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Supplementary Material: Pressure-induced electronic to ionic phase transition and recurrence of ferroelectricity in $PbTiO_3$

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We conducted XRD measurements of polycrystalline sample powders and compared the results with the PDF No. 06-0425 as shown in Fig. S1.

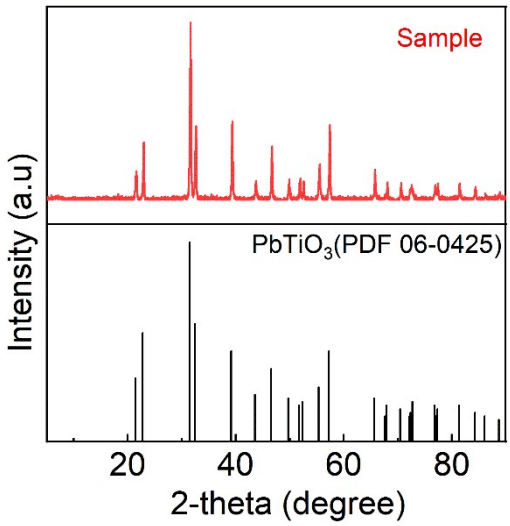

Fig. S1 XRD spectra of the polycrystalline sample and comparison with the PDF card No. 06-0425.

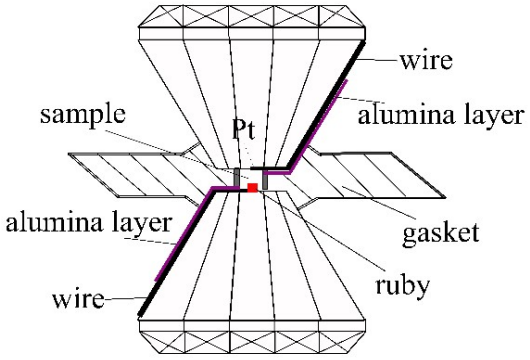

Fig. S2 The schematic of the DAC setup for pressurizing, mainly involving the specific configuration of components and electrode arrangement in the pressurization system.

Three corresponding equivalent circuits are used to fit the impedance spectra. The Nyquist representations of the impedance spectra at 1.5 GPa, 7.0 GPa, 10.9 GPa, 37.2 GPa are shown in Fig. S3(a)-(d). At 1.5 GPa, the impedance spectrum has two semicircular arcs in different radius which can be fitted by two groups of parallel *R* and CPE circuits in series, representing the electron conduction process of the grain and grain boundary. Its impedance can be expressed algebraically by Eq. 1. As the pressure reaches 7.0 GPa, ionic conduction begin to emerge and coexist with the electronic conduction. As a consequence, the spectra cannot be fitted with the equivalent circuit

anymore as shown in Fig. S3(a). Only when ions conduction added, the spectra can be well fitted again as shown in Fig. S3(b), where its impedance can be expressed algebraically as Eq. 2. Above 10.9 GPa, the electronic conduction disappears completely and the ionic conduction is the only electrical transport process in $PbTiO_3$ as shown in Fig. S3(c)-(d). We can fit the impedance spectrum with a pure ionic conducting circuit, and the impedance can be obtained using Eq. 3.

$$Z = \frac{1}{\frac{1}{R_e} + \frac{1}{Z_{Q_1}}} + \frac{1}{\frac{1}{R_{\mathrm{gb}}} + \frac{1}{Z_{Q_2}}} \tag{1}$$

$$Z = \frac{1}{\frac{1}{R_e} + \frac{1}{Z_{Q_1}} + \frac{1}{R_i + Z_W}} + \frac{1}{\frac{1}{R_{\mathrm{gb}}} + \frac{1}{Z_{Q_2}}} \tag{2}$$

$$Z = \frac{1}{\frac{1}{R_i + Z_W} + \frac{1}{Z_{Q_1}}} + \frac{1}{\frac{1}{R_{\mathrm{gb}}} + \frac{1}{Z_{Q_2}}} \tag{3}$$

where R_{i} is the transferring resistance of ions through grains, R_{e} is the transferring resistance of electrons through grains, and R_{gb} is the total grain boundary resistance of both ions and electrons. Z_{W} and Z_{Q} are the impedances of the Warburg elements and the constant phase element (CPE). The CPE represents the charge and discharge process between the electrodes. With those circuits, all the impedance spectra can be fitted well, indicating that the circuit diagrams describing the electrical transport behavior of $PbTiO_3$ carriers are correct.

