

Synthesis and characterization of BGO with different chelating compounds by the polymeric precursor method, and their effect on luminescence properties



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ABSTRACT

In the present work, $\text{Bi}_3\text{Ge}_4\text{O}_{12}$ (BGO) was synthesized by the polymeric precursor method using different chelating agents. We present a comparative analysis of each chelate formation and how the physicochemical properties of the BGO were affected, specifically its luminescence. In this work we used citric acid (CTR), ethylenediaminetetraacetic acid (EDTA), ethylene glycol (EG), nitrilotriacetic acid (NTA) and tartaric acid (TA), since they are the most reported chelating agents for this type of synthesis. The BGO materials were characterized by scanning electron spectroscopy (SEM), X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FTIR) and photoluminescence (PL), and showed that the luminescence properties of the synthesized BGO was affected by the formation of secondary phases. The changes in the BGO luminescence properties with the use of each chelating agent are discussed.

1. Introduction

Bismuth germanate ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$ or BGO) has been extensively studied because its interesting luminescent properties, like short decay time, photo and radioluminescence. These properties make BGO compounds suitable to be applied as scintillators in medicine, in geological explorations, nuclear physics and high energy physics [1,2].

BGO powders are commonly synthesized by the sol-gel method, which is a well-established method for the synthesis of complex oxides, since this method allows us to obtain pure phase products. It is a powerful tool to obtain materials at the nanoscale because the parameters are easy to control and the cost is convenient [3,4].

The polymeric precursor method, a modified Pechini's technique, is a modified sol-gel process, with the aim to stabilize metallic cations into a homogeneous matrix generated by a chelating agent, thus inhibiting the segregation and precipitation of the cations in the system. The Resin formation occurs in three steps: metallic chelate formation, ester formation and polyesterification [2].

The selection of chelating compounds and changes upon its concentration parameters affects the morphology and structure of the

resulting material, due to each chelating compound produces a different gel network. This gel network collapses when the chelating compound is evaporated at room temperature, and this leads to the formation of a rigid pore structure, which is different for each chelating agent. [5]. The chelating agents used in this study were chosen because they are the most frequently used in this type synthesis.

Herein we report the synthesis of BGO by a polymeric precursor method using different chelating compounds to obtain a pure phase of BGO. Also report the effect of each chelating compound in the optical properties, to determine the optimal precursor agent to obtain BGO with enhanced optical properties.

2. Experimental

2.1. Materials

2.1.1. Bismuth germanate

$\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) was synthesized by a polymeric precursor method using bismuth oxide (Bi_2O_3 , 99.99%, Sigma Aldrich) and germanium oxide (GeO_2 , 99.99%, Sigma Aldrich) as precursors. Different chelating

Abbreviations: BGO, bismuth germanate; CTR, citric acid; EDTA, ethylenediaminetetraacetic; EG, ethyleneglycol; NTA, nitrilotriacetic acid; PL, Photoluminescence; TA, Tartaric acid

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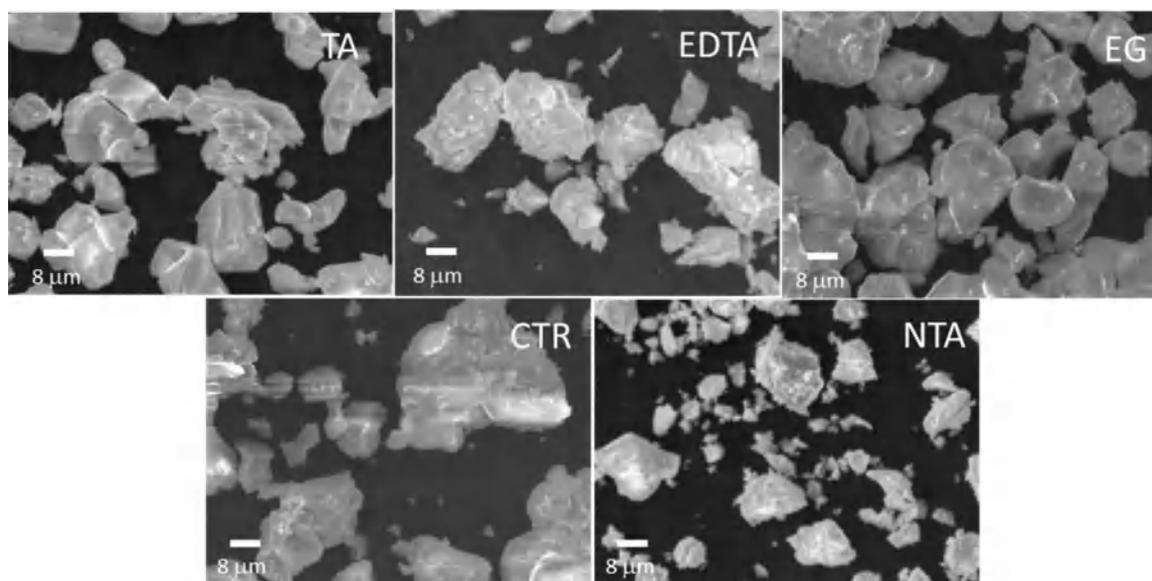


