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Laser irradiation-induced α to δ phase transformation in Bi_2O_3 ceramics and nanowires

M. Vila, C. Díaz-Guerra,[a] and J. Piqueras
Departamento de Física de Materiales, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain

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The α-Bi_2O_3 to δ-Bi_2O_3 phase transformation has been locally induced by laser irradiation in ceramic samples and single-crystal nanowires of this oxide. The threshold power densities necessary to induce this transformation, as well as the corresponding transformation kinetics and its temporal stability, have been investigated in both kinds of samples by micro-Raman spectroscopy. The appearance of the δ phase was also monitored by spatially resolved photoluminescence spectroscopy. An emission band peaked near 1.67 eV, not observed in α-Bi_2O_3, is tentatively attributed to δ-Bi_2O_3 near band gap transitions. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4747198]

Oxide materials with high values of ionic conductivity are a subject of increasing interest for potential applications in energy generation and storage technology. Bismuth trioxide (Bi_2O_3) is a semiconductor with interesting physical properties, such as a wide optical band-gap, high refractive index and dielectric permittivity, good photoconductive response, and ionic conductivity, which make this material suitable for applications in solid oxide fuel cells, gas sensing, optical coatings, catalysis, and optoelectronics.[1–3] Bi_2O_3 has 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 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. The cubic δ-Bi_2O_3 phase is one of the best oxygen ion conductors known ($\sigma \sim 1.5$ S cm^{-1}) and is considered as a reference material within the field of solid electrolytes.[6] This phase can be stabilized by addition of rare earth oxides, but the conductivity drops by about two orders of magnitude. In the past years, δ-Bi_2O_3 thin films have been synthesized by electrodeposition and magnetron sputtering.[7,8] In the present work, we investigate the possibility to induce a local and permanent α-Bi_2O_3 to δ-Bi_2O_3 phase transformation in bulk materials as well as in nanowires by laser irradiation. The ability to locally modify the electrical conductivity and optical properties of a wide range of materials is of great interest for the development of sensing and storage applications. In this framework, local laser irradiation is a useful technique able to modify the structure, composition, and physical properties of several oxides,[9–11] chalcogenides,[12] and metallic alloys.[13] Laser irradiation of the Bi_2O_3 samples was carried out by using a confocal microscope. The induced transformation was monitored *in situ* as a function of irradiation time and laser power by micro-Raman and photoluminescence (PL) spectroscopies.

Two kinds of Bi_2O_3 samples were investigated in the present work, ceramics and nanowires (Fig. 1). α-Bi_2O_3 ceramic samples were prepared following the procedure described in Ref. 14. In order to grow the nanowires, a mixture containing 80 wt. % Bi powder (Goodfellow, 99.997%) and 20 wt. % Er_2O_3 powder (STREM, 99.9%) was compacted under compressive load to form disk-shaped samples of about 7 mm diameter and 1 mm thickness. These samples were then annealed at 800 °C for 4 h in a horizontal tube furnace under Ar flow. The treatment leads to the growth of a high density of single crystalline α-Bi_2O_3 nanowires, as revealed by x-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM).[15] Energy dispersive x-ray microanalysis performed in scanning and transmission electron microscopes (SEM, TEM) did not detect the presence of Er in the Bi_2O_3 nanowires. The addition of Er_2O_3 alters the oxidation kinetics in the growth of the nanostructures, probably influencing the nucleation and oxidation process. Actually, nanowires were not obtained when similar treatments were carried out using pure Bi as the only precursor material, so that Er_2O_3 was used here to favor the growth of these nanostructures.

The morphology of the samples before and after laser irradiation was investigated by using a FEI Inspect SEM. Micro-Raman and PL 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 grating. The size of the laser spot on the sample was 2 μm approximately. In order to adjust the applied power densities, the excitation light was attenuated by using neutral density filters. Both ceramics and nanowires were attached to the confocal microscope sample holder by using a conductive adhesive carbon tape.

Figure 1 shows SEM images of both kinds of samples prior to irradiation. α-Bi_2O_3 ceramics show sintered grains with well defined grain boundaries and sizes in the (5–20) μm range. The investigated nanowires are (100–200) nm wide and up to 10 μm long. In order to carry out the

[a]e-mail: cdiazgue@fis.ucm.es.

