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Neodymium as a magnesium tetraborate matrix dopant and its applicability in dosimetry and as a temperature sensor

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ABSTRACT

MgB_4O_7 doped with lanthanides such as Dy^{3+} and Tm^{3+} are phosphors with very well established use in routine personal dosimetry. Certain characteristics, for example linearity in a broad dose range, low energy dependence, Z_{eff}=8.5, high sensitivity and a relatively simple thermoluminescent (TL) emission curve make MgB_4O_7 a good material for thermoluminescent dosimetry. With the aim of analyzing other doping possibilities, this paper presents some preliminary results on the use of Nd^{3+} as a dopant in the MgB_4O_7 matrix. Furthermore, we evaluated the effect of using two different lanthanides, Nd and Dy, in the host matrix. In the present work, the phosphors were produced through solid state synthesis and X-ray diffraction confirmed the success of the technique. The TL behavior of MgB_4O_7:Nd was assessed when irradiated with gamma (^{60}Co) and beta radiation, to determine the effect of the dopant concentration and the dose–response over a broad dose range. We also evaluated the dose–response of MgB_4O_7:Nd,Dy when irradiated with ^{60}Co. The TL responses of the phosphors were compared with that of MgB_4O_7:Dy. These preliminary studies show that for the absorbed dose range studied, the sensitivity of MgB_4O_7:Nd,Dy was 3.8 and 28 times higher than that of MgB_4O_7:Dy and MgB_4O_7:Nd. The materials also presented linearity from 5 to 40 Gy. Above this value, the dose response curve exhibited sublinear behavior. These preliminary results will assist in developing a new temperature sensor based on a MgB_4O_7 dosimeter.

1. Introduction

The applicability of MgB_4O_7 in solid state dosimetry, specifically in thermoluminescent (TL) dosimetry, has been a focus of interest over the years, i.e. since the early 1980s, when the first reports of its functionality for dosimetry were studied [1–3]. MgB_4O_7:Dy has essential characteristics for use in dosimetry, exhibiting a single thermoluminescent peak at approximately 200 °C with linearity of the dose–response curve over a broad dose range (μGy–kGy) [1]. Its TL emission is about 10 times more sensitive for dose detection of beta, gamma and neutron radiation than TLD-100, and shows minimal fading [4].

The MgB_4O_7 host matrix is also attractive due to its low effective atomic number, which implies a small photon energy dependence. The high TL intensity and low light sensitivity also makes MgB_4O_7 useful for temperature sensing applications [5]. One example of an application in temperature sensors using TL materials can be described in situations where it is desired to determine the temperature experienced by small particles in order to assess energy release processes and the dynamics of energetic materials for use in bio-agent protection [6]. The decrease in the concentration of trapped charges with temperature increases during the TL readout can also be useful for thermometry in geological and archeological applications, research on fire-damaged concrete and on explosions. Since each trapping center has a different thermal stability, if an irradiated sample is exposed to a temperature profile, the trapped charge concentration will be altered. This change can be detected by recording the TL curve after the sample has been exposed to a temperature profile (temperature versus time), and comparing it with the TL curve of a control sample that has not been exposed to the temperature profile [7]. $Li_2B_4O_7$:Cu,Ag, MgB_4O_7:Dy,Li, and $CaSO_4$:Ce,Tb have been tested for temperature sensing applications and their properties are suitable for these applications [5].

Many studies in the literature have already described the main TL features of tetraborate when doped/codoped with lanthanide elements such as Dy, Tb, Pr, Tm, or Mn [8–10]. A class of thermoluminescent dosimeters (TLD) is formed by lanthanide doped inorganic compounds, e.g. $CaSO_4$:Dy^{3+} and $CaSO_4$:Tm^{3+}. Since the 4f shell of the lanthanides is screened by the filled $5s^2$ and $5p^6$ shells of the Xe-core, the 4f electrons experience a weak

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crystal field interaction and their chemical properties as well as the ionic radius do not vary much with increasing numbers of 4f electrons [11]. All 15 lanthanides have similar interactions with the host lattice and the numerous optical transitions between the 4f states have made the lanthanides the most popular activator ions for lighting. The very intense TL peak from MgB_4O_7:Dy (~250 °C), characterized by emissions at 480 nm, has been extensively reported and is attributed to 4f–4f transitions from Dy^{3+} ($^4F_{9/2}$–$^6H_{15}$) [5,12,18]. The lanthanide neodymium (Nd) has already been described in the literature as a dopant for MgB_4O_7 and is known to generate TL emission peaks from low to high temperatures. The most intense TL peak is located above 350 °C and is due to emission of Nd^{3+} at 600 nm [5]. For temperature sensing applications, it is required that the material presents multiple TL peaks that can capture information over a wider temperature range [5]; therefore, it seems that MgB_4O_7:Nd is a good candidate for this application.

This study aimed to describe some TL features of MgB_4O_7:Nd and the effect of Dy^{3+} as a codopant (MgB_4O_7:Nd,Dy). It is expected that some codopants enhance the TL sensitivity of phosphors based on MgB_4O_7 [12]. The behavior of MgB_4O_7:Nd as a temperature sensor was also investigated; the preliminary TL results showed that the material presents two TL emissions peaks located below 200 °C and one major TL peak in the high temperature region (> 350 °C).

