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Synthesis of $Bi_4Ge_3O_{12}$ ceramic scintillators by the polymeric precursor method

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Abstract Bismuth germanate ceramic powders were synthesized for the first time by the polymeric precursor method (Pechini's method). Differential thermal analysis and thermogravimetric techniques were used to study the decomposition of the resin precursor, which indicated a suitable calcination temperature at 600 °C. It was observed that the mass loss occurs in two main stages that are associated with two exothermic reactions. The crystalline phases of the powders were inspected by the X-ray diffraction technique after thermal treatment between 300 and 600 °C. Single phase $Bi_4Ge_3O_{12}$ ceramic bodies were obtained after sintering at 840 °C for 10 h. The sintered ceramics presented a luminescence band emission centred at around 530 nm when excited with X-rays and UV radiation.

Keywords Bismuth germanate · Ceramic scintillators · Radioluminescence

Introduction

Bismuth germanate ($Bi_4Ge_3O_{12}$—BGO) is a synthetic material with a cubic eulytine structure, space group $I\bar{4}3d$, containing four molecules per unit cell. This material has several interesting features such as electro-optical, electro-mechanical and scintillator properties [1, 2]. Due to this last one, BGO has been widely used as the main radiation detector in medical diagnostics, high-energy physics and in industrial applications [3]. Single crystals present high light yield (9×10^3 photons/MeV) and density of 7.1 g cm^{-3} [1], but the use of these scintillators also presents some difficulties, related to its high production cost, limited size during the growth and poor dopant distribution. For this reason, the development of BGO ceramics has been widely studied in order to obtain good scintillator properties. The advantages of using ceramics instead of single crystals are a more uniform doping and reduced costs for large samples, which can be produced in a variety of shapes and sizes thus improving the scintillator applicability. Due to these attractive properties, considerable efforts have been devoted to the preparation and characterization of ceramic scintillators [2–6].

Frequently, bismuth germanate powders have been synthesized through solid state reactions using Bi_2O_3 and GeO_2 as precursor materials [4–6]. In this method, a calcination temperature of 810 °C is commonly used and the powders obtained present micrometric size particles. Recently, we have reported the synthesis of BGO submicrometric powders for the first time through the self-propagating high-temperature method (SHS—combustion synthesis) [7]. It was observed that the synthesis method did not affect the scintillator properties of the sintered ceramics.

On the other hand, the polymeric precursor method (Pechini's method) has been reported as a powerful route to obtain nanocrystalline powders in several compositions. This method allows the formation of a polymeric net (resin) containing the metallic ions homogeneously distributed. The resin formation occurs in three steps: metallic chelate formation, ester formation and polyesterification [8–11]. The main advantage of this method is the good control of the stoichiometry, high purity, easy dopant incorporation and formation of nanometric or sub

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micrometric particles with controlled particle size. In this paper we have studied for the first time the synthesis of $Bi_4Ge_3O_{12}$ powders by the polymeric precursor method. Radio- and photoluminescence spectra were also obtained and compared with the results presented in the literature.

Experimental procedure

$Bi_4Ge_3O_{12}$ powders were synthesized by the polymeric precursor method using bismuth oxide (Bi_2O_3; VETEC, P.A.) and germanium oxide (GeO_2; Alfa Aesar, 5N) as precursor materials. Figure 1 shows the flowchart of the synthesis process. The Ge and Bi solutions were prepared, respectively, by dissolving GeO_2 in distilled water at about 90 °C in a concentration of 0.005 g mL^{-1} [12], and Bi_2O_3 in nitric acid solution (1:1—HNO_3:distilled water) in a concentration of 0.125 g mL^{-1}. These cationic solutions were separately mixed to the citric acid (CA; VETEC, P.A.) previously dissolved in distilled water (0.1 g mL^{-1}), at the molar ratio of 1:3 (Cation:CA). After this dissolution, ethylenediamine (ED; VETEC, P.A.) was added to bismuth citrate in order to control the pH value at about 9. This step was essential to the solution stability. In some tests driven with ammonium hydroxide for pH control, the stability of the solution was not achieved. In order to promote the citrate polymerization by polyesterification reaction, the citrate solutions were heated at 90 °C and mixed with ethylene glycol (EG; Grupo Quimica, P.A.) at a mass ratio Cation:EG = 3:2. The (Bi, Ge) resin was prepared by mixing bismuth and germanium solutions stoichiometrically and keeping the pH value constant and equal to 9. The resulting solution was then heated up to 120 °C in order to eliminate water excess and a homogeneous, transparent and stable solution was obtained.

