Thermal and structural properties of magnesium tetraborate produced by solid state synthesis and precipitation for use in thermoluminescent dosimetry

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ARTICLE INFO

Keywords:
Dosimetry
Dysprosium
Magnesium tetraborate
SEM images
Sintering
Thermoluminescence
Thermal analyses

ABSTRACT

Magnesium tetraborate is a phosphor with relevant characteristics for radiation dosimetry purposes. One of the main challenges on this material is still the understanding of its structure and luminescent processes involved in dosimetric performance. In this work, all the steps of the material production through DTA/TG, XRD and SEM techniques were evaluated to understand the main physical and chemical changes during the thermal process (calcination and sinterization) to produce the MgB₄O₇ samples. Two synthesis processes of MgB₄O₇ were studied: precipitation (P.S) and solid state (S.S). Finally, the luminescence efficiency of the pellets was investigated in function of different sintering temperatures. The initial stage of DTA/TG curves of the material just after the mixing of starting materials, regardless the synthesis, is marked by endothermic events caused by dehydration, decomposition of hydroxyl groups and hydrated borate phases. At higher temperatures, the curves are marked by exothermic events related to crystalline transitions, but the peak obtained for the S.S is better defined in comparison to P.S. Moreover, the DTA/TG analyses of the pellets prior and after the sinterization, showed that the process is more relevant for the MgB₄O₇ pellets produced by S.S (950 °C), dramatically reducing its hygroscopicity. The SEM images reinforce the importance of the sintering process to create a resistant detector and with a more homogenous and cohesive surface, therefore increasing it luminescence properties. The thermoluminescent (TL) sensitivity of MgB₄O₇:Dy₀.₅% pellets produced via S.S, sintered at 950 °C, is 4 times higher compared to the ones sintered at 950 °C, via P.S. The materials produced via P.S did not present relevant changes in their TL sensitivity for sintering temperatures above 400 °C.

1. Introduction

Since 1980, borates are of great interest for thermoluminescent dosimetry (TLD), once they present better sensitivity (∼ 10 times higher) compared to the commercial TLD-100 (LiF:Mg,Ti), when exposed to gamma and beta radiation (Prokic, 1993, 2007). Some borate-based materials also can detect thermal neutrons (E < 0.25 eV), when produced with enriched boron (boron-10) (Yukihara et al., 2017). MgB₄O₇, for example, has an effective atomic number (Zₑff) for photoelectric absorption equal to 8.4, which is comparable to 7.4, for water and soft biological tissue, which is crucial for personal dosimetry (Prokic, 1986; Yukihara et al., 2017). Among the borates, the most useful for radiation dosimetry are barium borate (BaB₂O₄), lithium tetraborate (Li₂B₄O₇), hydrated borate phases at higher temperatures, the curves are marked by exothermic events related to crystalline transitions, but the peak obtained for the S.S is better defined in comparison to P.S. Moreover, the DTA/TG analyses of the pellets prior and after the sinterization, showed that the process is more relevant for the MgB₄O₇ pellets produced by S.S (950 °C), dramatically reducing its hygroscopicity. The SEM images reinforce the importance of the sintering process to create a resistant detector and with a more homogenous and cohesive surface, therefore increasing it luminescence properties. The thermoluminescent (TL) sensitivity of MgB₄O₇:Dy₀.₅% pellets produced via S.S, sintered at 950 °C, is 4 times higher compared to the ones sintered at 950 °C, via P.S. The materials produced via P.S did not present relevant changes in their TL sensitivity for sintering temperatures above 400 °C.

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https://doi.org/10.1016/j.radphyschem.2019.108382
Received 18 February 2019; Received in revised form 13 May 2019; Accepted 22 June 2019
Available online 24 June 2019
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It is already known that the synthesis process may change the luminescent efficiency of a detector and consequently its dosimetric properties, recently, it was reported how two different routes, solid state synthesis and precipitation synthesis (wet reaction), affect the dosimetric properties (e.g. dose response) of the MgB₄O₇:Dy, upon beta irradiation (Souza et al., 2015, 2017).

Hereby, the present work aimed to evaluate this change in a different perspective and to a deeper understanding why the synthesis changes the final TL properties in the MgB₄O₇ matrices. With this purpose, solid state and precipitation syntheses (S.S and P.S, respectively) were used to prepare the tetraborate; it was analyzed from the initial stage, which is the mixing of starting reactants for the MgB₄O₇ production, to the final stage, consisting in the pellets’ sinterization. To characterize these steps, differential thermal and thermogravimetry techniques (DTA/TG) were used. DTA/TG are important techniques for monitoring the chemical and physical changes of materials under increasing temperature. X-ray diffraction (XRD) was used to confirm the crystalline phase of the MgB₄O₇ matrices. The morphological characteristics of the pellets were examined through scanning electronic microscopy (SEM). Finally, the effect of different sintering temperature was checked in the final TL emission of MgB₄O₇:Dy produced by both S.S and P.S.