Fig. 1. Typical SEM images of pure $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ synthesized with assistance of chelating compound: tartaric acid (TA), citric acid (CTR), ethylenediaminetetraacetic acid (EDTA), ethylene glycol (EG) and nitrilotriacetic acid (NTA).

agents were tested as stabilizing polymers. L (+)-tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$, 99.5%, Sigma Aldrich), ethylenediaminetetraacetic acid ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$, 99.995%, Sigma Aldrich), nitrilotriacetic acid ($\text{C}_6\text{H}_9\text{NO}_6$, 99%, Sigma Aldrich), citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99.5%, Sigma Aldrich) and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, 99.8%, Alfa Aesar) were each used as the chelating agent for the polymeric precursor method.

2.2. Synthesis conditions

BGO was synthesized via the polymeric precursor method described in [6]. All reagents were of analytic grade. They were used as received without further purification. The precursor oxides were used in stoichiometric proportion. These oxides were dissolved in 50 mL of 70% HNO_3 and the mixture was stirred for 24 h at room temperature. After 24 h, the chelating agent (ethylene glycol, tartaric acid, ethylenediaminetetraacetic acid or citric acid) was dissolved in 15 mL of de-ionized water, mixed with the precursors and placed under constant stirring for another 3 h. Then, the mixture was additionally heated to 80 °C for 2 h. The sol was heated to 120 °C until dry to form the xerogel. Finally, the as-synthesized powders were annealed at 850 °C for 4 h with a heating rate of 2 °C/min. The same process was followed for each chelating compound.

3. Characterization

3.1. X-rays diffraction (XRD)

The annealed powders were analyzed by X-ray diffraction (XRD). The diffraction patterns were collected with a Philips X'pert diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm). Measurements in a $2\theta = 10\text{--}70^\circ$ range were taken with a step size of 0.02 and a 0.5 s dwell per point. Crystallite size was calculated using line broadening analysis based on the Scherrer equation:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where, D = crystallite size (nm), λ = radiation wavelength, θ = diffraction angle, and β = full width half maximum (FWHM) of the diffraction peak.

3.2. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) images were obtained with a JEOL JSM 5300 a 3500 \times . Each sample for SEM analysis was placed on a carbon tape for analysis.

3.3. Fourier transform infrared spectroscopy (FTIR)

Samples were analyzed with a Nexus-760 FTIR spectrometer with in situ Harrick cell, which was used for diffuse reflectance. All measurements were performed in air and at room temperature.

3.4. Luminescence

Luminescence properties of the samples were studied with a fluorescent spectrophotometer (Hitachi FL-4500) using 280 nm excitation wavelength. This wavelength produced the highest photoluminescence (PL) emission. All optical measurements were performed in air and at room temperature.

4. Results and discussion

$\text{Bi}_4\text{Ge}_3\text{O}_{12}$ samples were synthesized by the polymeric precursor method assisted with citric acid (AC), ethylenediaminetetraacetic acid (EDTA), ethylene glycol (EG), nitrilotriacetic acid (NTA) and tartaric acid (TA), and analyzed by SEM, XRD, PL and FTIR.

