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

Luiza F. Souza^a, Patrícia L. Antonio^b, Linda V.E. Caldas^b, Divanizia N. Souza^{a,*}^a Departamento de Física, Universidade Federal de Sergipe, UFS, Av. Marechal Rondon s/n, 49100-000 São Cristóvão, Sergipe, Brazil^b Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear, IPEN/CNEN-SP, Av. Prof. Lineu Prestes 2242, CEP 05508-000 São Paulo, Brazil

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ABSTRACT

MgB₄O₇ doped with lanthanides such as Dy³⁺ and Tm³⁺ are phosphors with very well established use in routine personal dosimetry. Certain characteristics, for example linearity in a broad dose range, low energy dependence, $Z_{\text{eff}}=8.5$, high sensitivity and a relatively simple thermoluminescent (TL) emission curve make MgB₄O₇ a good material for thermoluminescent dosimetry. With the aim of analyzing other doping possibilities, this paper presents some preliminary results on the use of Nd³⁺ as a dopant in the MgB₄O₇ 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 MgB₄O₇:Nd was assessed when irradiated with gamma (⁶⁰Co) 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 MgB₄O₇:Nd,Dy when irradiated with ⁶⁰Co. The TL responses of the phosphors were compared with that of MgB₄O₇:Dy. These preliminary studies show that for the absorbed dose range studied, the sensitivity of MgB₄O₇:Nd,Dy was 3.8 and 28 times higher than that of MgB₄O₇:Dy and MgB₄O₇: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 MgB₄O₇ dosimeter.

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1. Introduction

The applicability of MgB₄O₇ 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]. MgB₄O₇: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 MgB₄O₇ 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 MgB₄O₇ 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]. Li₂B₄O₇:Cu,Ag, MgB₄O₇:Dy,Li, and CaSO₄: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. CaSO₄:Dy³⁺ and CaSO₄:Tm³⁺. Since the 4f shell of the lanthanides is screened by the filled 5s² and 5p⁶ shells of the Xe-core, the 4f electrons experience a weak

* Corresponding author.

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 $\text{MgB}_4\text{O}_7:\text{Dy}$ ($\sim 250^\circ\text{C}$), characterized by emissions at 480 nm, has been extensively reported and is attributed to 4f–4f transitions from Dy^{3+} ($^4\text{F}_{9/2} - ^6\text{H}_{15}$) [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 $\text{MgB}_4\text{O}_7:\text{Nd}$ is a good candidate for this application.

This study aimed to describe some TL features of $\text{MgB}_4\text{O}_7:\text{Nd}$ and the effect of Dy^{3+} as a codopant ($\text{MgB}_4\text{O}_7:\text{Nd,Dy}$). It is expected that some codopants enhance the TL sensitivity of phosphors based on MgB_4O_7 [12]. The behavior of $\text{MgB}_4\text{O}_7:\text{Nd}$ 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 ($> 350^\circ\text{C}$).

The TL responses of both materials ($\text{MgB}_4\text{O}_7:\text{Nd}$ and $\text{MgB}_4\text{O}_7:\text{Nd,Dy}$) were compared with that of $\text{MgB}_4\text{O}_7:\text{Dy}$ [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 $\text{MgB}_4\text{O}_7:\text{Nd}$ was determined by scanning electron microscopy (SEM).

2. Materials and methods

$\text{MgB}_4\text{O}_7:\text{Nd}$ and $\text{MgB}_4\text{O}_7:\text{Nd,Dy}$ were produced through solid state synthesis. This route has been described in the literature for the production of $\text{MgB}_4\text{O}_7:\text{Dy}$ [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, $\text{MgB}_4\text{O}_7:\text{Nd}$ 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 $180\ \mu\text{m}$. For the test, five pellets of each $\text{MgB}_4\text{O}_7:\text{Nd}$ 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 $\text{MgB}_4\text{O}_7:\text{Nd,Dy}$, 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 $75\ \mu\text{m}$ was used. For the TL study, all pellets were produced from the powder (between 75 and $180\ \mu\text{m}$) by cold

compaction in a hydraulic press at $100\ \text{kg}/\text{cm}^2$. 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 $300^\circ\text{C}/30\ \text{min}$ and $400^\circ\text{C}/90\ \text{min}$.

