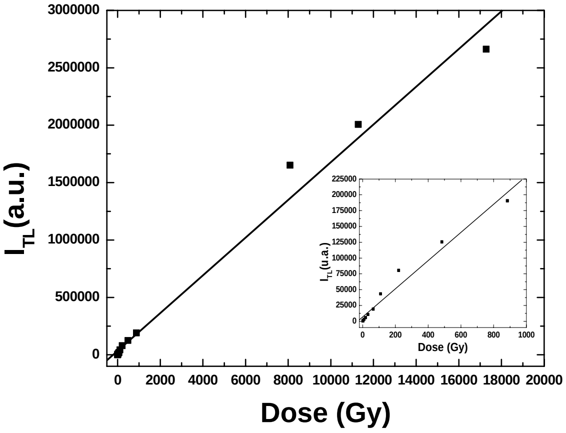

Fig. 9. TL output of ^{137}Cs exposed $K_2B_4O_7$:Dy at different doses.

Since the addition of rare earth dopants increases the TL efficiency of materials it is advisable to investigate the TL properties of $K_2B_4O_7$ doped with Ce, Nd, Sm, Eu, and Ho.

4. Conclusions

During the thermoluminescent (TL) process a proportion of the electron population is excited to one or more sets of metastable levels as a result of energy absorption by the material placed in a radiation field. In the last decay, the thermoluminescence of borates attracted the researchers' attention due to their suitability for personal dosimetry. A complete characterization of a thermoluminescent material cannot be done without indications concerning the kinetic parameters such as activation energy (E) of the traps involving in the TL emission, the order of kinetics (b) and the frequency factor (s). The knowledge of these parameters is essential due to its connection with the stability of the traps. Using different methods described in the literature for calculus of the kinetics parameters mentioned above, similar results for the studied materials were obtained.

References

[1] Z. D. Spurny, Kernenenergie **5**, 611 (1962)
[2] B. Bjärngard, Luminescence Dosimetry (F. H. Attix ed.), USAEC, Conf-650637, pp. 192-203, 1967.
[3] R. L. Dixon, K. E. Ekstrand, J. Lumin. **8**, 383 (1974).
[4] U. Madhusoodanan, M. T. Jose, A. Tomita, A. R. Lakshmanan, J. Lumin. **87-89**, 1300, (2000).
[5] C. X. Zhang, Q. Tang, D L. Luo, Z. R. Qiu, P. L. Leung, M. J. Stokes, Rad. Measur. **35**, 161, (2002).
[6] P. Christensen, "Manganese-Activated Lithium Borate as a Thermoluminescent Dosimetry Material" Risö Report, **161** (1967).
[7] M. Prokič, Rad. Prot. Dosim. **47**, 191 (1993).
[8] C. Furetta, G. Kitis, P. S. Weng, T. C. Chu, Nucl. Instr. and Meth. **A420**, 441 (1999).
[9] J. Li, J. Hao, C. Zhang, Q. Tang, Y. Zhang, Q. Su, S. Wang, Nucl. Instr. and Meth. **B222**, 577 (2004).
[10] J. Manam, S. K. Sharma, Nucl. Instr. and Meth. **B 217**, 314 (2004).
[11] U. Kümmel, E. Krautz, R. Knütter, Phys. Stat. Sol., **11**, 181 (1972).
[12] B. D. Bhasin, R. Sasidharan, C. M. Sunta, Health Phys. **30**, 139 (1976).
[13] C. Bettinali, "Thermoluminescence and color centers in some irradiated vitreous and crystalline silicates, borates and phosphates", Interaction of Radiation with Solids, Plenum Press, p. 273-280, 1967.
[14] S. M. Naranje, S. V. Moharil, Phys. Stat. Sol. A **165**, 489 (1998).
[15] K. Madhukumar, H. K. Varma, M. Komath, T. S. Elias, V. Padmananabhan, C. M. K. Nair, Bull. Mater. Sci. **30**, 527 (2007).
[16] J. H.Schulman, F. H. Attix, E. J. West, R. J. Ginther, Rev. Sci. Instrum. **31**, 1263 (1960); Nucleonics **18**, 92 (1960).
[17] R. P. Gonzales, C. Furetta, E. C. Zaragoza, Nucl. Instr. and Meth. **B243**, 349 (2006).
[18] W. L. Medlin, J. Chem. Phys. **30**, 451 (1959).
[19] V. Pagonis, Rad. Measur. **29**, 45 (1998).
[20] E. D. Taylor, H. G. Hecht, J. Phys. Chem. Solids **29**, 865 (1967).
[21] P. J. Kelly, M. J. Laubitz, J. Am. Ceramic Soc. **50**, 540 (1967).
[22] C. Soliman, Nucl. Instr. and Meth. **B251**, 441 (2006).
[23] J. C. A. Vega, J. A. Nieto, M. G. Hipolito, T. R. Montalvo, Rad. Measur. **42**, 613 (2007).
[24] K. Maduhkumar, K. R. Babu, K. C. A. Prasad, J. James, T. S. Elias, V. Padmanabhan, C. M. K. Nair, Bull. Mater. Sci. **29**, 119 (2006).
[25] G. Kitis, M. Spiropulu, J. Papadopoulos, S. Charalambous, Nucl. Instr. and Meth. In Phys. Res. **73**, 367 (1993).
[26] G. F. J. Garlick, A. F. Gibson, Proc. Phys. Soc. **60**, 574 (1948)
[27] Furetta C., "Handbook of Thermoluminescence" World Scientific, Singapore, 2003
[28] M. Balarin, J. Therm. Anal. **17**, 319 (1979).
[29] R. Chen, J. Electrochem. Soc. **116**, 1254 (1969).
[30] L. J. Grossweiner, J. Appl. Phys. **24**, 1306 (1953).
[31] C. B. Lushchik, Dokl. Akad. Nauk. SSSR **101**, 641 (1955).
[32] R. Chen, S. A. A. Winer, J. Appl. Phys. **41**, 5227 (1970).
[33] W. F. Hornyak, R. Chen, J. Lumin. **44**, 73 (1989).
[34] D. Yossian, Y. S. Horowitz, J. Phys. **28**, 1495 (1995).
[35] C. Furreta, G. Kitis, P. S. Weng, T. C. Chu, Nucl. Instr. and Meth. **A420**, 441 (1999).
[36] C. Furetta, G. Kitis, C. H. Kuo, Nucl. Instr. and Meth. **B160**, 65 (2000).
[37] L. Liu, Y. Zhang, J. Hao, C. Li, S. Wang, Q. Su, J. Phys. Chem. Solids **68**, 1745 (2007).

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*Corresponding author: jipasilviu@yahoo.com