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Synthesis and Characterization of Dysprosium-Doped Magnesium Tetraborate

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Abstract—We have identified optimal conditions for the synthesis of highly sensitive MgB_4O_7:Dy thermoluminescent phosphor and examined the effect of alkali metals (lithium and sodium) as additional dopants that improve the performance of the thermoluminescent phosphor.

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INTRODUCTION

The use of ionizing radiation is an integral part of modern science and technology. To monitor irradiation doses, use is made of sensors that take advantage of thermally stimulated luminescence (thermoluminescence). Lithium and magnesium borates are among the most promising thermoluminescent phosphors [1–3]. They offer high thermoluminescence sensitivity and tissue equivalence, which allows them to be used in personal, clinical, and radiobiological dosimetry of weak ionizing radiation. To improve the dosimetric characteristics of the thermoluminescent phosphors, Prokic [4] and Furetta et al. [5] doped them with lithium and sodium, but they did not describe in detail the synthesis of the thermoluminescent phosphors.

In connection with this, the purpose of this work was to study the effect of synthesis conditions (annealing time and temperature and doping level) on the thermoluminescence sensitivity of polycrystalline dysprosium-doped magnesium tetraborate (MgB_4O_7:Dy).

EXPERIMENTAL AND RESULTS

The starting materials used were MgO (pure grade), B_2O_3 (extrapure grade), Dy_2O_3 (grade "zh" DyO), Li_2CO_3 (reagent grade), and Na_2CO_3 (reagent grade). Stoichiometric ratios of the starting materials were homogenized in ethanol. A predried reaction mixture was annealed in a Nabertherm L3 muffle furnace. The phase composition of the sample was checked by X-ray diffraction on a Bruker D8 Advance AXS diffractometer (CuK_α radiation).

Thermoluminescence analysis was performed using an experimental setup that incorporated a heater, temperature controller, chart recorder, and photomultiplier tube. It detected the optical signal from the thermoluminescent phosphor as a function of temperature. Test samples were exposed to the radiation from a strontium–yttrium ($^{90}Sr + {}^{90}Y$) control beta source. The exposure time was 30 min, which corresponded to 7.5 mGy. Thermoluminescence glow curves of MgB_4O_7:Dy were obtained at a constant heating rate of 5°C/s. The measured thermoluminescence intensity was normalized to the signal from a standard: TLD-580 thermoluminescent phosphor.

Synthesis. Because of the low doping level, the results of our experiments depend significantly on homogenization. The materials were homogenized by ball milling, ultrasonication, and manual grinding in an agate mortar. Among the approaches used, manual grinding ensured the highest thermoluminescence sensitivity. Homogenization was performed by a method of "equal amounts," in which the starting materials were ground stepwise, in equal weights.

According to Davis and Knight [6], MgB_4O_7 experiences solid-state decomposition above 1050°C. The presence of excess MgO leads to $Mg_2B_2O_5$ formation. The samples prepared by the method of equal amounts and containing 0.5 wt % Dy were annealed at temperatures of 750, 800, 850, and 900°C for 6 h. We failed to synthesize MgB_4O_7 at annealing temperatures under 750°C. The results of our experiments are presented in Fig. 1a. The highest thermoluminescence intensity was obtained at an annealing temperature of 850°C. The samples containing 0.5 wt % Dy were annealed at a temperature of 850°C for 2, 4, 8, 10, 16, 24, 36, 40,

