

International Conference on Luminescence

## Photoluminescence of bismuth germanate phosphors with a silica-shell structure

M. J. Oviedo<sup>a</sup>, J.K. Han<sup>b</sup>, O. Contreras<sup>c</sup>, Z.S. Macedo<sup>d</sup>, G. A. Hirata<sup>c\*</sup> and J. McKittrick<sup>b,e</sup>

<sup>a</sup>Programa de Posgrado en Física de Materiales, CICESE-UNAM, carretera Ensenada-Tijuana No. 3918, Ensenada, B.C., México.

<sup>b</sup>University of California at San Diego, Materials Science and Engineering Program, La Jolla, CA 92093-0418

<sup>c</sup>Centro de Nanociencias y Nanotecnología, UNAM, Ensenada, B.C., México

<sup>d</sup>Departamento de Física, Universidade Federal de Sergipe, Sao Cristóva, SE, Brazil

<sup>e</sup>University of California at San Diego, Mechanical and Aerospace Engineering, La Jolla, CA 92093-0411

Received 25 July 2011; accepted 25 August 2011

### Abstract

An intense bluish-white emitting phosphor  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  (BGO) was synthesized by tartaric acid-assisted sol-gel method and covered with a  $\text{SiO}_2$  nanolayer by the sol-gel method. The cubic crystal structure of BGO was confirmed by X-ray diffraction. Transmission electron microscopy analysis revealed the particle size to be in the range of 6-20 nm. Under excitation with 4.3 eV photons the BGO powders showed a PL contribution centered at 2.43 eV that corresponds to the typical BGO luminescence associated with  $^3\text{P}_1 \rightarrow ^1\text{S}_0$  of  $\text{Bi}^{3+}$  electron transitions. Radioluminescence measurements showed the predominant emission centered at 2.43 eV due to the intra-ionic  $\text{Bi}^{3+}$  transitions. The PL emission of the silica coated BGO nanoparticles presented a luminescence enhancement of more than 200% compared with the uncoated nanoparticles. This enhancement in photoluminescence is proposed to be related to the reflectivity (refractive index) between air-silica-BGO layers.

© 2012 Published by Elsevier B.V. Selection and/or peer-review under responsibility of the organizing committee represented by Stephen C. Rand and the guest editors. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

**Keywords:** bismuth germanate; sol-gel; silica coating; photoluminescence

\*Corresponding author. Tel: +52-646-174-4602; fax: +52-646-174-4603.  
Ee-mail address: [hirata@cny.unam.mx](mailto:hirata@cny.unam.mx)

## 1. Introduction

Bismuth germanate  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  (BGO) is a cubic crystal with a space group  $\bar{4}3d$  of the eulytine-type structure with the  $\text{Bi}^{3+}$  site coordinated by a distorted octahedron of oxygen ions, and is used as a scintillator [1]. Scintillators are materials that produce light under ionizing radiation. They are utilized as detectors in scientific research, industry and medicine [2–4], and are often used in the single crystalline form. Due to the difficulty in producing good quality, large samples, there is a motivation for finding polycrystalline ceramics that can be used in place of single crystals [5]. The advantages of using polycrystalline samples are a more uniform doping and reduced costs for large samples, additionally which can be produced in a variety of shapes and sizes that can broaden the scintillator applicability [6].

BGO powders have been synthesized by solid state reaction, combustion synthesis and by a polymeric precursor method [7,8]. Chemical methods, such as the sol-gel, are versatile techniques used to produce nanoparticles. The sol gel technique has been used to prepare  $\text{Y}_2\text{O}_3$  nanoparticles using tartaric acid and nitric acid as complexing agents [9]. Nanoparticles are a topic of extensive research for the development of new luminescent materials, which are essential components for emerging technologies in imaging, lighting and display devices. There is a considerable interest in particles covered with silica (core/shell morphologies) due to their enhanced luminescent properties [10], which presents several advantages in the field of biological and imaging applications [11,12]. The silica shell performs two important functions: (a) it allows the functionalization by biological groups and (b) increase the optical response of luminescent cores used as optical tags [13]. This paper presents a study of the optical and structural properties of BGO nanoparticles with and without silica coatings produced by sol-gel method and post-annealed by a slow thermal treatment.