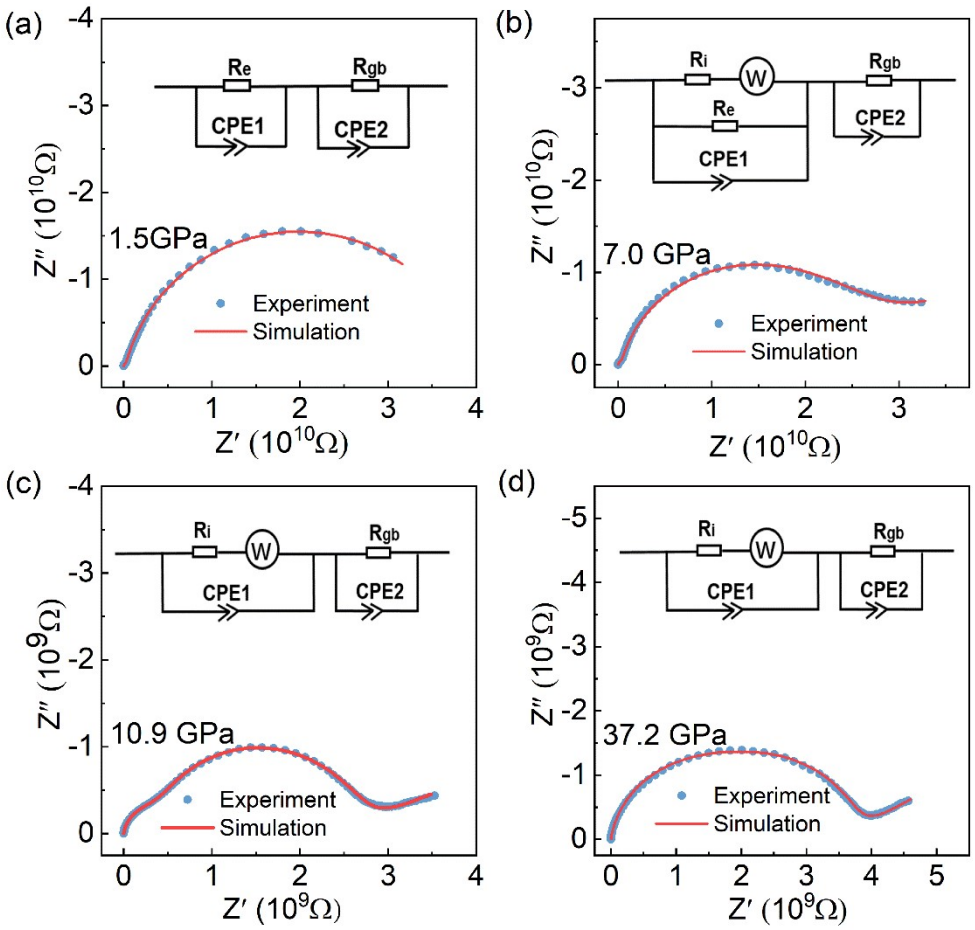

Fig. S3 Selected fitting results of the Nyquist diagram and equivalent circuit diagrams at 1.5 GPa, 7.0 GPa, 10.9 GPa and 37.2 GPa, respectively.

Table S1 *dH/dP* of $PbTiO_3$ in different structures.

