Communication

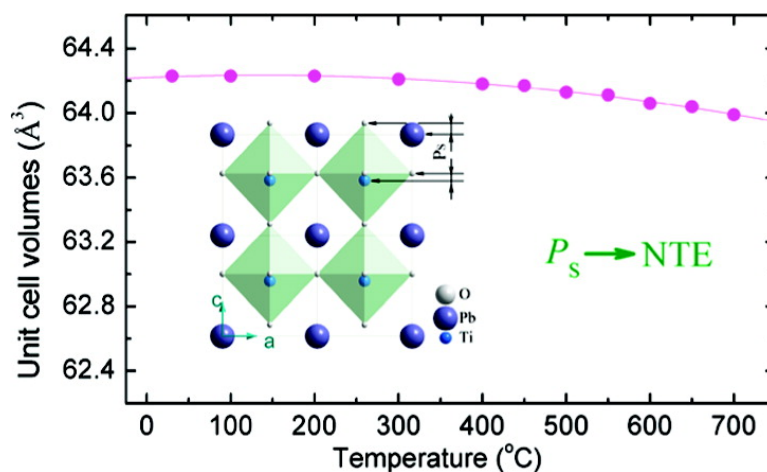# Zero Thermal Expansion in PbTiO-Based Perovskites

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Zero Thermal Expansion in PbTiO$_3$-Based Perovskites

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Most materials expand on heating, known as positive thermal expansion. There are some instances most of which have been discovered in the past decade to exhibit a negative thermal expansion (NTE).[1−9] The nature of NTE behavior originates from the effect of atomic vibrations, (e.g., the low-energy transverse mode (ice),[2] the coupled rotation of rigid polyhedra (ZrW$_2$O$_8$, Fe[Co-(CN)$_6$]),[1,4] and active vibration modes of carbon fullerenes and nanotubes),[7] from the effect of magnetic transition (Invar alloy),[3] or from the changes in electron configuration (Sm$_{2.72}$C$_{60}$, YbCuAl).[8] The occurrence of NTE materials immediately found their important technical applications in many fields, because the overall thermal expansion coefficient (TEC) could be tailored by introduction of NTE materials.[1,2] In particular, zero thermal expansion (ZTE) is very interesting, where the volume neither expands nor contracts with the temperature fluctuation.[3−6] The ZTE could be achieved to form composite by combining the materials with positive thermal expansion with NTE materials. However, the fabrication of ZTE composite is hampered by the poor thermal stability of NTE compounds. For example, ZrW$_2$O$_8$ will be decomposed at a relatively low temperature (777 °C).[1] The requirement of ZTE will be satisfied if the ZTE is available in a single phase. Up to now, rare materials exhibit the novel ZTE, such as Invar alloys and Fe-[Co(CN)$_6$].[3,4] Moreover, the ZTE generally appears in a low temperature (below room temperature). The ZTE over a wider temperature range would be very useful for the applications.

PbTiO$_3$ (PT) as an important perovskite-type multifunctional material exhibits a unique NTE in the perovskite family.[9,10] The unit cell volume of PT contracts over a wide temperature range in the ferroelectric phase (25−490 °C) with an average intrinsic volumetric TEC (-1.99×10^{-5} °C^{-1}).[9b] The NTE of PT-based compounds can be controlled over a large range from -0.11×10^{-5} to -3.92×10^{-5} °C^{-1}, which covers the range found in almost all other known NTE oxides.[9] However, a low or ZTE could only be achieved by sacrificing the temperature range, that is, reducing the Curie point (T_C), such as for Pb$_{0.80}$La$_{0.20}$TiO$_3$ (-0.11×10^{-5} °C^{-1}, 25−130 °C).[9b] It is a challenge to expand ZTE to the high-temperature range. On the basis of our previously studied PbTiO$_3$-based compounds, we could only access a low expansion or ZTE by reducing the tetragonality (c/a), resulting in the decrease in the ZTE temperature range (region II in Figure 1). To obtain the ZTE in a wider temperature range, a kind of PbTiO$_3$-based compound should be found in the region I where c/a is large and the absolute value of TEC is low (Figure 1). Recently, in the PbTiO$_3$−BiMeO$_3$ (Me is cations with an average valence +3), the Bi substitution plays an unusual role in which both T_C and c/a are considerably enhanced, owing to the strong coupling between the Pb/Bi cations and the B-site cations with strong ferroelectricity activity, such as Ti, Zn, and Fe.[11] It is possible to find the novel ZTE in the PbTiO$_3$−Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ and its related solid solutions. In this study, we report a ZTE in PbTiO$_3$−Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$-based solid solutions over
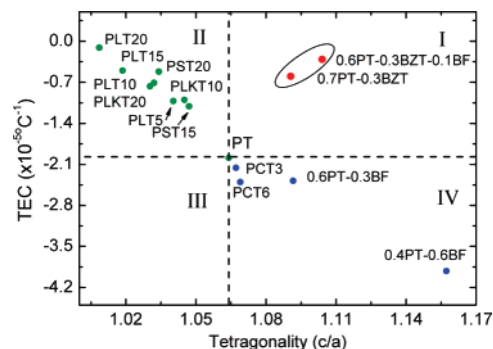

