Polymorphism peculiarities in Bi$_2$W$_{1-x}$Me$_x$O$_{6-y}$ and Bi$_2$Mo$_{1-x}$Me$_x$O$_{6-y}$ Systems (Me = Nb, Ta, Sb).
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Bi$_2$WO$_6$ and Bi$_2$MoO$_6$ are archetypal (n= 1) members of the large family of layered perovskite-related compounds with the general formula (Bi$_2$O$_2$)(An$_{-1}$BnO$_{3n+1}$) (Aurivillius phases). These compounds attract attention as ferroelectrics, piezoelectrics, oxide-ion conductors, catalytic materials. Three phase transitions were found in pure Bi$_2$WO$_6$ and Bi$_2$MoO$_6$: ferroelectric between two polar orthorhombic phases $\gamma \rightarrow \gamma'''$ (310ºC for Bi$_2$MoO$_6$, 640-660ºC for Bi$_2$WO$_6$, ferroelectric between polar and nonpolar orthorhombic phases $\gamma''' \rightarrow \gamma''$ (604ºC for Bi$_2$MoO$_6$, 930ºC for Bi$_2$WO$_6$), reconstructive between orthorhombic and high temperature monoclinic phases $\gamma'' \rightarrow \gamma'$ (604ºC for Bi$_2$MoO$_6$, 930ºC for Bi$_2$WO$_6$). Reconstructive between orthorhombic and high temperature monoclinic phases $\gamma'' \rightarrow \gamma'$ (604ºC for Bi$_2$MoO$_6$, 930ºC for Bi$_2$WO$_6$), is fully suppressed in Bi$_2$W$_{1-x}$Nb$_x$O$_{6-y}$ solid solutions ($x = 0.1$). In the case of Ta ($x = 0.1$) and Sb ($x = 0.04$) a mixture of $\gamma''$ and $\gamma'$ phases have been observed at long exposure at 940-1000oC. Ferroelectric $\gamma''' \rightarrow \gamma''$ 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 $\gamma''$ phase significantly increases from 30 to 200 degrees.

Doping Mo with Nb results in significant shift of ferroelectric $\gamma''' \rightarrow \gamma''$ and reconstructive $\gamma'' \rightarrow \gamma'$ transitions into high temperature region. According to X-ray data, Bi$_2$MoNbO$_{6-y}$ 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 $\gamma''' \rightarrow \gamma''$ 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$_2$WO$_6$ or Bi$_2$MoO$_6$. The higher concentration of Nb and Ta dopants leads to decrease in electrical conductivity.

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