Phase	*Pressure region(GPa)*	*dH/dP(mev/GPa)*
P4mm	0-8	1.47
I4/mcm	10.9-26.7	-1.56
I4cm	26.7-40.2	3.59

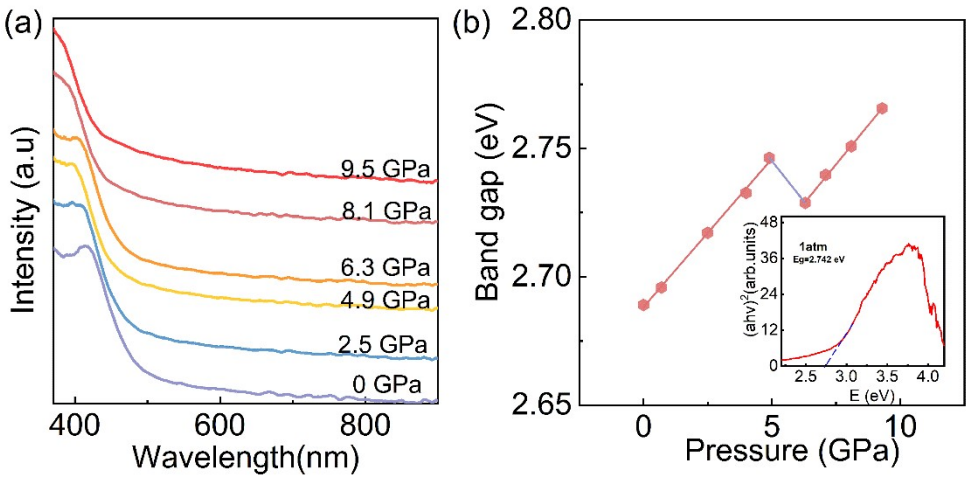

Fig. S4 (a) Absorption spectra of $PbTiO_3$ as a function of pressure. (b)The pressure dependence of band gaps of $PbTiO_3$.The inset in (b) is the Tauc−Mott plots of the absorption spectra for $PbTiO_3$ under ambient condition.

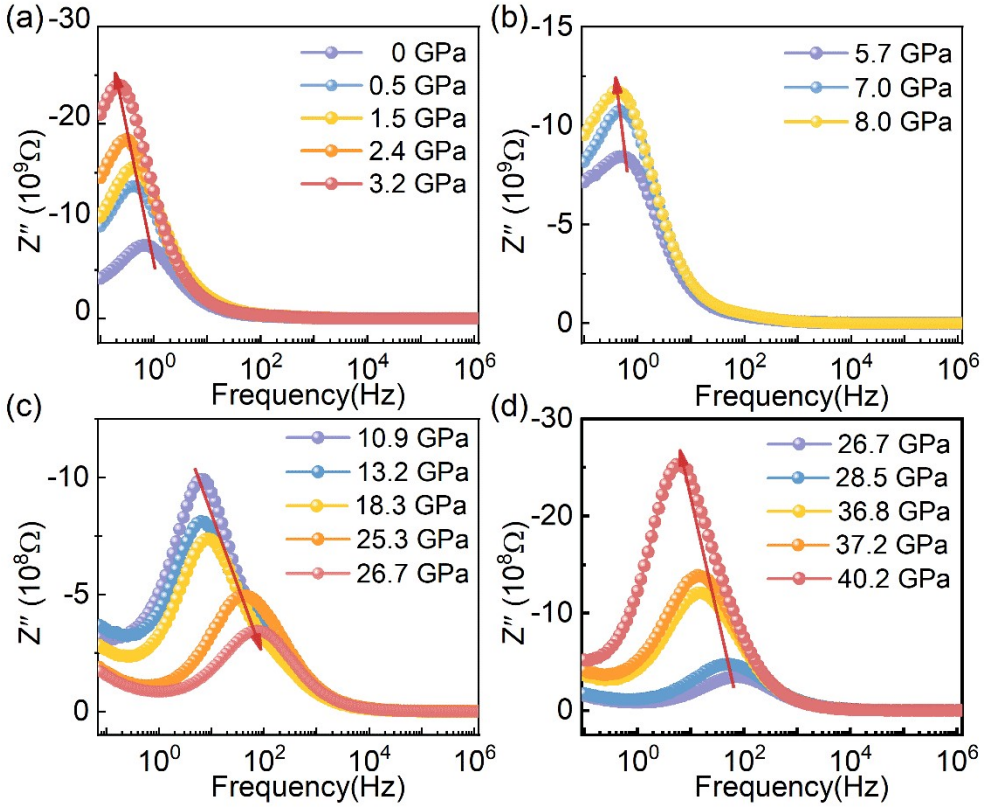

Fig. S5 The *Z*''–*f* plots of the impedance spectra for $PbTiO_3$ at several pressures.