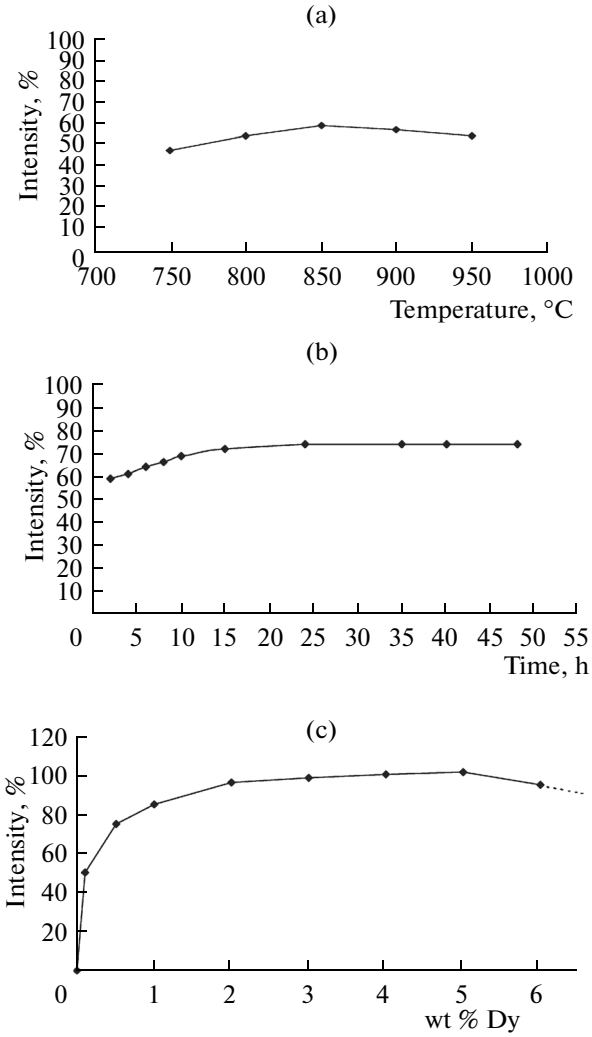

Fig. 1. MgB_4O_7 thermoluminescence intensity as a function of (a) synthesis temperature (0.5 wt % Dy; synthesis time, 2 h), (b) synthesis time (0.5 wt % Dy; synthesis temperature, 850°C), and (c) dysprosium content (synthesis temperature, 850°C; synthesis time, 24 h).

and 48 h (Fig. 1b). High thermoluminescence intensities were offered by the samples annealed for 24, 36, 40, and 48 h. The effect of doping level on the thermoluminescence intensity was studied for the samples annealed at a temperature of 850°C for 24 h (Fig. 1c). In all of our experiments, the relative uncertainty in thermoluminescence intensity was within 3%. In this way, we identified optimal conditions for the synthesis of highly sensitive MgB_4O_7:Dy thermoluminescent material ($t = 850$°C, $\tau = 24$ h, 5 wt % Dy).

We examined the effect of a second dopant (lithium or sodium) on the thermoluminescence intensity. A sample additionally doped with 0.5 wt % lithium had the highest thermoluminescence intensity (Fig. 2). Sodium doping slightly increased the thermoluminescence intensity in magnesium tetraborate, but the results were poorly reproducible. Lithium and sodium

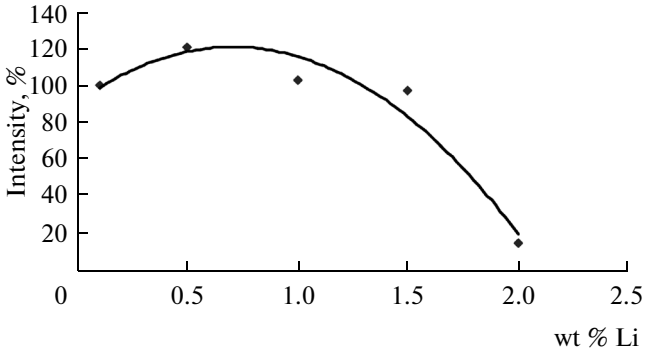

Fig. 2. Thermoluminescence intensity as a function of additional dopant (Li) content.

as additional dopants increase the thermoluminescence intensity relative to magnesium tetraborate singly doped with dysprosium.

