Study of local structure of α- and δ- Bi2O3 polymorphs by means temperature dependent XAS

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Bismuth trioxide (Bi2O3) is a polymorph semiconductor with interesting physical properties, such as a wide optical band-gap, high refractive index and dielectric permittivity, and ionic conductivity, which make this material suitable for applications in gas sensing, optical coatings, catalysis, and optoelectronics. Bismuth trioxide (Bi2O3) has four main polymorphs, labelled as α (monoclinic), β (tetragonal), γ (bcc), and δ (fcc), with different physical properties. The α - phase is stable up to 1003 K, when the transition to the δ - phase occurs. This phase is an anion deficient fluorite structure, which is responsible of its high ion conductivity (1.5 Scm-1). The cubic δ phase is considered as a reference material in the field of solid electrolytes, and therefore, the understanding of the local lattice disorder and its structural properties near the α to δ – Bi2O3 phase transition is crucial for the development of new devices.

Bi2O3 nanowires and ceramics have been synthesized and structural, compositional as well as morphological characterization has been carried out. Additionally, ionic conductivity measurements have been performed in order to study the abrupt increase in the conductivity due to the α to δ phase transition.

The aim of this experiment was to study the temperature dependence of structure spectra of both Bi2O3 nanowires and ceramics in order to investigate the local structure of the different Bi2O3 phases and obtain information at the alpha - delta phase transition. α - Bi2O3 is stable from room temperature up to 1003 K. At 1003 K, this phase undergoes a transition to the δ - Bi2O3 phase, which remains stable up to its melting point (1098 K). On the other hand, γ - Bi2O3 and β - Bi2O3 are obtained as metastable phases during the cooling of δ - Bi2O3. Below 913 K approximately, these metastable phases are transformed into α - Bi2O3.

Direct evidences of the oxygen vacancies arrangement and local structure of different phases have been obtained by means X-Ray Absorption Spectroscopy in function of temperature. These results have been correlated with temperature dependent High Resolution Powder Diffraction study of both Bi2O3 nanowires and ceramics samples.