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Research Article

Influence of the Uniaxial Hot-Pressing Sintering Condition on $Bi_4Ge_3O_{12}$ Ceramic Scintillators

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The production of high-density bismuth germanate ($Bi_3Ge_4O_{12}$) ceramic scintillators by uniaxial hot pressing was investigated as a function of different applied pressure conditions. The X-ray diffraction showed that the sintering process was able to eliminate the undesirable secondary phase present in the nonsintered samples. The height changes from samples with higher applied pressure rate and applied pressure duration lead to a better relative density value, >95% for samples sintered under a pressure of 0.14 and 0.18 MPa. The radioluminescence results showed that all samples have the characteristic emission spectra of $Bi_3Ge_4O_{12}$ and that the hot-pressed samples have higher radioluminescence emission efficiency.

1. Introduction

The eulytite crystals like bismuth germanate ($Bi_4Ge_3O_{12}$, BGO) have a considerable importance due to their remarkable characteristics such as large light output, fast luminescent decay time, low afterglow, and good radiation hardness [1]. Other characteristics of the BGO are very high effective atomic number ($Z_{eff} = 74$) that promotes a good attenuation of ionizing radiation, very low hygroscopicity, and high density ($\rho = 7.1\ g{\cdot}cm^{-3}$). These characteristics made them an important material for scintillation applications [2, 3], such as positron detection [4], calorimetry [5], positron emission tomography (PET), and fusion controllers [2], always using single crystals.

The BGO crystals growth process is reasonably expensive [6–8]. However, the use of polycrystalline ceramics has shown some advantages, in comparison with single crystal form, such as easier preparation and lower production costs [9]. The sintering process is the experimental technique used to produce polycrystalline ceramic bodies, and it has a huge importance in the development of high-density ceramics [10]. There are many different sintering processes that produce good relative densities values such as hot pressing [11], spark plasma [12], microwave [13], and laser sintering [2]. The hot pressing is relatively a simple technique, in which the sample is heated under a uniaxial or isostatic mechanical load, and this additional energy accelerates the kinetics of the densification process [14].

In previous work, we have shown that, for sintered BGO ceramics, the light output when exposed to X-ray photons is much higher than for single crystal form [15]. In this paper, we have carried out a study of the uniaxial hot pressing sintering to prepare BGO ceramics and investigate its luminescence when exposed to the X-ray source. The crystalline structure of ceramic powder and sintered samples was analyzed by X-ray diffraction. Different sintering conditions such as load rate and uniaxial pressure load were investigated in function of the relative density of the sintered samples and their relationships with scintillating efficiency.

2. Experimental

The BGO powder was produced by the solid-state reaction. The precursor oxides were used as starting materials in stoichiometric amounts of 2 : 3 of Bi_2O_3 and GeO_2 (99, 99% purity grade, Alfa Aesar, Danvers, MA), respectively. These

