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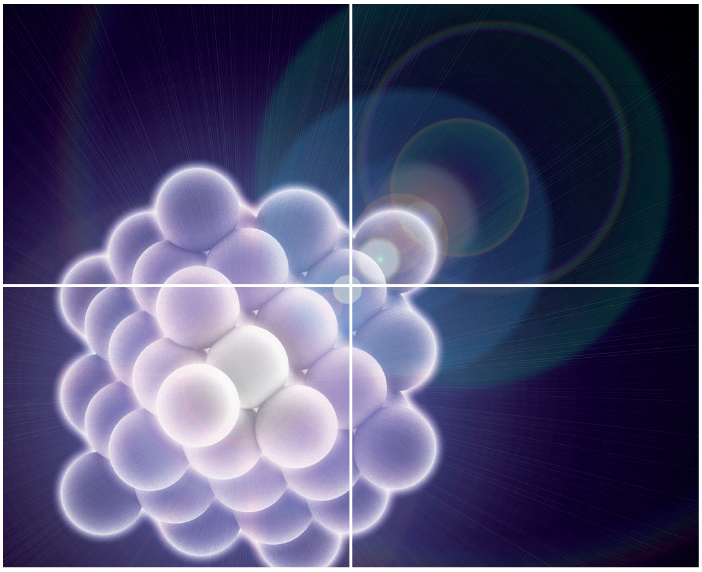

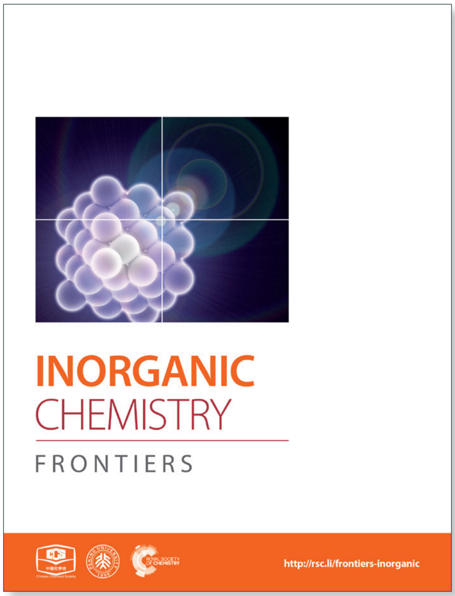

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ARTICLE

Cation deficiency effect on negative thermal expansion of ferroelectric $PbTiO_3$

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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It is known that negative thermal expansion (NTE) in $PbTiO_3$ (PT) ferroelectrics can be controlled by chemical substititions. In the present work, however, we report a method to change the NTE of PT by introducing cation deficiency at both the *A* (Pb^{2+}) and *B* sites (Ti^{4+}). We investigated the spontaneous polarization, tetragonality c/a, coefficient of thermal expansion, and Curie temperature T_C at 8% Pb^{2+} deficiency PT ($P_{92}T$), 2% Ti^{4+} deficiency PT (PT_{98}), and pure PT. We found that while Pb^{2+} deficiency disdinctively weakens the NTE, the effect on B-site deficiency could be ignored. These phenomena are ascribed to the NTE mechanism of spontaneous volume ferroelectrostriction. The present study provides a possible way to control the NTE of PT-based materials.

Introduction

It is well known that most materials expand upon heating due to the inherent anharmonicity of bond vibrations. Over the past decades, however, negative thermal expansion (NTE) has been reported in some materials,[1-15] and its discovery has made it possible to reduce thermal shock for various applications. $PbTiO_3$ (PT) is a very popular NTE material featuring a spontaneous polarization (P_S) parallel to the polar direction of the *c* axis.[16,17] In our group, the NTE of PT was found in the temperature range of 25-490°C.[15] Systematic investigations have been taken to adjust NTE in PT-based compounds afterward.[18-22] Chemical substitutions of Pb and Ti cations is used to achieve wide control of the coefficient of thermal expansion (CTE). For example, in the systems of $(1\text{-}x)PbTiO_3\text{-}xBiFeO_3$[18] and $(Pb_{1\text{-}x}Cd_x)TiO_3$[19], chemical substitutions enhanced NTEs, resulting in a CTE of -3.92×10^{-5} °C^{-1} for x=0.6 and -2.40×10^{-5} °C^{-1} for x=0.06 in the corresponding compound. Furthermore, In $(1\text{-}x)PbTiO_3\text{-}xBi(Zn_{1/2}Ti_{1/2})O_3$[20] and $(1\text{-}x)PbTiO_3\text{-}xBi(Ni_{1/2}Ti_{1/2})O_3$[21], near zero thermal expansions were achieved. Cation doping cripples NTE of PT in most cases. For example, the NTEs of $PbTi_{1\text{-}x}Fe_xO_3$ are reduced to -1.49×10^{-5} °C^{-1} and -1.13×10^{-5} °C^{-1} when x=0.05 and 0.10,[22] respectively. All these evidences[16] show a strong correlation between the spontaneous polarization and NTE for the PT-based ferroelectrics, known as spontaneous volume ferroelectrostriction (SVFS), which is a newly identified mechanism in ferroelectric NTE compounds.[23]

