

PbTiO₃ Nanofibers with Edge-Shared TiO₆ Octahedra

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In this communication, we report a new tetragonal phase for PbTiO₃ nanofibers, characterized by a one-dimensional (1D) columned structure with edge-shared TiO₆ octahedron pairs stacking over adjacent pairs in an interlaced manner along the *c*-axis.

Perovskite oxides with a formula of ABO₃ are an important family of materials for their piezoelectricity, ferroelectricity, and colossal magnetoresistivity, which make them highly attractive for fundamental research and various technical applications.^{1–3} In perovskite oxides, BO₆ octahedra usually share the corners forming a three-dimensional (3D) network structure.⁴ A postperovskite MgSiO₃, in which partial SiO₆ octahedra share edges and form a two-dimensional (2D) layered structure, was discovered.⁵ Very recently, high-pressure monoclinic and rhombohedral perovskite phases of PbTiO₃ were reported, in which TiO₆ octahedra still share corners to form a 3D network structure.⁶ Herein, we report a new PbTiO₃ phase, containing edge-shared TiO₆ octahedron pairs and stacking over adjacent pairs in an interlaced manner along the *c*-axis, which was synthesized by a polymer-assisted hydrothermal method developed in our previous work.⁷

For sample preparation, chemistry grade tetrabutyl titanate ((C₄H₉O)₄Ti) and lead nitrate Pb(NO₃)₂ were used as the starting materials. Potassium hydroxide (KOH) was added as a mineralizer, and polyvinyl alcohol (PVA), poly(acrylic acid) (PAA), and poly(ethylene glycol) (PEG) were added as additives. The hydrothermal treatment was performed in an autoclave at 200 °C for 12 h. The products were filtered and washed several times with distilled water and absolute ethanol and finally oven-dried in air at 60 °C for 24 h, resulting in the formation of white powders. Details are given in the Supporting Information.

The morphology of the as-prepared PbTiO₃ sample was examined by a scanning electron microscope (SEM) (Figure 1a and b) and transmission electron microscope (TEM) (Figure 1c and d). PbTiO₃ square nanometer-sized tubes, with an outer edge size of approximately 80–300 nm, an inner edge size of approximately 20–40 nm, and a length of a few to tens of micrometers, are fabricated. Figure 1d shows a TEM image of a typical longitudinal section of a nanofiber with outer and inner sizes of approximately 102 and 20 nm, respectively, which has an asymmetrical wall thickness with a thick side of 46 nm and a thin one of 36 nm. Figure 1e–g show the SAED pattern and the experimental and simulated HRTEM images along [110] zone axis. A good match between the experimental image and simulated one is obtained.

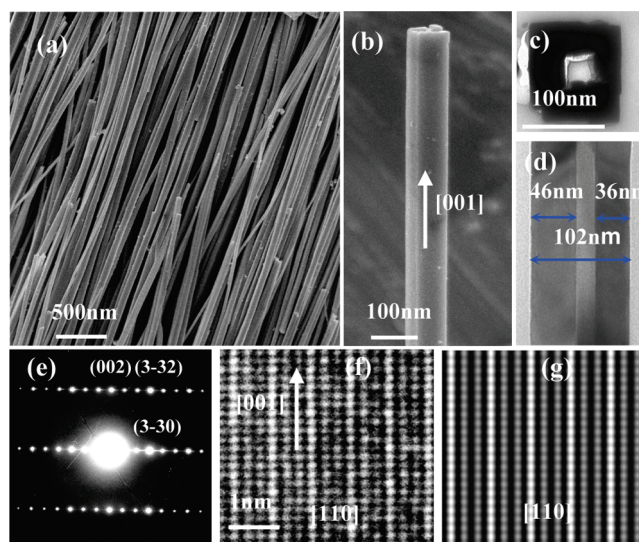


Figure 1. (a) SEM image of the as-prepared PbTiO₃ sample. (b) SEM image of a single PbTiO₃ nanofiber. (c and d) TEM images of the cross section and longitudinal section of the PbTiO₃ nanofiber. (e–g) SAED pattern as well as experimental and simulated HRTEM images of as-prepared PbTiO₃ nanofibers along [110].