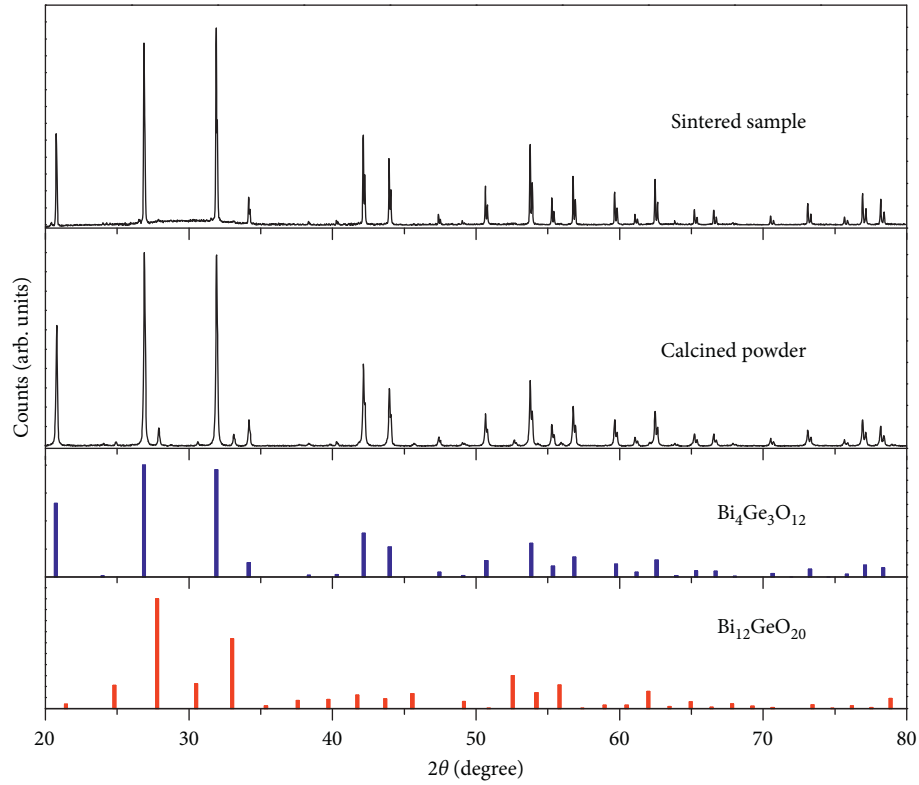

Figure 1: XRD patterns of the BGO calcined powders and sintered ceramics. Before sintering, the samples showed main $Bi_4Ge_3O_{12}$ crystalline phases with some XRD peaks due to the $Bi_{12}GeO_{20}$ crystalline phase. Sintered ceramics show only the $Bi_4Ge_3O_{12}$ crystalline phase.

oxides were ball milled with zirconia balls and isopropyl alcohol in a volumetric proportion of 10 : 60 : 30, respectively, for 80 hours, followed by the drying process and calcination at 800°C for 8 hours. Later, the powder was milled again for 24 hours due to undesirable grain growth in the calcination step. To produce the pellets, the powder was mixed to a drop of a binder solution of polyvinyl alcohol (PVA, 0.1 g·ml^{-1}) and uniaxially pressed under 15 MPa into samples of 6 mm of diameter and ~1.2 mm thick.

The pellets, also known as green ceramic pellets, must have at least 50% of relative apparent density in order to attain final densities in the sintered ceramics that are high enough to be useful (usually higher than 90%). The apparent density of the green ceramic pellets was obtained using the geometric method in which the mass, diameter, and height were measured and the relative densities were calculated in the following equation:

$$D_r = \frac{m}{\pi r^2 h/7.1} * 100, \quad (1)$$

where D_r is the relative density, m, r, and h is the mass, radius, and height of pellets, respectively, and 7.1 is the density of the BGO single crystal in g·cm^{-3}.

BGO ceramics were sintering in a thermomechanical analyzer (TMA, 60 Shimadzu) with different pressures (0, 0.10, 0.14, and 0.18 MPa) and heated between two alumina disks. The sintering programs are called BGO I and BGO II. In the BGO I program, the pressure load was continuously raised during the sintering temperature plateau and released before the cooling step. In the BGO II program, full pressure was applied at the beginning of the sintering plateau and kept until the end of the cooling process. In both cases, the heating rate was 10°C·min^{-1}, the binder was burned at 450°C for 30 min, the sintering temperature was 840°C for 4 hours, and maximum pressure values of 0.10 MPa, 0.14 MPa, or 0.18 MPa were tested.

The crystalline phases present in the calcined powder and the sintered ceramic pellets were investigated using powder X-ray diffraction analysis using Cu Kα radiation in a Bruker D8 Advance diffractometer in the Bragg–Brentano geometry, operating at 40 kV/40 mA in the continuous scanning mode, over a 2θ range from 20° to 80°. The relative densities of ceramics were measured according to the Archimedes method. The radioluminescent (RL) measurements were done using an Oxford X-ray tube (Oxford Instruments™) operating at 45 kV/0.75 mA, with radiation from W target. An optical fiber coupled to an Ocean Optics HR2000 spectrometer was used to collect the light output signals.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the BGO calcined powders and sintered ceramics. For the powder, it is possible to see the presence of two different phases of bismuth germanate compounds. The main phase is attributed to the typical cubic $Bi_4Ge_3O_{12}$ crystalline phase with space group 43m, according to card no. 084-0505 from ICSD. A small