The morphology and microstructure of the synthesized samples were analyzed by Scanning Electronic Microscopy (SEM) (Fig. 1). Particle size of all samples was between 3 and 4 μm ; no significant changes in particle morphology were observed, even when using a different chelating compound. The micrographs show BGO particles of undefined shape.

The chelating agents tend to form stable complexes with a variety of metals over fairly wide pH ranges, and are simply combined with the metal cations in solution to form precursors that are subsequently calcined by pyrolysis of the organic species [5].

The chelating compounds chosen for this investigation are the most frequently reported to assist in the polymeric precursor method. Moreover, each compound should possess at least one hydroxo ligand, necessary for the condensation to occur and, hence, the gel formation. The gel network is formed by the esterification of the chelating agent

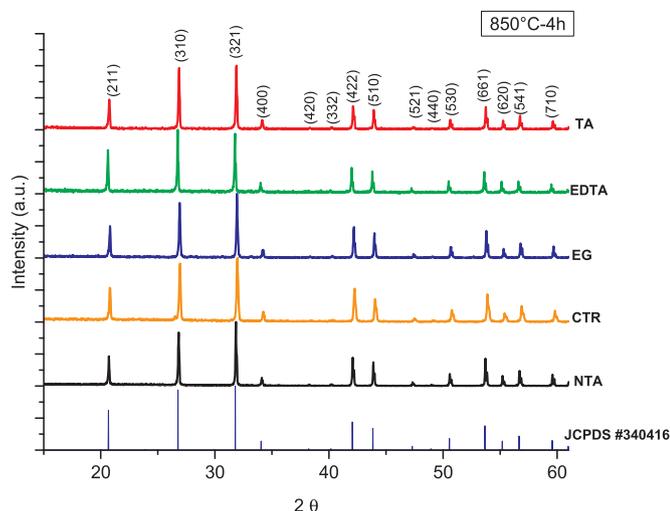


Fig. 2. XRD patterns of BGO samples obtained by polymeric precursor method synthesis assisted by chelating compounds (TA, EDTA, EG, CTR or NTA).

[7,8]. The hydroxo ligand is also necessary as a nucleophile site since it gives each chelating agent the affinity to the metal ions [9].

The diffraction peaks of the five BGO samples were indexed in agreement with the JCPDS card N. 340416 for cubic $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (Fig. 2). The synthesized BGO samples crystallized as typical body-centered cubic structures of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ with a group space I43d [2]. No other obvious diffraction peaks of the impurity phase were present, which indicates that the powders were in pure phase.

A well-defined narrow and sharp peak was observed for powders synthesized with NTA indicating a sample of large crystallite size. Crystallite size was calculated using line-broadening analysis based on Scherrer's formula obtained variations in crystallite size between 65.02 nm (NTA) and 51.36 nm (CTR). No further difference in particle size was found between CTR and other chelating compounds. Crystallite sizes are shown in Table 1.

The TA and NTA-assisted BGO samples displayed two characteristic bands at ~ 250 and ~ 280 nm, associated to Bi^{3+} optical absorption. The transitions $^1S_0 \rightarrow ^3P_1$ and $^1S_0 \rightarrow ^1P_1$ were assigned to each band respectively, and can be directly associated to the excitation and reflection spectra of BGO. The spectra also reveal that in the BGO samples assisted with EG, EDTA and CTR, a well-defined excitation band appears at ~ 290 nm associated with the transition $^1S_0 \rightarrow ^1P_1$ of the Bi^{3+} ion and also show the attenuation for the first band (~ 250 nm) for both samples [1] (Fig. 3).

The PL emission spectra of the BGO samples are shown in Fig. 4. The measurements of excitation were recorded at 280 nm, the wavelength with the highest response band during the excitation process. This value is also close to the band gap edge of BGO crystals. The PL spectra exhibit the characteristic emission of BGO centered at ~ 478 nm [10].