## Experimental

Bismuth germanate oxides were prepared by l-tartaric acid assisted sol-gel method. The high purity starting materials bismuth oxide [ $\text{Bi}_2\text{O}_3 \cdot \text{XH}_2\text{O}$  Puratronic 99.999%] and germanium oxide [ $\text{GeO}_2$  Alfa Aesar 99.98%] were weighed according to stoichiometric calculations and dissolved in minimum amount of 25 ml of diluted  $\text{HNO}_3$ . l-tartaric acid (Aldrich, USA) was dissolved in de-ionized water and the individual solutions were mixed under constant stirring. The dissolved mixture was further stirred for 24 h at room temperature and after the pH was measured at 0.5. Then, the mixture was heated under constant stirring at  $80^\circ\text{C}$  for 2 h, which produced a more dense sol. Subsequently, the sol was heated at  $120^\circ\text{C}$  until a gel was produced and dried to form the precursor. The precursor was annealed in air in a muffle furnace, starting gradually from room temperature to  $900^\circ\text{C}$  at a heating rate of  $1^\circ\text{C}/\text{min}$ , maintained at this high temperature for 4 hr and then cooled at  $1^\circ\text{C}/\text{min}$ . Later, the silica coating was applied to the as-synthesized powders using colloidal silica (Aldrich, LUDOX-AM-30). First, 1 g of BGO powder was dispersed into a solution of 100 ml of deionized water with 10 ml of LUDOXAM-30. Then, the suspension was stirred gently for 1 hr at room temperature followed by a filtering and washing procedure with ethanol. The final powder resulted after an annealing (drying) at  $800^\circ\text{C}$  for 1 hr.

The annealed powder was analyzed by x-ray diffraction (XRD). The diffraction patterns were collected with a Phillips X'pert diffractometer equipped with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ). Measurements in a  $2\theta = 15\text{--}65^\circ$  range were taken with a step size of  $0.1^\circ$  and a 1 sec dwell time per point. Transmission electron microscopy (TEM) images were obtained with a JEOL-2010 operated at 200 kV accelerating voltage. The photoluminescent (PL) properties of the samples were studied with a fluorescence spectrophotometer (Hitachi FL-4500). In order to compare the optical properties between

coated and uncoated samples, the same amount of material (0.2 g) was analyzed in the PL system. Radioluminescence (RL) measurements were performed at the Brazilian Synchrotron Light Laboratory by using an X-ray beam of 7 keV. All optical measurements were performed in air at room temperature.

## Results and discussions

XRD patterns of the annealed powders are shown in Fig. 1, which were indexed according to JCPDS Card No. 34-0416 for cubic  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ . The relative intensity of diffraction peaks for powders are quite similar to those reported in the standard. A few low intensity diffraction peaks appeared in both kinds of samples, which have been identified as small traces of  $\beta\text{-Bi}_2\text{O}_3$  and  $\text{Bi}_2\text{GeO}_5$  phases, labeled in Fig. 1 with a “ $\beta$ ” and “+”, respectively. Excellent crystallinity of the powders is confirmed from the high signal/noise ratio of the diffraction patterns. The size of the crystallites is  $\sim 12$  nm, as calculated by the Scherrer formula. The inset in Fig. 1 shows the Scherrer adjustment and line width for the uncoated sample. XRD patterns for both kinds of samples are practically identical. The thermal treatment at  $900^\circ\text{C}$  is optimum to obtain high crystallinity powders.

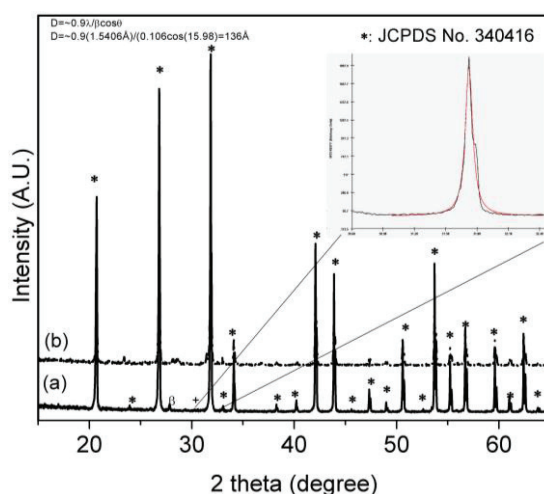


Fig. 1. XRD patterns of the BGO synthesized by sol-gel method (a) annealed at  $900^\circ\text{C}$  uncoated and (b) with silica coated. The  $\beta\text{-Bi}_2\text{O}_3$  (JCPDS #270050) and  $\text{Bi}_2\text{GeO}_5$  (JCPDS #771641) phases, labeled with a “ $\beta$ ” and “+”, respectively. The inset shows the Scherrer adjustment and line width for the uncoated BGO sample.