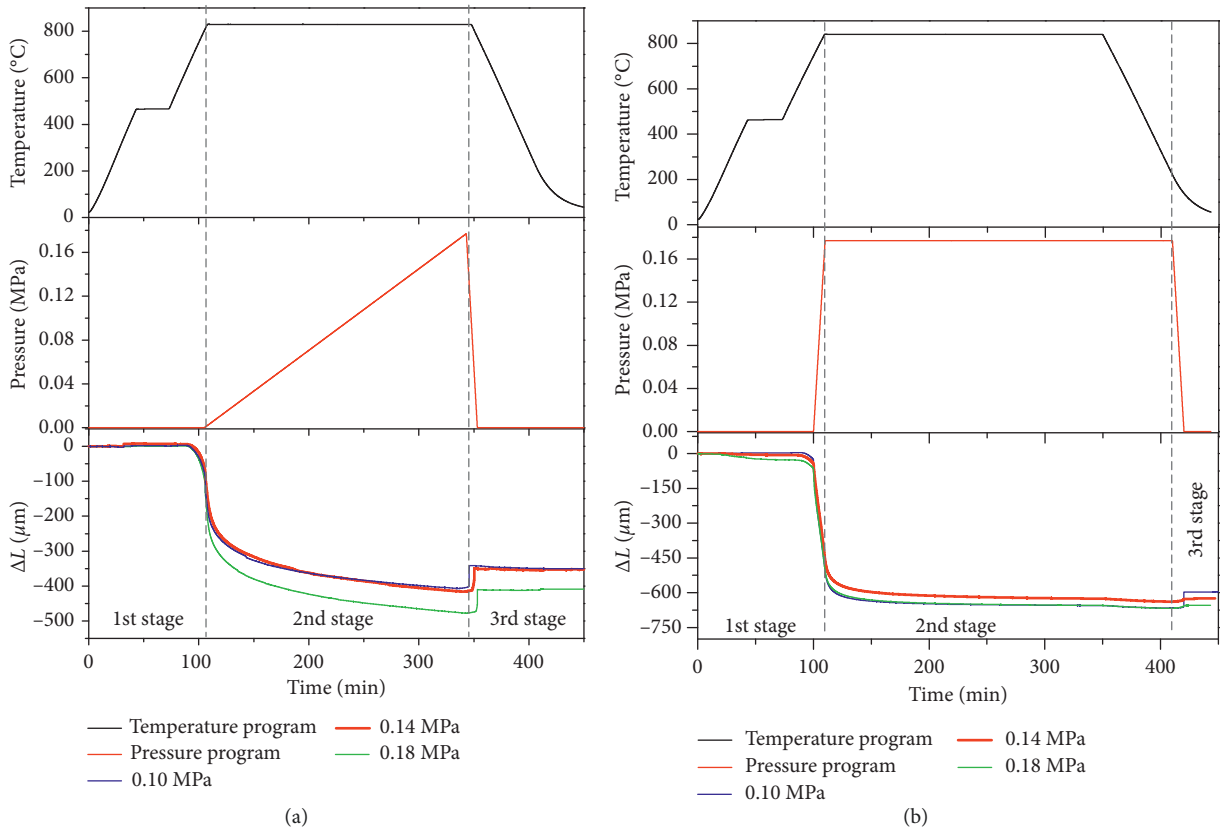

Figure 2: Height changes of the samples during the hot-pressing procedure using three different pressure factors. The solid black line represents the heating program. In the first stage, the sample is heated up to 840°C; in the second stage, the sample is maintained under 840°C for 4 h; and in the third stage, the sample is cooled down to room temperature. (a) BGO I, (b) BGO II.

amount of the $Bi_{12}GeO_{20}$ crystalline phase was also found, identified by the presence of the two main peak of this phase at 27.81 and 30.52 degrees, according to card no. 077-0861 from ICSD. However, a small amount of the $Bi_{12}GeO_{20}$ is frequently found after the synthesis of $Bi_4Ge_3O_{12}$. This secondary phase is undesirable since it does not exhibit luminescent properties [16]. The crystallization of both phases, occurred due to the enthalpy of formation of $Bi_{12}GeO_{20}$, which is lower than for $Bi_4Ge_3O_{12}$, that is, 920.70 and 588.265 eV, respectively [17].