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 $3.5\ \mu\text{m}$. 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 $^{90}\text{Sr}/^{90}\text{Y}$ 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 $10^\circ\text{C}/\text{s}$. After the TL measurements, the samples were thermally treated at $400^\circ\text{C}/\text{h}$ for TL bleaching.

In order to evaluate the TL behavior of $\text{MgB}_4\text{O}_7:\text{Nd}$ 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 $\text{MgB}_4\text{O}_7:\text{Nd}$ and $\text{MgB}_4\text{O}_7:\text{Nd,Dy}$ are shown in Fig. 1. The XRD diffractograms obtained for both materials pro-

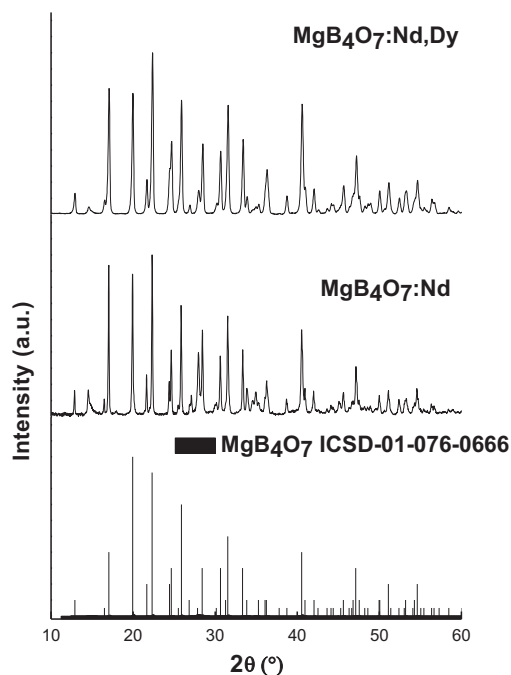


Fig. 1. X-ray diffraction of the calcined $\text{MgB}_4\text{O}_7:\text{Nd}$ and $\text{MgB}_4\text{O}_7:\text{Nd,Dy}$ powder and the respective reference pattern of MgB_4O_7 .

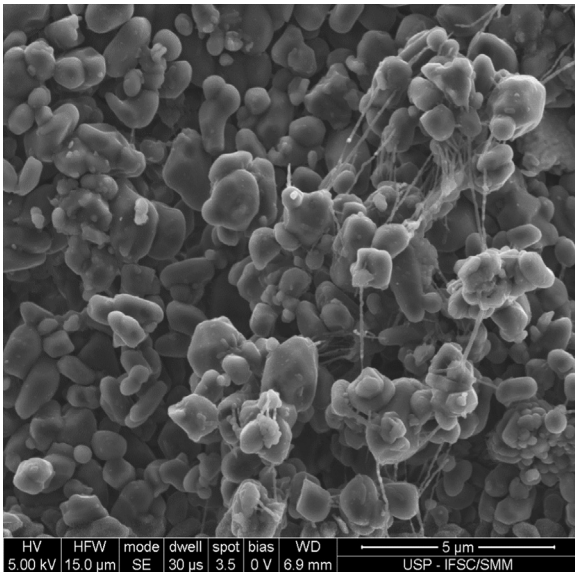


Fig. 2. SEM of $\text{MgB}_4\text{O}_7\text{:Nd}$.

duced by solid state synthesis were in accordance with the ICSD 01-076-0666 standard, corresponding to magnesium tetraborate with an orthorhombic crystal system. The crystallographic parameters were as follows: a (Å): 13.73, b (Å): 7.97, c (Å): 8.62; α (deg): 90; β (deg): 90; γ (deg): 90, thus showing the success of the technique in producing the polycrystal.

Some experimental peaks had different intensities than those presented by the pattern; this effect was possibly related to some preferential direction acquired by the crystals, thus interfering with the diffraction planes.