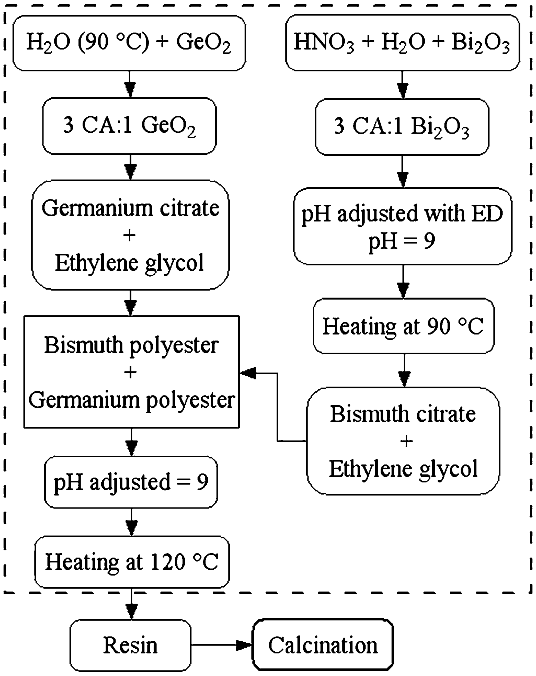

Fig. 1 Flowchart of the synthesis of $Bi_4Ge_3O_{12}$ by the polymeric precursor method

After stabilization, the resin was calcined in open furnace under air flow and a heating rate of 2 °C min^{-1}. Several maximum temperatures were tested and in all the tests a free cooling rate was adopted, which means that the cooling followed Newton's exponential law. The calcined powders were ball-milled for 24 h and conformed by uniaxial pressing as discs with 6 mm diameter and 2.0 mm thickness with green density of 58%. The sintering was made at 840 °C for 10 h with heating rate of 10 °C min^{-1} and cooling rate of 2 °C min^{-1} [5, 13]. The ball-milling was made in plastic recipients containing the powders, isopropyl alcohol and zirconia balls, in the volumetric proportion of 10:30:60, respectively. The relative density of the sintered ceramics was determined by the fluid displacement (Archimedes) method, using distilled water.

Thermal analysis of the dried resin was performed from room temperature up to 900 °C in a simultaneous DTA/TG (SDT 2960—TA INSTRUMENTS) system, with a heating rate of 10 °C min^{-1} and synthetic air flow. The crystalline phases of the powder and sintered ceramics were inspected by X-ray diffraction (XRD—Rigaku RINT 2000/PC), in continuous scanning mode using Cu K_α radiation, in the 2θ range between 10° and 80°. The particle size of the calcined powders was determined by scanning electron microscopy (SEM—JSM-5900 INSTRUMENT).

The luminescence properties of the samples were inspected via photo- and radioluminescence techniques at room temperature. The photoluminescence (PL) spectra of the scintillators were measured using an Ocean Optics HR 2000 spectrometer (resolution of 0.5 nm) under excitation of 280 nm, using a 300 W Xenon lamp. Radioluminescence (RL) was registered under excitation of X-rays ($\sim$9 keV), by the same spectrometer used in the PL tests.

Results and discussion

Figure 2 presents the DTA/TG curves of the resin dried at 100 °C for 24 h. These curves clearly show two main thermal events: the first one, from room temperature up to 350 °C, is characterized by a mass loss of approximately 50% and an exothermic peak (onset at 200 °C). This event can be attributed to dehydration and oxidation reactions followed by the formation and elimination of NO_x; the second event, with onset at 400 °C, presents a high exothermic peak and a mass loss of about 37% which can be

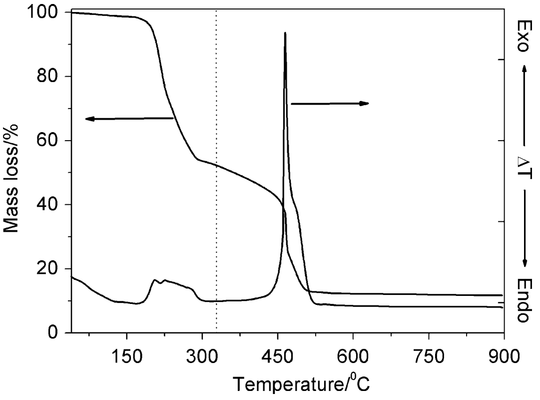

Fig. 2 DTA/TG curves of the BGO precursor resin dried at 100 °C for 24 h

associated to combustion reactions, organic decomposition and subsequent crystalline phase formation. Since there is no thermal event above 600 °C, this temperature was firstly adopted for the powder calcination.

