Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary information:

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

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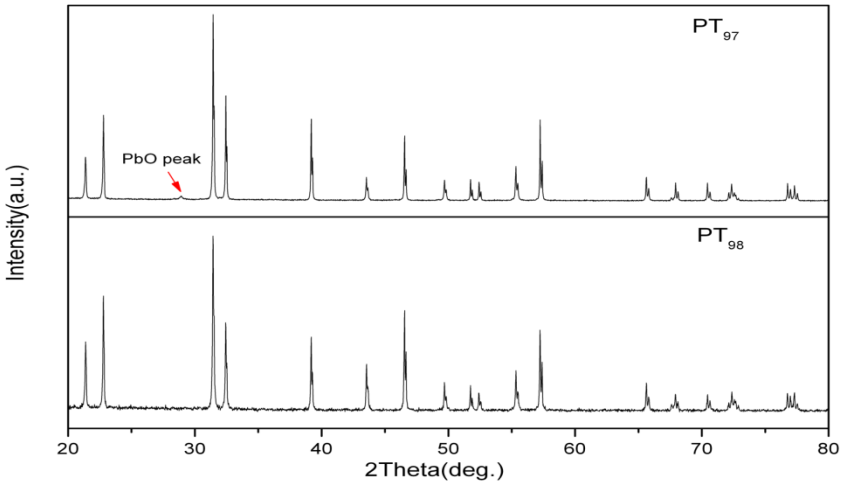

b.

Fig.S1 The XRD patterns of PT_{98} and PT_{97}

XRD patterns of PT_{98} and PT_{97} samples are shown in Fig S1. we can easily find that PT_{98} is in single phase while PT_{97} is not in a pure phase. It has obvious PbO inpure phase in PT_{97} XRD pattern.

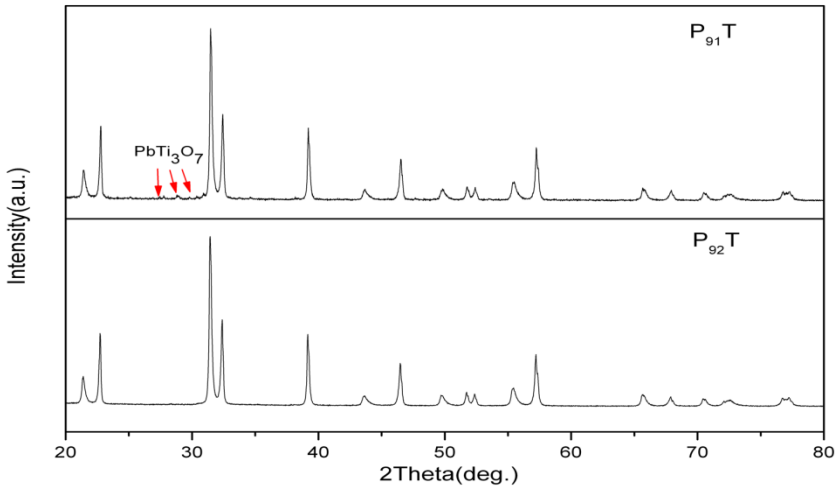

Fig.S2 The XRD patterns of $P_{91}T$ and $P_{92}T$

In Fig.S2, the xrd pattern of $P_{92}T$ shows single phase but $P_{91}T$ does not. In $P_{91}T$, it has obvious $PbTi_3O_7$ inpure phase.

