The Serbian Society for Ceramic Materials

Institute for Multidisciplinary Research, University of Belgrade

Institute of Physics, University of Belgrade

Center of Excellence for the Synthesis, Processing and Characterization of Materials for use in Extreme Conditions "CEXTREME LAB" - Institute of Nuclear Sciences "Vinča", University of Belgrade

Faculty of Mechanical Engineering, University of Belgrade



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THE INFLUENCE OF DREDGE WASTE AND EFFLUENT TREATMENT PLANTS SLUDGE ON THE PORTLAND CEMENT CLINKER MANUFACTURE

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Alternative materials such as industrial wastes and by-products can be easily and economically utilized as raw material in Portland cement clinker manufacture. These materials are generated in abundance as a result of growing worldwide industrialization. Two types of wastes from mining industry were used as secondary raw material in a concentration ranging from 1.4 to 3.5%. CEM I cements were obtained from these clinkers and compressive strength was determined. The chemical and mineralogical compositions of the wastes and raw meals were determined. The influence of homogeneous raw mixes containing different concentrations of wastes on all steps of burning in a laboratory furnace to form a Portland cement clinker was investigated. It was noticed in the case of mining wastes an improved burnability and no apparent deterioration in clinker quality.

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HIGHLY CONDUCTIVE V-DOPED δ-Bi₂O₃ WITH 3×3×3 SUPERSTRUCTURE

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Due to the increasing demands for new highly efficient and environmentally friendly energy conversion technologies, the oxide ion conductors applicable in solid oxide fuel cells (SOFCs) have widely been investigated. The high temperature δ -Bi₂O₃ phase has been proposed as a good candidate for electrolyte in SOFCs because it is the fastest known ionic conductor.

In this study, the possibility to stabilize O^{2-} ion conductors related to the δ -Bi₂O₃ polymorph in Bi₁₂V_xO_{18+5x/2} (x = 0.5-1) system was investigated. Six starting mixtures of α -Bi₂O₃ and V₂O₅ were dry homogenized in an agate mortar, heat treated at 1000 °C for 1 h and then slowly furnace cooled. The samples were characterized by XRD, TEM/SAED, optical microscopy, DTA and EIS techniques.

Based on XRD and TEM/SAED, if $x \ge 0.6$ the high-temperature reaction between α -Bi₂O₃ and V₂O₅ resulted in formation of microcrystalline single-phase specimens containing the phase based on δ -Bi₂O₃. The obtained phases showed main diffraction peaks corresponding to the cubic δ -Bi₂O₃ (space group *Fm*-3*m* and $a \approx 5.6$ Å). However, the detected weak reflections indicate that the true unit cell is the 3×3×3 supercell with $a \approx 16.6$ Å. An expected decrease of the unit cell parameters with the dopant amount was found as the consequence of smaller dopant ionic radius { $r_i(V^{5+}) = 0.54$ Å and $r_i(Bi^{3+}) = 1.03$ Å in the six-coordinated environment [1]}. In the case of Bi₁₂V_{0.5}O_{19.25}, traces of α -Bi₂O₃ were also found.

The XRD data of $Bi_{12}V_{0.7}O_{19.75}$ were used for the Rietveld refinement giving $Bi_{102}V_6O_{168}$ as the composition of the $3 \times 3 \times 3$ supercell. The octahedrally coordinated V^{5+} ions fully occupy 4a Wyckoff position, *i.e.* the corners and face centers of cubic supercell, and partially occupy 32f. The Bi³⁺ ions are placed at the rest of 32f and at 24e and 48h with full occupation. At the 32f site, the cations are surrounded by five oxide ions making a square pyramid. At the 24e site, the Bi³⁺ ions with four oxide ions form a square pyramid with the cation at the apex. The coordination of Bi³⁺ at the 48h is square planar.

Cyclic DTA curves showed that the following $3 \times 3 \times 3 \rightarrow \gamma$ -Bi₂O₃ $\rightarrow \delta$ -Bi₂O₃ \rightarrow Bi₂O₃(1) consecutive phase transitions occur on heating. On cooling, δ -Bi₂O₃ crystallizes from the melts and remains stable to about 530 °C. At this temperature, an order-disorder transition takes place, *i.e.* δ -Bi₂O₃ $\rightarrow 3 \times 3 \times 3$.

The sintered disk-shaped pellets were characterized by EIS at temperatures between 760 and 820 °C. The sample with x = 0.6 demonstrates one of the highest known conductivity among the published O²⁻ ion conductors, *i.e.* 0.66 S cm⁻¹ at 760 °C with the lowest activation energy of 0.21(1) eV.

1. R. D. Shannon, Acta Cryst. A 32 (1976) 751