SYNTHESIS AND PROPERTIES OF $Bi_{26}Mo_{10}O_{69}$ SUBSTITUTED WITH NONMETALS

Levina A.A.,[a] Michailovskaya Z.A.,[a] Klimova A.V., [a] Buyanova E.S,[a] Petrova S.A.,[b]

[a]Ural Federal University named after the first President of Russia B.N.Yeltsin,
Mira street 19, Ekaterinburg, 620002, Russia,
e-mail: anastasia.levina@urfu.ru
[b]Institute of Metallurgy, Ural Brunch of Russian Academy of Sciences,
Amundsena street 101, Yekaterinburg, 620016, Russia

The present work is devoted to the synthesis and investigation of properties and structure of S-,P-and Sb- substituted bismuth molybdate $Bi_{26}Mo_{10}O_{69}$. The $Bi_{26}Mo_{10}O_{69}$ has unique structure what contains columns $[Bi_{12}O_{14}]_n$, $[MoO_m]$ polyhedra and isolated Bi ions and shows one-dimensional oxygen-ionic conductivity at mediate temperatures. The $Bi_{26}Mo_{10}O_{69}$ -based solid solutions crystallizes in monoclinic symmetry at the temperatures above ~310°C, or it has triclinic distortion below this temperature. Substitution in $Bi_{26}Mo_{10}O_{69}$ can be realized by doping molybdenum or isolated bismuth positions resulting to the formula $Bi_{26-2x}Me_{2x}Mo_{10}O_{69-d}$ or $Bi_{26}Mo_{10-2y}Me_{2y}O_{69-d}$.In this work the solid solutions $Bi_{26}Mo_{10-2y}S_{2y}O_{34.5}$, $Bi_{26}Mo_{10-2y}P_{2y}O_{34.5-d}$ and $Bi_{26}Mo1_{0-2y}Sb_{2y}O_{34.5-d}$ were investigated. The complex oxide samples have been synthesized using conventional solid state method from metal oxides, and $(NH_4)_2SO_4$ /Sb_2O_3/$(NH_4)_2HPO_4$. The phase composition was defined by XRPD. The dopant concentration homogeneity ranges were determined to be y=0.6-0.7 for all dopants. The ranges of stabilization of the monoclinic form is observed at y>0.4. The IR FT spetroscopy and Rietveld full profile structure refinement at XRPD data showed substitution of Mo by S, P and Sb and forming SO_4 and PO_4 groups. The laser diffraction and SEM were used for investigation of morphology of powder samples. The geometrical sizes of particles lie in the range of 1-10 μm in powder samples and 50-100 μm in dense ceramic samples. Porosity of samples was examd by hydrostatic weighting and was determined to be less then 5%. Electrical conductivity has been studied using impedance spectroscopy method. The impedance measurements were carrying out in the range of 523-1123 K over the respective frequency ranges 3 MHz to 10 Hz with two Pt electrodes. For analysis of impedance plots the equivalent electrical circuits method was used Zview. According to the results of the impedance measurements the temperature and concentration curves of electrical conductivity were plotted. The maximum of conductivity is ~10^{-2} S×cm^{-1} at 973K and ~10^{-4} S×cm^{-1} at 623K As a result $Bi_{26}Mo_{10-2y}(S/P/Sb)_{2y}O_{34.5}$ family can be recommended as a high ionic conductive material.

This work was supported RFBR, project №18-33-00921.