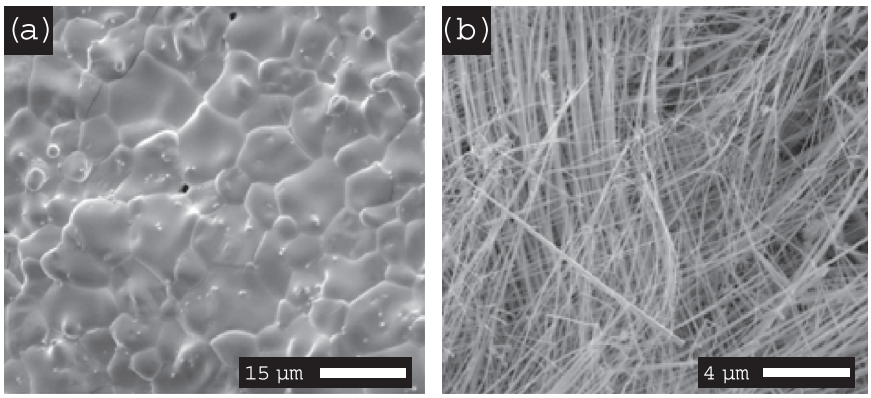

FIG. 1. SEM images of α-Bi_2O_3 ceramics (a) and nanowires (b) prior to laser irradiation.

irradiation experiments, the nanowires were gently detached from the disk-shaped substrates. SEM observations of both kinds of samples after irradiation revealed no morphological changes irrespective of the power density used or the exposure time to the laser beam. The development of the Bi_2O_3 structural change was monitored in ceramics and nanowires by Raman spectroscopy, using laser power densities ranging from 10^5 to 10^2 W/cm^2 (Fig. 2). Spectra recorded at power densities below 10^4 W/cm^2 show, in both kinds of samples, Raman bands peaked at about 212, 284, 315, 414, 447, and 535 cm^{-1}. These bands can be assigned to the α-Bi_2O_3 phase

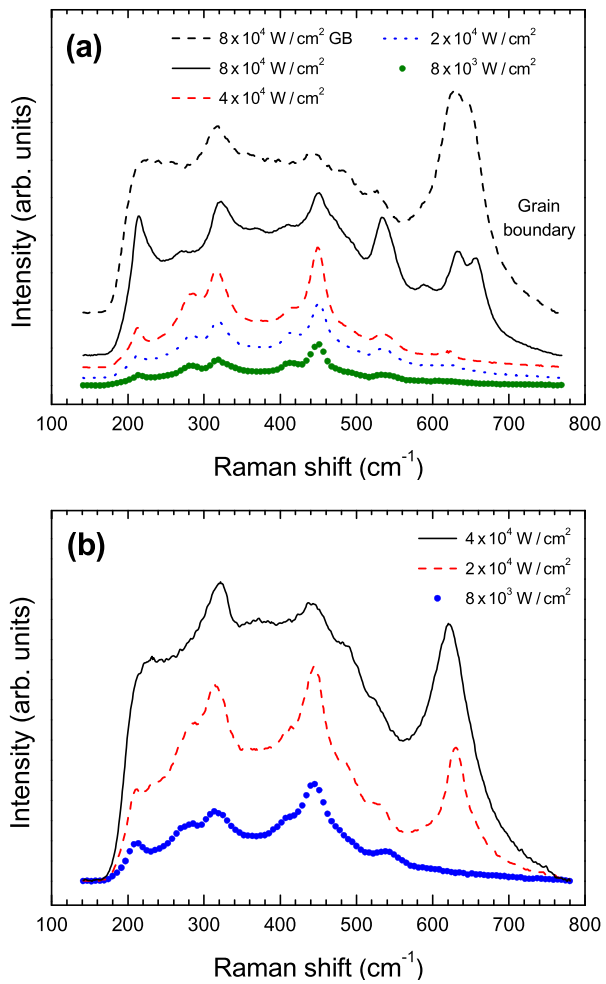

FIG. 2. Raman spectra, shifted for clarity, of Bi_2O_3 ceramics (a) and nanowires (b) as a function of laser power density. Spectra shown in (a) were recorded at a grain interior unless otherwise indicated.

