Thermoluminescent borates for environmental purposes

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Abstract. Ceramic samples based on lithium and divalent metal borates were obtained by solid-state reaction and their thermoluminescent response were tested. It is shown that calcium borate has the maximum thermoluminescent sensitivity. Co-doping of magnesium and calcium borates with monovalent metals result in an increase of the thermoluminescence intensity and appearance of a second thermoluminescence peak for calcium borate.

1. Introduction

With the increase of nuclear energy in many countries, questions arise about the monitoring of the environment near nuclear reactors. In this area of dosimetry, the measurement of small additional doses caused by artificial radiation over the natural radiation of the environment is a difficult task. The dosimeter should properly measure both the space and ground components of natural radiation. Various dosimetric systems based on thermoluminescence (TL), radiophotoluminescence, optically stimulated luminescence, etc. are used to determine the doses of radioactive radiation. Thermoluminescent systems are the most common [1].

The most promising material for use in environmental dosimetry is LiF:Mg,Cu,P. Its thermoluminescent sensitivity is 30 times higher than LiF:Mg,Ti [2, 3], nevertheless LiF:Mg,Ti is still the most commonly used TL material. Based on the latest large-scale international comparison of environmental dosimeters, organized by the Environmental Measurements Laboratory of the USA, where calcium sulfate and LiF:Mg,Ti were the most commonly used types of TL detectors. The results showed that the use of supersensitive TL materials is increasing [4].

Lithium and magnesium borates are among the most promising TL phosphors [5–8]. They offer high TL sensitivity which allows them to be used in personal, clinical, and environmental dosimetry of weak ionizing radiation. In connection with this, the purpose of this work was to study TL sensitivity of synthesized polycrystalline lithium and magnesium borates and their derivatives.

2. Models and Methods

The samples were prepared by solid state reactions using ceramic technology [9]. The chemically pure grade H₃BO₃ (99%), Li₂CO₃ (99.9%), MgO (99%), Dy₂O₃ (99.9%), CaO (99%), BaO (99%), SrO (99%), CdO (99%) components were used as initial reagents. Temperatures were measured with a Pt–PtRh thermocouple. The temperature was controlled to be within ±2 °C up to 1200 °C with an OMRON controller. After the heat treatment, the sample was slowly cooled to room temperature together with the furnace and the estimated cooling rate was 12 °C/min. Phase equilibrium was monitored by X-ray powder analysis at room temperature (D8 diffractometer Bruker AXS, CuKα-radiation, Germany).
TL analysis was performed using an experimental setup that incorporated a heater, temperature controller, chart recorder, and photomultiplier tube (Figure 1). It detected the optical signal from the TL phosphor as a function of temperature. Test samples were exposed to the radiation from a strontium–yttrium ($^{90}\text{Sr} + ^{90}\text{Y}$) beta source. The exposure time was 30 min, which corresponded to 7.5 mGy. TL glow curves of samples were obtained at a constant heating rate of 5 °C/s. The measured TL intensity was normalized to the signal from a standard – TLD-580.

3. Results and Discussion

3.1. Synthesis of Mg$_2$B$_2$O$_5$:Dy, Mg$_3$B$_2$O$_6$:Dy

The MgO–B$_2$O$_3$ binary system contains 3 compounds, namely, MgO·2B$_2$O$_3$, 2MgO·B$_2$O$_3$, 3MgO·B$_2$O$_3$ [10]. These compounds were doped with dysprosium for the TL response. The crystallographic and thermal characteristics of the studied borates are presented in Table 1. The formation of these borates is confirmed by X-ray powder analysis. TL analysis of these compounds showed an insignificant TL response.

3.2. Synthesis of LiMg$_{0.5}$B$_4$O$_7$:Dy and LiMgBO$_3$:Dy

Magnesium and lithium double borates doped dysprosium (LiMg$_{0.5}$B$_4$O$_7$:Dy and LiMgBO$_3$:Dy) were synthesized for testing their TL responses. LiMg$_{0.5}$B$_4$O$_7$:Dy was obtained by substituting half of the Mg atoms for Li in MgB$_4$O$_7$:Dy, and a compound of the LiMgBO$_3$ composition exists in the ternary system MgO–Li$_2$O–B$_2$O$_3$ [12]. Both specimens are obtained in the glass form, due to the low melting points of these compounds. The TL intensity of LiMg$_{0.5}$B$_4$O$_7$:Dy and LiMgBO$_3$:Dy is higher than that of magnesium borates.
Table 1. Crystallographic and thermal characteristics of borates [11].

| Compounds          | Space group | $T_{\text{melt}}$ (°C) |
|--------------------|-------------|------------------------|
| MgB$_4$O$_7$       | $Pbca$      | 995 (incongruent)      |
| Mg$_2$B$_2$O$_5$   | $P21/c$     | 1381 (incongruent)     |
| Mg$_3$B$_2$O$_6$   | $Pnmn$      | 1400 (congruent)       |
| LiMg$_{0.5}$B$_4$O$_7$ | -          | -                      |
| LiMgBO$_3$ [12]    | $P21/c$     | -                      |
| CaB$_6$O$_{10}$    | $P2_1/c$    | -                      |
| BaB$_4$O$_7$       | $P21/c$     | 910                    |
| SrB$_4$O$_7$       | $Pnm21$     | 930                    |
| CdB$_4$O$_7$       | $Pbca$      | -                      |