The electronic energy levels involved in the excitation of ns^2 cations (e.g. Sn^{2+} , Pb^{2+} and Bi^{3+}) are the ground state (1S_0) and the four excited states ($^3P_{0,1,2}$, 1P_1). The 3P_1 level undergoes mixing with 1P_1 by

Table 1

Obtained values of crystallite size associated with different $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ samples obtained by Scherrer's equation.

Chelate compound	Size (nm)
NTA	65.02
EDTA	61.67
TA	61.37
EG	58.64
CTR	51.36

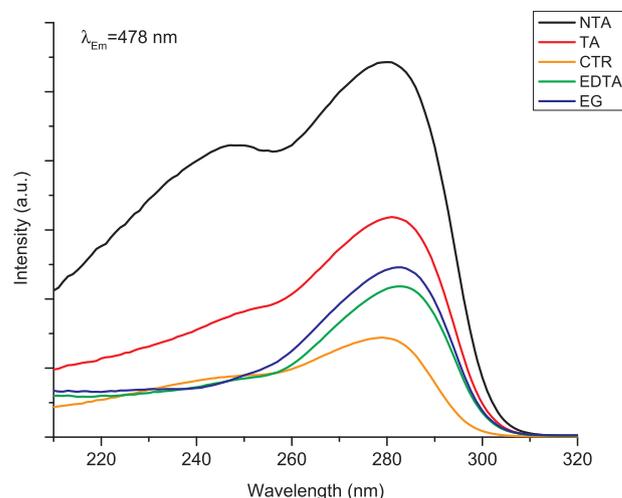


Fig. 3. Photoluminescence excitation spectra of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ samples synthesized by the polymeric precursor method and assisted by different chelating compounds. The measurement was made at 478 nm emission wavelength.

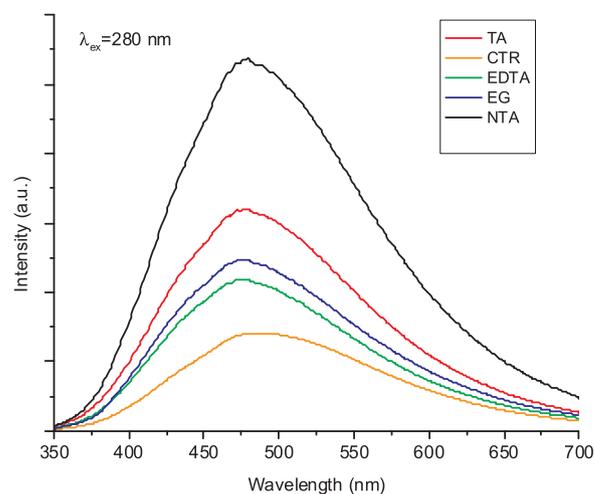


Fig. 4. PL emission spectra of BGO samples synthesized by the polymeric precursor method assisted with different chelating compounds. The measurements were performed at 280 nm excitation wavelength.

spin-orbit coupling allowing the $^3P_1 \rightarrow ^1S_0$ radiative transition [10,11].

The structure of BGO is gradually formed during calcination process and a crystalline field is formed around Bi^{3+} ions by GeO_4 tetrahedral structures. The luminescence of BGO arises from the radiative recombination between Bi^{3+} and O^{2-} ions as reported by Polosan et al. [12]. Hence, the aforementioned process describes the PL emission for each sample.

The XRD patterns showed no differences between the five samples, since all materials showed a BGO pure phase. Despite a significant reduction in PL intensity was achieved, the samples synthesized with the assistance of EG, EDTA, and CTR chelating agents displayed lower intensity compared to the samples synthesized with assistance of NTA and TA.

The decrease in intensity can be correlated to the presence and attenuation of the two excitation bands feature; the NTA-assisted sample shows both well-defined bands and the highest emission intensity, while the TA-assisted sample shows the second-highest intensity, and is attenuated at the ~ 250 nm excitation band. For the other samples (CTR, EDTA and EG), which showed lower intensity compared to NTA and TA, the first band associated to the characteristic excitation process almost disappeared.

