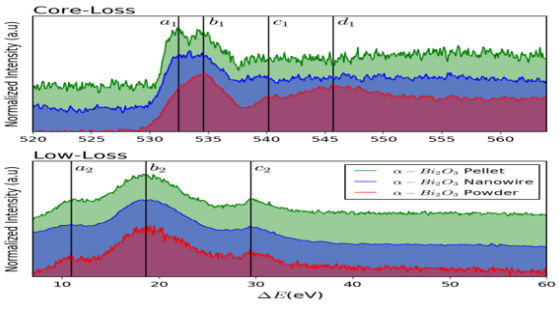
EELS + DFT on the study of oxygen deficient α-Bi_2O_3

Coll, C.[1], Torruella, P.[2,3], Martín, G.[2,3], López, L.[2,3,4], Vila, M.[5,6], Díaz-Guerra, C.[6], Varela, M.[6], Ruiz-González, M.L.[7], Piqueras, J.[6], Estradé, S.[2,3] and Peiró, F.[2,3]

[1] University of Barcelona, Spain, [2] LENS-MIND, Departament d'Enginyeria Electrònica i Biomèdica, Universitat de Barcelona, Spain, [3] IN2UB - Institute of Nanoscience and Nanotechnology, Universitat de Barcelona, Spain, [4] Unitat TEM-MAT, Centres Científics i Tecnològics de la Universitat de Barcelona (CCiTUB), Spain, [5] IMDEA Materials Institute, Spain, [6] Departamento de Física de Materiales, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Spain, [7] Departamento de Química Inorgánica, Facultad de Químicas, Universidad Complutense de Madrid, Spain

Density Functional Theory (DFT) calculations are widely used in the understanding of the electronic structure of the materials. Combined with Electron Energy Loss Spectroscopy (EELS) it is a powerful tool to elucidate all the features which appear in the experimental spectra [1]. In the present work we address the characterization of bismuth oxide, an interesting material with potential applications in the fields of optics, electrochemistry and in fuel cells, using EELS and DFT [2]. One the most promising properties of Bi_2O_3 is its abnormally high oxygen conductivity, which is normally discussed in terms of oxygen vacancy generation and transport [3]. However, most of the literature about this material are studies performed at the macroscopic level and even though local properties such as the electronic environment of the oxygen would be highly interesting, little experimental work has been done in this matter [4]. We have performed pioneering core and low-loss EELS studies in three different alpha-Bi_2O_3 samples which exhibit different oxygen conductivity values. These are the first reported core-loss EELS measurements of this material to our knowledge and as such, how spectral features relate to structural and electronic properties remains unclear.

Detailed EELS measurements have revealed significant differences in the Electron energy-loss near-edge structure (ELNES) of the respective oxygen K edges. Since there are not reported EEL spectra of alpha-Bi_2O_3 the interpretation of the ELNES features required DFT calculations. First, the bulk alpha-Bi_2O_3 ELNES (without oxygen vacancies) was simulated using WIEN2k [5]. Then DFT simulations of oxygen deficient Bi_2O_3 were carried out. The theoretical data obtained from DFT was compared to the experimental data. Several simulations were performed considering a different fraction of oxygen deficiency. The results showed a shift of the O K edge depending on the amount of vacancies. Furthermore, EELS analysis together with DFT enabled to discern, from the non equivalent O crystallographic sites in the unit cell, which was the site where the oxygen vacancies appear, in addition to establishing a relationship between the fraction of oxygen vacancies and the shift of the O K edge.



[1] Hébert, C., Micron 2007, 38, 12–28.
[2] Torruella, P et al., Journal of Physical Chemistry C 121 (39) (2017).
[3] Takahashi, T. et al., *J. Appl. Electrochem.* 5 (1975) 187 - 195.
[4] Walsh, A., J. *Phys. Rev. B* 23 (2006) 1-13.
[5] Blaha, P.; Comput. Phys. Commun. 1990, 59 (2), 399–415.

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