For sintered ceramics, the presence of $Bi_{12}GeO_{20}$ was not detected by XRD measurements. This effect was discussed in a previous work [2], in terms of the melting points of $Bi_{12}GeO_{20}$ and $Bi_4Ge_3O_{12}$ are 1050°C and 870°C, respectively, and during the sintering process, the melting of the $Bi_{12}GeO_{20}$ phase occurs. During the cooling step, this phase solidifies in an amorphous structure, inhibiting its detection by XRD.

Figure 2 shows the height change for different pressure loads used during the hot-pressing procedure, where a higher pressure leads to an increase in the total shrinkage of the BGO ceramics. The obtained relative densities are shown in Table 1. Although the samples sintered with higher pressure loads seem to present the highest shrinkage, the final relative density did not follow this behavior. This can be because of nonuniformity of the surface of the starting pellets (before sintering). Nevertheless, the main result from Figure 2(a) is promising showing that all samples displayed relative density higher than 94%. This value is bigger than the ones obtained by Andrade de Jesus et al. [18] where the authors used conventional sintering method in BGO nanoparticles produced by combustion synthesis obtaining relative densities between 68% and 84% for different BGO preparation conditions.

Table 1: Relative densities and RL efficiency for BGO I and II samples.

	Relative density		RL efficiency	
	BGO I	BGO II	BGO I	BGO II
0 MPa	95.28 ± 0.5	95.28 ± 0.5	—	—
0.10 MPa	94.87% ± 0.01	95% ± 2	+7.2%	+0.13%
0.14 MPa	94.07% ± 0.01	94.2% ± 0.4	+7.1%	+0.79%
0.18 MPa	94.67% ± 0.01	95% ± 2	+8.3%	−3.70%

Figure 2(a) also showed that after removing the pressure load, the samples showed a small expansion, marked in the figure as the 3rd stage.

Figure 2(b) shows the height change of the BGO ceramics submitted to the hot-pressing program BGO II. This new condition is based on the increase of the rate of applied load just before reaching the sintering temperature and in keeping it applied for the rest of the thermal cycle until it