We employed the Forcite module of Materials Studio 8.0 to conduct molecular dynamics simulations. The COMPASS force field and force field assigned charges were utilized, while atom-based summation methods were employed to handle

electrostatic and van der Waals interactions. An electric field strength of 10 kcal/(mol·Å) was applied, with the electric field direction set along the *X*, *Y*, and *Z* axes, respectively.

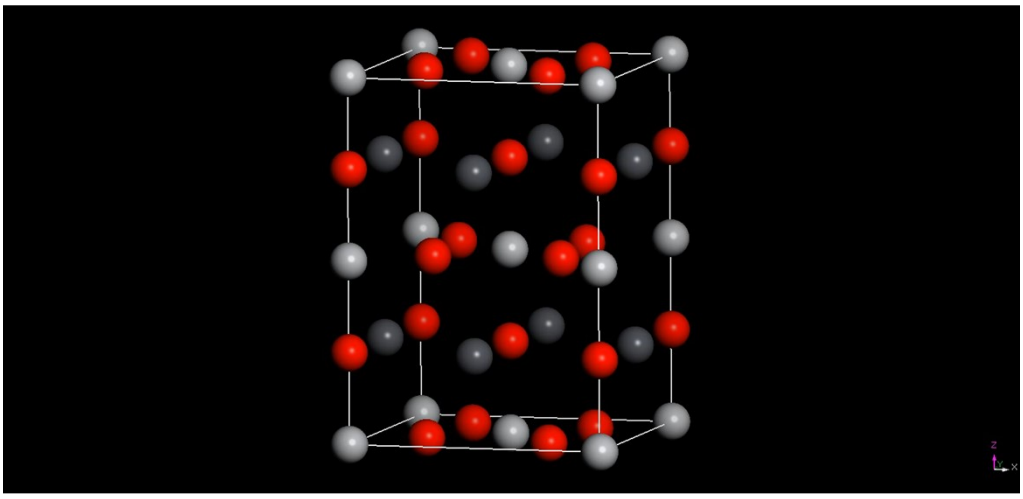

Fig. S6 Molecular dynamics simulations of $PbTiO_3$ in *I*4/*mcm* phase at a temperature of 60 K without an applied electric field. Pb, Ti, and O atoms are represented by black, gray, and red spheres, respectively. (Multimedia view).

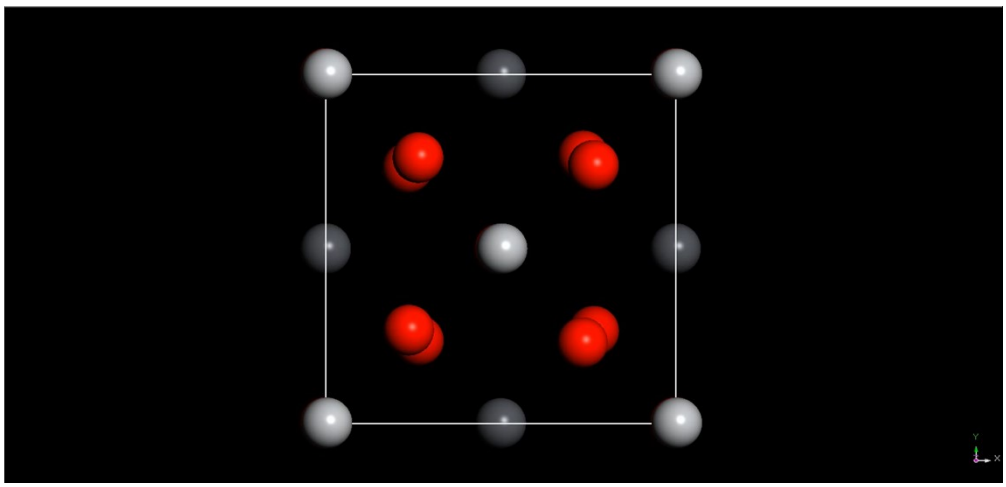

Fig. S7 Molecular dynamics simulations of $PbTiO_3$ in *I*4/*mcm* phase at a temperature of 60 K with an electric field applied in the *X*-direction. Pb, Ti, and O atoms are represented by black, gray, and red spheres, respectively. (Multimedia view).