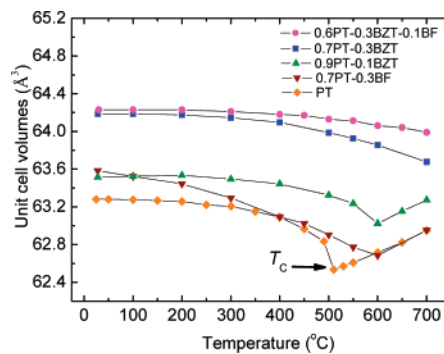**Figure 1.** Average volumetric TEC as a function of c/a in the PbTiO$_3$-based solid solutions studied previously.[9]

Figure 2. Temperature evolution of unit cell volume in (1-x-y)PbTiO$_3$-xBi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$-yBiFeO$_3$ solid solutions. The data of 0.7PT-0.3BF is shown for comparison.[9a]

a large temperature range up to 500 °C and show an evidence for a relationship between NTE and ferroelectricity.

(1-x-y)PbTiO$_3$-xBi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$-yBiFeO$_3$ solid solutions (labeled as PT-BZT-BF) were synthesized by a modified solid-state reaction method. The details of high-temperature X-ray diffraction and Raman scattering spectroscopy are reported in the Supporting Information. The lattice parameters of PT-based solid solution are calculated based on the XRD patterns.

As shown in Figure 2, the temperature dependence of unit cell volume gives an abnormal behavior as the BZT is introduced to the PT lattice. With increasing content of BZT, the sharp variation of volume becomes more and more obscure, which is different than the known PbTiO$_3$-based compounds.[9] The T_C is, moreover, more enhanced, indicating a broader NTE temperature range. As a little magnitude of BF (10 mol %) is introduced to 0.7PT-0.3BZT, the volume nearly does not depend on a wide temperature fluctuation. From room temperature to 500 °C, 0.7PT-0.3BZT and 0.6PT-0.3BZT-0.1BF exhibit a neglectable volume change with an average volumetric TEC of −0.60 and −0.31 × 10^{-5} °C^{-1}, respectively (region I of Figure 1). These values are smaller than that of large
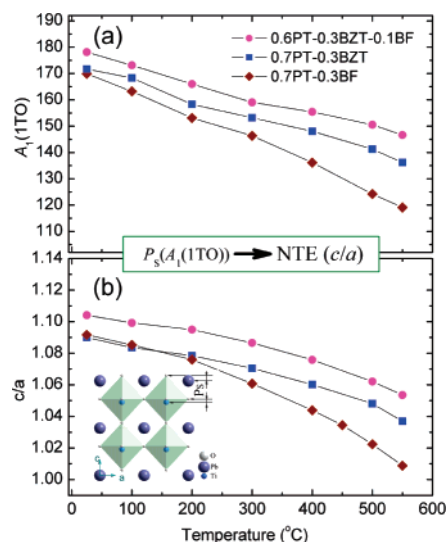
Figure 3. (a) A_1(1TO) frequency, and (b) c/a as a function of temperature in PbTiO$_3$-based solid solutions. The insert of panel b shows the P_S of PbTiO$_3$.