3.2. SEM

The grain size is a very important characteristic for TL and also for temperature sensing application materials. For TL applications, MgB_4O_7 in nanocrystalline form exhibits very poor sensitivity [11], so the ideal is to produce MgB_4O_7 with larger grains (microcrystalline form). For temperature sensing applications, the ideal is to use material with crystallite sizes $< 20\text{--}30\ \mu\text{m}$, in order to guarantee a fast response time of the material to a short heating pulse [5]. In the SEM image in Fig. 2, the $\text{MgB}_4\text{O}_7\text{:Nd}$ produced by solid state synthesis tended to crystallize in a spherical shape with an average diameter of $1.37 \pm 0.45\ \mu\text{m}$, which is an ideal grain size for both applications.

3.3. Dopant concentration

In Fig. 3, it can be seen that the highest TL emission was exhibited by the pellets with 0.5 wt% (weight) of the dopant. From 1.0 to 1.5 wt%, a decrease in TL intensity was observed, which can be attributed to the concentration quenching effect [16,17]. A possible explanation for quenching is that an increase in the dopant concentration may cause an intensification of competition between traps during the irradiation process or TL readout, giving rise to non-radiative transitions (via electron–phonon coupling), which in turn leads to a decrease in the efficiency of luminescence. Based on these results, the phosphor with 0.5 wt% Nd^{3+} was found to be the best among the samples analyzed.

3.4. TL response

The TL glow curves of the $\text{MgB}_4\text{O}_7\text{:Nd}$ (0.5 wt%) samples irradiated with beta radiation ($^{90}\text{Sr} + ^{90}\text{Y}$) are shown in Fig. 4.

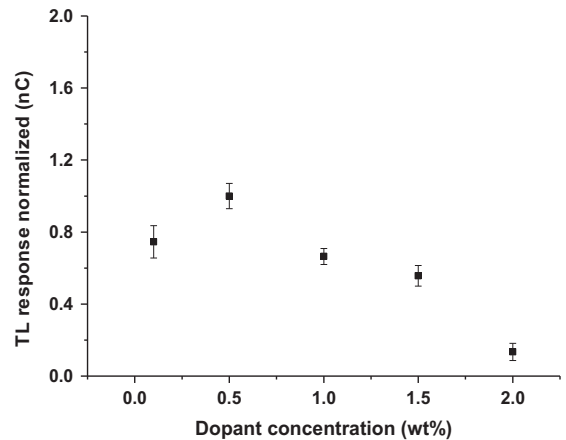


Fig. 3. Sensitivity of MgB_4O_7 as a function of the Nd concentration.

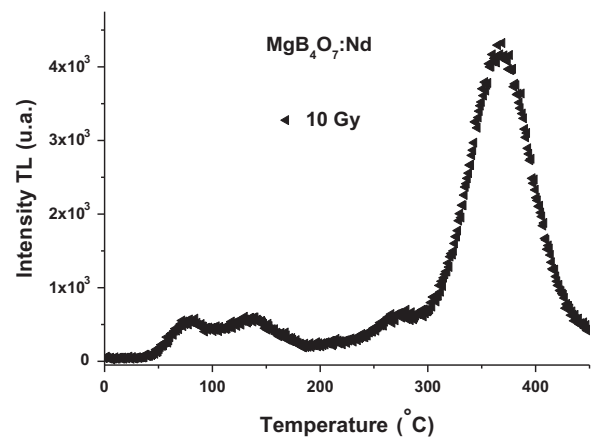


Fig. 4. Typical TL emission curve of $\text{MgB}_4\text{O}_7\text{:Nd}$ exposed to a beta source. The sample was irradiated with an absorbed dose of 10 Gy ($^{90}\text{Sr}/^{90}\text{Y}$).

The presence of two less intense TL peaks was observed, between $0\ ^\circ\text{C}$ and $200\ ^\circ\text{C}$, while the final and most intense peak was found in the high temperature region ($> 350\ ^\circ\text{C}$). This TL emission indicates the possible existence of three different trap sites (luminescent centers) [16]. The third peak increased proportionally with the absorbed dose, as expected during TL dosimetry. Another important feature for dosimetric applications (e.g., personal and environmental) is the linear TL response to dose; the TL response was linear over the dose range studied, i.e. between 2 and 20 Gy for electrons ($^{90}\text{Sr}/^{90}\text{Y}$) and from 0.2 to 54 Gy for gamma radiation (^{60}Co) (Figs. 5 and 6).

