Journal of Crystal Growth ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Novel bismuth tri-iodide nanostructures obtained by the hydrothermal method and electron beam irradiation

Ivana Aguiar [a,*], Alvaro Olivera [b], Maia Mombrú [a], Heinkel Bentos Pereira [b], Laura Fornaro [b]

[a] Grupo de Desarrollo de Materiales y Estudios Ambientales, Cátedra de Radioquímica, Departamento Estrella Campos, Facultad de Química, Universidad de la República, General Flores 2124, Montevideo, Uruguay

[b] Grupo de Desarrollo de Materiales y Estudios Ambientales, Departamento de Desarrollo Tecnológico, Centro Universitario Regional del Este, Universidad de la República, Ruta 9 and Ruta 15, Rocha, Uruguay

Keywords:
A1. Nanostructures
A1. Radiation
B1. Halides
B2. Semiconducting materials

A B S T R A C T

Bismuth tri-iodide is a layered compound semiconductor which has suitable properties as material for ionizing radiation detection devices. Monocrystals and polycrystalline thin films have been studied for this application, but only recently, the development of nanostructures of this compound has emerged as an interesting alternative for using such nanostructures in new types of radiation detectors or for including them in other applications. Considering this, we present in this work BiI_3 nanoparticles successfully synthesized by the hydrothermal method, using a Teflon-lined stainless steel autoclave, at a temperature of 180 °C during 8–20 h, with $BiCl_3$ and NaI as source materials. We characterized the nanoparticles by X-ray diffraction (XRD), transmission electron microscopy (TEM) and electron dispersive spectroscopy (EDS). We obtained small rounded or hexagonal particles (10–20 nm in size) and larger structures. The maximum orientation of the nanostructures is along the *(0 0 l)* family planes and occurs after 16 h of synthesis, which arises as the best condition for obtaining BiI_3 oriented nanostructures. When a 100 kV TEM electron beam was converged on the larger structures, we obtained highly oriented BiI_3 hexagonal and rod shaped nanostructures. We found that particles' shape does not depend on the synthesis time. In addition, results were compared with the ones obtained for nanoparticles synthesized from solution. The present work is an advance in the synthesis of BiI_3 nanostructures by the hydrothermal method, and is also the first step on seeking the amenable control of morphology and size of such structures using electron beam irradiation. This last process may be particularly appropriate for producing nanostructures for future applications in new devices.

1. Introduction

Since the discovery of inorganic fullerene-like and nanotubes, nanostructures of layered compounds have attracted remarkable attention for their novel properties and, consequently, for their new potential applications. Considerable advances have been reached in theoretical and experimental studies in the field of chalcogenides such as WS_2 and MoS_2 [1–3], and in their application as solid lubricants [4,5]. However, there are not many reports related to the synthesis of halides nanostructures, possibly due to the high reactivity and the high vapor pressure of those compounds at their melting point and below it, which make them difficult to handle. Among others, there are reports about PbI_2 nanocrystals synthesized by the hydrothermal method [6] and BiI_3 and HgI_2 nanocrystals obtained by solution [7–9] and hydrothermically [10–12]. Until now, the structures obtained hydrothermically were unsatisfactory, because of their non-uniformity in size and morphology. Besides, nanostructures of CdI_2, PbI_2 and SbI_3 have been synthesized via electron beam irradiation, with and without WS_2 inorganic nanotubes as templates, and BiI_3@WS_2 core–shell nanotubes were obtained by wetting and capillary filling of inorganic nanotubes [13–15].

On the other hand, BiI_3 is an anisotropic semiconductor with rhombohedral structure, with a layer of Bi^{3+} sandwiched between two hexagonally closed packed layers of iodide. The band gap of bulk BiI_3 was reported to be 1,67 eV [16], and crystals and films of this material have been studied for ionizing radiation detection [17–21].