and are attributed to displacements of the O atoms with respect of the Bi atoms causing Bi-O elongation.[16,17] However, for power densities above 2×10^4 W/cm^2 in nanowires and approximately 4×10^4 W/cm^2 in ceramic samples, a new Raman band is observed peaked between 619 and 628 cm^{-1}. The intensity of this band increases by increasing the excitation density in all the investigated samples and is the dominant band in spectra recorded in irradiated grain boundaries of ceramic samples. These results evidence a laser-induced α to δ phase transformation during the irradiation of both Bi_2O_3 ceramics and nanowires. Raman spectra of the δ-Bi_2O_3 phase usually show a wide and asymmetric band centered between 610 and 640 cm^{-1}.[7,8,18,19] In the present case, the band characteristic of the δ phase appears centered between 619 and 625 cm^{-1} in Raman spectra of the nanowires and between 624 and 628 cm^{-1} in those measured in ceramic samples. δ-Bi_2O_3 may be regarded as an anion deficient fluorite structure, where Bi occupies the *fcc* sites, having a defect oxygen sublattice the structure of which is still under discussion. In fact, the oxygen sublattice is characterized by a complicated disorder, while there is still no clear understanding of the oxygen vacancies arrangement.[20] Moreover, the δ phase is likely to involve a thermal average of a range of different local environments.[21] This structural disorder may account for the somewhat different peak frequencies of the δ-Bi_2O_3 Raman band found in nanowires and ceramics. Raman bands characteristic of α-Bi_2O_3 can still be observed in the Raman spectra of the strongly irradiated areas, suggesting that this thermally driven process probably takes place in the central part of the area irradiated by the laser spot, where temperature reaches its highest value due to the Gaussian intensity profile of the laser beam. The temperature distribution is less homogeneous in bulk material than in nanowires due to the existence of grain boundaries and other extended defects. Moreover, the size of the laser spot is much smaller than the size of the polycrystalline samples, which is not the case for the irradiated nanowires. This may explain the occasional appearance of a Raman peak at about 656 cm^{-1} only in spectra from irradiated ceramics, in agreement with Raman observations reported by Fan *et al.*[18] in annealed δ-Bi_2O_3. These authors tentatively attributed a Raman peak centered at 655 cm^{-1} to the metastable γ-Bi_2O_3 phase by comparison of XRD and Raman measurements.

Transformation kinetics was investigated *in situ* in both ceramics and nanowires by irradiating the samples with power densities above the previously mentioned threshold

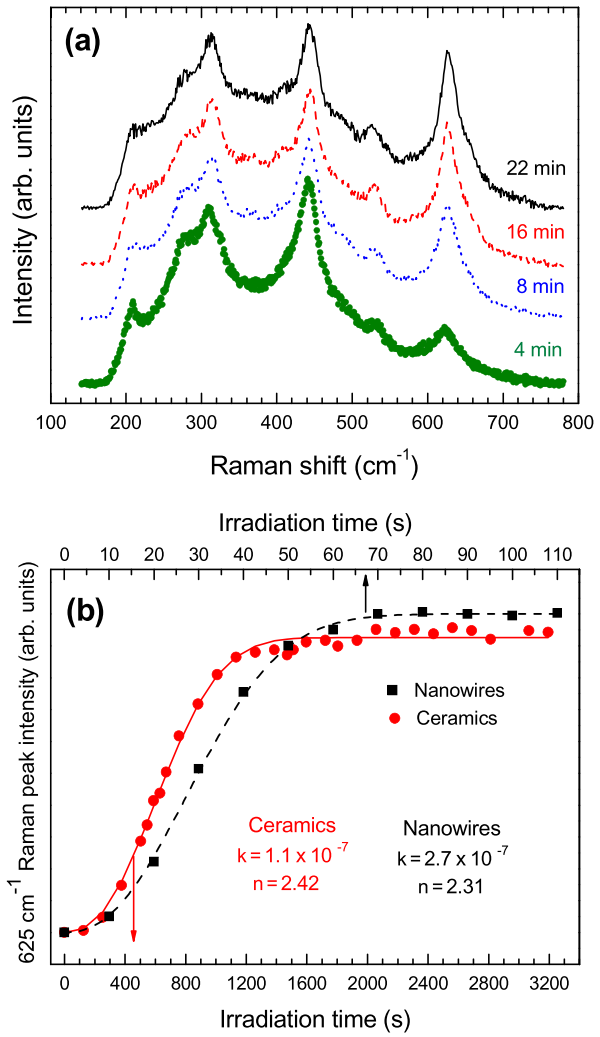

FIG. 3. (a) Raman spectra of Bi_2O_3 ceramics after different irradiation times. (b) Temporal intensity evolution of the 625 cm^{-1} Raman peak in ceramic samples and nanowires. Dots correspond to experimental data while solid lines correspond to fits to the JMA model. Data correspond to power densities of 8×10^4 W/cm^2 (ceramics) and 4×10^4 W/cm^2 (nanowires).