The TL glow curves of $\text{MgB}_4\text{O}_7\text{:Dy}$, $\text{MgB}_4\text{O}_7\text{:Nd}$ and $\text{MgB}_4\text{O}_7\text{:Nd,Dy}$ pellets are compared in Fig. 7. The TL peak of $\text{MgB}_4\text{O}_7\text{:Dy}$ around $200\ ^\circ\text{C}$ was from Dy^{3+} emissions, which act as recombination/luminescent centers [18,19]. The TL peak of $\text{MgB}_4\text{O}_7\text{:Nd,Dy}$ was located at a high temperature (around $350\ ^\circ\text{C}$) in the same region as the main TL peak of $\text{MgB}_4\text{O}_7\text{:Nd}$. These peaks may be associated with recombination in deep traps with emissions at around $550\ \text{nm}$ [5].

The dose–response curves for both materials ($\text{MgB}_4\text{O}_7\text{:Nd}$ and $\text{MgB}_4\text{O}_7\text{:Nd,Dy}$) were compared with the dose–response curve of $\text{MgB}_4\text{O}_7\text{:Dy}$ [13], considering the area below the highest TL emission peak. According to Fig. 8, it was observed that in the absorbed dose range studied, the $\text{MgB}_4\text{O}_7\text{:Nd,Dy}$ dosimeter had almost 3.8 times greater sensitivity than $\text{MgB}_4\text{O}_7\text{:Dy}$ and about 28 times more than $\text{MgB}_4\text{O}_7\text{:Nd}$. The Dy codopant may act as a charge compensator, helping to improve the incorporation of Nd in the MgB_4O_7 crystal lattice, thereby increasing its TL sensitivity. Alkali

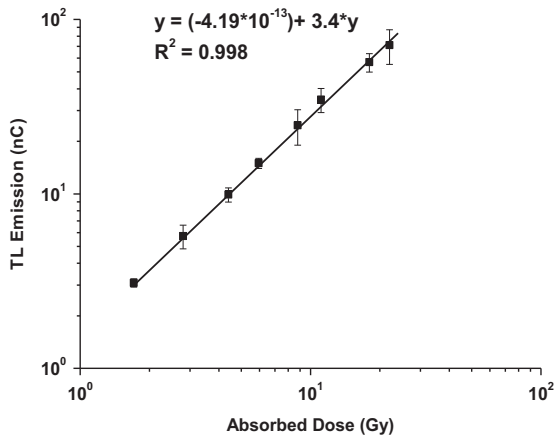


Fig. 5. Dose–response curve of $\text{MgB}_4\text{O}_7:\text{Nd}$ pellets irradiated from 2 to 20 Gy ($^{90}\text{Sr}+^{90}\text{Y}$ source) at room temperature.

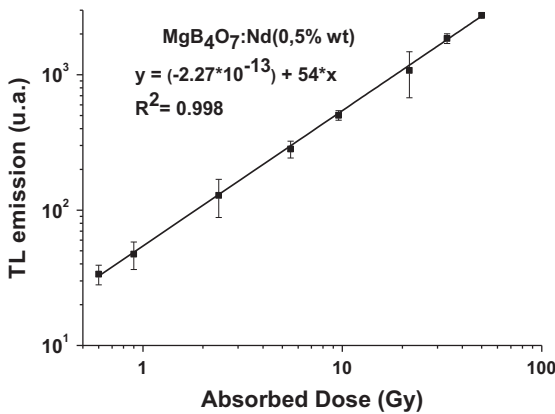


Fig. 6. Dose–response curve of $\text{MgB}_4\text{O}_7:\text{Nd}$ pellets irradiated from 0.2 Gy to 54 Gy (^{60}Co source) at room temperature.