The crystallization processes that occur during the thermal decomposition of the resin were monitored by X-ray diffraction measurements. Figure 3 presents the XRD pattern of the samples calcined at different temperatures for 6 h. The powder heated up to 300 °C is predominantly amorphous, but after calcinations at 400 °C it presents three phases of the bismuth–germane system, namely $Bi_4Ge_3O_{12}$, Bi_2GeO_5 and $Bi_{12}GeO_{20}$. Yet, when the powder was calcined at 500 and 600 °C, the majority phase was $Bi_4Ge_3O_{12}$ with very small amounts of GeO_2, Bi_2GeO_5 and $Bi_{12}GeO_{20}$. These undesirable phases were eliminated after the sintering process at 840 °C, as will be shown below. In order to verify the elimination of the spurious GeO_2, Bi_2GeO_5 and $Bi_{12}GeO_{20}$, DTA measurements of the powder pre-calcined at 500 °C for 6 h were performed (Fig. 4). As expected, the main exothermic peak presented at Fig. 2 was eliminated after the pre-calcination, so a broad band between 780 and 900 °C (with onset at 700 °C), corresponding to the single phase formation, was observed.

In order to reduce the coalescence between the particles, the powders calcined at 600 °C for 6 h were ball-milled for 24 h before sintering [14]. Figure 5 presents a SEM image of this powder. Particles can be observed in the beginning of the coalescence process with an average grain size of 600 nm. After the milling, the powder was dried, pressed to a green density of 58% and sintered at 840 °C for 10 h reaching a relative final density of 85.5 ± 0.5%. Figure 6 shows the XRD patterns of the sintered ceramic. As mentioned above, sintered ceramics presented only the $Bi_4Ge_3O_{12}$ phase.

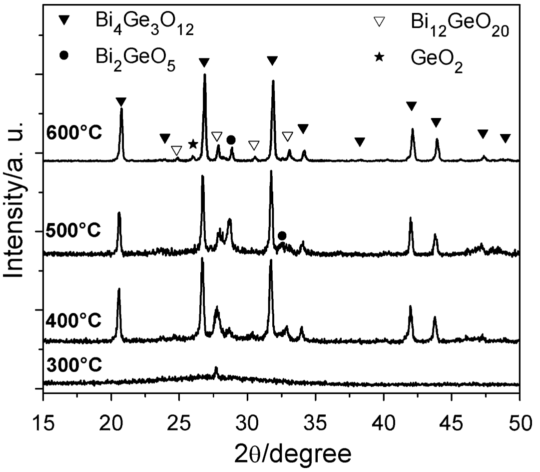

Fig. 3 XRD patterns of the samples calcined for 6 h, at the temperature indicated at each pattern. The peaks were indexed using JCPDS database: $Bi_4Ge_3O_{12}$ (PDF# 84-0505), Bi_2GeO_5 (PDF# 78-1334), $Bi_{12}GeO_{20}$ (PDF# 77-0861) and GeO_2 (PDF# 83-2480)