2. Materials and methods

For the solid state synthesis, high temperatures are used to promote the formation of the desired phase of MgB₄O₇. In the precipitation synthesis, the compounds are obtained using aqueous solutions and so lower calcinations temperatures are needed (Souza et al., 2015; Yukihiro et al., 2013, 2014; Chiang et al., 1997; Subanakov et al., 2014).

For both routes, the starting materials used were: MgO (Merck, 99.9% purity) and H₃BO₃ (Merck, 99.9% purity). For doped samples (MgB₄O₇:Dy₄₋ₓ₁₀), dysprosium oxide (Dy₂O₃) (Sigma-Aldrich, 99.9% purity) was utilized. The stoichiometric proportion of raw materials at temperature are better defined in comparison with the showed loss of mass. For the P.S, the reactants and dopants, when it is the case, were diluted in nitric acid (HNO₃) with the main purpose of accelerating the chemical transformations of the samples upon heating. The TG (dotted line) records changes in the samples mass along of this process.

For both methods, stage III (Fig. 1a and b) is marked by exothermic events related to crystalline transitions (Brown, 2004), but the exothermic peak at 170 °C, with weight loss of 5% in the range of 152-165 °C. In stage II there is an endothermic peak at 115 °C, accompanied by a loss of weight of 25% between 21 °C and 150 °C. For the S.S case, at the first stage, an endothermic peak is seen at 115 °C, accompanied by a loss of weight of 25% between 21 °C and 150 °C. In stage II there is an endothermic peak at 170 °C, with weight loss of 5% in the range of 152-265 °C.

3. Results and discussion

3.1. Thermal analyses and XRD diffraction

DTA/TG curves of the samples produced by S.S and P.S prior the calcination are shown in Fig. 1(a) and (b), respectively. The DTA (full line) represents chemical and physical changes in the samples during the temperature raising. The TG (dotted line) records changes in the samples mass along of this process.

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obtained by S.S at 900 °C for 7 h. The XRD results indicate that the crystalline phase of MgB₄O₇ is the dominating one for these calcination temperatures.

The DTA/TG analyses in the MgB₄O₇ pellets prior and after the sinterization are shown in Figs. 3 and 4, respectively. In Fig. 3 (a) is shown the thermal analyses of MgB₄O₇ produced by P.S, prior the sinterization at 850 °C for 2 h, where two weak exothermic broad bands are seen around 40 °C and 120 °C approximately. These bands are related to an adsorption process whereby water molecules adhere to the surface, due to the porosity presented by non-sintered pellets. After the sintering process [Fig. 3 (b)], the two small peaks are replaced by a broad exothermic band. The loss of mass of the pellet prior sinterization is 10% compared to 4% observed after the sinterization.

The sintering process has a higher relevance for MgB₄O₇ pellets obtained through the S.S. As can be seen in Fig. 4 (a), the DTA/TG curve of a non-sintered pellet shows two strong endothermic peaks at 114 °C and 214 °C, which is related to the occurrence of water molecules decomposition. An exothermic peak is seen at 539 °C, which can be related to the recrystallization process of the borates (Pekpak et al., 2010; Yukihara et al., 2013). After the sintering process at 950 °C, the pellets did not present relevant thermal changes during the temperature interval of the DTA/TG. The loss of 16% of mass for these pellets without sinterization, and just after the sintering the loss of mass is only 4%.

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The DTA/TG curve of a sintered MgB₄O₇ pellet, at 950 °C for 2 h, is very similar to that obtained for a sintered MgB₄O₇ pellet prepared via precipitation [Fig. 3 (b)]; it is composed of one exothermic broad band around 100 °C and an endothermic broad band between 600 °C and 800 °C, also with insignificant loss of mass (3%).

Through SEM images it was possible to see the surface of the MgB₄O₇ pellets before and after the sintering. In Figs. 5 and 6, it is seen that the sintering reduces the porosity of the pellets and thus improve their cohesion and surface homogeneity. For dosimetric purposes pellets must have a homogeneous surface and should be as cohesive as possible, to improve the optical and thermal conductivity properties, once that reproducibility of the luminescent signal is reduced by porous surfaces (Galmarini, 2011). In addition to increasing mechanical resistance of MgB₄O₇ pellet, the sintering process is a fundamental tool to reduce the sample hygroscopicity, and the DTA/TG results obtained before and after sintering process corroborate this affirmation [Figs. 3 and 4].

3.3. Sintering effect on TL sensitivity

The influence of different sintering temperature on the final thermoluminescent (TL) emission of MgB₄O₇:Dy₀.₅% is shown in Fig. 7. In the figure, each point in the graphs represents the average value of the areas below the TL peak at 240 °C exhibited by the pellets produced through S.S and that one at 225 °C by the samples obtained via P.S (Fig. 8).