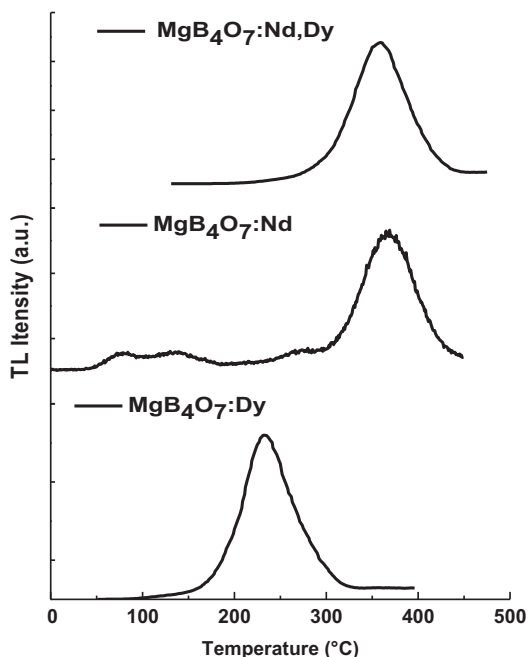


Fig. 7. TL glow curves of both materials ($\text{MgB}_4\text{O}_7:\text{Nd}$ and $\text{MgB}_4\text{O}_7:\text{Nd,Dy}$) in comparison with $\text{MgB}_4\text{O}_7:\text{Dy}$.

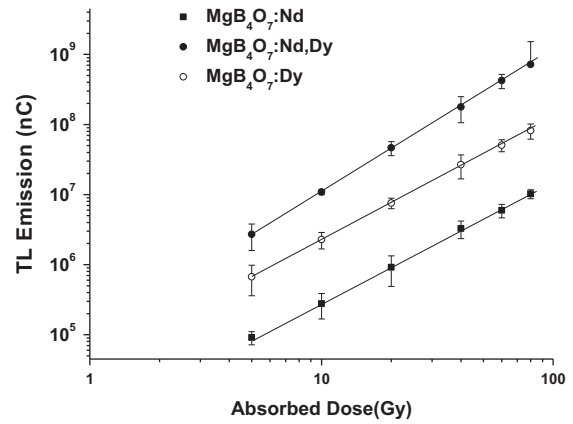


Fig. 8. Dose–response curves for $\text{MgB}_4\text{O}_7:\text{Nd}$, $\text{MgB}_4\text{O}_7:\text{Nd,Dy}$, and $\text{MgB}_4\text{O}_7:\text{Dy}$ irradiated from 5 Gy to 80 Gy (^{60}Co source) at room temperature.

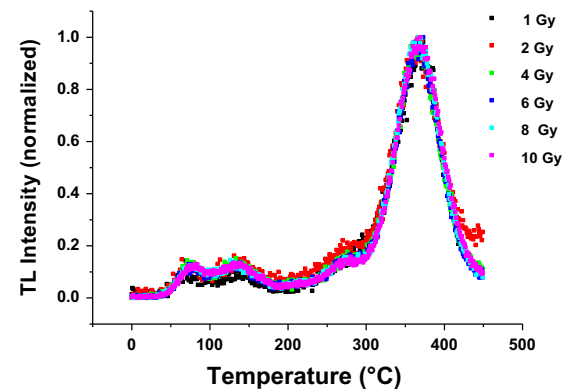


Fig. 9. Normalized TL curves from the dose–response of $\text{MgB}_4\text{O}_7:\text{Nd}$ over a dose range of about 1–10 Gy.

metals such as Na, Li and K have been reported in the literature as codopants that increase the TL sensitivity of MgB_4O_7 , as they also act as charge compensators and enhance incorporation of the dopant into the lattice [18]. Linearity of dose–response is a rare behavior over 10 Gy of absorbed dose, which makes $\text{MgB}_4\text{O}_7:\text{Nd}$, $\text{MgB}_4\text{O}_7:\text{Nd,Dy}$ and $\text{MgB}_4\text{O}_7:\text{Dy}$ rather distinct amongst other dosimeters in that they present linearity from 5 to 40 Gy. Above 40 Gy, the TL glow curves began to exhibit sublinear behavior with a loss of proportionality between the absorbed dose and the TL signal. However, this region (sub-linearity) can still be used with previous calibration of the dosimeter [20].

