

# Thermo-luminescence of Rare Earths Activated Potassium Tetraborate

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Potassium tetraborate was synthesized by high-temperature solid state reaction. The influence of rare earths (La, Ce, Nd, Sm, Eu, Gd, Dy, Ho and Yb) as dopants was investigated. Relative thermoluminescence (TL) efficiency for the  $K_2B_4O_7$  activation is given. The TL kinetic parameters were evaluated by employing the peak shape method and the results suggest that activated tetraborate systems obey the intermediate order kinetic ( $1 < b < 2$ ). An attempt was made to explain the thermo-luminescence mechanism according to frequency factor magnitude. The TL dose response is linear ranging from 3 Gy to 6 kGy and there is no indication on response saturation.

**Keywords:** thermo-luminescence, potassium tetraborate, trivalent rare earth ions, trapping parameters

The chemistry of various structures of glassy and crystalline inorganic borates are of the considerable interest for thermo-luminescence dosimetry (LTD) [1 – 13]. The advantages of this sort of materials are near tissue-equivalent absorption coefficient linear relationship between gamma dose and thermoluminescence response, easy handling and low cost.

One of the promising research directions for developing TL phosphors is the investigations on alkaline and alkaline-earth tetraborates as hosts for trivalent rare-earth (RE) ions. Thus, one may be expected that trivalent RE ions can contribute to the increasing the sensitivity of thermo-luminescence dosimetric phosphors.

To our knowledge, no reports on  $K_2B_4O_7:RE^{3+}$  have been noted up to this time. In this paper the thermo-luminescence properties of potassium tetraborate doped with individual La, Ce, Nd, Sm, Eu, Gd, Dy, Ho and Yb were investigated. The recorded thermo-luminescence curves provide information on the localized energy level in these solids. Kinetic parameters (activation energy, E, kinetic order, b, and frequency factor, s) were determined by applying standard analysis methods.

## Experimental part

The preparation of potassium tetraborate was performed by mixing potassium carbonate and boric acid in the stoichiometric ratio. Potassium tetraborate was further mixed with each of selected rare earth oxides ( $RE_2O_3$ ) and the resulted mixtures were melted in air at 900°C in an electrically heated furnace. Excepting the cases of cerium ( $Ce_2(SO_4)_3 \cdot 4H_2O$ , Loba) and samarium ( $Sm(NO_3)_3 \cdot 5H_2O$ , Merck), the high purity other oxides of La, Nd, Eu, Gd, Dy, Ho and Yb were used for doping. The activator concentration was 1.5 mole %. All these reagents were of analytical grade purity.

Vitrification was obtained by rapid cooling at room temperature. The resultant vitreous mass was ground and sieved to a size of 200  $\mu m$ . Gamma irradiation was performed at room temperature using  $^{137}Cs$  GAMMATOR M-38-2 (USA) installation at a dose rate of 0.4 kGy.h<sup>-1</sup>.

For the thermo-luminescence measurements (LTM Fimel, Harshaw apparatus), glass powders (~ 4 mg) were used. The thermo-luminescence glow curves of the investigated samples were obtained on the temperature range between room temperature and 450°C. The linear heating rate was set at 5°C/s and all measurements were taken in ambient atmosphere.

## Results and discussion

The RE-doped potassium tetraborates can be classified into two groups according to their common TL features. The representative glow curves of  $K_2B_4O_7:A^{3+}$  ( $A^{3+}$ :  $Ce^{3+}$ ,  $Sm^{3+}$ ,  $Eu^{3+}$ ,  $Yb^{3+}$ ) and  $K_2B_4O_7:B^{3+}$  ( $B^{3+}$ :  $La^{3+}$ ,  $Nd^{3+}$ ,  $Gd^{3+}$ ,  $Dy^{3+}$ ,  $Ho^{3+}$ ) samples with 1.5 mole % are shown in figures 1 a and 1b, respectively; in these figures the deconvolution is also presented.

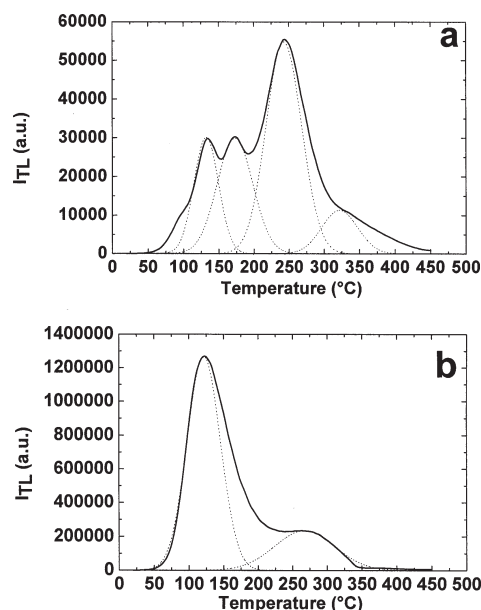


Fig. 1. Glow curves for (a)  $K_2B_4O_7:Sm$  and (b)  $K_2B_4O_7:Dy$  recorded after irradiation. (dopant concentration: 1.5 mole %; dose 6 kGy; heating rate: 5°C/s)