NTE 0.4PT-0.6BF (-3.92×10^{-5} °C^{-1})[9a] and ZrW$_2$O$_8$ (-2.73×10^{-5} °C^{-1})[1] and close to that of ZTE Fe[Co(CN)$_6$] (-0.44×10^{-5} °C^{-1}).[4]

Owing to the special properties of NTE and ferroelectricity of PT in the perovskite family,[9,10,12] we propose that the ferroelectricity might be entangled in the explanation of NTE behavior. As the temperature is below T_C, PT exhibits ferroelectricity and NTE; while it loses NTE in the paraelectricity above T_C. In the ferroelectric phase, the increased volume can be maintained by the high lattice distortion (c/a) that resulted from the strong spontaneous polarization (P_S).[12] Therefore, how the P_S, reflecting the magnitude of ferroelectricity, varies with temperature will directly affect the value of c/a, that is, the NTE.[13]

According to lattice dynamical theory, it is well-known that the frequency of the A_1(1TO) soft mode is proportional to the order parameter P_S of PT-based solid solutions. The variation of the A_1(1TO) soft mode indicates how P_S evolves with the temperature below the T_C.[14] Thus, Raman scattering spectra of 0.7PT-0.3BF, 0.7PT-0.3BZT, and 0.6PT-0.3BZT-0.1BF were measured from room temperature up to T_C.[15] The temperature dependence of c/a and A_1(1TO) for these three PT-based compounds are shown in Figure 3. In particular, it is interesting to find a much different behavior of c/a and A_1(1TO) dependent on temperature for 0.7PT-0.3BF and 0.7PT-0.3BZT (Figure 3). Although their c/a and A_1(1TO) soft mode frequency is nearly the same at room temperature, they gradually separate with increasing temperature. As temperature is raised up to T_C, the lattice distortion (c/a) of 0.7PT-0.3BF reduces rapidly, indicating a strong NTE property (-2.38×10^{-5} °C^{-1}),[9a] while it decreases slightly for 0.7PT-0.3BZT, resulting in a low NTE property (-0.60×10^{-5} °C^{-1}). The A_1(1TO) mode of 0.7PT-0.3BF becomes continually softer than that of 0.7PT-0.3BZT and 0.6PT-0.3BZT-0.1BF with increasing temperature, indicating that the P_S can be maintained in the 0.7PT-0.3BZT and 0.6PT-0.3BZT-0.1BF, and become lower in 0.7PT-0.3BF as the temperature raises to T_C. As shown in Figure 3, one can see how the c/a, , that is NTE, is affected by the P_S. The ZTE property of 0.7PT-0.3BZT and 0.6PT-0.3BZT-0.1BF is ascribed to the strong coupling of P_S displacements of Pb/Bi and Ti/Zn with a strong ferroelectric activity. As the temperature increases up to T_C, the volume of 0.7PT-0.3BZT

and 0.6PT-0.3BZT-0.1BF can be kept close to that at room temperature by the high P_S, and thus the ZTE is produced; however, in 0.7PT-0.3BF, the rapidly decreased P_S results in the rapid decrease in c/a ratio and thus a greatly enhanced NTE. Therefore, the NTE of PbTiO$_3$-based compounds is controlled by the behavior of the temperature dependence of P_S.

In conclusion, PT-BZT solid solutions exhibit an unusual NTE, while their tetragonal character and Curie temperature are considerably increased. The 0.7PT-0.3BZT and 0.6PT-0.3BZT-0.1BF solid solution exhibits a ZTE over a wide temperature range. The lattice dynamics results indicated that the NTE property of PT-based solid solutions is strongly correlated with the ferroelectricity, which is a new mechanism for NTE oxide. In the future search of ZTE materials, ZTE could be found in those ferroelectrics where the ferroelectric soft mode could be well maintained with increasing temperature.

