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Enhanced Tetragonality in $(x)$PbTiO$_3$-(1-$x$)Bi($B'B''$)O$_3$ systems: Bi($Zn_{3/4}W_{1/4}$)O$_3$

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Enhanced Tetragonality in \((x)\text{PbTiO}_3-(1-x)\text{Bi}(B^\prime B^\prime \prime)\text{O}_3\) systems: \(\text{Bi}(\text{Zn}_3/4\text{WN}_1/4)\text{O}_3\)

Abstract
Solid solutions in the \((x)\text{PbTiO}_3-(1-x)\text{Bi}(\text{Zn}_3/4\text{W}_1/4)\text{O}_3\) system have been examined by x-ray diffraction, dielectric measurements, and thermal analysis. \(\text{Bi}(\text{Zn}_3/4\text{W}_1/4)\text{O}_3\) increases the tetragonality and Curie temperature of \(\text{PbTiO}_3\) which reach a value of 1.08 and 530 °C, respectively, at the limit of the single-phase perovskite forming region \((x \approx 0.8)\). The observation of a sustained increase in the tetragonality in this system is similar to the behavior of the \((x)\text{PbTiO}_3-(1-x)\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\) system and highlights the unique properties of Bi-based systems when the \(B\) sites contain high concentrations of highly polarizable cations.

Comments
Enhanced tetragonality in (x)PbTiO$_3$–(1 − x)Bi($B'$ $B''$)O$_3$ systems: Bi(Zn$_{3/4}$W$_{1/4}$)O$_3$

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Solid solutions in the (x)PbTiO$_3$–(1 − x)Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ system have been examined by x-ray diffraction, dielectric measurements, and thermal analysis. Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ increases the tetragonality and Curie temperature of PbTiO$_3$ which reach a value of 1.08 and 530 °C, respectively, at the limit of the single-phase perovskite forming region (x ~ 0.8). The observation of a sustained increase in the tetragonality in this system is similar to the behavior of the (x)PbTiO$_3$–(1 − x)Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ system and highlights the unique properties of Bi-based systems when the B sites contain high concentrations of highly polarizable cations. © 2006 American Institute of Physics. [DOI: 10.1063/1.2357871]

The discovery of the PbTiO$_3$–BiScO$_3$ perovskite system renewed research focus on solid solutions of PbTiO$_3$ (PT) and Bi-based end members as possible replacements for lead zirconate titanate in piezoelectric and ferroelectric applications. Predictions of enhanced tetragonality and responses in systems such as BiGaO$_3$ have provided additional impetus for the synthesis of new Bi perovskites, and recently the preparation of highly tetragonal BiCoO$_3$ in perovskite form at high pressure was reported. For piezoelectric applications lead titanate solid solutions typically show the highest responses at compositions close to a morphotropic phase boundary (MPB). The substitution of almost all known Pb- or Bi-based additives reduces the tetragonality of lead titanate and induces the formation of a MPB. The position of the MPB is strongly influenced by the crystal chemistry of the additive and becomes increasingly PT rich for lower tolerance factor substitutions. First principles calculations have shown that the composition of the MPB is also influenced by the magnitude of the ionic displacement of “ferroelectrically active” cations on the B-site sublattice. High concentrations of FE active cations, such as Ti, Nb, Zn, etc., induce a relative enhancement in the stability of the tetragonal structure and the position of the MPB shifts away from the PT end member. An unexpectedly large manifestation of this effect was recently discovered in the PbTiO$_3$–Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ (PT-BZT) system, where the tetragonality (c/a ratio) of lead titanate systematically increased with the addition of BZT, reaching values as high as 1.11 at the limit of substitution (∼50% BZT) at ambient pressure. Prior to that study, BiFeO$_3$ and Bi(Zn$_{3/4}$Nb$_{1/4}$)O$_3$ were the only other additives known to sustain enhanced tetragonality in PbTiO$_3$. The high c/a’s in the PT-BZT system were suggested to arise from a strong coupling of the Bi and Zn/Ti displacements; because the W$^{4+}$ cation can also undergo octahedral off centering, the PbTiO$_3$–Bi(Zn$_{3/4}$W$_{1/4}$)O$_3$ (PT-BZW) system was identified as another promising candidate for promoting enhanced tetragonality. This letter reports on the synthesis, structure, and properties of PT-BZW solid solutions. Although the single-phase perovskite forming region is narrower than PT-BZT, similar enhancements in tetragonality were observed.