These results reveal that PbTiO₃ square nanofibers synthesized here are single crystal and grow along [001] with surfaces enclosed by {110}.

The crystallographic structure of the as-prepared PbTiO₃ square nanofibers is examined by neutron diffraction (ND) in Figure 2a and X-ray diffraction (XRD) (Figure S1). We note that no impurity phases such as pyrochlore (Pb₂Ti₂O_{7–y}) or fluorite (Pb_{2+x}Ti_{2–x}O_{7–y}) have been detected from these patterns, which easily exist in the low temperature preparation of perovskite PbTiO₃ materials.⁸ Both data are refined by Rietveld refinement. All parameters obtained from ND and XRD are listed in Tables 1 and S1, respectively. All the diffraction peaks can be refined by a tetragonal unit cell with *a* = 12.367(8) Å, *c* = 3.808(4) Å, and space group *I4/m* (87) within experimental uncertainty. This new structure (Figure 2b and c) differs from the normal perovskite PbTiO₃⁹ with *a* = 3.905 Å, *c* = 4.156 Å, and space group *P4mm* (Figure 2f and g) and the postperovskite-type structure (Figure 2d and e). This new structure can transfer to a normal perovskite PbTiO₃ phase by annealing treatments in air in Figure S2.

In this new PbTiO₃ structure, the unit cell contains 40 atoms with Pb/Ti/O = 1:1:3 (Figure S3). TiO₆ octahedra share edges and stack along the *c* axis in an interlaced manner to form a 1D column. Pb²⁺ cations are located between isolated columns. The shortest

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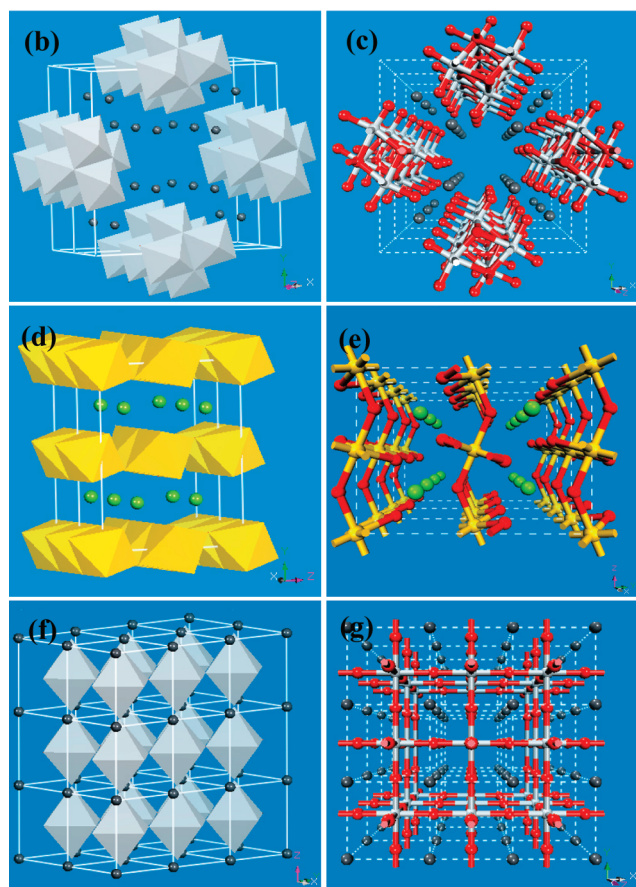
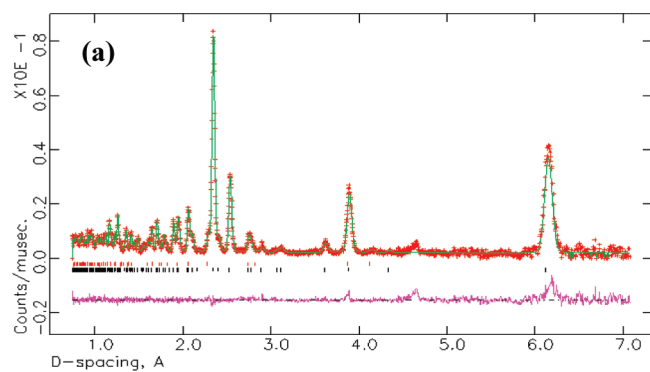