values and collecting Raman spectra at fixed time intervals. Fig. 3(a) shows spectra of Bi_2O_3 ceramics irradiated for different times. A progressive increase of the relative intensity of the band centered near 625 cm^{-1}, characteristic of the δ-Bi_2O_3 phase, is observed by increasing the exposure time to the laser beam. After approximately 20 min of laser irradiation, the intensity of the mentioned band reaches a saturation value [Fig. 3(b)]. A similar behavior is observed for nanowires, but the transformation takes place much faster. Actually, saturation is reached just 1 min after irradiation started. The observed thermal conductivities of oxide nanostructures are frequently lower than the corresponding bulk values, which is mainly attributed to an increased phonon-boundary scattering rate.[22] Such behavior is in agreement with our Raman measurements, since the threshold power density required to trigger the α to δ phase transformation is lower for nanowires than for ceramics, while saturation of the 625 cm^{-1} band is reached faster in nanowires than in ceramics.

The temporal intensity evolution of the 625 cm^{-1} Raman signal of both kinds of samples is plotted in Fig. 3(b). Assuming that the intensity of such band is proportional to the volume of transformed material,[9] from α-Bi_2O_3 to δ-Bi_2O_3, the experimental data were fitted to the Johnson-Mehl-Avrami (JMA) equation:[23]

$$X = 1 - \exp(-Kt^n).$$

This model, originally proposed to describe crystallization kinetics for isothermal annealing conditions, has been frequently applied to describe phase transformation induced by laser irradiation in different materials.[9,24] X represents the transformed volume fraction in the irradiated area, K is an effective rate constant and the Avrami exponent, n, is related to the nucleation rate and/or the growth morphology. The obtained values, 2.3 for nanowires and 2.4 for ceramics, suggest that crystallization proceeds by a diffusion-controlled growth mode with nearly constant nucleation rate.[25] The disorder characteristic of δ-Bi_2O_3 can be structurally derived from the α phase. As a consequence of the growing degree of oxygen site disorder with increasing temperature, the oxygen sublattice exhibits a liquid-like behavior which promotes higher oxygen ion diffusion only when a certain degree of the structural disorder is achieved, mimicking a process which is analogous to a pre-melting phenomenon.[26]

The time stability of the laser induced δ-Bi_2O_3 phase was investigated for both types of samples. In order to do that, ceramics and nanowires were irradiated with laser power densities above their respective threshold values and for times longer than the saturation values shown in Fig. 3(b). Precisely, nanowires were irradiated during 90 s and ceramics during 20 min by using a power density of 8×10^4 W/cm^2. Raman spectra were recorded before beginning irradiation and at different time lapses after the end of irradiation, using, in all cases, a low laser power density of 8×10^3 W/cm^2. The absence of Raman bands above 600 cm^{-1} before irradiation and its presence 2 h after irradiation (Fig. 4) reveal the stability of the induced δ-Bi_2O_3 phase. Actually, an intensity decrease of the mentioned

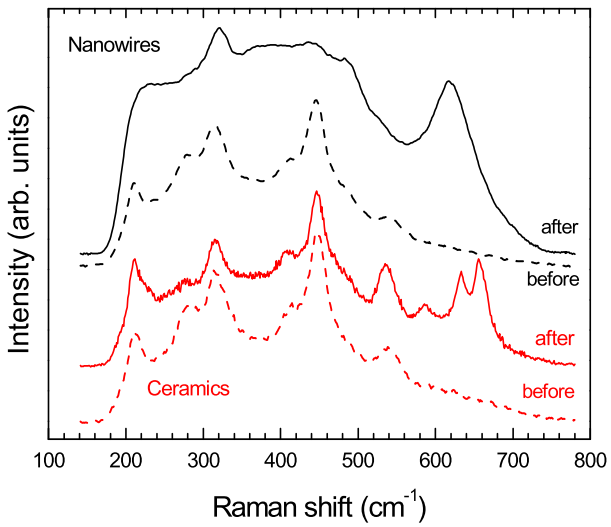

FIG. 4. Raman spectra of ceramics and nanowires before and 2 h after laser irradiation. Nanowires were irradiated during 90 s and ceramics during 20 min by using a power density of 8×10^4 W/cm^2 in both cases. Spectra were recorded by using a laser power density of 8×10^3 W/cm^2.