In light of these antecedents, we believe that nanoparticles of this compound may have special applications, for instance, for

Abbreviations: XRD, X-ray diffraction; SEM, scanning electron microscopy; TEM, transmission electron microscopy; EDS, energy dispersive spectroscopy; TC, texture coefficient

* Corresponding author.
E-mail addresses: iaguiar@fq.edu.uy (I. Aguiar), alvarobq@gmail.com (A. Olivera), maiam@fq.edu.uy (M. Mombrú), yandinoca@gmail.com (H. Bentos Pereira), lfornaro@gmail.com (L. Fornaro).

http://dx.doi.org/10.1016/j.jcrysgro.2016.06.024
0022-0248/

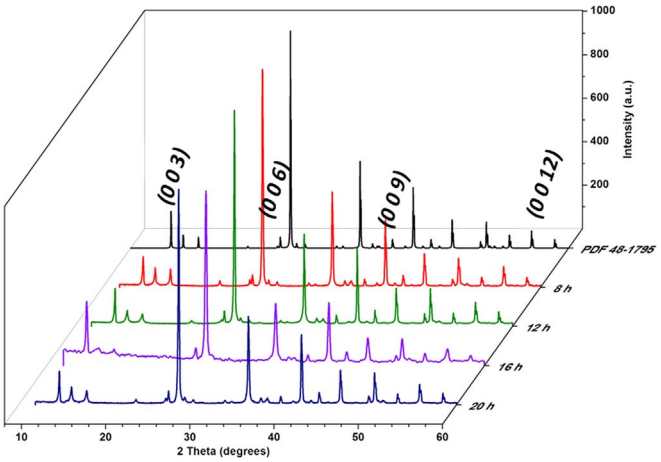

Fig. 1. XRD patterns of the BiI_3 samples synthesized at different times, compared with the BiI_3 PDF file 48-1795.

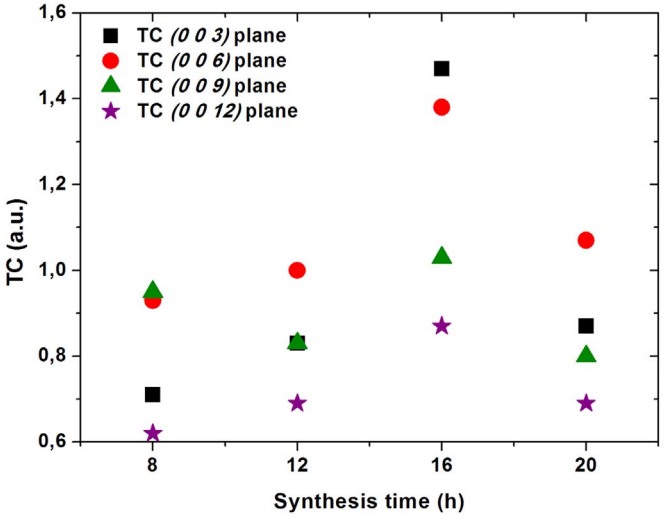

Fig. 2. TC for *(0 0 l)* planes as a function of the synthesis time.

preparing radiation detectors or as acceptors in inorganic–organic solar cells.

In this report, we focus our work on the synthesis and characterization of BiI_3 nanostructures by the hydrothermal method. Furthermore, we studied electron beam irradiation as a new way of producing novel structures, and we provided some comprehensive insights in the formation mechanism of the nanostructures.

2. Materials and methods

Bismuth tri-iodide nanoparticles have been synthesized by the hydrothermal method. $BiCl_3$ (Aldrich, ˃98%) and NaI (Dolder) were used as starting materials, and distilled water was used as solvent. In a typical synthesis, $2{,}8 \times 10^{-3}$ mol of $BiCl_3$ were dissolved in 10 mL of HCl 4.5 M, and $1{,}4 \times 10^{-2}$ mol of NaI were dissolved in 5 mL of distilled water. Subsequently, the NaI solution was slowly dropped into the $BiCl_3$ solution under vigorous stirring, and a transparent orange-colored solution precursor was obtained. Finally, the solution was transferred into a home-made Teflon-lined autoclave and heated at 180 °C for 8, 12, 16 and 20 h. After the system was cooled down to room temperature, the final product was isolated by centrifugation at 5000 rpm and dried at 60 °C for 24 h.