The TL responses of both materials (MgB_4O_7:Nd and MgB_4O_7:Nd, Dy) were compared with that of MgB_4O_7:Dy [13], produced elsewhere. The phosphors were also characterized by X-ray diffraction. Some TL properties such as luminescent efficiency for different dopant concentrations, the TL emission curve, and the dose–response were analyzed after the samples were irradiated with beta and gamma sources. In addition, the grain size of MgB_4O_7:Nd was determined by scanning electron microscopy (SEM).

2. Materials and methods

MgB_4O_7:Nd and MgB_4O_7:Nd,Dy were produced through solid state synthesis. This route has been described in the literature for the production of MgB_4O_7:Dy [13–15]. For the synthesis, analytical grade MgO (Merck, 99.9% purity), H_3BO_3 (Merck, 99.9% purity), neodymium oxide (Nd_2O_3; Sigma-Aldrich, 99.9%) and dysprosium oxide (Dy_2O_3; Sigma-Aldrich, 99.9%), in the case of the codoped material, were used as starting reactants in stoichiometric ratios. The compounds were uniformly homogenized using an agate mortar and pestle. The mixtures were calcined in a muffle furnace (EDG-1800) at 900 °C for 6 h, followed by slow cooling to room temperature (25 °C). Initially, MgB_4O_7:Nd was produced with five different dopant concentrations (0.1, 0.5,1.0, 1.5 and 2.0 wt%) in order to investigate the concentration that enabled the highest TL emission from the polycrystals. The resulting powders were granulated; the grain size selected for pellet production was between 75 and 180 μm. For the test, five pellets of each MgB_4O_7:Nd concentration (0.1–2 wt%) described above were irradiated under the same conditions with 5 Gy of gamma radiation from ^{60}Co. For the production of MgB_4O_7:Nd,Dy, the reactants and dopants (1 wt% of Nd and 0.5 wt% of Dy) were also mixed uniformly and then calcined under the same conditions used for the other phosphors.

Crystal structures were confirmed by X-ray diffraction (XRD) with a Rigaku model DMAX 2000. CuK_α radiation was used, with the tube operating at 40 kV/20 mA in step scan mode with steps of 2θ (deg)=0.5 in the interval of the 2θ scan from 10° to 80°, with 10 s per step at room temperature. For the XRD analysis, a grain size less than 75 μm was used. For the TL study, all pellets were produced from the powder (between 75 and 180 μm) by cold compaction in a hydraulic press at 100 kg/cm^2. Each pellet had a final mass of 40.0 mg, and was 6.0 mm in diameter and 2.0 mm in thickness. The samples were thermally treated sequentially at 300 °C/30 min and 400 °C/90 min.

The morphology of the grains was determined using the *Inspect Microscope F*-50 with an acceleration voltage of 5 kV and a spot size of 3.5 μm. The SEM samples were covered with a thin carbon layer to promote electrical conductivity in order to obtain microscopic images. The grain size was determined using *Image Pro Plus* 6.0 software.

The radiation used for the tests was from a beta source of ^{90}Sr/^{90}Y of a dermatological applicator type, with an absorbed dose rate of 7.4 mGy/s, and a ^{60}Co Gammacell gamma irradiator (dose rate of 1139 Gy/h). The irradiations were performed at room temperature (RT). For gamma irradiation, the samples were fixed between 3 mm-thick Lucite plates to ensure electronic equilibrium conditions during irradiation.

To evaluate the TL response of the pellets, a Harshaw TL reader system (model TLD-2500) was used. TL glow curves were recorded at a heating rate of 10 °C/s. After the TL measurements, the samples were thermally treated at 400 °C/h for TL bleaching.

In order to evaluate the TL behavior of MgB_4O_7:Nd when it is submitted to a temperature profile, step annealing experiments were performed to analyze how the TL curve changed. The pellets were irradiated (10 Gy) and preheated from zero to a given temperature T_{stop} (100, 150, 200, 250 or 300 °C), then cooled back to room temperature. The whole TL curve was recorded from room temperature up to the maximum readout temperature, and the sequence was repeated for the five different temperatures described above.

3. Results and discussion

3.1. XRD

The XRD results for MgB_4O_7:Nd and MgB_4O_7:Nd,Dy are shown in Fig. 1. The XRD diffractograms obtained for both materials pro-

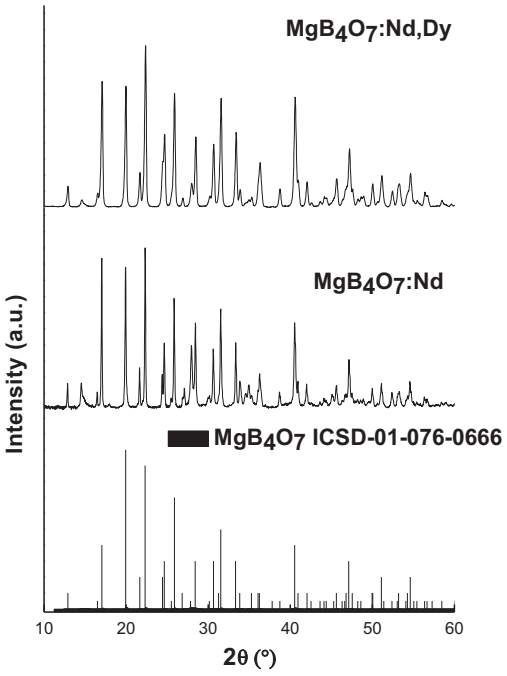

Fig. 1. X-ray diffraction of the calcined MgB_4O_7:Nd and MgB_4O_7:Nd,Dy powder and the respective reference pattern of MgB_4O_7.