Figure 2. (a) Observed (red crosses), calculated (green solid line) neutron diffraction intensities of the new structured PbTiO_3 at room temperature using space group $I4/m$. In the final refinement, $RI = 0.044$, $RF = 0.030$. The lower plot represents the difference between observed and calculated intensities. Short vertical lines show the Bragg peak positions of the new phase (black lines, lower) and normal perovskite phase of PbTiO_3 (red lines, upper). (b–g) Illustrations of three possible cells of perovskite-type oxides with a formula of ABO_3 . The one-, two-, and three-dimensional arrays of BO_6 octahedra in the new structured PbTiO_3 (b and c), postperovskite (d and e), and normal perovskite (f and g), respectively. Gray sphere, Pb; red sphere, O; white sphere, Ti; shallow green, Mg; yellow sphere, Si atom.

Ti–O and Pb–O distances in the new PbTiO_3 structure are 1.707 and 2.166 Å, respectively (Table 1), significantly smaller than the counterparts of normal perovskite PbTiO_3 (1.78 and 2.53 Å),¹⁰ indicating a stronger covalent bonding in the new PbTiO_3 structure than that in normal perovskite PbTiO_3 . This is further confirmed

Table 1. Crystallographic Data and Structural Refinement of Neutron Diffraction Intensities of the New-Structured PbTiO_3 at Room Temperature

Crystal system: Tetragonal $a = b = 12.367(8)$ Å		Space group: $I4/m$ (No.87) $c = 3.808(4)$ Å	
Atomic coordinates	x	y	z
Pb(8h)	0.165	0.151	0.5
Ti(8h)	0.471	0.142	0.5
O1(8h)	0.605	0.028	0.5
O2(8h)	0.169	0.289	0
O3(8h)	0.543	0.260	0.5
Bond distance (Å)			Average
Ti–O	1.707(9), 1.931(10), 1.958(2)($\times 2$), 2.187(10), 2.319(9)		2.01
Pb–O	2.166(6), 2.504(4)($\times 2$), 2.560(5)($\times 2$)		2.46

by first principles calculations on the electronic structure and density of states of the new PbTiO_3 structure.

It is found that O2p states strongly hybridize with Ti3d and Pb6s states, leading to a strong covalent bonding (Figure S4). We believe that stronger Pb–O covalent bonding is the key point to form the new PbTiO_3 structure with a 1D-stacking manner, which clearly differs from the 2D layered structure of postperovskite MgSiO_3 (Figure 2d and e) and the 3D network structure of normal perovskite PbTiO_3 (Figure 2f and g).

In summary, we synthesized PbTiO_3 nanofibers with a tetragonal unit cell, $a = 12.367(8)$ Å, $c = 3.808(4)$ Å, and space group $I4/m$ at room temperature and ambient pressure, by a polymer-assisted hydrothermal method. This new structure is characterized by a 1D columned structure of an edge-shared TiO_6 octahedron along the c -axis, which is the first 1D structured perovskite-type oxides with a formula of ABO_3 . This new material will trigger more studies on its mechanical, optical, and electric properties and also stimulate more investigations for other 1D structured perovskite-type oxides.

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Supporting Information Available: Experimental details, characterization and simulation data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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