Dosimetric characteristics of MgB_4O_7:Dy. The thermoluminescence glow curve of MgB_4O_7:Dy has a well-resolved glow peak at a temperature of 190°C (Fig. 3a), which allows the intensity and area of the thermoluminescence peak to be readily measured. The thermoluminescence sensitivity of the synthesized MgB_4O_7:Dy samples was calculated as the peak area divided by the mass of the dosimeter and beta dose [TL/(mg Gy)], and the values obtained were compared to data for TLD-580 and LiF:Mg,Ti (DTG-4) (Fig. 3c). It can be seen that the sensitivity of our MgB_4O_7:Dy samples exceeds that of TLD-580 by 5–10% and that of LiF:Mg,Ti (DTG-4) by a factor of 3–4. To assess the reproducibility of ionizing radiation dose measurements with MgB_4O_7:Dy, we performed a number of repeated irradiations and heatings. The results demonstrate that such dosimeters can measure a beta dose of 7.5 mGy with a relative uncertainty less than 3%, as quantified by the standard deviation for ten sequential measurements. To estimate fading, MgB_4O_7:Dy samples were annealed and then irradiated to a dose of 0.1 Gy. The MgB_4O_7:Dy samples were stored in the dark at room temperature for 1, 1.5, 2, 7, 14, 21, and 30 days, and then thermoluminescence glow curves were obtained. The fading of MgB_4O_7:Dy was determined to be approximately 5% over a month when the sample was stored in the dark at an ambient temperature of 25 ± 27°C. Thermoluminescent materials with a fading under 10% are thought to be suitable for dosimetry.

The activation energy and frequency factor were determined by heating the phosphor at different rates [7]. To evaluate the activation energy and frequency factor of MgB_4O_7:Dy, we used the equation [8]

$$\frac{E}{kT_m^2} = \frac{\delta_0}{q} e^{-\frac{Er}{kT_m}}, \quad (1)$$

where E is the activation energy, δ_0 is the frequency factor, k is Boltzmann's constant, T_m is the peak emis-