Nanoparticles were characterized by X-Ray diffraction (XRD) with a Shimadzu XRD 7000 Diffractometer, using Ni-filtered CuKα radiation ($\lambda = 1.5406$ Å).

In order to study any preferred growth orientation of the nanoparticles, texture was estimated by the Texture Coefficient (TC), defined as

$$TC(hkl)_i = \frac{I(hkl)_i / I_0(hkl)_i}{\frac{1}{N}\sum_N \frac{I(hkl)_n}{I_0(hkl)_n}} \quad (1)$$

where $I(hkl)_i$ is the observed intensity of the $(hkl)_i$ plane, $I_o(hkl)_i$ is the intensity of the $(hkl)_i$ reflection of a polycrystalline sample, N is the total number of reflections taken into account, and (hkl) denotes the Miller indices of the lattice planes of a given signal [22].

BiI_3 nanoparticles were also characterized by transmission electron microscopy (TEM), using a JEOL JEM-1010 instrument

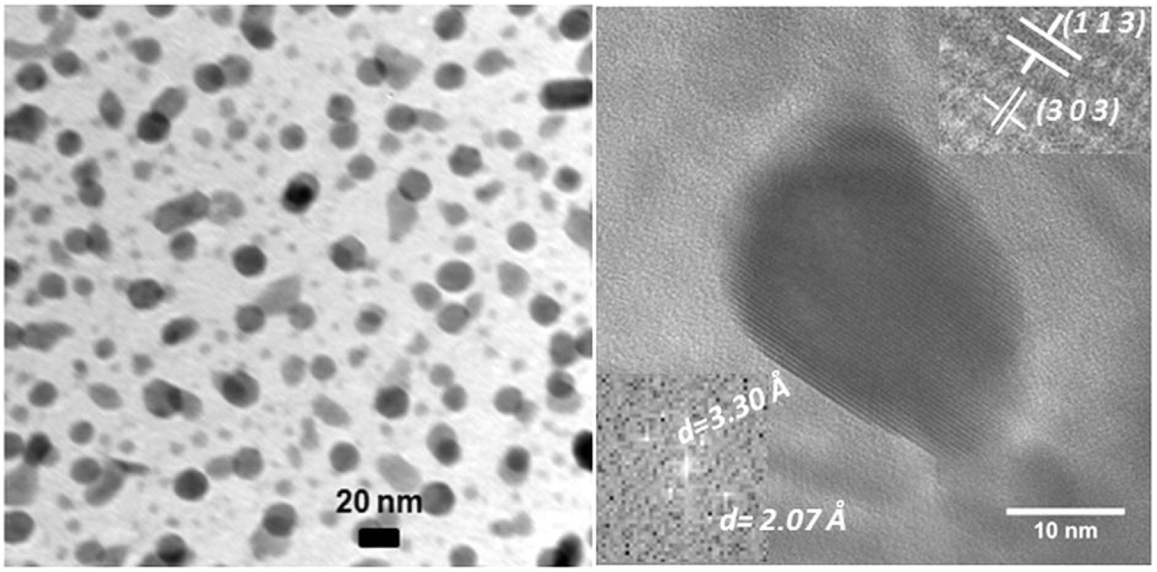

Fig. 3. a: TEM image (100 kV), b: High resolution TEM image (200 kV) of a representative structure. Inset: Fourier transform of a section of the image.

Please cite this article as: I. Aguiar, et al., Journal of Crystal Growth (2016), http://dx.doi.org/10.1016/j.jcrysgro.2016.06.024