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Activator	Ionic radius (Å)	Peak temperatures and corresponding TL intensities							
		T <sub>m1</sub>	I <sub>1</sub>	T <sub>m2</sub>	I <sub>2</sub>	T <sub>m3</sub>	I <sub>3</sub>	T <sub>m4</sub>	I <sub>4</sub>
		(°C)	(a.u.)	(°C)	(a.u.)	(°C)	(a.u.)	(°C)	(a.u.)
Ce	1.034	132	10340	168	4837	247	9408	-	-
Sm	0.964	133	23134	173	13810	245	54573	354	3306
Eu	0.947	120	2145	167	1952	248	1459	414	874
Yb	0.858	130	14677	170	10599	247	26807	345	2644

**Table 1**  
GLOW CURVE TEMPERATURES AND THE MAIN PEAKS INTENSITY FOR K<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:A<sup>3+</sup> SAMPLES.

**Table 2**  
GLOW CURVE TEMPERATURES AND THE MAIN PEAKS INTENSITY FOR K<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:B<sup>3+</sup> SAMPLES

Activator	Ionic radius (Å)	Peak temperatures and corresponding TL intensities			
		T <sub>m1</sub>	I <sub>1</sub>	T <sub>m2</sub>	I <sub>2</sub>
		(°C)	(a.u. * 10 <sup>5</sup> )	(°C)	(a.u. * 10 <sup>5</sup> )
La	1.061	125	5.29	250	1.73
Nd	0.995	140	7.16	255	1.45
Gd	0.938	123	4.22	290	2.58
Dy	0.912	128	13.20	254	18.50
Ho	0.901	119	1.68	278	4.37

The glow curves recorded for K<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:A<sup>3+</sup> systems (A<sup>3+</sup>: Ce<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Yb<sup>3+</sup>) have certain common features. A low intensity glow peak resulting from the superposition of several individual glow peaks lies in the temperature region between 100 and 175°C (table 1). Between 245 and 248°C there follows other peak with higher intensity which is considered a main peak.

The glow curve obtained for K<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:B<sup>3+</sup> compositions (B<sup>3+</sup>: La<sup>3+</sup>, Nd<sup>3+</sup>, Gd<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>) showed two peaks: the first is placed between 119 and 140°C, which is considered as prominent peak, and the second one, between 245 and 278°C (table 2).

The major glow peaks recorded for these samples are activator – induced maxima, because they do not appear in „pure” sample prepared by the same technique. The TL efficiency (TL intensity divided by radiation dose) for the main peaks in glow curves is profoundly different for the samples doped with rare earths. The TL efficiency decreases in the following order:

$$\text{Dy} > \text{Nd} > \text{La} > \text{Gd} > \text{Ho} \gg \text{Sm} > \text{Yb} > \text{Ce} > \text{Eu}$$

The most strong thermo-luminescent sample emitted light about 10<sup>3</sup> times as intense as most weak thermo-luminescent system, both being subjected to the same radiation dose.

There are trends on which some glow peak temperatures vary as a function on the ionic size of the rare earth atoms (fig. 2). This behavior suggests that the rare-earth ions are active both in the trapping and luminescence steps. The thermo-luminescence recorded from K<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:RE<sup>3+</sup> can be satisfactorily explained on the basis of the following mechanism. The electrons and holes created under ionizing radiation are trapped on lattice imperfections in the host material and then, during thermal stimulation, the released electrons or holes recombine with partners at some of these defects. The recombination energy can be transferred to nearby closed RE<sup>3+</sup> site, which serves as luminescence center, when the material is heated to emit TL quanta [14].

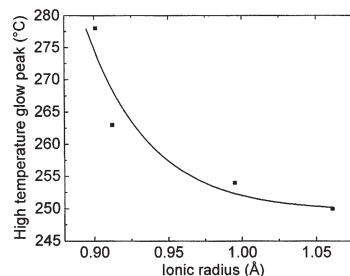


Fig. 2. High temperature glow curve dependence on some rare-earth ionic radius for K<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:RE<sup>3+</sup>

Several methods are currently employed for obtaining the activation energy of thermo-luminescence glow peaks. Details on these methods are given elsewhere [15-18].

In order to find the kinetic parameters of TL main peaks, the geometrical factor ( $\mu_g$ ), Balarin's parameter ( $\gamma$ ) and the kinetic order ( $b$ ) were calculated by means of the following expressions [19, 20]:

$$\mu_g = \frac{T_2 - T_m}{T_2 - T_1}; \quad \gamma = \frac{T_2 - T_m}{T_m - T_1}; \quad b = 0.0563 \cdot 10^{2.95\mu_g}$$

where T<sub>m</sub> is the maximum temperature of the TL peak, T<sub>1</sub> and T<sub>2</sub> are the temperatures at the half-widths of the peak, T<sub>1</sub> < T<sub>2</sub>. If  $\mu_g = 0.42$ , the kinetics is of the first order ( $b = 1$ ), while  $\mu_g = 0.52$  corresponds to the second order kinetics ( $b = 2$ ). Tables 3 and 4 summarize these parameters and the results were obtained applying the various methods to determine the activation energy (or trap depth), E, and frequency factor (or pre-exponential factor), s.

