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Luminescence and Raman study of α-Bi_2O_3 ceramics

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ABSTRACT

Cathodoluminescence in the scanning electron microscope and photoluminescence in a confocal microscope have been used to investigate the luminescence properties of the stable monoclinic α-phase of Bi_2O_3. Powders of this oxide have been sintered at temperatures of 500 °C and 750 °C in air or in nitrogen atmospheres. Spectra of the starting powder and of the samples treated at 500 °C show luminescence bands at 1.50 eV and 1.95 eV as well as a band at 2.1 eV, more prominent in nitrogen treated samples. Sintering at 750 °C leads to quenching of the 1.50 eV infrared emission and the formation of a broad band with emission above 3 eV. The evolution of Raman bands with the sintering treatments has also been investigated.

1. Introduction

Bismuth trioxide (Bi_2O_3) is a semiconductor with interesting physical properties, such as a wide optical band-gap, high refractive index and a good photoconductive response, which make this material suitable for applications in gas sensing, optical coatings, catalysis and optoelectronics [1–3]. In spite of the technological interest of Bi_2O_3, some of its main optical and electronic properties are not well known. One of the problems in Bi_2O_3 studies is the existence of four main polymorphs [4,5], labeled as α (monoclinic), β (tetragonal), γ (bcc) and δ (fcc), with different physical properties. α-Bi_2O_3 is stable from room temperature up to 730 °C. At 730 °C, this monoclinic phase transforms into the δ-Bi_2O_3 phase, which remains stable up to its melting point (825 °C). β-Bi_2O_3 and γ-Bi_2O_3 are obtained as metastable phases during the cooling of δ-Bi_2O_3. Below 640 °C approximately, these metastable phases are transformed into α-Bi_2O_3. Mixtures of different phases have been observed in Bi_2O_3 thin films [6], while the growth of α [7], β [8] and mixed (α + β) Bi_2O_3 nanowires [9] has been also reported. The room temperature band gaps of the α and β-Bi_2O_3 phases measured by optical absorption are 2.85 eV and 2.58 eV, respectively [10–12]. Nevertheless, a range of band gap values of up to 3.5 eV has been reported for α-Bi_2O_3 nanowires as a function of size [7]. Due to the different optical applications of Bi_2O_3, its luminescence behavior has been increasingly investigated in the last years. Most of the results are explained in the frame of the reported band gap values for the different phases or the influence of size in the case of nanostructures. Photoluminescence (PL) spectra of α-Bi_2O_3 microcrystals [13] show a peak at 2.81 eV, attributed to band-to-band recombination, and a peak at 2.98 eV explained by surface states, while for α-Bi_2O_3 nanoparticles a band edge PL emission at 3.12 eV was reported [14]. In α-Bi_2O_3 ceramics the spectra were found to consist of three bands with maxima at 2.75 eV, 2.40 eV and 1.97 eV [15], which were associated to processes in complexes containing the Bi ion in closest oxygen environment. β phase nanowires and nanorods show a PL band at 2.75–2.90 eV [8] and two phase (α and β) nanowires show a broad emission in the range 1.5–2.5 eV [9,16]. Contrary to the case of other oxides of technological interest, the information on the luminescence emission related to the presence of native defects, or other defect states, in the stable α-Bi_2O_3 phase is scarce. Previous reports on the luminescence of α-Bi_2O_3 refer to PL studies [13–15], while we are not aware of cathodoluminescence (CL) reports on this material Moreover, a correlation between the observed emission bands and the defect structure of this oxide was not clearly established in the previously mentioned PL works. In the present work, the luminescence of α-Bi_2O_3 ceramics – sintered in air or in nitrogen atmosphere – was investigated by CL in the scanning electron microscope (SEM) and by PL. The structural and compositional properties of the samples were also characterized by X-ray diffraction (XRD), energy dispersive spectroscopy (EDS) and micro-Raman spectroscopy.

2. Experimental method

The starting material used was commercial Bi_2O_3 powder (Sigma–Aldrich) of 99.999% purity. The powder consisted of particles of about (4–5) μm. The powders were compacted under compressive load to form disk-shaped samples of about 7 mm diameter and 1 mm thickness. Some of the samples were then sintered in air or in nitrogen at temperatures of 500 °C or 750 °C for 10 h. In order to control possible phase transformation during the thermal treatments, XRD measurements were carried out in the