Transmission electron microscopy analysis revealed the structure as well as the morphology of the synthesized cubic  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ . The general morphology of the uncoated powders consists of faceted nanocrystallites with a diameter size in the range of 6-20 nm (see Fig. 2(a)). The uncoated particles have a well defined surface whereas the coated sample, Fig. 2(b), has nano-sized silica agglomerates ranging from 10 to 20 nm in size deposited surrounding the particle surface. A higher magnification of a silica coated particle is shown in the inset in Fig. 2 (b). The thickness of the silica layer was estimated to be around 30 nm and this layer is observed in all phosphor nanoparticles analyzed by TEM.

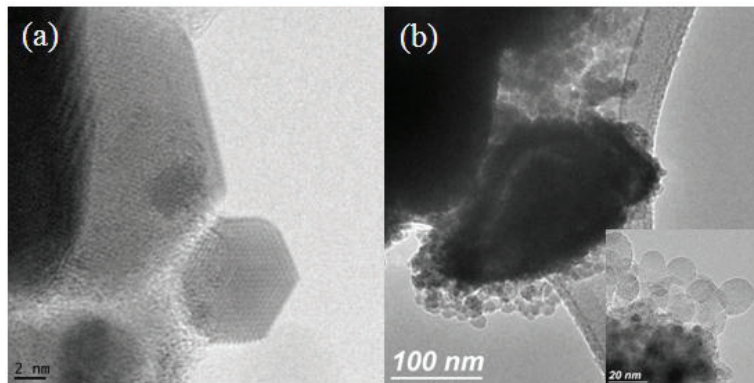


Fig. 2. TEM micrographs of the  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  powder annealed at  $900^\circ\text{C}$ : (a) uncoated and (b) silica coated.

An optimum excitation wavelength region was determined through a series of PL excitation measurements, finding maximum excitation energy at 4.30 eV (288 nm). Photoluminescence measurements taken from the samples with 4.30 eV excitation are illustrated in Fig. 3. Both kinds of powders yielded a bluish-white luminescence. Uncoated powders show a broadband emission in the region of 2.0 - 3.1 eV with a maximum emission at 2.43 eV (Fig 3(a)). This light emission corresponds to an electron transition from the  $6p6s$  ( $^3P_{0;1;2}$ ,  $^1P_1$ ) level to the fundamental electronic state  $6s_2$  ( $^1S_0$ ) of  $\text{Bi}^{3+}$  ions [14] in the BGO single crystals.

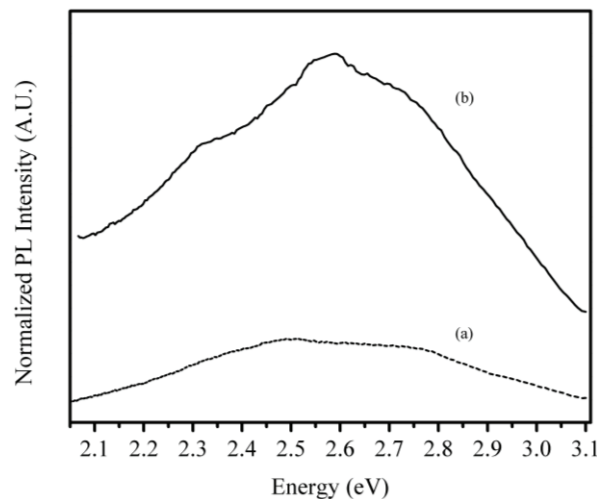


Fig. 3. Photoluminescence spectra of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  particles: (a) uncoated and (b) coated with colloidal silica.

Fig. 3(b) shows the luminescence enhancement in the BGO nanoparticles when they are covered with the colloidal silica nanoparticles. Both measurements were performed using the same amount of BGO powders. Thus, a reflectivity phenomenon of UV light from the particle surface is proposed to be the mechanism for an increased emission intensity in the silica coated BGO system. The indices of refraction of air ( $n = 1.000$ ),  $\text{SiO}_2$  ( $n = 1.505$ ) and  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  ( $n = 2.150$ ) were used in Fresnel's equation.

Dispersion of the excitation light is reduced when the refractive index of the silica coating has a value between that of the suspension medium (air) and core particle [15]. In our case, the reflectivity between air and BGO is 13.3%, air-SiO<sub>2</sub> is 4.04% and SiO<sub>2</sub>-BGO is 3.11%. Thus, more UV photons are transmitted into the BGO particles due to the silica coating and consequently enhancing the PL emission intensity.

