[MS20-P01] Polymorphism peculiarities in Bi2W1-xMexO6-y and Bi2Mo1-xMexO6-y Systems (Me = Nb, Ta, Sb).

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Bi_2WO_6 and Bi_2MoO_6 are archetypal (n= 1) members of the large family of layered perovskite-related compounds with the general formula $(Bi_2O_2)(A_{n-1}B_nO_{3n+1})$ (Aurivillius phases). These compounds attract attention as ferroelectrics, piezoelectrics, oxide-ion conductors, catalytic materials. Three phase transitions were found in pure Bi_2WO_6 and Bi_2MoO_6: ferroelectric between two polar orthorhombic phases γ → γ''' (310ºC for Bi_2MoO_6, 640-660ºC for Bi_2WO_6, ferroelectric between polar and nonpolar orthorhombic phases γ''' → γ'' (604ºC for Bi_2MoO_6, 930ºC for Bi_2WO_6), reconstructive between orthorhombic and high temperature monoclinic phases γ'' → γ' (680oC for Bi_2MoO_6, 960oC for Bi_2WO_6). The monoclinic γ'-phases do not belong to Aurivillius structure, and the last transition is irreversible in the case of Bi^2MoO^6 and reversible with destruction of crystalline samples in the case of Bi_2WO_6 that is unfavorable for technical applications. An influence of dopants on this transition has not been investigated.

The aim of present work is synthesis of $Bi_2W_{1-x}Me_xO_{6-y}$ and $Bi_2Mo_{1-x}Me_xO_{6-y}$ (Me = Nb, Ta, Sb) solid solutions and investigation of their polymorphism and properties. Polycrystalline samples of $Bi_2W_{1-x}Nb_xO_{6-y}$ (x = 0.02, 0.05, 0.1), $Bi_2W_{1-x}Ta_xO_{6-y}$ (x = 0.02, 0.05, 0.1, 0.15), $Bi_2W_{1-x}Sb_xO_{6-y}$ (x = 0.02, 0.03, 0.04, 0.05) and $Bi_2Mo_{1-x}Nb_xO_{6-y}$ (x = 0.02, 0.05, 0.5), $Bi_2Mo_{1-x}Me_xO_{6-y}$ (Me = Ta, Sb; x = 0.02, 0.05) were obtained by solid state synthesis in air. According to X-ray analysis, at room temperature, all samples belong to Aurivillius family and are isostructural with γ-Bi_2WO_6 and γ-Bi_2MoO_6 phases.

Increase of Me = Nb, Ta concentration in $Bi_2W_{1-x}Me_xO_{6-y}$ leads to shift of reconstructive γ'' → γ' transition into high temperature region. It is fully suppressed in $Bi_2W_{1-x}Nb_xO_{6-y}$ solid solutions (x = 0.1). In the case of Ta (x = 0.1) and Sb (x = 0.04) a mixture of γ'' and γ' phases have been observed at long exposure at 940-1000oC. Ferroelectric γ''' → γ'' transition does not suppressed by the dopants. For Me = Nb, Ta it strongly shifts to lower temperatures, thus the temperature region of existence of the nonpolar orthorhombic γ'' phase significantly increases from 30 to 200 degrees.

Doping Mo with Nb results in significant shift of ferroelectric γ''' → γ'' and reconstructive γ'' → γ' transitions into high temperature region. According to Xray data, Bi_2MoNbO_{6-y} sample (50%Nb) keeps the Aurivillius-type structure, even after prolonged exposure above 800ºC. Below the melting point (1050ºC) DSC shows only one slight anomaly at 950ºC, which presumably corresponds to ferroelectric γ''' → γ'' transition.

Substitution of W^{6+} and Mo^{6+} with Nb^{5+}, Ta^{5+} and Sb^{5+} leads to formation of oxygen vacancies. As a result the conductivity of samples with low dopant concentration (5-10 at.%) increases by 1-2 orders of magnitude in comparison with pure Bi^2WO^6 or Bi^2MoO^6. The higher concentration of Nb and Ta dopants leads to decrease in electrical conductivity.

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