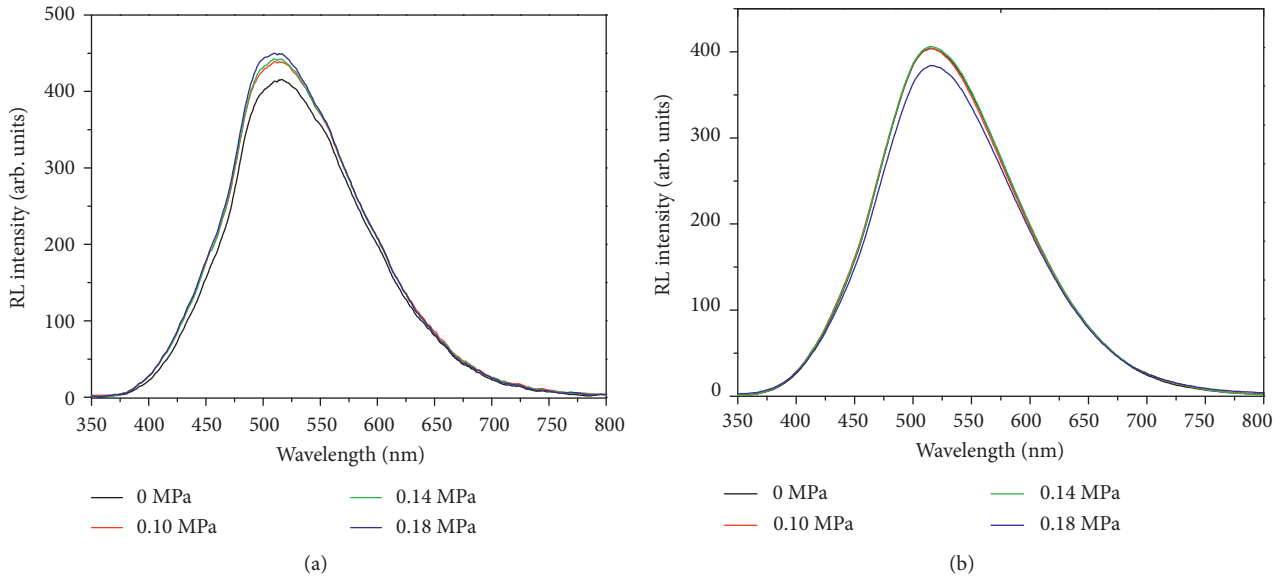

Figure 3: Radioluminescent spectra of ceramics sintered under the hot-pressing programs BGO I (a) and BGO II (b) using different load conditions, as compared to samples obtained with the same thermal cycle but with no applied load.

cooled back to room temperature. This procedure was adopted after observing that, in the BGO I program, the samples expanded in the 3rd stage after the pressure load was removed. The sample shrinkages observed using the BGO II program were at least 40% higher than the ones obtained using the BGO I condition. Table 1 shows the values of relative densities for all sintering conditions. The values in the table are average values, and the respective standard deviation, of density measurements for groups of ceramic pellets sintered in the same conditions.

The relative density measurements did not show any significant difference between the groups of samples, although the linear shrinkage was observed to be quite different for different pressure loads and also dependent on the way the pressure load is applied during sintering. One possible explanation is that the Archimedes method is not sensitive enough to show the density difference since all sample groups showed quite high relative density, above 94%. The fluctuation in the relative densities for the samples in group BGO II was observed to be much higher than the samples in group BGO I, and this may also be associated with the fact that, on applying the pressure load during all the sintering temperature plateaus and keeping it until the sample was cooled down to room temperature, there is a few variation in the total time of the applied load due to small differences during the cooling steps that is governed in the final steps due to the natural convection currents and the thermal energy exchange between the sample oven and the laboratory room temperature. Nevertheless, the important and crucial result obtained is that the pressure loads do help the sintering processes of the samples increasing the final relative density of the ceramic pellets to values above the ones usually obtained in the literature when only temperature is used for the same total time of sintering. In a previous work [15], total sintering temperature program for more than 14 h was needed to obtain ceramic pellets of similar relative densities. In the present work, a total time of only 7.5 hours were enough to produce ceramic pellets of densities higher than 94% and that represents a reduction in time of about 46% and energy consumption of about 37%.

Figures 3(a) and 3(b) show the radioluminescence (RL) of BGO-sintered ceramics. All samples showed only the well-known BGO emission from the $^3P_{0,1,2}$, $^1P_1$ excited states to the fundamental $^1S_0$ state of the Bi^{3+} ions [19]. Figure 3(a) shows the comparison of the RL emission efficiency of the ceramics submitted to sintering program BGO I. The RL of the sample which was sintered in the same temperature cycle but with no pressure load (0 MPa curve) is also shown and presents lower light emission output, as compared to the ones sintered under the uniaxial load. The samples sintered at the BGO I condition under 0.18 MPa of uniaxial pressure showed the highest RL intensity, and its RL is 8.3% higher than the RL of the sample sintered following the same temperature program but with 0 MPa loads. The samples sintered with 0.10 and 0.14 MPa pressure loads (under BGO I condition) also showed RL intensities 7.2 and 7.1% higher than the sample sintered with no load proving that the hot-pressing procedure was efficient to enhance the RL efficiency of the BGO ceramic pellets. The Archimedes method did not show a considerable improvement in the relative densities of the samples, but according to RL measurements, there is an increment in the intensity of the samples sintered under different conditions. This behavior happens due to a decrease in the pore concentrations, since residual pores, either on grain boundaries or entrapped, can act as efficient scattering centers [9].

