

CRYSTAL STRUCTURE AND DIELECTRIC PROPERTIES OF THE MIXED-LAYER AURIVILLIUS PHASES $\text{Bi}_7\text{Ti}_{4+x}\text{W}_x\text{Nb}_{1-2x}\text{O}_{21}$ ($x=0.1, 0.2, 0.3, 0.4, 0.5$)

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Ferroelectric materials on the base of layered bismuth oxides have been extensively studied in view of their applications in nonvolatile computer memories and high-temperature piezoelectric transducers. Among bismuth layered-structured compounds, most of members have the Aurivillius phase (APs) type of the crystal structure. The general chemical formula for APs is $\text{Bi}_2\text{A}_{m-1}\text{B}_m\text{O}_{3m+3}$, where the A site can be occupied by large cations such as Bi^{3+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Na^+ , K^+ , Th^{4+} or rare earth ions and the B site by highly charged small cations such as Ti^{4+} , Nb^{5+} , Ta^{5+} , W^{6+} , Mo^{6+} , Fe^{3+} , Mn^{4+} , Cr^{3+} , Ga^{3+} , *ets.* The crystal structure of all APs consist of perovskite-like $[\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]^{2-}$ units which are regularly interleaved with $[\text{Bi}_2\text{O}_2]^{2+}$ layers. The integer $m=1-5$ corresponds to the number of oxygen octahedra layers in the perovskite-like slabs. Besides these simple members of APs, the mixed-layer APs intergrowths ($m=1+2$, $2+3$ and *ets*) have been prepared as pure phases. In this work pure polycrystalline $\text{Bi}_7\text{Ti}_{4+x}\text{W}_x\text{Nb}_{1-2x}\text{O}_{21}$ ($x=0.1, 0.2, 0.3, 0.4, 0.5$) ceramics ($m=2+3$) with APs structure were prepared by traditional solid state reaction. The crystal structures of APs $\text{Bi}_7\text{Ti}_{4+x}\text{W}_x\text{Nb}_{1-2x}\text{O}_{21}$ ($x=0.1, 0.2, 0.3, 0.4, 0.5$) have been analyzed by powder X-ray diffraction. All these APs have been refined in orthorhombic space group $I2cm$ (46), with $a=5.4114$ Å, $b=5.4449$ Å, $c=58.0131$ Å ($\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$), $a=5.3995$ Å, $b=5.4338$ Å, $c=57.9060$ Å ($\text{Bi}_7\text{Ti}_{4.1}\text{W}_{0.1}\text{Nb}_{0.8}\text{O}_{21}$), $a=5.3977$ Å, $b=5.4321$ Å, $c=57.8444$ Å ($\text{Bi}_7\text{Ti}_{4.2}\text{W}_{0.2}\text{Nb}_{0.6}\text{O}_{21}$), $a=5.3921$ Å, $b=5.4204$ Å, $c=57.7603$ Å ($\text{Bi}_7\text{Ti}_{4.3}\text{W}_{0.3}\text{Nb}_{0.4}\text{O}_{21}$), $a=5.4013$ Å, $b=5.4040$ Å, $c=57.6529$ Å ($\text{Bi}_7\text{Ti}_{4.4}\text{W}_{0.4}\text{Nb}_{0.2}\text{O}_{21}$), $a=5.4106$ Å, $b=5.3877$ Å, $c=57.5455$ Å ($\text{Bi}_7\text{Ti}_{4.5}\text{W}_{0.5}\text{O}_{21}$).

The dielectric properties of APs were investigated in the frequency range of 25Hz- 1MHz and the temperature range of 25⁰C- 900⁰C. In each case, a double anomaly in temperature dependence of dielectric permittivity was found. The temperatures of the anomaly correspond to ferroelectric-ferroelectric and ferroelectric-paraelectric phase transitions. The Curie temperatures t_c for APs $\text{Bi}_7\text{Ti}_{4+x}\text{W}_x\text{Nb}_{1-2x}\text{O}_{21}$ are dependent on parameter x ($t_c=849^0\text{C}$ at $x=0$, $t_c=826^0\text{C}$ at $x=0.1$, $t_c=786^0\text{C}$ at $x=0.2$, $t_c=760^0\text{C}$ at $x=0.3$, $t_c=742^0\text{C}$ at $x=0.4$ and $t_c=712^0\text{C}$ at $x=0.5$). The activation energies E_a for charge carriers in APs calculated using the dependence of conductivity vs. $1/T$ were obtained to vary from 1.26 to 1,74 eV at high temperature ($> 400^0\text{C}$).