3.3. Synthesis and TL properties of Mg$_{1-x}$A$_x$B$_4$O$_7$::Dy ($A = Ca, Cd, Sr, Ba; x = 0.1, 0.5, 1$)

Further search is continued by isovalent magnesium substitution of MgB$_4$O$_7$::Dy for divalent metals – Ca, Cd, Sr, Ba. Polycrystalline specimens were obtained by solid-phase reactions. The X-ray diffraction analysis of Mg$_{1-x}$A$_x$B$_4$O$_7$::Dy ($x = 0.1, 0.5, 1$) shows that a complex comprises both phases MgB$_4$O$_7$ and CaB$_6$O$_{10}$ [13]. Samples were studied by TL analysis. The increase in divalent metal A content in Mg$_{1-x}$A$_x$B$_4$O$_7$::Dy ($A = Cd, Sr, Ba$) results in a decrease in TL intensity and, on the contrary, increases for calcium (Table 2). The TL intensity of CaB$_6$O$_{10}$::Dy, biphasic mixtures of magnesium and calcium borates, Mg$_{0.5}$Cd$_{0.5}$B$_4$O$_7$::Dy, Mg$_{0.5}$Sr$_{0.5}$B$_4$O$_7$::Dy is higher than commercial TL material TLD-580.

Magnesium, calcium and cadmium borates have a TL response; we note that the ionic radii of Mg (0.72 Å), Sr (1.32 Å) and Ca (1.14 Å) are comparable to the ionic radius of Dy (1.052 Å) [14]. Perhaps this is due to the replacement of the divalent metal with dysprosium. The TL intensity is reduced from calcium borate (CaB$_6$O$_{10}$) to magnesium borate (MgB$_4$O$_7$) and the minimum intensity is observed in cadmium borate (CdB$_4$O$_7$).

Table 2. The relative TL intensity of Mg$_{1-x}$A$_x$B$_4$O$_7$::Dy ($A = Cd, Sr, Ba; x = 0.1, 0.5, 1$), CaB$_6$O$_{10}$: Dy, biphasic mixtures of magnesium and calcium borate.

| Metal | x=0.1 | x=0.5 | x=1 |
|-------|-------|-------|-----|
| Ca    | MgB$_4$O$_7$::Dy and traces of CaB$_6$O$_{10}$::Dy | MgB$_4$O$_7$::Dy and CaB$_6$O$_{10}$::Dy | CaB$_6$O$_{10}$::Dy |
| $I_{\text{rel.}}$, % | 132.3 | 148.7 | 166.3 |
| Cd    | Mg$_{0.5}$Cd$_{0.5}$B$_4$O$_7$::Dy | Mg$_{0.5}$Cd$_{0.5}$B$_4$O$_7$::Dy | CdB$_4$O$_7$::Dy |
| $I_{\text{rel.}}$, % | 113.0 | 111.6 | 49.6 |
| Sr    | Mg$_{0.5}$Sr$_{0.5}$B$_4$O$_7$::Dy | Mg$_{0.5}$Sr$_{0.5}$B$_4$O$_7$::Dy | SrB$_4$O$_7$::Dy |
| $I_{\text{rel.}}$, % | 37.0 | 10.8 | 0 |
| Ba    | Mg$_{0.5}$Ba$_{0.5}$B$_4$O$_7$::Dy | Mg$_{0.5}$Ba$_{0.5}$B$_4$O$_7$::Dy | BaB$_4$O$_7$::Dy |
| $I_{\text{rel.}}$, % | 78.0 | 31.2 | 0 |

$a - I_{\text{rel.}}$, % = \left( \frac{I_{\text{sample}}}{I_{\text{TLD-580}}} \right) \times 100$

3.4. Co-doping of MgB$_4$O$_7$::Dy,Me and CaB$_6$O$_{10}$::Dy, Me (Me = Li, Na, Tl)

The effect of the second doping elements on the TL properties of MgB$_4$O$_7$::Dy,Me and CaB$_6$O$_{10}$::Dy, Me (Me=Li, Na, Tl) was studied. With the co-doping of magnesium borate by Li, Na, Tl, a more intense and wider single TL peak is observed. In the series MgB$_4$O$_7$::Dy,Me (Me=Li, Na, Tl), the TL intensity falls. When co-doping calcium borate with lithium, sodium and thallium, two TL peaks are observed and CaB$_6$O$_{10}$::Dy,Na possesses maximum TL intensity (Table 3).
Table 3. The relative TL intensity of CaB$_6$O$_{10}$:Dy, MgB$_4$O$_7$:Dy,Me.

| Co-doping element, Me | MgB$_4$O$_7$:Dy,Me | CaB$_6$O$_{10}$:Dy,Me (1st peak) | CaB$_6$O$_{10}$:Dy,Me (2nd peak) |
|----------------------|-------------------|---------------------------------|---------------------------------|
|                      | I$_{rel}$, %a      |                                 |                                 |
| Li                   | 187               | 62.6                            | 148.4                           |
| Na                   | 118               | 110                             | 150                             |
| TI                   | 68                | 49                              | 94                              |

I$_{rel}$, % = (I$_{sample}$/I$_{TLD-580}$)*100

4. Conclusion

Thus, magnesium borates (Mg$_2$B$_2$O$_5$:Dy and Mg$_3$B$_2$O$_6$:Dy) and double borates of lithium and magnesium (LiMg$_{0.5}$B$_4$O$_7$:Dy and LiMgBO$_3$:Dy) doped with dysprosium have an insignificant level of TL. It is shown that the intensity of TL in CaB$_6$O$_{10}$, AB$_4$O$_7$:Dy borates (A = Cd, Sr, Ba) depends on the ionic radius of the cations. Co-doping of magnesium and calcium borates with monovalent metals result in an increase of the TL intensity and appearance of a second TL peak for calcium borate.

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