Figure 3(b) shows the comparison between the RL emission spectra of the BGO ceramics sintered using the BGO II procedure again compared with the sample sintered with no load (0 MPa). The total RL efficiency of the sample, obtained via the area under the RL emission spectra, is also shown in Table 1. The values were normalized considering

that the RL intensity of the sample sintered with no load is 100%. It is possible to see that the samples produced using the BGO II procedure displayed lower RL efficiency, even lower than the sample sintered with no load. For the samples sintered under 0.18 MPa load, the RL intensity of the sample produced via the BGO II procedure is 12% lower than that sintered following the BGO I procedure.

The main differences between BGO I and BGO II programs are when and for how long the load is applied during the sintering process. However, the relative density found for batches of samples sintered under both programs showed no appreciable differences, within the experimental errors of the Archimedes method (Table 1). This may lead to the erroneous conclusion that there would be no direct relation between the density and RL efficiency for BGO ceramics.

There are a number of factors that will influence the RL efficiency of a scintillator material, or in other words, the measured efficiency. One of them is the relative density of the material and that is connected with the way the light is collected. A sample that is 100% dense (the measured density is exactly the expected density as if all the sample volume was filled with just the material of interest) will not be porous, and the sample will be transparent. Consequently, depending on where the light detector is, just part of the light produced by the sample will be collected, unless a spherical light collector is used. Since such detection is easy to find, just part of the light generated by the material will arrive at any RL detection, meaning that, unless the samples have comparable transparency, the RL efficiency is often not the true RL efficiency of the sample but a combination of the actual response of the samples convoluted with the efficiency of the detection geometry (or the solid angle of the detection system combined with de angular response of it). This is true no matter how the RL efficiency is measured, either using a transmission-type detection system or a reflection-type (or fluorescence-type) detection system. If samples with different transparencies were compared, they will favor one specific characteristic of the sample or the other.

The measuring geometry used in the present work is of the reflection type where the X-ray tube and the light detection are facing the same surface of the sample. In this geometry, if the sample becomes more transparent, less light will arrive at the detection system and that will be translated as a false lower efficiency, if care is not taken. It is true that less light is being collected by the detector but that is not necessarily a consequence of poorer sample quality but may just be related to actually a better sintering and more dense material that will produce a better transparence. However, since the important aspect of any scintillator is its actual use and certainly requirement of one particular geometry of light detection certainly, it is important that not only the values of the scintillation efficiency are quoted but also how it was measured. For applications that require a reflection-type (or fluorescence-type) detection system, very good transparent materials are not always good, mainly when very low levels of ionizing radiation intensities are to be measured. It is rather preferable that not transparent detection system is used and all the light generated is guided to the detection system.

The results obtained in the present work can now be revisited considering this framework. If one would have to choose samples to be used in reflection-type detection geometry, one should pick the samples sintered following the BGO I procedure with 0.18 MPa load. However, if a certain degree of transparency is needed, the samples sintered following the BGO II procedure could be more suitable and specifically the one sintered with 0.18 MPa load is probably the best one. The transparency versus detection geometry is the explanation for the fact that the measured RL efficiency decreased as the load increased for samples sintered via the BGO II procedure and also why they showed apparent lower efficiency as compared to the sample sintered with no load.

4. Conclusions

The applicability of $Bi_4Ge_3O_{12}$ (BGO) ceramics produced by uniaxial hot pressing as scintillators was confirmed in the present investigation. The hot-pressed samples have better radioluminescence emissions efficiency, but no more intense than samples sintered without any load during the sintering temperature cycle. This effect was explained in terms of the transparence of the sintered ceramics and of the geometry of the detection system used in this work. The samples sintered using the BGO I condition under a pressure of 0.18 MPa showed a slightly better intensity than all the other ones analyzed in the present work, being 8.3% more intense in comparison to the sample sintered without load. The samples sintered using the BGO II procedure, using a higher applied pressure rate and applied pressure duration led to higher changes in their heights, which makes this condition better to produce ceramics with higher relative densities values. This methodology allows the production of ceramic bodies with relative density values higher than 94%. The comparison between relative density and RL efficiency showed that the Archimedes method was not enough sensitive to quantify the slight differences in the relative densities. Furthermore, RL efficiency results also indicated that the samples with higher relative density show a dependence of the scintillating light collection with the geometry of the detection system.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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