STABILISATION OF DELTA BI_2O_3 PHASE IN NANOCOMPOSITES DOWN TO ROOM TEMPERATURE BY TWIN–ROLLERS TECHNIQUE

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Polycrystalline bismuth (III) oxide is very well known for its occurrence in α, β, γ and δ phases (Fig. 1), which is widely reported in the literature. Furthermore, Bi_2O_3 seems to exhibit different properties, according to its crystalline phase, which makes it an exceptionally interesting material from the perspective of science path for solid state matter, along with possible practical applications. In particular, the δphase of Bi_2O_3 exhibits the highest conductivity in high temperature range (1 S/cm at 750 °C) from among all known oxygene ion conductors. However, it is stable only in a narrow temperature range from 730 to 825 °C [1].

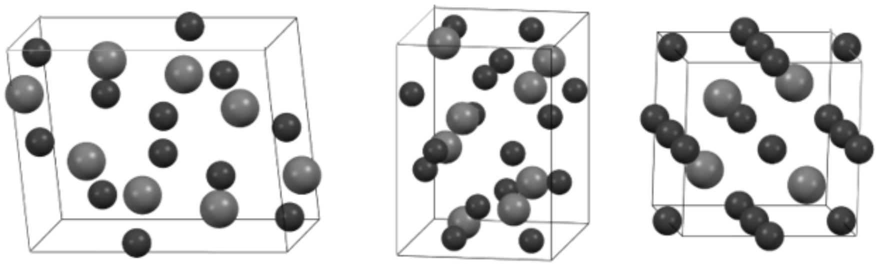

Fig. 1. Unit cells of the most important phases of bismuth (III) oxide (from left to right): ($P2_1/C$) monoclinic (α); ($P42_{1C}$) tetragonal (β); (Pn-3m) fluorite-type fcc (δ), generated by Mercury software [2] from CIFs no. 1010004, 1545547, 1010311, respectively.

Its very high ionic conductivity has motivated many researchers to look for a method to stabilise this fluorite-type structure to lower temperature. So far the successful strategies to achieve the stabilisation of the delta phase have included doping (e.g. by rare-earth elements [3]) or synthesis in form of thin layers [4]. Our approach to reach the same goal is significantly different. Previous experience with studies on V_2O_5 has shown that via twin–rollers technique one may obtain this material directly as a nanocomposite. Moreover, different cooling rates applied upon synthesis can significantly alter the properties of the samples [5].

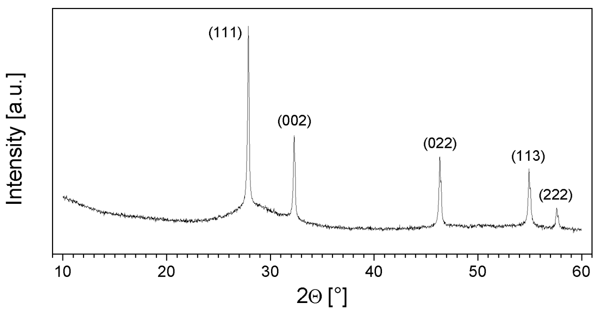

Fig. 2. Room temperature XRD pattern of as-synthesized material. Miller indexes of δ–Bi_2O_3 phase, assigned to experimental diffraction lines, prove that the fcc phase was obtained.

Similarly to V_2O_5, Bi_2O_3 remains amoderate glass former. Therefore our idea, presented in this work, is to apply twin–rollers technique in order to obtain bismuth oxide nanocomposites. An additional investigation path was to examine, how parameters of the synthesis (e.g. cooling rate) affect thermal stability of as-received materials. X-ray diffraction measurements (XRD) have shown that via twin–rollers technique we succeeded in synthesising nanocomposites in the desired δ–phase, which remained stable at room temperature (Fig. 2). Moreover, studies executed by X-ray diffraction in function of temperature (HT–XRD) revealed that this phase remains stable up to ca. 550 °C, depending on parameters of the synthesis.

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[1] H. A. Harwig, On the structure of bismuthsesquioxide: the α, β, γ, and δ phase, Journal of Inorganic and General Chemistry, **444**, 151–166 (1978).
[2] http://www.ccdc.cam.ac.uk/mercury/
[3] M. Leszczynska, X. Liu, W. Wrobel et al., Oxide ion distribution, vacancy ordering and electrical behaviour in the $Bi_3NbO_7Bi_3YbO_6$ pseudo-binary system, Journal of Materials Chemistry **A2**, 18624–18634 (2014).
[4] H. T. Fan, S. S. Pan, X. M. Teng et al., δ–Bi_2O_3 thin films prepared by reactive sputtering: Fabrication and characterization, Thin Solid Films **513**, 142–147 (2006).
[5] T.K. Pietrzak, M. Maciaszek, J.L. Nowiski et al., Electrical properties of V_2O_5 nanomaterials prepared by twin rollers technique, Solid State Ionics **225**, 658–662 (2012).