To date, the influence of *A*/*B*- site deficiency on NTE in $PbTiO_3$ has not been reported. In the present work, we prepared nonstoichiometric PT sample to introduce Pb^{2+}/Ti^{4+} deficiencies. The Pb^{2+}/Ti^{4+} deficiencies can cause a spontaneous polarization displacement change, which in turn cause a distortion of the primitive cell, and thus controls its CTE. The experimental results show that the CTE of PT with 2% Ti^{4+} deficiency (PT_{98}) is nearly equal to that of pure PT, while the NTE of 8% Pb^{2+} deficiency compound ($P_{92}T$) has significantly weakened.

Experimental

Solid solution samples of Pb^{2+}/Ti^{4+} deficiency were prepared by a conventional solid state reaction route. Analytic reagent grade raw materials of PbO and TiO_2 are weighed in stoichiometric proportion and pestled for an hour in ethanol medium. The mixed powders were calcined at 850 °C for 5 hours for perovskite phase formation. Then, the solid solution samples were sintered at 900 °C for two hours. In the *A*-site deficiency experiment, we set TiO_2:PbO =1:x, x<1; And in the *B*-site deficiency testing, we set PbO:TiO_2 =1:x, x<1. The x-ray diffraction (XRD) patterns of sintered samples were taken using a laboratory diffractometer (PANalytical X' PertIII, Holland) (Cu Kα radiations). The high-temperature powder X-ray diffraction patterns were collected in the same diffractometer and an Anton Paar HTK 1200 high-temperature attachment was used. Data was collected from 25-700 °C over a 2θ range from 20 to 80°. The heating rate was 10 °C/min, and the sample was held for 5 min at a specified temperature to reach heating equilibrium. The structure was refined by the Rietveld method using FULLPROF software. The T_C

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Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

(temperature where the ferroelectric transforms into a paraelectric one in lead titanate) of these samples was defined by using DSC (Labsys Evo, Setaram, France). The heating rate was 10 °C/min in air condition and the rate of airflow was 25 mL/min. Raman measurements were performed with a LabRAM HR Evolution Raman spectrometer (Jobin Yvon, France). The 532 nm line of an argon ion laser was used as exciting light. The output power of the laser was kept within 0.4 mW. The compositions of samples were identified by energy-dispersive spectroscopy (SEM-EDS) (FE-SEM, SUPRA-40, Carl Zeiss) and inductively coupled plasma optical emission spectroscopy (ICPOES; Thermo IRIS Intrepid II). Ion oxidation states in the samples were analyzed by X-ray photoelectron spectroscopy (ESCALAB 250Xi, Thermo Fisher). Experimental detail is included in Supporting Information (SI).

Results and Discussion

PT has a perovskite structure (ABO_3) where large Pb atoms occupy the A-site and small Ti atoms occupy the B-site. It is known that perovskite structure has a flexible crystal structure that allows cation deficiency at the A/B site. Single perovskite phase can be achieved in various concentration of A/B site deficiency, and while a larger amount of deficiency can be stabilized at the A site, an impure phase appears when more deficiency is introduced. To study the B-site deficiency of PT, we set Pb^{2+} : Ti^{4+}= 1 : *x*. The prepared sample is not in a single phase when $x < 0.98$. Similarly, in the A-site Pb^{2+} deficiency situation with the chemical ratio of Ti^{4+}: Pb^{2+}= 1:*x*, the impurity is detected in the sample with $x<0.92$. For example, the PbO and $PbTi_3O_7$ impurity phases are detected in the nominal PT_{97} and $P_{91}T$ samples. To study the actual compositions of the prepared samples, the SEM-EDS measurements were carried out. The averaged measured results (Table 1) agree well with the nominal compositions (error < 5%, the individual ones could be seen in Table S2-S4 in SI). The EDS results of different areas are close to each other, indicating the compositional homogeneity. Also the ICP tests were adopted to confirm the results. The Pb^{2+} /Ti^{4+} ratio from ICP tests are 1/1.00, 1/0.97 and 0.94/1 for PT, $P_{92}T$ and PT_{98}, respectively, confirmed the EDS measurements. In addition, the XPS results reveal that the valence states of Ti^{4+} and Pb^{2+} ions exist only, while oxygen vacancies increases with more

Table 1 Crystal structure at room temperature, *Tc*, P_S and CTE of the PT, $P_{92}T$, and PT_{98}.