Supporting Information Available: Details of XRD and Raman scattering spectra for PbTiO$_3$-based compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Mary, T. A.; Evans, J. S. O.; Vogt, T.; Sleight, A. W. *Science* **1996**, *272*, 90−92.
(2) (a) Sleight, A. W. *Inorg. Chem.* **1998**, *37*, 2854−2860. (b) Evans, J. S. O. *J. Chem. Soc., Dalton Trans.* **1999**, 3317−3326. (c) Barrera, G. D.; Bruno, J. A. O.; Barron, T. H. K.; Allan, N. L. *J. Phys.: Condens. Matter* **2005**, *17*, R217−R252.
(3) Mohn, P. *Nature* **1999**, *400*, 18−19.
(4) Margadonna, S.; Prassides, K.; Fitch, A. N. *J. Am. Chem. Soc.* **2004**, *126*, 15390−15391.
(5) Sleight, A. *Nature* **2003**, *425*, 674−676.
(6) Roy, R.; Agrawal, D. K.; McKinstry, H. A. *Annu. Rev. Mater. Sci.* **1989**, *19*, 59−81.
(7) Kwon, Y.-K.; Berber, S.; Tománek, D. *Phys. Rev. Lett.* **2004**, *92*, 015901-1−4.
(8) (a) Arvanitidis, J.; Papagelis, K.; Margadonna, S.; Prassides, K.; Fitch, A. N. *Nature* **2003**, *425*, 599−602. (b) Mattens, W. C. M; Hölscher, H.; Tuin, G. J. M.; Moleman, A. C.; de Boer, F. R. *J. Magn. Magn. Mater.* **1980**, *15−18*, 982−984.
(9) (a) Chen, J.; Xing, X. R.; Liu, G. R.; Li, J. H.; Liu, Y. T. *Appl. Phys. Lett.* **2006**, *89*, 101914-1−3. (b) Chen, J.; Xing, X. R.; Yu, R. B.; Liu, G. R. *J. Am. Ceram. Soc.* **2005**, *88*, 1356−1358. (c) Chen, J.; Xing, X. R.; Yu, R. B.; Liu, G. R. *Appl. Phys. Lett.* **2005**, *87*, 231915-1−3. (d) Chen, J.; Xing, X. R.; Deng, J. X.; Liu, G. R. *J. Alloy Compd.* **2004**, *372*, 259−266. (e) Xing, X. R.; Chen, J.; Deng, J. X.; Liu, G. R. *J. Alloy Compd.* **2004**, *360*, 286−289.
(10) Taylor, D. *Br. Ceram. Trans. J.* **1985**, *84*, 181−188.
(11) (a) Grinberg, I.; Suchomel, M. R.; Dmowski, W.; Mason, S. E.; Wu, H.; Davies, P. K.; Rappe, A. M. *Phys. Rev. Lett.* **2007**, *98*, 107601-1−4. (b) Grinberg, I.; Suchomel, M. R.; Davies, P. K.; Rappe, A. M. *J. Appl. Phys.* **2005**, *98*, 094111-1−10.
(12) Cohen, R. E. *Nature* **1992**, *358*, 136−138.
(13) Based on the NTE of the PT-based solid solutions studied previously, all the a,b lattice parameters increase slightly with the same trends, while the c axis has a very different temperature evolution (Figure S2). Thus, the unit cell volume mainly depends on the variation of the tetragonality (c/a), and the behavior of temperature dependence of c/a will directly reflect the NTE.
(14) (a) Burns, G.; Scott, B. A. *Phys. Rev. B* **1973**, *7*, 3088−3101. (b) Foster, C. M.; Grimsditch, M.; Li, Z.; Karpov, V. G. *Phys. Rev. Lett.* **1993**, *71*, 1258−1260.
(15) Although 0.7PT-0.3BF and 0.7PT-0.3BZT are very similar in lattice parameters and c/a at room temperature, the NTE property shows the reverse behavior (Figure S2). The NTE of 0.7PT-0.3BF is much enhanced (-2.38×10^{-5} °C^{-1}), while that of 0.7PT-0.3BZT is conversely much reduced (-0.60×10^{-5} °C^{-1}), in comparison to PT (-1.99×10^{-5} °C^{-1}). Therefore, 0.7PT-0.3BF, 0.7PT-0.3BZT, and 0.6PT-0.3BZT-0.1BF were selected to study what the difference in behavior of A_1(1TO) soft mode, that is, P_S, could be.

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