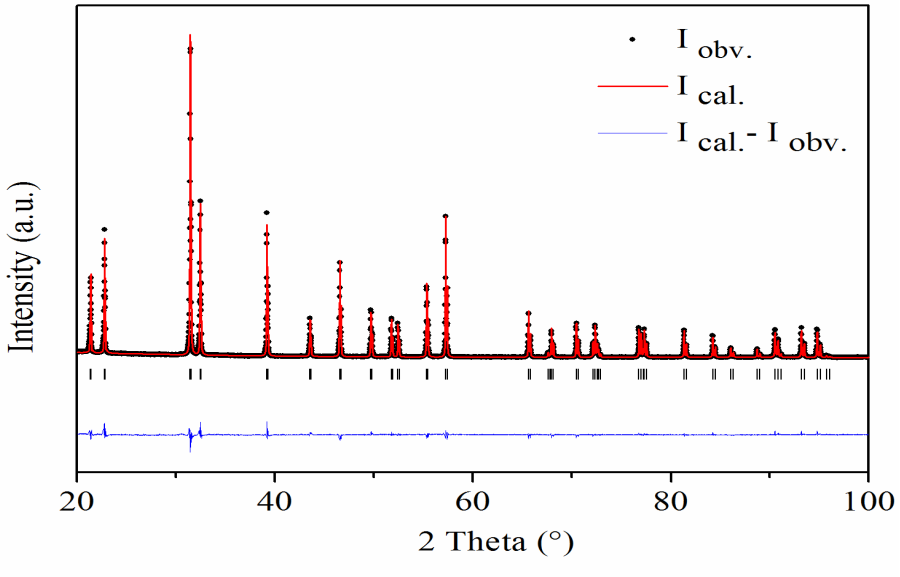

Fig. S3 Observed (point), calculated (line) and difference profiles at room temperature after Rietvrld refinement using *P*4*mm* space group for PT

Table.S1 Refined structure parameters of the PT, $P_{92}T$ and PT_{98}

	PT	**$P_{92}T$**	**PT_{98}**
Z_{Pb}	0	0	0
Z_{Ti}	0.5309(7)	0.5370(9)	0.5298(10)
$Z_{O(I)}$	0.1263(12)	0.1112(13)	0.1255(14)
$Z_{O(II)}$	0.6259(8)	0.6247(9)	0.6266(9)
R_p	3.91	5.79	4.35
R_{wp}	5.22	7.65	5.62
Chi^2	4.34	12.3	3.25

The structure of PT was adopted as the initial structure model to refine the structure of PT, $P_{92}T$ and PT_{98}. Atomic positions of compounds were acquired based on the space group *P*4*mm* (No. 99). In the *P*4*mm* space group, Pb, Ti, O(I), and O(II) occupy the 1*a* Wycoff site at (0, 0, 0), 1*b* site at (1/2, 1/2, Z_{Ti}), 1*b* site at (1/2, 1/2, $Z_{O(I)}$), and 2*c* site at (1/2, 0, $Z_{O(II)}$), respectively. All of the Rietveld refinements were

performed and accomplished through the software FULLPROF. After the anisotropic profile broadening model was taken into account, a satisfying refining result was obtained. The compositional fluctuation and the diffuse scattering might have caused the anisotropic profile broadening, which was teamed up with the locally disordered regions within the vicinity of the domain walls.

For the displacive type $PbTiO_3$-based ferroelectrics, the spontaneous polarization (P_S) depends on the atom shifts between the centers of positive and negative charges. We first calculate the relative atomic displacement by the atom position and then we could know the spontaneous displacement. By assuming standard atomic ionizations state, we could get the P_S.

P_S and P_S displacement calculated by:

$$\delta_{ZTi}=\left(\frac{4Z_{O(II)}+Z_{O(I)}+\left(1+Z_{O(I)}\right)}{6}-Z_{Ti}\right)\times c$$

$$\delta_{ZPb}=\frac{4Z_{O(II)}+4(Z_{O(II)}-1)+4Z_{O(I)}}{12}\times c$$

$$P_S=Z\left(\frac{\delta_{ZPb}\times q_{Pb}}{V}+\frac{\delta_{ZTi}\times q_{Ti}}{V}\right)$$

where δ is the cation shifts along the ferroelectric axis; q is a charge of the ion carrying; V is the unit cell volume and $Z = 1$.