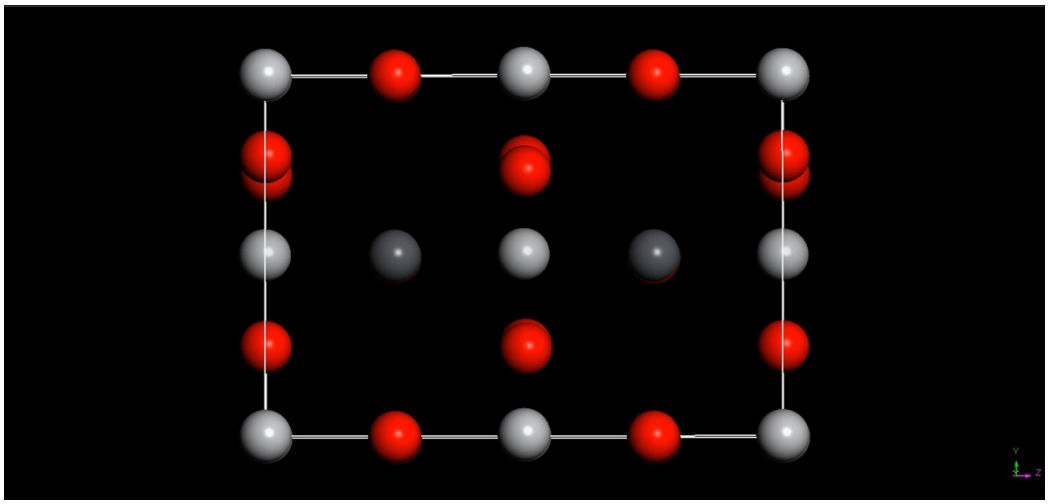

Fig. S8 Molecular dynamics simulations of $PbTiO_3$ in *I*4/*mcm* phase at a temperature of 60 K with an electric field applied in the *Y*-direction. Pb, Ti, and O atoms are represented by black, gray, and red spheres, respectively. (Multimedia view).

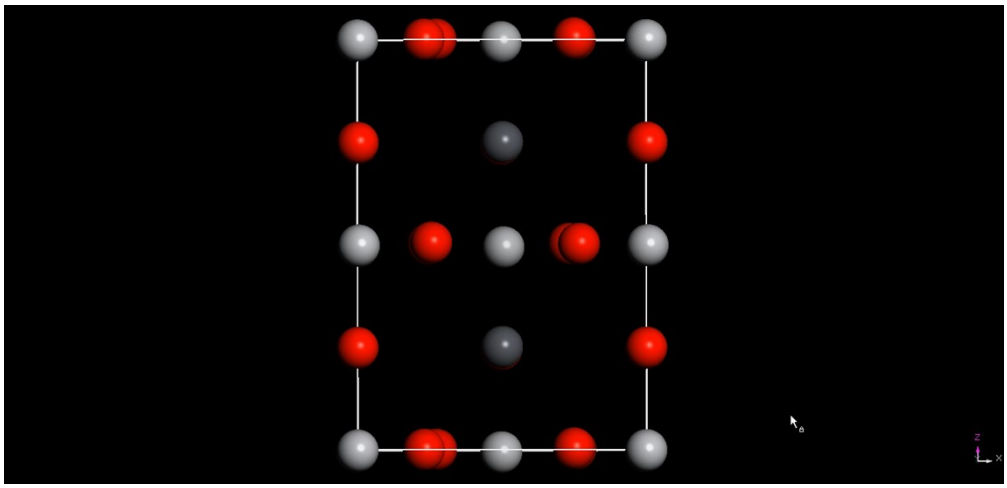

Fig. S9 Molecular dynamics simulations of $PbTiO_3$ in *I*4/*mcm* phase at a temperature of 60K with an electric field applied in the *Z*-direction. Pb, Ti, and O atoms are represented by black, gray, and red spheres, respectively. (Multimedia view).