Samples of the (x)PT–(1 − x)BZW solid solutions were prepared by traditional solid state methods from the component oxides and from a route involving prereaction of the oxides of the B-site components (Ti, Zn, W). Stoichiometric mixtures of the starting reagents were ball milled in ethanol with yttria-stabilized zirconia balls for 5 h. To avoid impurities at compositions with x = 0.85 and x = 0.80, the titanium-, zinc-, and tungsten-containing reagents were premixed and calcined at 1100 °C prior to the addition of the lead and bismuth components. To achieve phase homogeneity the powders were calcined multiple times between 850 and 1100 °C. After calcination the powders were isostatically pressed into pellets, surrounded by sacrificial powder of the same composition to avoid any loss of the more volatile components, and sintered for 5 h between 1000 and 1100 °C depending on the composition. Powder x-ray diffraction (XRD) patterns of calcined powders were recorded in the 2θ scan range of 15°–60°; lattice parameters were calculated via the least-squares method. Ferroelectric phase transition temperatures were monitored by differential scanning calorimetry (DSC) at heating and cooling rates of 10 °C/min from 350 to 700 °C. Dielectric properties were investigated as a function of frequency and temperature using an impedance analyzer on pellets that were coated with a fired Ag paint (Heraeus ST1601-14 type) to provide electrical contacts for Pt leads.

The room temperature XRD scans for selected compositions in the (x)PT–(1 − x)BZW system in Fig. 1 indicate that a single-phase tetragonal perovskite region exists between 1.0 ≥ x > ∼ 0.80; for lower values of x the patterns contained additional peaks associated with pyrochlore-related impurity phases. Similar to the PT-BZT system, the enhanced tetragonality of the BZW-containing solid solution was clearly exhibited by the increased splitting of peaks such as the {200} reflections. Figure 2 highlights the change in the lattice parameters, as well as the c/a ratio, for the substitution of BZW into PT. The enhanced tetragonality, which reaches ∼1.08 for x = 0.8, is primarily due to an increase in the c-lattice parameter, while the a parameter decreases only slightly across the solid solution. The molar volume in-
structure of PbTiO$_3$ should be contrasted to the behavior of limited range of solid solubility. The effect of BZW on the
Compared to PT-BZT, the PT-BZW system shows a similar
increase in $c/a$ for equal substitution, but with a much more limited range of solid solubility. The effect of BZW on the structure of PbTiO$_3$ should be contrasted to the behavior of its magnesium counterpart, Bi$_{3/4}$Zn$_{1/4}$O$_3$, which has similar crystal chemistry (cation radius and tolerance factor) but reduces the tetragonality of PbTiO$_3$.

Dense sintered pellets of all compositions with $x < 0.95$ were obtained by using slow heating and cooling rates through the ferroelectric-paraelectric transition to avoid strain induced cracking. Dielectric data were obtained at various frequencies between 100 Hz and 1 MHz; no evidence for frequency dispersion was observed and the 100 kHz data are used in the plot of the temperature dependence of the real part of the permittivity in Fig. 3. Consistent with the enhancement in tetragonality, the $T_C$ of PT increases with BZW substitution, though the limited solubility prevents the gains from being more than moderate ($\sim 525$ °C for 20% substitution). Similar to the PT-BZT system there is an increasing thermal hysteresis with BZW substitution, likely due to the kinetics of the nucleation and growth of the highly distorted tetragonal phase.