To maintain charge balance, there are two possible ways: 1, the valence states of Ti and Pb ions are changed; 2. the amount of oxygen vacancies are increased. The Pb and Ti XPS signals showed only one spinorbit doublet, i.e. Pb $4f_{7/2}$= 137.9± 0.2 eV, Pb $4f_{5/2}$= 142.8± 0.2 eV, Ti $2p_{3/2}$= 457.8± 0.2 eV and Ti $2p_{1/2}$= 463.6± 0.2 eV, which indicate that here are no obvious valence state change of these samples. If the valence state changes, the Ti $2p_{1/2}$, Ti $2p_{3/2}$, Pb $4f_{7/2}$ and Pb $4f_{5/2}$ peaks would split into two components, respectively. The nominal single O 1s peak could be decomposed into the main peak Oa (at 529.4± 0.2 eV) and two satellites Ob (at 531.0± 0.2 eV) and Oc (at 532.4± 0.2 eV). The Oa peaks correspond to the perovskite lattice oxygen. The Ob peak could be related to the concentration of oxygen vacancies. And the Oc peak could be attributed to absorbed oxygen such as OH, CO, and CO_2.[1,2] The ratio of the area under the Ob and the Oa peaks increases with increasing oxygen vacancy concentration. The ratios for PT, PT_{98} and $P_{92}T$ are 14.82%, 17.35%, and 22.68% respectively, which indicates that there are accompanying oxygen vacancies with cation vacancies increasing.