A close scrutiny of our results reveals that we obtained intermediate order kinetics, which are defined by  $0.42 < \mu_g < 0.52$  and  $0.8 < \gamma < 1.05$ . The order of magnitude for the frequency factor gives us some conclusions about the nature of recombination mechanism involved in the TL process. The frequency factor observed in the recombination processes due to delocalized transitions (without retrapping) are  $s \leq 10^5 \text{ s}^{-1}$ , whereas for the typical recombination processes involving carriers via the conduction or valence band (retrapping) are placed on the range  $s = 10^{10} - 10^{12} \text{ s}^{-1}$  [14, 21, 22]. Therefore, in all studied materials, the recombination process of carriers occurs as a result of thermal release from a trap and diffusion of

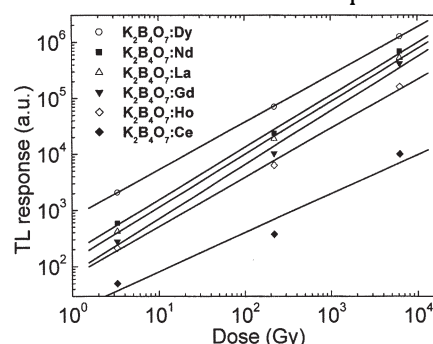


Fig. 3. TL output of <sup>137</sup>Cs exposed K<sub>2</sub>B<sub>4</sub>O<sub>7</sub>:RE<sup>3+</sup> at different doses

**Table 3**  
TRAPPING PARAMETERS OF TL MAIN GLOW PEAK FOR  $K_2B_4O_7:A^{3+}$  USING DIFFERENT METHODS

Activator	$\mu_g$	$\gamma$	b	Activation energy (eV) evaluated by method					Frequency factor, s ( $s^{-1} * 10^9$ )	
				Chen	Balarin	Halperin-Braner		Lushchik		Mean
				(Chen, 1969)	(Balarin, 1979)	(Halperin and Braner, 1960)	(Lushchik, 1956)			
Ce	0.50	1.00	1.68	1.09	1.01	0.93	1.04	1.02	1.98	
Sm	0.49	0.97	1.57	1.13	1.04	0.95	1.09	1.05	4.34	
Eu	0.48	0.92	1.46	1.17	1.09	0.97	1.17	1.10	11.80	
Yb	0.48	0.95	1.46	1.09	1.01	0.90	1.07	1.02	1.95	

**Table 4**  
TRAPPING PARAMETERS OF TL MAIN GLOW PEAK FOR  $K_2B_4O_7:B^{3+}$  USING DIFFERENT METHODS

Activator	$\mu_g$	$\gamma$	b	Activation energy (eV) evaluated by method					Frequency factor, s ( $s^{-1} * 10^8$ )	
				Chen	Balarin	Halperin-Braner		Lushchik		Mean
				(Chen, 1969)	(Balarin, 1979)	(Halperin and Braner, 1960)	(Lushchik, 1956)			
La	0.49	0.96	1.57	0.88	0.81	0.74	0.86	0.82	84	
Nd	0.47	0.92	1.37	0.76	0.70	0.60	0.76	0.71	1.23	
Gd	0.49	0.96	1.57	0.91	0.83	0.77	0.88	0.84	176	
Dy	0.50	1.00	1.68	0.79	0.73	0.67	0.76	0.73	4.68	
Ho	0.50	1.03	1.68	0.88	0.81	0.78	0.83	0.82	135	

electrons or holes to a recombination center via the conduction or the valence band.

The TL output of the samples exposed with different doses of  $^{137}Cs$  gamma radiation is shown in figure 3. The samples have responded linearly in the range between 3 Gy and 6 kGy. It should be noticed that on this dose range, there are no indications on response saturation.

These results present a real interest for the studies concerning the  $K_2B_4O_7:RE^{3+}$  phosphors, offering the possibility of further studies. Permanent efforts have to be made to improve our understanding on the influence of various parameters on the characteristics of thermoluminescence systems.

### Conclusions

The study emphasizes that defect centers play an important role in TL. The release of electrons/holes from defect centers at characteristic trap initiates the thermoluminescence process in gamma radiation exposed material.

The TL glow curves in the range 25-450°C from  $K_2B_4O_7$  individually doped with rare-earth ions were analyzed.

The symmetry parameters of the main glow peaks show intermediate kinetics between first and second order.

Kinetic parameters (activation energy and frequency factor) were determined using different methods based on both glow curve shape and maximum temperature. The obtained values suggest that  $RE^{3+}$  ions can efficiently capture charge carriers and they serve simultaneously as recombination and luminescent centers.

The TL outputs of  $K_2B_4O_7:RE^{3+}$  phosphors were linear up to 6 kGy.

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