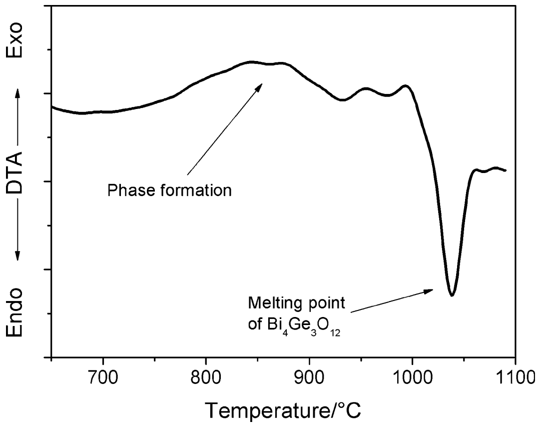

Fig. 4 DTA curve of the BGO powder previously calcined at 500 °C for 6 h

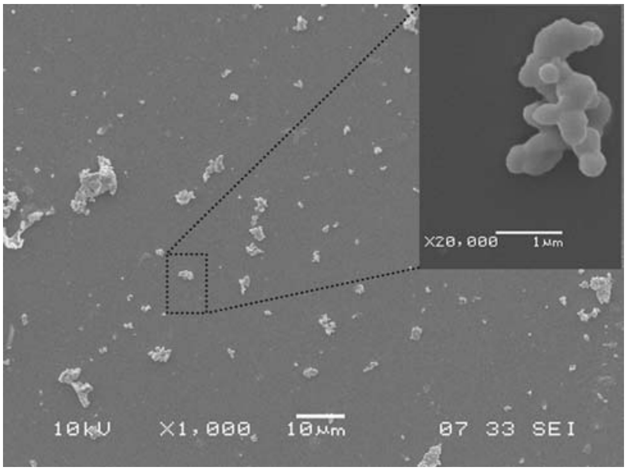

Fig. 5 SEM image of the powder calcined at 600 °C for 6 h and ball milled for 24 h, presenting some coalescence process

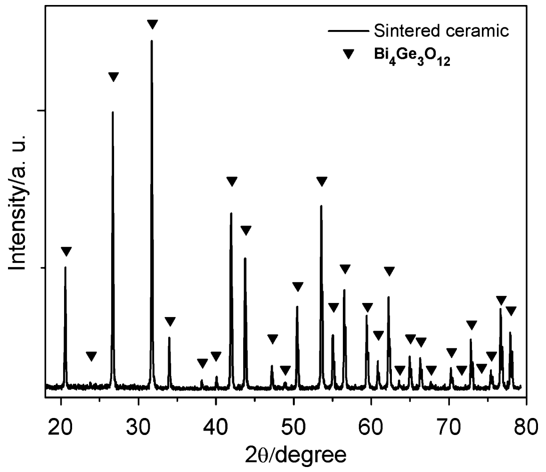

Fig. 6 XRD pattern of the BGO ceramic sintered at 840 °C for 10 h. The peaks are indexed according to the PDF# 84-0505 from JCPDS database

Figure 7 presents the normalized curve of the photoluminescence spectra of the sintered ceramics excited at 280 nm. This curve presents the wavelength corresponding to the maximum intensity at 520 nm while the wavelength of the single crystal is centred at 515 nm. Figure 8 (normalized curve) shows the radioluminescence spectra of the same ceramics excited with X-rays (8 keV), it can be seen that the emission is centred at 534 nm and for the single crystal the maximum intensity is at 515 nm. These two results are the same if we take into account the standard deviation of the measurements, so it can be concluded that the luminescence results from the same emission process, regardless the excitation energy. For $Bi_4Ge_3O_{12}$ the luminescent emission is associated with the transition from the level 6p6s ($^3P_{0;1;2}$, $^1P_1$) to the fundamental state $6s_2$ ($^1S_0$) of Bi^{3+} [15].

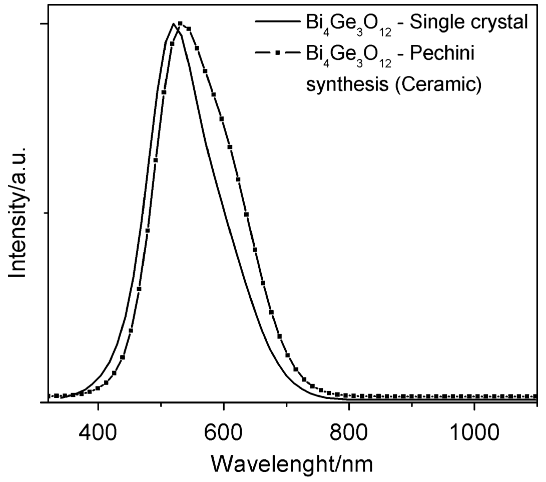

Fig. 7 Luminescence spectra of the $Bi_4Ge_3O_{12}$ ceramics under ultraviolet (UV) excitation