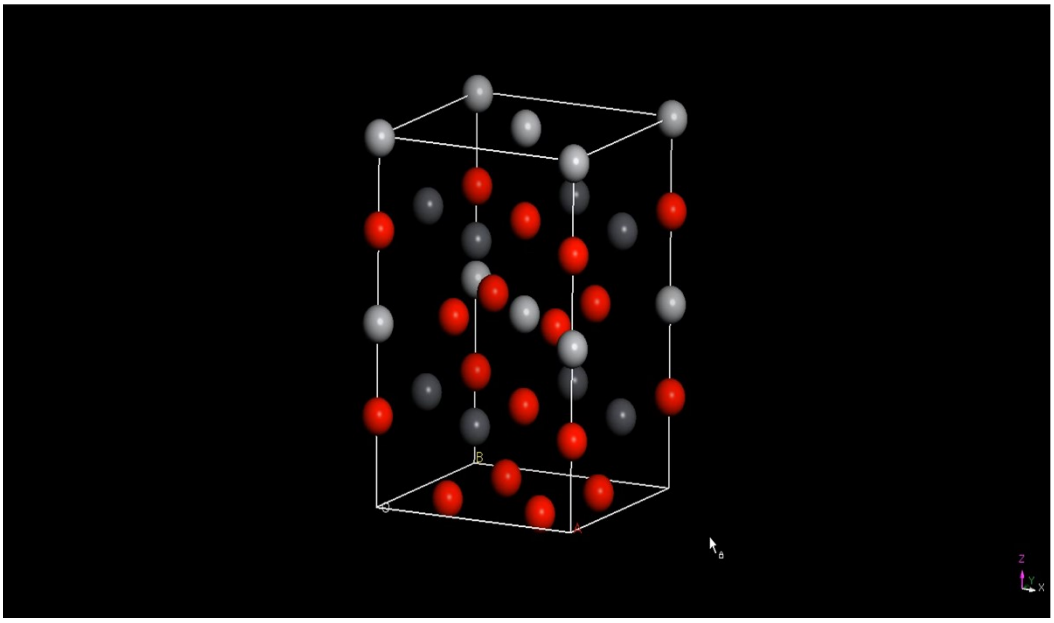

Fig. S10 Molecular dynamics simulations of $PbTiO_3$ in *I*4*cm* phase at a temperature of 60 K without an applied electric field. Pb, Ti, and O atoms are represented by black, gray, and red spheres, respectively. (Multimedia view).