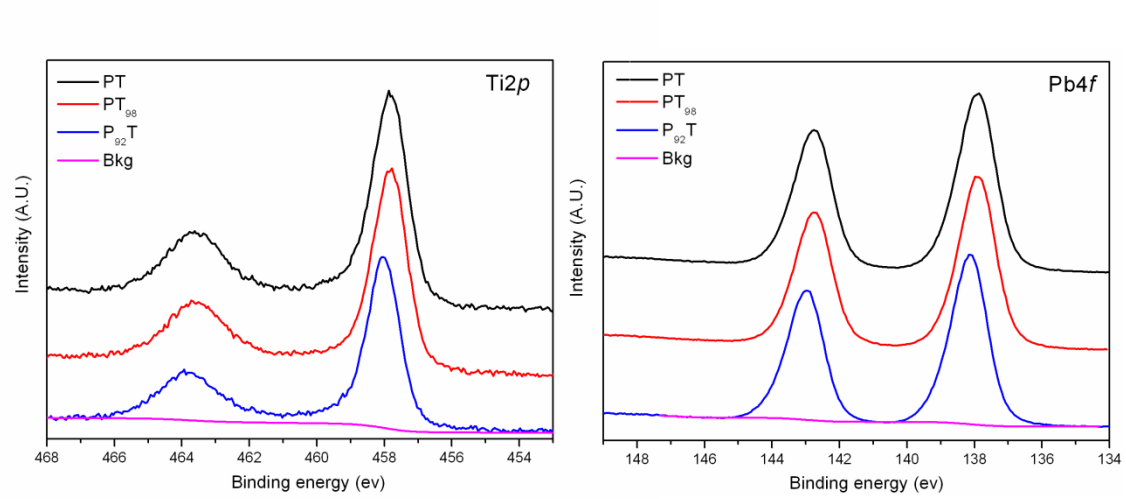

Fig. S4. Pb 4f and Ti 2p XPS spectra of PT, PT_{98} and $P_{92}T$

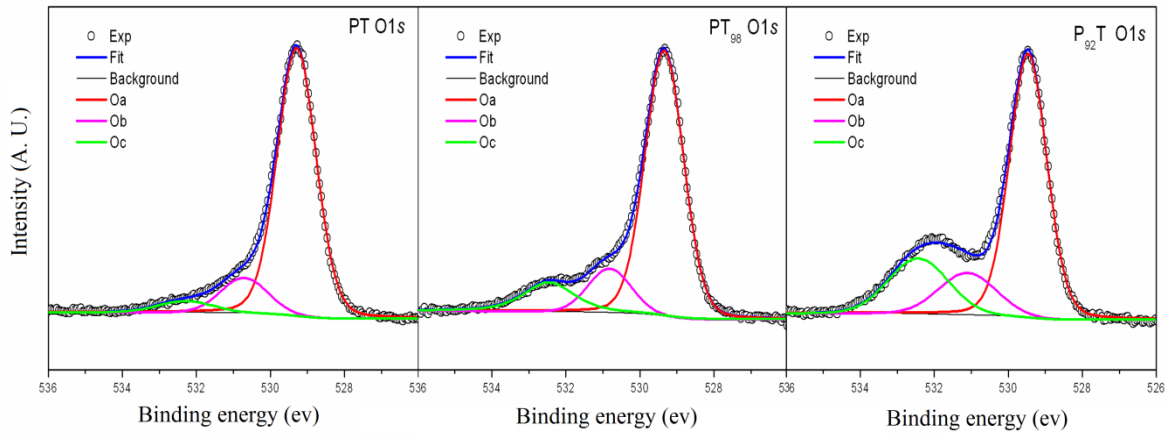

Fig. S5. O 1s XPS spectra of PT, PT_{98} and $P_{92}T$ with peak fitting

We carried out the SEM -EDS to figure the actual compositions of the samples. The EDS results were collected from ten randomly selected areas for each sample (see the tables below and SI). The resultant local compositions in different areas are approximate. The average compositions of PT is Pb: Ti= 0.9979:1; of PT_{98} is Pb: Ti= 1: 0.9843; of $P_{92}T$ is Pb: Ti=0.9395: 1. Also we added the ICP tests for the three samples. The results of ICP tests are Pb: Ti= 1:1.00 for PT, Pb: Ti= 1: 0.97 for PT_{98}, Pb: Ti=0.94: 1 for $P_{92}T$. The above results suggest that the samples are homogeneous and the actual compositions agree with the nominal ones.

Table S2 Local and average compositions measured by EDS for PT. The data were collected on 10 randomly selected areas were also listed.

Area. No.	Pb (Atom%)	Ti (Atom%)
1	50.21	49.79
2	49.40	50.60
3	50.20	49.80
4	49.81	50.19
5	49.51	50.19
6	50.31	49.69
7	49.90	50.10
8	50.47	49.53
9	50.11	49.89
10	49.72	50.28
Average	49.96(0.9979)	50.04(1.0000)

Table S3 Local and average compositions measured by EDS for PT_{98}. The data were collected on 10 randomly selected areas were also listed.

Area No.	Pb (Atom%)	Ti (Atom%)
1	51.33	48.67
2	50.92	49.08
3	50.89	49.11
4	49.66	50.37
5	50.03	49.97
6	50.46	49.54
7	50.51	49.49
8	50.02	49.98
9	50.48	49.42
10	49.68	50.32
Average	50.40(1.0000)	49.60(0.9843)

Table S4 Local and average compositions measured by EDS for $P_{92}T$. The data were collected on 10 randomly selected areas were also listed.

Area No.	Pb (Atom%)	Ti (Atom%)
1	48.27	51.72
2	49.2	50.8
3	48.44	51.56
4	48.21	51.79
5	48.57	51.43
6	47.26	52.74
7	48.63	51.37
8	48.37	51.63
9	48.73	51.27
10	48.47	51.53
Average	48.41(0.9395)	51.59(1.0000)

[1] Y. Wang, W. J. Chen, X. Y. Zhang, W. J. Ma, B. Wang and Y. Zhang, *Act. Mec. Sin.*, 2014, **30**, 526

[2] S. Bhaskar, S. B. Majumder, E. R. Fachini and R. S. Katiyar, *J. Am. Ceram. Soc.*, 2004, **87**, 384