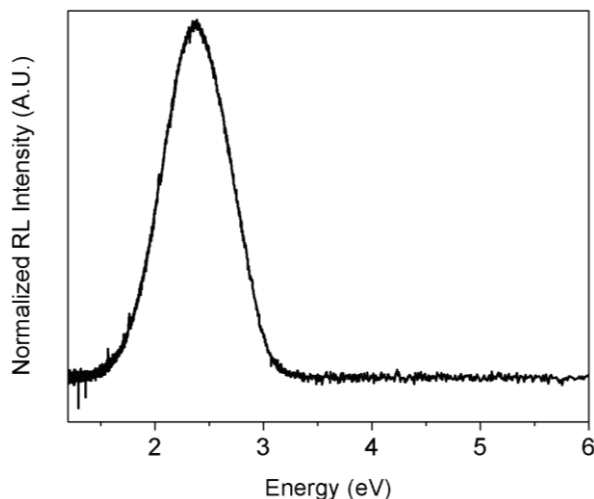


Fig. 4. Radioluminescence spectra of Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> powders without the silica coating at room temperature.

The RL spectrum of the BGO powders is shown in Fig. 4. Under a monochromatic high energy 7 keV X-ray beam, it can be seen that a single emission peak appears around 2.43 eV, very close to the value reported for RL in single crystal BGO, 2.37 eV [13]. The RL emission at 2.43 eV derives from the  $^3P_1 \rightarrow ^1S_0$  electron transition of Bi<sup>3+</sup>. Thus, the powder sample offers applicability as a scintillator material.

## Conclusions

Bismuth germanate (Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub>, BGO) nanoparticles (6-20 nm) were successfully synthesized by the sol-gel method. The BGO nanoparticles were coated with amorphous silica resulting in colloidal silica attached to the phosphor surface. Photoluminescence and radioluminescence measurements of the uncoated samples show the typical optical properties of BGO. Silica coated BGO nanoparticles show a significant increase in the photoluminescence intensity.

## Acknowledgements

Support from DGAPA-UNAM (Grant No. IN114010 and IN101509), CONACYT (Grant No. 100555) and U.S. DOE (Grant DE-EE0002003) is acknowledged. Technical assistance from E. Aparicio, F. Ruiz, I. Gradilla, E. Flores, J. Palomares, I. Perez Monfort, D. Dominguez and J.A. Diaz is also appreciated. We are grateful with the Brazilian Synchrotron Light Laboratory for RL measurements.

## References

- [1] M.J. Weber, *J. Lumin.*, 100 (2002) 35.
- [2] K. Nitsh and M. Rodova, *J. Therm. Anal. Calorim.* 91 (2008) 137.
- [3] C. Chang and C.C. Chan, *J. Radioanal. Nucl. Chem.*, 180 (1994)131.
- [4] Z.S. Macedo, R.S. Silva, M.E.G. Valerio, A.C. Hernandez, *Nucl. Instrum. Meth., B* 218 (2003)153.
- [5] C. Greskovich, N.V. Ivannikova, V.N. Shlegel, Y.V. Vasiliev and V.A. Gusev, *J. Cryst. Growth*, 229 (2001) 305.
- [6] F.A.A. De Jesus, R.S. Da Silva and Z.S. Macedo, *J. Therm. Anal. Calorim.*, 100 (2009) 537.
- [7] F. de Jesus, R. Silva, A. Hernandez and Z.S. Macedo, *J. Europ. Ceram. Soc.*, 29 (2009) 125.
- [8] S. Polosan, *Mat. Res. Bull.*, 45 (2010) 1492.
- [9] V.B. Taxak, S.P. Khatkar, S.D. Hanb, R. Kumar and M. Kumar, *J. Alloys Comp.*, 469 (2009) 224.
- [10] B.I. Won, S.Y. Hyoung, V. Sivakumar, K. Ki Hyuk, J.P. Hyung, K. Yong-Il and Y.J. Duk, *Mater. Chem. Phys.*, 115 (2009) 161.
- [11] M. Bruchnez, M. Moronne, P. gin, S. Weiss and A.P. Alivisatos, *Science*, 281 (1998) 2013.
- [12] C. Seydel, *Science* 300 (2003) 80.
- [13] C. Louis, S. Roux, g. Ledoux, C. Dujardin, O. Tillement, B.L. Cheng and P. Perriat, *Chem. Phys. Lett.*, 429 (2006) 157.
- [14] M.J. Webber, R.R. Monchamp, *J. Appl. Phys.*, 44 (1973) 495.
- [15] J.K. Han, G.A. Hirata, J.B. Talbot and J. McKittrick, *Mater. Sci. Eng. B*, 176 (2011) 436.