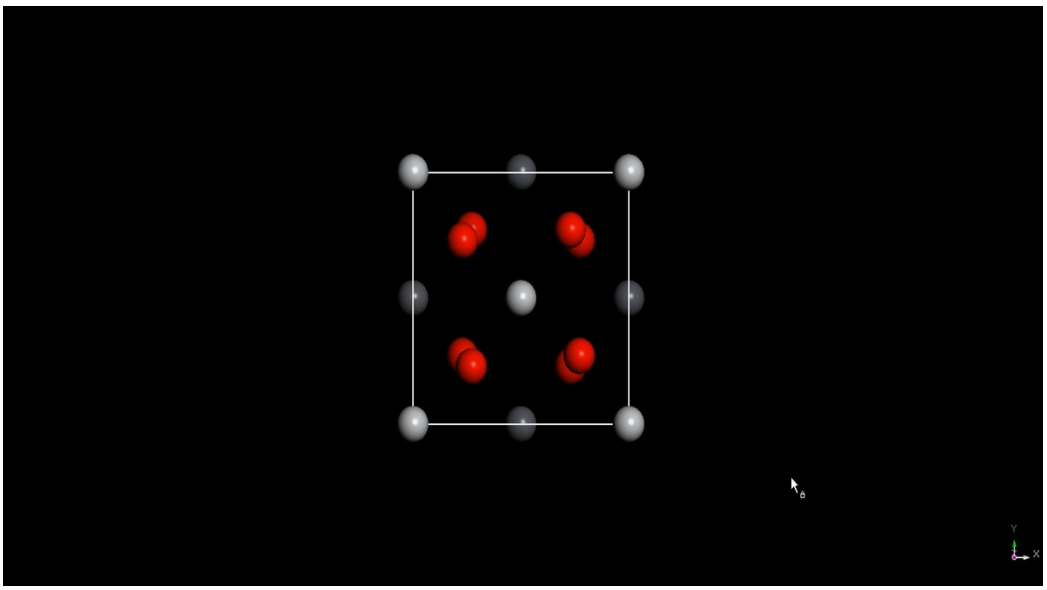

Fig. S11 Molecular dynamics simulations of $PbTiO_3$ in *I*4*cm* phase at a temperature of 60 K with an electric field applied in the *X*-direction. Pb, Ti, and O atoms are represented by black, gray, and red spheres, respectively. (Multimedia view).

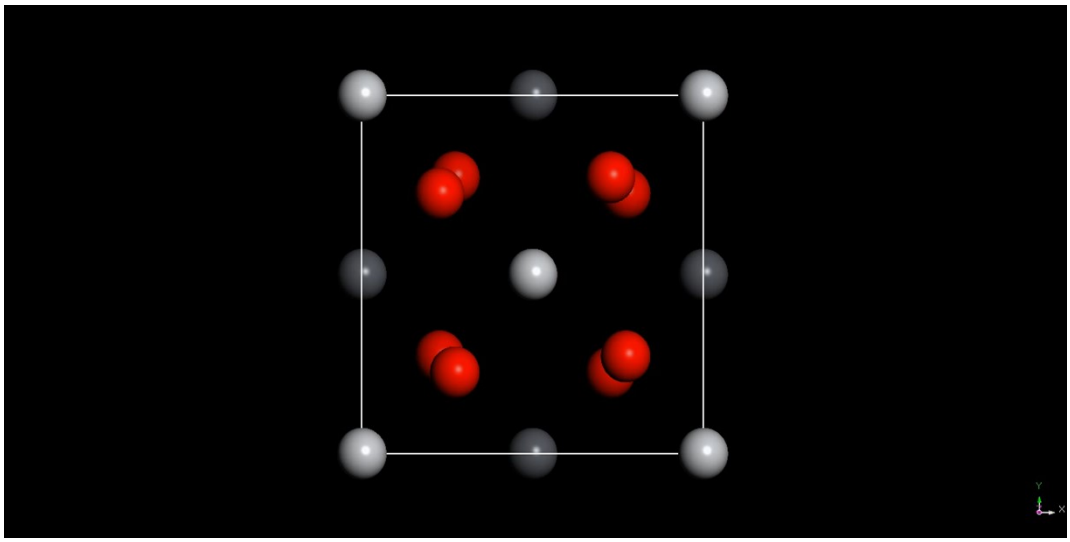

Fig. S12 Molecular dynamics simulations of PbTiO3 in *I*4*cm* phase at a temperature of 60 K with an electric field applied in the *Y*-direction. Pb, Ti, and O atoms are represented by black, gray, and red spheres, respectively. (Multimedia view).