DSC data were used to corroborate the $T_C$ data from the dielectric measurements and to obtain data for compositions with higher $x$ that could not be sintered. The combined dielectric and DSC data for $T_C$ are shown as a function of BZW substitution in Fig. 4. The plotted points reflect the average $T_C$ values and the error bars represent the extent of the thermal hysteresis. For the largest substitution of BZW, there is an increase in $T_C$ of 30–40 °C, depending on the measurement technique. While the rate of increase of the $c/a$ ratio with substitution of PT is nearly equal in both the PT-BZT and PT-BZW systems, the rate of increase of $T_C$ is smaller for PT-BZW, illustrating that the Curie temperature is a function of the specific chemistry and ionic displacements and not just the structure. To further illustrate this point, the enhancements in tetragonality and $T_C$ of lead titanate solid solutions with Bi(Zn$_{3/4}$W$_{1/4}$)O$_3$, Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$, BiFeO$_3$, and Bi(Zn$_{2/3}$Nb$_{1/3}$)O$_3$ are compared in Fig. 5. Although the range of solubility in PT-BiFeO$_3$ is complete and BiFeO$_3$-rich compositions induce formation of a MPB and a rhombohedral phase region, the rate of increase of $c/a$ with replacement of PT is much higher in the BZT- and BZW-containing systems. We believe that this is due to the larger $B$-site displacements and increased cooperative Bi/$B$-site coupling for the [Zn, Ti] and [Zn, W, (Ti)] combinations. The data in this figure also reinforce the absence of a direct correlation between the actual magnitude of $c/a$ and $T_C$; the increase in the latter is higher for the Zn-based systems, presumably because of larger ionic displacements on the $B$ site. For comparison, Fig. 5 also includes a limited selection of data for additives that exhibit “normal” behavior and reduce the tetragonality to induce a MPB, in particular, BiScO$_3$ and BiFeO$_3$. 

FIG. 1. XRD patterns of compositions in the $(x)$PbTiO$_3$ – $(1-x)$Bi(Zn$_{3/4}$W$_{1/4}$)O$_3$ system. Enhanced tetragonality is highlighted by increased [002] splitting.

FIG. 2. Lattice parameters and $c/a$ ratio as a function of composition in the $(x)$PbTiO$_3$ – $(1-x)$Bi(Zn$_{3/4}$W$_{1/4}$)O$_3$ (PT-BZT) system.

FIG. 3. Dielectric permittivity ($\varepsilon_r$) vs temperature in the $(x)$PbTiO$_3$ – $(1-x)$Bi(Zn$_{3/4}$W$_{1/4}$)O$_3$ system ($f=100$ kHz). Arrows indicate direction of thermal ramp.

FIG. 4. Compositional dependence of Curie temperature ($T_C$) in the $(x)$PbTiO$_3$ – $(1-x)$Bi(Zn$_{3/4}$W$_{1/4}$)O$_3$ system. The dotted line is a polynomial fit of the average $T_C$ values, as measured by DSC.
the Mg-containing Bi$^{2+}$/H$_2$O$_{84}$Mg$_{3/4}$W$_{1/4}$O$_3$, Bi$^{2+}$/H$_2$O$_{85}$Mg$_{2/3}$Nb$_{1/3}$O$_3$, and Bi$^{2+}$/H$_2$O$_{84}$Mg$_{1/2}$Ti$_{1/2}$O$_3$ systems.\cite{1,4,8,9}

In conclusion, the substitution of Bi$^{2+}$/H$_2$O$_{84}$Zn$_{3/4}$W$_{1/4}$O$_3$ increases the tetragonality and Curie temperature of PbTiO$_3$ with a maximum $c/a$ ratio (1.08) and $T_C$ (530 °C) occurring at the limit of the single-phase perovskite forming region (20% substitution). The behavior of the PbTiO$_3$–Bi(Zn$_{3/4}$W$_{1/4}$)O$_3$ system supports the prediction of enhanced tetragonality in bismuth-containing lead titanate solid solutions when the $B$ sites are fully populated by ferroelectrically active cations such as Zn, Ti, Nb, and W.\cite{4} This system also provides another example of the unique behavior of Zn-containing chemistries compared to their Mg counterparts.

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