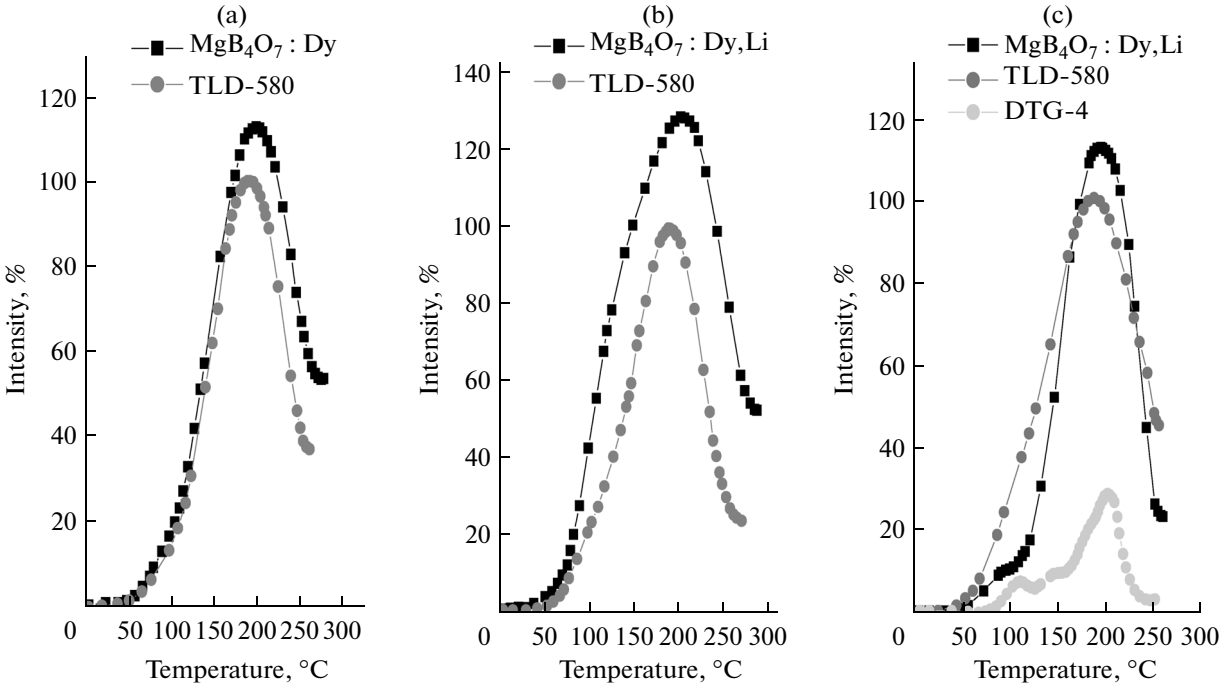

Fig. 3. Thermoluminescence glow curves of (a) MgB_4O_7:Dy and (b) MgB_4O_7:Dy,Li samples; (c) comparison of the thermoluminescence intensities of MgB_4O_7:Dy, TLD-580, and DTG-4.

sion temperature of the thermoluminescence peak, and q is the heating rate.

At heating rates of 44.6, 5.8, 2.87, and 0.7°C/s, the peak emission temperatures of the thermoluminescence peaks were 406, 316, 266, and 103°C, respectively. Using Eq. (1), the activation energy and frequency factor were determined to be $E = 0.8–0.9$ eV and $\delta_0 = 7.1 \times 10^6$ s^{-1}.

As a result of our studies, we obtained a MgB_4O_7:Dy thermoluminescent phosphor suitable for personal, clinical, radiobiological, radiation engineering, and reactor dosimetry of low-energy ionizing radiation, such as beta radiation and accelerated neutron radiation. The advantages of MgB_4O_7:Dy over other thermoluminescent materials are its tissue equivalence (the ability to absorb ionizing radiation like biological tissue: $Z_{eff}(MgB_4O_7) = 8.4$, Z_{eff}(biol. tissue) = 7.4), which simplifies absorbed dose calculation, and its high thermoluminescence sensitivity, which enables measurements of low irradiation doses, typical of low-energy ionizing radiation, and allows one to use modified thin-film dosimeters (close in thickness to the epidermal basal layer, which absorbs ionizing radiation) containing small amounts of MgB_4O_7:Dy.

The synthesis temperature and time were chosen so as to obtain a thermoluminescent host (MgB_4O_7) best suited for maximum thermoluminescence intensity. However, according to Furetta et al. [5], some thermoluminescent phosphors contain a mixture of magnesium borates (70% MgB_4O_7 and 30% MgB_2O_4). Under the conditions of this study, single-phase MgB_4O_7 was obtained.

The table lists the activation energies and frequency factors of some thermoluminescent phosphors. The highest activation energy so far has been reported for $Li_2B_4O_7$:Cu,In [11]. Accordingly, this thermoluminescent phosphor has low fading. Its ther-

Activation energies and frequency factors of thermoluminescent phosphors

Material	Activation energy (E), eV	Frequency factor (δ_0), s^{-1}	Source
MgB_4O_7:Tm	0.98 ± 0.03	1.42×10^9	[7]
$EuGa_2S_4$:Er	0.1–0.2	–	[9]
MgB_4O_7:Dy;Tm	1.07 ± 0.03	4.2×10^{10}	[10]
$Li_2B_4O_7$:Cu;In	1.62	2×10^{14}	[11]
$Li_2B_4O_7$:Cu;In;Ag	1.45	5×10^{13}	[11]
MgB_4O_7:Dy	0.8–0.9	7.1×10^6	This work

moluminescence sensitivity is also low. $EuGa_2S_4$:Er has the lowest activation energy [9] and holds no promise as a dosimetric material.

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