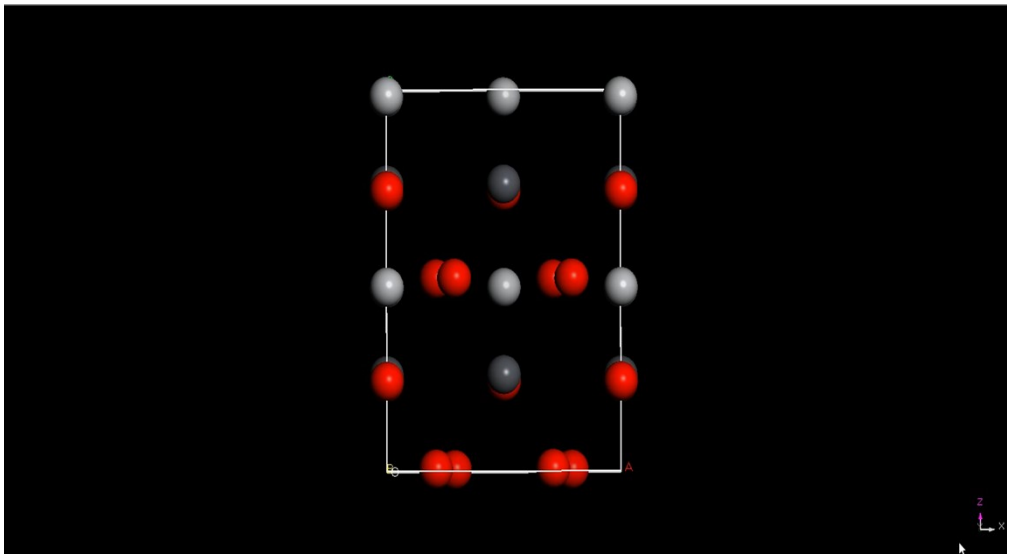

Fig. S13 Molecular dynamics simulations of $PbTiO_3$ in *I*4*cm* phase at a temperature of 60 K with an electric field applied in the *Z*-direction. Pb, Ti, and O atoms are represented by black, gray, and red spheres, respectively. (Multimedia view).

Among the three types of atoms (Pb, Ti, and O) in *I*4/*mcm* and *I*4*cm* phase, the vibration of O atoms is the most obvious and makes irregular motion when the temperature is 60 K and no electric field is applied (as shown in Fig. S6 and S10). From Fig. S6-S13, we found that O atoms move significantly along the direction of the electric field. Therefore, we believe that ion diffusion in $PbTiO_3$ results from O^{2-} ions movement.

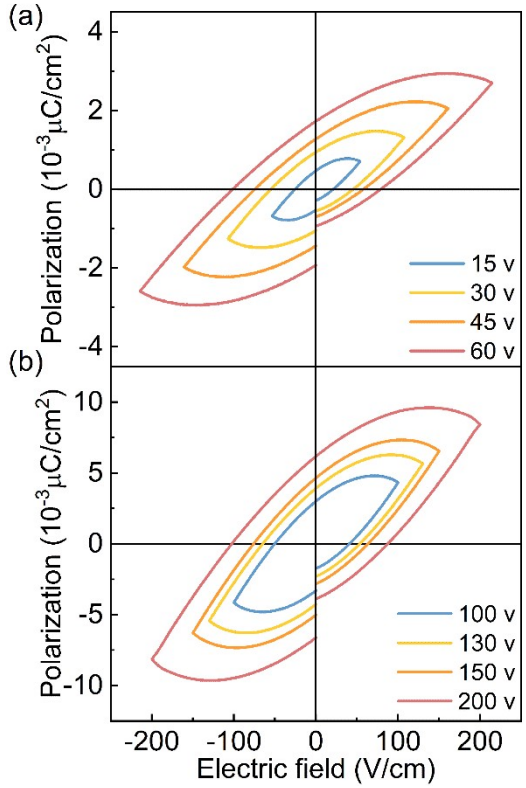

Fig. S14 P–E hysteresis loops of $PbTiO_3$ measured with different voltage ranges under normal pressure.

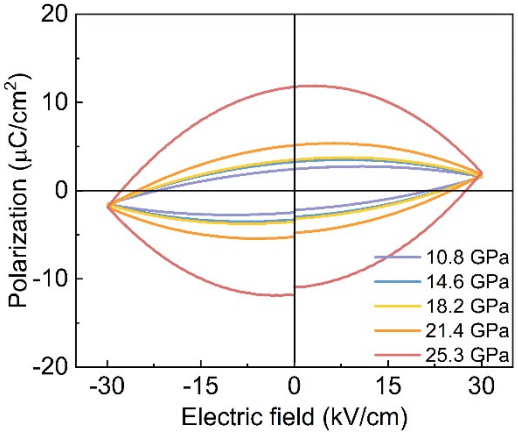

Fig. S15 P–E hysteresis loops of $PbTiO_3$ measured with the pressure range of 10.8-25.3 GPa.