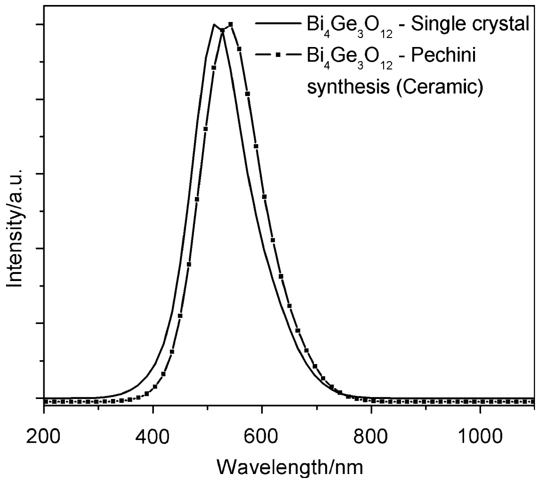

Fig. 8 Luminescence spectra of the $Bi_4Ge_3O_{12}$ ceramics under X-rays excitation

Conclusions

Bismuth germanate sintered ceramics were successfully synthesized for the first time through the polymeric precursor method, and pH control at 9 was essential for the solution stability at room temperature. Thermal decomposition of the resin was monitored by both DTA/TG and X-ray diffraction techniques. The formation of the majority $Bi_4Ge_3O_{12}$ phase was observed after calcination at 600 °C for 6 h and single phase after the sintering process at 840 °C for 10 h. At these conditions the samples presented a final relative density of 85.5%. Photo- and radioluminescence spectra of the sintered ceramics presented a typical $Bi_4Ge_3O_{12}$ behaviour, with emission band centred at 530 nm, indicating that this new route did not affect the luminescent centres in this material.

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References

1. Blasse G. Scintillator materials. Chem Mater. 1994;6:1465–75.
2. Trnovcová V, Furár I, Schultze D. Electrical properties of bismuth phosphate and bismuth germanate single crystal. Solid State Ionics. 2008;179:131–4.
3. Nitsch K, Rodová M. Crystallization study of Na-Gd phosphate glass using non-isothermal DTA. J Therm Anal Calorim. 2008;91(1):137–40.
4. Macedo ZS, Silva RS, Valerio MEG, Hernandes AC. Radiation detectors based on laser sintered $Bi_4Ge_3O_{12}$ ceramics. Nucl Instrum Meth Phys Res B. 2004;218:153–7.
5. Macedo ZS, Silva RS, Valerio MEG, Martinez AL, Hernandes AC. Laser-sintered bismuth germanate ceramics as scintillator devices. J Am Ceram Soc. 2004;87(6):1076–81.

6. Mello ACS, Santana GC, Jackson RA, Macedo ZS, Moreira SGC, Valerio MEG. Optical properties of pure and Cr^{3+} doped BGO ceramic scintillators. Phys Stat Sol C. 2007;4(3):980–3.
7. Jesus FAA, Silva RS, Hernandes AC, Macedo ZS. Effect of pH on the production of dispersed $Bi_4Ge_3O_{12}$ nanoparticles by combustion synthesis. J Eur Ceram Soc. 2008;29:125–30.
8. Pechini MP. US Patent No. 3.330.697, 11 July 1967.
9. Silva RS, Bernardi MIB, Hernandes AC. Synthesis of non-agglomerated $Ba_{0.77}Ca_{0.23}TiO_3$ nanopowders by a modified polymeric precursor method. J Sol-Gel Sci Technol. 2007;42:173–9.
10. Gouveia DS, Rosenhaim R, Maurera MA, Lima SJ, Paskocimas CA, Longo E, et al. Thermal study of $Co_XZn_{7-x}Sb_2O_{12}$ spinel obtained by Pechini method using different alcohols. J Therm Anal Calorim. 2004;75:453–60.
11. Matraszek A, Szczygieł I. Modified Pechini synthesis of $Na_3Ce(PO_4)_2$ and themochemistry of its phase transition. J Therm Anal Calorim. 2008;93:689.
12. Shimomura S, Sakurai H, Morita H, Inoue M. Preparation of standard germanium solution. Anal Chim Acta. 1977;91:421–3.
13. Santana GC, Mello ACS, Valerio MEG, Macedo ZS. Scintillating properties of pure and doped BGO ceramics. J Mater Sci. 2007;42:2231–5.
14. Antonelli E, Silva RS, Vicente FS, Zanatta AR, Hernandes AC. Electrophoretic deposition of $Ba_{0.77}Ca_{0.23}TiO_3$ nanopowders. J Mater Process Technol. 2008;203:526–31.
15. Weber MJ, Monchamp RR. Luminescence of $Bi_4Ge_3O_{12}$: spectral and decay properties. J Appl Phys. 1973;44:5495–9.