	PT	$P_{92}T$	PT_{98}
Composition (Pb:Ti)	0.9979:1	0.9395:1	1:0.9843
***a*/Å**	3.8990(1)	3.9019(2)	3.8994(1)
***c*/Å**	4.1542(1)	4.1384(3)	4.1540(1)
c*/*a	1.065	1.060	1.065
V/Å^3	63.153(2)	63.006(7)	63.163(2)
δz_{Ti}/Å	0.395(7)	0.368(8)	0.400(9)
δz_{Pb}/Å	0.523(4)	0.497(4)	0.524(4)
$P_S/\mu C(cm)^{-2}$	66.6(9)	62.7(10)	67.1(11)
***Tc*/°C**	490.6	484.3	491.3
CTE/°C^{-1}	-1.99×10^{-5}	-1.68×10^{-5}	-2.00×10^{-5}

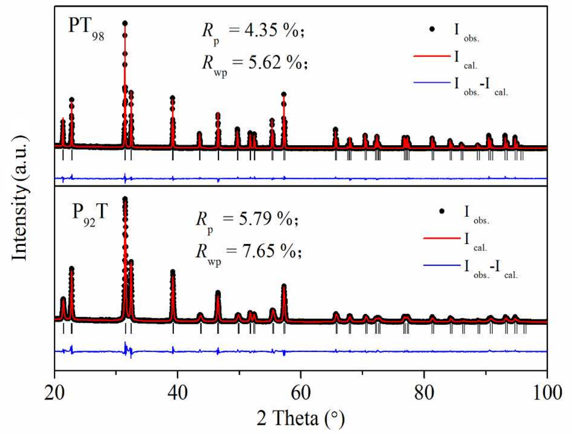

Fig.1 XRD patterns of PT_{98} and $P_{92}T$. Observed (point), calculated (line) and difference profiles at room temperature after Rietveld refinement using *P4mm* space group for the PT_{98} and $P_{92}T$.

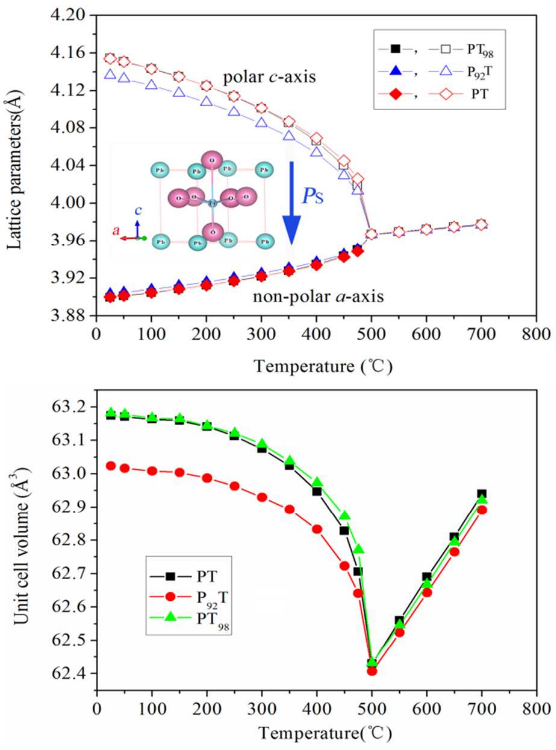

Fig.2 Temperature dependence of (a) lattice constant, and (b) unit cell volume of the PT, $P_{92}T$ and PT_{98}. The error bar is too small to view than the experimental data icon.