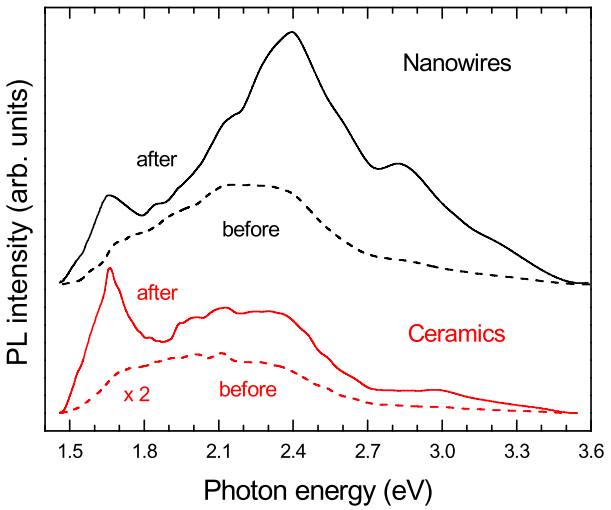

FIG. 5. PL spectra of ceramics and nanowires before and 2 h after laser irradiation. Irradiation was carried out by using a power density of 8×10^4 W/cm^2. Spectra shown in this figure were recorded by using a laser power density of 8×10^3 W/cm^2.

Raman signal with time was neither observed in nanowires nor in ceramic samples after finishing the corresponding irradiation periods.

The appearance of the δ phase was also monitored by PL spectroscopy. Besides emission in the (3.20–2.85) eV range, usually attributed to band gap transitions, PL emission in the visible range has been frequently attributed in α-Bi_2O_3 to radiative transitions involving Bi ions with different charge states.[14,27–29] Figure 5 shows PL spectra of our bismuth oxide ceramics and nanowires before and after laser irradiation. A broad, complex, emission peaked between 2.4 and 2.0 eV can be observed before irradiation in all the samples investigated. Laser irradiation enhances PL intensity and induces significant changes in the spectral distribution of the emission. In particular, a dominant band peaked near 2.41 eV, with well resolved shoulders at 2.82 eV and 2.21 eV, can be clearly appreciated in spectra from the irradiated nanowires. Emission in the (3.1–2.2) eV spectral range has usually been attributed to Bi^{3+} intraionic transitions or charge transfer transitions between oxygen ligands and Bi^{3+} ions[14,27,28] in α-Bi_2O_3, while luminescence bands in the (2.10–1.87) eV range were commonly assigned to Bi^{2+} intraionic transitions.[14,29] Furthermore, laser irradiation gives rise—in PL spectra of ceramics and nanowires—to an intense band centered at 1.67 eV, not observed in samples with the α-Bi_2O_3 structure. This band can be tentatively attributed to δ-Bi_2O_3 near band gap transitions. Actually, such emission appears only in the PL spectra of strongly irradiated areas, where the corresponding Raman spectra reveal the formation of the δ phase. In addition, the peak energy of the mentioned PL band is very close to the band gap value of 1.73 eV measured by optical absorption in δ-Bi_2O_3 thin films[8] and is in agreement with recent theoretical calculations.[30]

In summary, an α-Bi_2O_3 to δ-Bi_2O_3 phase transformation can be locally induced by laser irradiation in ceramic samples and single crystal nanowires of this oxide, which may be of interest for electronic and optoelectronics applications due to the different conductivity and optical properties of such polymorphs. A threshold power density for the irradiation induced phase transformation of 2×10^4 W/cm^2 in nanowires and approximately 4×10^4 W/cm^2 in ceramic samples was determined by μ-Raman spectroscopy in a confocal microscope. Transformation kinetics can be described by the Johnson-Mehl-Avrami equation. The time stability of this laser induced phase transformation was also established. Irradiation induces changes in the luminescence emission of both ceramics and nanowires. A PL emission band peaked near 1.67 eV, not observed in α-Bi_2O_3, is tentatively attributed to δ-Bi_2O_3 near band gap transitions.

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