3.5. Temperature sensing applications

In addition to TL dosimetry, the $\text{MgB}_4\text{O}_7:\text{Nd}$ dosimeter can be used as a temperature sensor. The $\text{MgB}_4\text{O}_7:\text{Nd}$ fulfills one of the main criteria for this particular application, i.e. it is a material with multiple TL peaks, which can capture information over a wider temperature range [5]. As can be observed in Fig. 3, $\text{MgB}_4\text{O}_7:\text{Nd}$ presents peaks below 200 °C and one major TL peak above 350 °C. For this particular application, the comparison of dose–response for TL materials at low doses (< 1 Gy) is not relevant. For these studies, the material should be irradiated with high doses before being submitted to a temperature profile, thus guaranteeing sufficient TL intensity in case a small amount of TL material is used.

The dose–response of $\text{MgB}_4\text{O}_7:\text{Nd}$ at high doses can be observed in Fig. 9. It was also observed that the main TL peak position (> 350 °C) did not vary with increasing dose, indicating

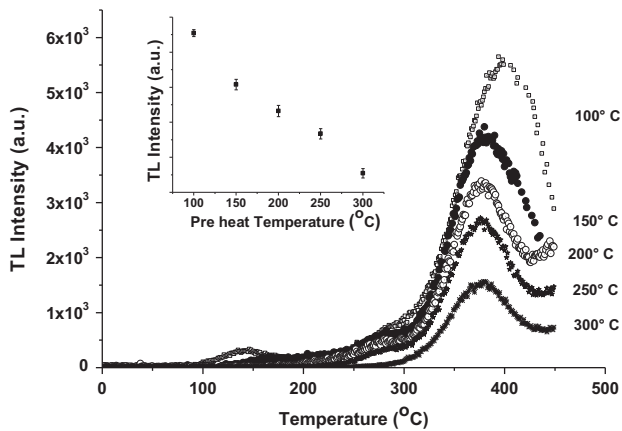


Fig. 10. Step annealing data for $\text{MgB}_4\text{O}_7:\text{Nd}$. T_{stop} is the annealing temperature used for the test and the heating rate for both the pre-heating and the readout was $5^\circ\text{C}/\text{s}$.

that the kinetic parameters of the TL peak are close to one (first-order kinetics); otherwise, the position of the TL emission peak would shift toward higher temperatures as the radiation dose increased, a feature typical of a TL emission peak approaching second-order kinetics [12,18]. It is important for TL materials used in temperature sensing applications to have a well-defined and separated TL emission peak. The results of step annealing experiments are shown in Fig. 10; as expected, the TL peaks were emptied as the T_{stop} increased and the TL emission curve barely shifted with increasing T_{stop} . This is another indication that the TL emission curve of $\text{MgB}_4\text{O}_7:\text{Nd}$ (350°C) is characterized by first-order kinetics.

4. Conclusion

The results of this study show that $\text{MgB}_4\text{O}_7:\text{Nd}$ and $\text{MgB}_4\text{O}_7:\text{Nd}, \text{Dy}$ phosphors can be produced successfully by solid state synthesis using a simple route, as shown by XRD analysis. The TL response of the pellets showed that $\text{MgB}_4\text{O}_7:\text{Nd}$ is sensitive to beta radiation and presents dose–response linearity from 2 to 20 Gy of absorbed dose for $^{90}\text{Sr}+^{90}\text{Y}$ and for ^{60}Co in the dose range from 0.2 to 80 Gy. Another possible application for $\text{MgB}_4\text{O}_7:\text{Nd}$ is in temperature sensing, due to the presence of TL emission peaks throughout the temperature range studied. Moreover, the main TL

peak is located in a high temperature range ($> 350^\circ\text{C}$). However, for dosimetry applications, the use of two dopants (Nd and Dy) in the MgB_4O_7 matrix produced a good thermoluminescent phosphor. $\text{MgB}_4\text{O}_7:\text{Nd}, \text{Dy}$ was about 3.8 times more sensitive than $\text{MgB}_4\text{O}_7:\text{Dy}$ and about 38 times more sensitive than $\text{MgB}_4\text{O}_7:\text{Nd}$.

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