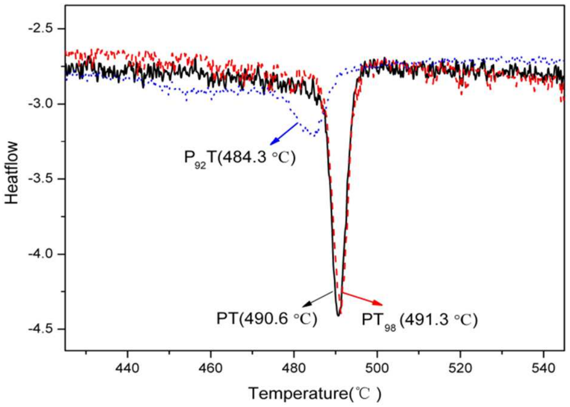

Fig. 3 DSC curves of PT, $P_{92}T$ and PT_{98} from 425 °C to 545°C

introduced cations (Fig. S4 and S5 in SI). These results show that a large amount of deficiencies can be stabilized at the A-site but not in the B-site. We know that TiO_6 octahedron is the framework of the perovskite structure of $PbTiO_3$, and the Pb atom is in the cave of the framework, surrounded by twelve oxygen atoms to form PbO_{12} polyhedron. We can thus reasonably speculate that this is why the amount of Pb^{2+} deficiency could be much bigger than Ti^{4+} deficiency in single phase PT.

As shown in Fig 1, PT_{98} and $P_{92}T$ samples are in pure tetragonal phase, and the crystal structure can be well refined using the same structure model with PT (*P*4*mm*). In Table 1, we compare $P_{92}T$, PT_{98} and PT on *c*/*a*, cell volume, P_S at room temperature and T_C. It is found that PT and PT_{98} are very similar in the structural properties, whereas $P_{92}T$ is greatly different from PT. The *c* axis of $P_{92}T$ is also smaller than that of PT while the *a* axis is bigger than PT. Thus, the *c*/*a* for $P_{92}T$(1.060) is smaller than that of the PT which has a value of 1.065. The unit cell volume of $P_{92}T$ at room temperature is also smaller than that of PT. It is known that the ferroelectric dipole is aligned with the direction of the *c* axis, which strongly correlates with the lattice and the *P*s displacement. As shown in Table 1, the *A*-site *P*s displacement of Pb^{2+}(δz_{Pb}) decreases from 0.524 Å of PT to 0.497 Å of $P_{92}T$, while the *B*-site *P*s displacement of Ti^{4+}(δz_{Ti}) decrease from 0.400 Å to 0.368 Å. This indicates that the reduction in the *c* axis is due to its close relation with the decrease in the *P*s displacement. Due to more covalent bonding of Ti with the four adjacent oxygens O2 in the ab plane (dsp hybridization), the linkage of the O1-Ti-O1 along the *c* axis becomes more flexible than the stiff Ti-O2 bonds[24,25] during compression and elongation. On the other hand, for the B-site deficiency, the crystal structural properties of PT are rarely affected due to the fact that only a small amount of the B-site vacancy concentration can be introduced. Therefore, the ferroelectric property cannot be significantly affected, and thus NTE does not change apparently.

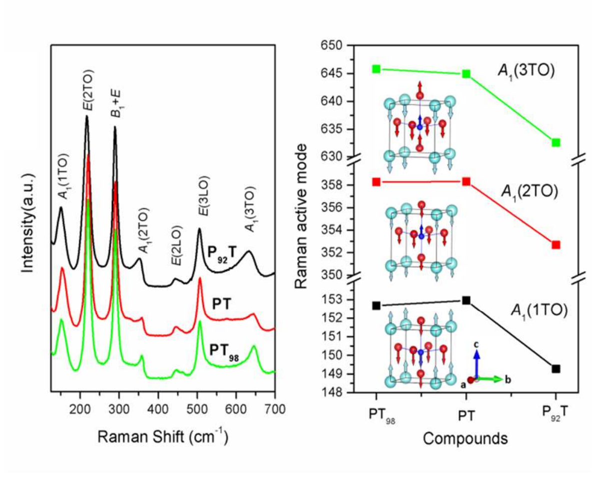

Fig. 4 (a) Raman spectra and (b) Raman active modes of PT, $P_{92}T$ and PT_{98} at room temperature

High temperature X-ray diffraction measurements from RT to 700 °C were performed to determine the evolution of cell parameters of the PT, $P_{92}T$ and PT_{98}. As shown in Figure 2(a), the *a* axis in all three compositions increases upon heating, while the *c* axis decreases with increasing temperature below T_C. The *c* axis of $P_{92}T$ is also smaller than the other two compositions, which reduces the unit cell volume (Fig. 2b). As a result, the NTE of $P_{92}T$ is weakened significantly, while the NTE of PT_{98} is nearly identical to that of PT. The CTE of $P_{92}T$ is -1.58 x 10^{-5}/°C, which is smaller than PT's -1.99 x 10^{-5}/°C. As shown in Fig. 2b, the difference in the NTE is mainly due to the change in the *c*-axis. It has been known that there is coupling between the *c*-axis and *Ps* for the PT-based ferroelectrics. In the $P_{92}T$ sample, the Ps displacements are reduced at both *A* and *B*-sites compared with PT, but not for PT_{98} (Table 1), thus indicating that ferroelectricity is reduced significantly in the $P_{92}T$. It is therefore possible to conclude that the weakened NTE of $P_{92}T$ is a result of the reduction in ferroelectricity. The present study is in good agreement with the previous studies.[1]

