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BOOK OF ABSTRACTS

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Tm(III)-doped δ-Bi_2O_3 for solid oxide fuel cells

Aleksandra Dapčević, Dejan Poleti, Jelena Rogan, Aleksandar Radojković*
Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade
**Institute for Multidisciplinary Research, University of Belgrade, Kneza Višeslava 1a, Belgrade*

The oxide ion conductors have widely been investigated because of their application in many devices with high economical and ecological interests, such as solid oxide fuel cells (SOFC). δ-Bi_2O_3 polymorph possesses the highest known O^{2-} ion conductivity, which is one to two orders of magnitude higher than that of stabilized zirconia at corresponding temperatures [1]. At the moment, the application of this high-temperature polymorph as an electrolyte in SOFC requires temperatures above 730 °C. However, the doping allows δ-Bi_2O_3 stabilization to room temperature and opens the possibility for construction of SOFC that will operate at intermediate temperatures (ca. 350 °C) [2].

As it is found that some lanthanides are suitable dopants [3], the possibility to stabilize O^{2-} ion conductors related to the δ-Bi_2O_3 polymorph in the Bi_2O_3–Tm_2O_3 system was investigated. Two starting mixtures with compositions $(Bi_{1-x}Tm_x)_2O_3$ (x = 0.04 and 0.20) were homogenized in an agate mortar, heat treated at 750 °C for 3 h and then slowly furnace cooled. The samples were characterized by XRPD, DTA and SEI techniques.

Based on XRPD, the single-phase tetragonal β-Bi_2O_3 was identified in the sample with x = 0.04. Its unit cell parameters, a = 7.742(2) and c = 5.650(2) Å, well-correspond to those of undoped β-Bi_2O_3 [4]. On the other hand, the cubic δ-Bi_2O_3 phase was obtained in the sample with x = 0.20. Its unit cell parameter was greater than the value reported for Tm-doped δ-Bi_2O_3 sample with x = 0.25 [3] (5.5033(9) *vs*. 5.478 Å). Both values are smaller than reported for undoped δ-Bi_2O_3 [4]. This means that the unit cell parameter of cubic δ-Bi_2O_3 decreases as Tm-content increases and it is in accordance with Tm^{3+} and Bi^{3+} ionic radii [5].

For the sample with x = 0.04, cyclic DTA curves showed one reversible β-Bi_2O_3 ↔ δ-Bi_2O_3 transition with corresponding temperatures: on heating, 660 °C, and, on cooling, 600 °C. Surprisingly, no phase transitions were observed in the sample with x = 0.20 which indicates that the obtained δ-Bi_2O_3 is stable within the whole investigated interval, *i.e.*, from room temperature to 1000 °C.

Electrochemical impedance of δ-Bi_2O_3 phase was measured in the following temperature range: 300 – 800 °C. At higher temperatures (600 – 800 °C) the conductivities are similar (0.11 – 0.32 S cm^{-1}), but with lowering temperature they rapidly decrease, and amount, for example, $2.1 \cdot 10^{-5}$ S cm^{-1} at 300 °C. As a consequence, two activation energies are found: 0.45(4) eV (600 – 800 °C), and 1.33(2) eV (300 – 600 °C).

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