It is also important to notice that the NTA sample displayed the

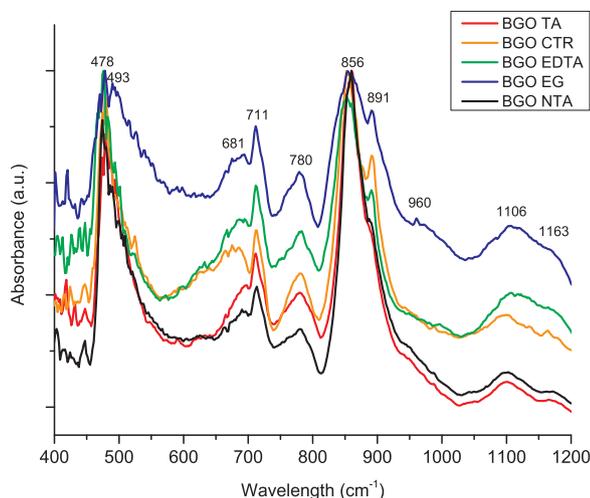


Fig. 5. FTIR spectra of BGO synthesized with assistance of different chelating compound (TA, CTR, EDTA, EG and NTA) by the polymeric precursor method.

highest intensity, both in excitation and emission, suggesting a direct correlation with the largest crystallite size. This results suggest that presence of structural defects can reduce the efficiency of the excitation and emission process of the Bi^{3+} ion [5].

The FTIR technique was used to explain the reduction in luminescence emission of each sample of BGO synthesized with different chelating agents.

Fig. 5 shows the room temperature FTIR absorption spectra of the different BGO samples. For each sample the first signal appeared at 478 cm^{-1} and was associated with the Bi-O bond vibrations in distorted BiO_6 units [13]. The band at $\sim 681\text{ cm}^{-1}$ was ascribed to Ge-O stretching vibrations in GeO_4 [14]. The band at 711 cm^{-1} was assigned to Ge-O stretching vibrations in GeO_4 units, while the band at 780 cm^{-1} was attributed to a GeO^- stretching mode also in GeO_4 units [13,15,16]. Both signals appear in each sample. Absorption at 856 cm^{-1} can be attributed to Bi-O bonds in BiO_6 units. The signal at 891 cm^{-1} appeared with high intensity for the samples synthesized with EG, EDTA and CTR and was ascribed to GeOGe stretching in amorphous GeO_2 [17]. The band at 1106 cm^{-1} can be assigned to Bi-O-Ge linkage vibrations [18].

Although the signal at 891 cm^{-1} is more evident for the EDTA, EG, and CTR samples, it is important to notice that the NTA and TA samples exhibit a shoulder at that position, which could indicate the formation of the GeO_2 but with a lesser amount. Although the presence of GeO_2 ion could be associated with the incomplete dissociation of the GeO_2 during the synthesis and constitute a remnant of the synthesis process, it should be noted that the amounts of GeO_2 and HNO_3 used for each synthesis were constant. For this reason, we concluded that it is not directly correlated with the incomplete dissociation of GeO_2 in the synthesis process.

In order to explain the presence of GeO_2 , it is important to consider factors such as the chelating affinity of the chelating compounds to the metal ions that is given by $-\text{OH}$ groups. In the reaction to synthesize BGO, the amount of Bi represents $\sim 67\%$ in the reaction, compared with Ge which represents $\sim 17\%$. Also, Bi is more highly electronegative compared with Ge. Then, according with our results, GeO_2 probably appears because the Ge and Bi ions compete for the nucleophile sites of each chelating agent, the Bi ions occupying more sites and the Ge ions leaving segregated, which then allows GeO_2 formation.

5. Conclusion

The present work demonstrated that it is possible to successfully obtain pure phases of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ by a polymeric precursor method using as chelating compounds: tartaric acid (TA), nitrilotriacetic acid (NTA),

citric acid (CTR), ethylenediaminetetraacetic acid (EDTA) and ethylene glycol (EG), with low reduction in optical features.

Our results suggest that the differences in the optical responses between each synthesized material can be associated to the formation of defects in the structure as influence of each chelating compound. The formation of GeO_2 ion can directly affect the optical response of the materials, since germanium oxide is not a luminescent material.

According to the results of this work, we conclude that the NTA-assisted BGO material, presented enhanced optical properties.

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