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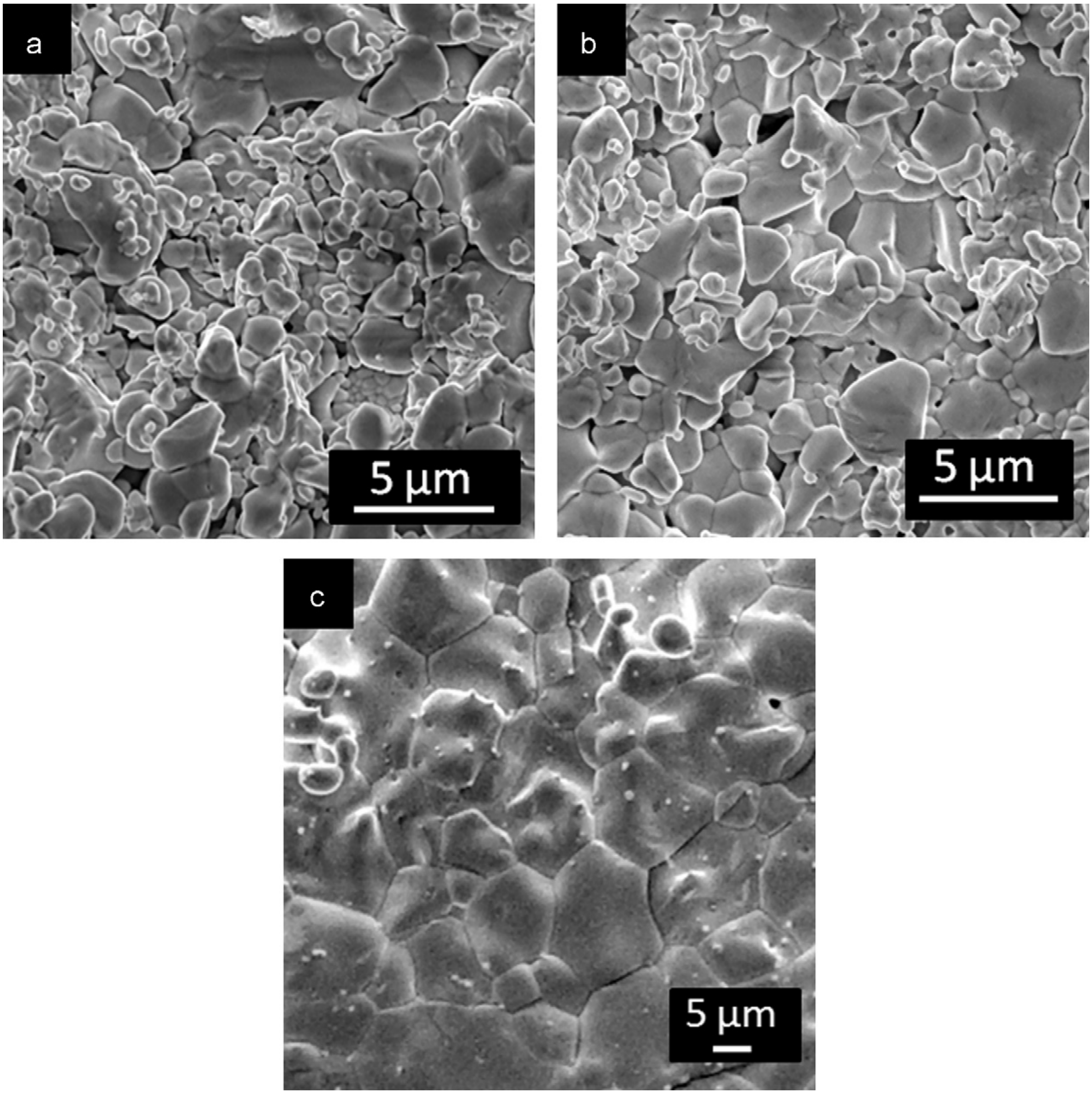

Fig. 1. SEM images of samples treated at 500 °C in nitrogen (a) and air (b). (c) SEM image of sample treated at 750 °C in nitrogen atmosphere.

starting material and in all treated samples, with an X'Pert PRO MRD diffractometer using Cu Kα radiation. Since diffraction maxima of several Bi_2O_3 phases appear at close angles, data were collected with a step width of 0.015° and step time of 5 s. Secondary electron observations were performed with a Leica 440 Steroscan SEM or with a Fei Inspect SEM. For EDS measurements, a Bruker AXS Quantax was used. CL investigations were carried out, at temperatures between 100 K and 300 K, in a Hitachi S2500 SEM using a Hamamatsu R928 photomultiplier working in photon counting mode. Micro-Raman and photoluminescence measurements were carried out at room temperature in a Horiba Jovin-Ybon LabRAM HR800 system. The samples were excited by a 325 nm He–Cd laser on an Olympus BX 41 confocal microscope with a 40× objective. A charge coupled device detector was used to collect the scattered light dispersed by a 2400 lines mm^{-1} grating.

3. Results and discussion

SEM images of samples treated at 500 °C show partial sintering and the presence of some pores. The grain size in the samples annealed in nitrogen at 500 °C (Fig. 1a) ranges from 0.5 μm to about 6 μm. The samples treated in air at the same temperature show a more uniform grain size, in the approximate range from 1 μm to 3 μm, and a slightly more developed sintering (Fig. 1b). Samples treated at 750 °C in air or in nitrogen present a similar appearance, with sintered grains with well defined grain boundaries and sizes in the (8–30) μm range (Fig. 1c). XRD measurements show (Fig. 2a) that the Bi_2O_3 starting powder contains a predominant α phase and only one small peak can be assigned to the cubic γ phase (JCPDS card 045-1344). XRD spectra of all the treated samples (Fig. 2b) are similar, and can be unambiguously indexed to the monoclinic α-Bi_2O_3 structure (JCPDS card 041-1449).

Raman spectroscopy measurements have been carried out in all samples, as an additional technique to assess the crystalline phase and to investigate the possible effect of annealing in different atmospheres on the Raman peaks of α-Bi_2O_3. Previous Raman studies enabled to assign specific bands to different Bi_2O_3 phases but, to our knowledge, no studies have been carried out on the relative intensity of the bands as a function of other structural features. Factor group analysis predict 30 active Raman modes ($15\,A_g + 15\,B_g$)