In Fig. 7 it is clear that the TL sensitivity of the pellets produced by S.S is much higher compared to the one produced by P.S, for non-sintered pellets and for all sintering temperature range evaluated. As an example, the TL emission of non-sintered S.S pellets is 6 times higher than the one produced by P.S.

The sintering at 400 °C for 2 h increases the TL emission of MgB₄O₇:Dy₀.₅% produced by P.S, in an order of two [Fig. 7 (b)]. Considering the other sintering temperature (> 400 °C), the TL emissions are within the uncertainties (type A) range.

The MgB₄O₇:Dy₀.₅% pellets obtained through the S.S and sintered at 300 °C for 2 h showed a similar TL sensitivity to the non-sintered pellets. For higher temperatures, from 300 °C to 950 °C, an increase was
observed in the TL efficiency by an order of 4. This behavior confirms how the sintering process is fundamental in the TL efficiency of the phosphorus, prepared by S.S.

The DTA/TG curves of non-sintered S.S MgB₄O₇ pellets [Fig. 3 (b)] exhibited endothermic events related to water release in their structure, due to its high porosity [Fig. 6 (a)]. During the TL reading, the presence of water molecules in the porous of MgB₄O₇:Dy₀.₅% pellet can easily absorb the luminescence emitted by the sample, creating a quenching effect and thus reducing its luminescence efficiency.

During the heating in the TL reading, the thermal conductivity among the pellets is also reduced with the presence of the porous: the transfer of heat through the pores is usually slow and inefficient, due to the presence of stagnant air and water (Yukihara et al., 2014; Somiya, 2013) and so this is another important factor which contributes to decrease the TL sensitivity of non-sintered MgB₄O₇:Dy₀.₅% pellets.

The sinterization process used in this work consisted in taking the tetraborate pellets to temperatures close to their fusion, which is approximately 1000 °C. High temperatures cause reduction of porosity,
improving the mechanical, thermal and optical properties of these pellets. Indeed, the sintering at higher temperatures causes better diffusion of the BO$_3^{3-}$ and BO$_4^{4-}$ vacancies at the MgB$_4$O$_7$ (Galmarini, 2011), which act as trapping centers in this lattice (Prokic, M., 1986. Magnesium borate in TL dosimetry. Radiat. Protect. Dosim. 17, 91-93).

Fig. 7. (a) - TL emission of MgB$_4$O$_7$:Dy$_{0.5\%}$ pellets obtained through the S.S and P.S syntheses. (b) Enlarged image of the P.S graph. All the pellets were irradiated with 1 Gy ($^{90}$Sr/$^{90}$Y).

Fig. 8. TL emission from MgB$_4$O$_7$:Dy$_{0.5\%}$ produced via the S.S synthesis and the precipitation method, after irradiation of 1 Gy ($^{90}$Sr/$^{90}$Y).

4. Conclusions

In this work the TL efficiency of tetraborate has been correlated with its synthesis steps, covering from the calcination process, were the borate is produced in its crystalline phase, to the sintering of the pellets. With the DTA/TG analyses of raw material, just after mixing, it was possible to identify the main physical and chemical events which occur with temperature raising. The graphs showed that the crystallization of the material prepared by P.S is accompanied by nitric acid liberation, causing the broad band seen within 600 °C and 800 °C (Fig. 1 (b)). The exothermic band at the S.S case is well defined and with a peak at 712 °C. It was also observed that the total loss of mass during the calcination process is 55%, for the P.S, and 37% for the material produced via S.S.

The DTA/TG graphs of the non-sintered and sintered pellets emphasize the importance of the sintering process to improve the cohesion of the pellets and also to reduce the porosity in their surface. This process is more relevant for the S.S MgB$_4$O$_7$:Dy$_{0.5\%}$ pellets in comparison to the ones produced by P.S. Such proprieties reflect directly in the TL efficiency of the pellets, and the SEM images corroborate this affirmation. Finally, it was observed that the TL sensitivity is improved with the increase of sintering temperatures. This effect was pronounced for the S.S MgB$_4$O$_7$:Dy$_{0.5\%}$ pellets, where an improving in the TL sensitivity from 350 °C to 950 °C was seen. Moreover, although the calcination temperature and time to prepare the MgB$_4$O$_7$ through P.S is much lower compared to the S.S, leading to less energy consumption, the technique is very cumbersome and the TL sensitivity of the detector is much lower compared to the TLDs produced by S.S (in an order of 6).

This aspect reinforces the assumption presented by previous papers (Souza et al., 2014, 2015), that the S.S has more advantages than the P.S, when producing the MgB$_4$O$_7$:Dy$_{0.5\%}$ for dosimetric purposes.

Acknowledgments

The authors gratefully acknowledge the support received by the Brazilian agency CNPq (301335/2016-8) and CAPES (88881.119743/2016-01).

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