Additionally, the phase transition temperatures of tetragonal to cubic have been measured by DSC measurements as shown in Fig. 3. The T_C of PT, $P_{92}T$ and PT_{98} are determined to be 490.6 °C, 491.3 °C and 484.3 °C, respectively. The reduction in T*c* indicates a reduced Ps, which is consistent with the structure refinement results.

The Raman spectra of PT, PT_{98} and $P_{92}T$ are shown in Fig. 4. PT has a tetragonal space group symmetry C_{4v}^1 with an ABO_3 formula unit cell., and is composed of 12 optical modes that can be divided into three categories: three A_1-symmetry modes, eight *E*-symmetry modes, and one B_1-symmetry mode. The three transverse optical (TO) modes of A_1-symmetry (A_1(1TO), A_1(2TO), and A_1(3TO)) are important for $PbTiO_3$-based ferroelectric compounds, because the vibrations are along the direction of the Ps.[26] Specifically, the A_1(1TO) soft mode is composed of displacement of the TiO_6 octahedron relative to lead atoms, while the A_1(2TO) soft mode is composed of displacements of the titanium ion relative to the oxygen and lead ions. In A_1(3TO) soft mode, titanium ions, with oxygen ions lying between, move in the *c*-axis direction.[26,27] The change in these A_1-symmetry modes are highly correlative with the Ps. The results show that Raman active modes of A_1(1TO), A_1(2TO) and A_1(3TO) soften from PT to $P_{92}T$, but remain relatively similar from PT to PT_{98} (Fig. 4). This indicates that the P_S displacements are reduced at both the *A*- and *B*-sites in the $P_{92}T$, but not in PT_{98}. Furthermore, the ferroelectricity is reduced in of $P_{92}T$, but not in the PT_{98}, which confirms the results described above.

In view of these findings, we can thus conclude that the decrease in the Ps displacement is caused by defects in PT. To clarify, the c axis is closely related with *P*s displacement such that the decrease of *P*s displacement triggers the decrease in the *c* axis. As shown in Table 1, both δz_{Ti} and δz_{Pb} of $P_{92}T$ are smaller than PT's at room temperature. This is why the *c* axis of $P_{92}T$ is much smaller than that of PT; on the other hand, the *a* axis is related with TiO_6 octahedron which is stable in a single phase, so the change of *a* axis is small. This explains why the unit cell volume of $P_{92}T$ is smaller than that of PT in the ferroelectric phase below *T*c (Fig. 2(b)). Furthermore, at *T*c, the ferroelectric phase transforms to paraelectric cubic one, and the *P*s displacements disappear, making the unit cell volume at *T*c similar for both PT and $P_{92}T$, thus causing the NTE of $P_{92}T$ to clearly decrease. In addition, the *T*c of $P_{92}T$ is found to be smaller than that of PT due to the small *P*s displacement of $P_{92}T$ and less energy is needed for phase transition, which can be described by the Landau theory.[28]

Conclusions

In summary, we studied the cation deficiency effect on negative thermal expansion in $PbTiO_3$. The resulting structural refinements and softening of A1(TO) modes suggest that Pb^{2+} deficiency in PT leads to a P_S displacement reduction and a slight decrease of Tc. As a result, the NTE is weakened from -1.99×10^{-5}/°C to -1.68×10^{-5}/°C correspondingly. However, due to the limited B-site vacancy concentration, Ti^{4+} deficiency sample does not show apparently changes on P_S displacement and CTE. The present study provides further evidence to support our previous finding that NTE of PT based compounds has a close relationship with the *P*s displacement. Our experiment result provides a possible method to control the NTE of PT-based compounds and other NTE materials by introduction of deficiency.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (grant no. 91022016, 91422301, and 21231001), the Program for Changjiang Scholars and the Innovative Research Team in University (IRT1207), and the Fundamental Research Funds for the Central Universities, China (Grant No. FRF-SD-13-008A).

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