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Research paper

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ABSTRACT

The external pressure is one of the essential parameters for regulating the structure and energy conversion properties of antiferroelectric AgNbO₃. For pure AgNbO₃, however, there has been still a blank of its real lattice structure under the stress field. Here, high-pressure lattice structures and phase transitions of AgNbO₃ have been explored by spectroscopic experiments and theoretical models. A successive phase transition process from *Pbcm* to *C222₁* to *P2₁* has been observed at the pressure range of 0–30 GPa, associated with displacive-type characterized by soft-mode kinetics. Note that the paraelectric phase cannot be achieved under high-pressure at room temperature. Significantly, the competition of long-range Coulomb force, short-range interatomic interaction, and covalent interaction in AgNbO₃ lattice were demonstrated under the stress field. The present work can provide fundamental guidelines to reveal the high-pressure phase transitions of AgNbO₃, which will open up possibilities for the designing device with functional properties at extremes.

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1. Introduction

The antiferroelectricity concept was introduced by Kittel in 1951, according to macroscopic phenomenological theory [1]. The antiferroelectrics have drawn increasing attentions for their potential applications in sensors, mining, high-density data storage and energy conversion, owing to the electric-field induced structure transition process between antiferroelectric (AFE) and

ferroelectric (FE) phases [2–7]. Recently, the emerging lead-free AgNbO₃-based AFE materials has emerged as a prospective alternative candidate to conventional lead-based antiferroelectrics such as PbZrO₃ in energy storage or conversion applications [8–10]. The performances of AFE materials are heavily dependent on the structural transition processes, mainly determined by the composition and external fields. Therefore, the construction of phase boundaries is one of the most productive methods to enhance energy storage, pyroelectric and piezoelectric properties. Considering the merit of the phase boundary, it is expected to construct and explore the phase boundary under the physical manipulations, such as the chemical doping, temperature, electric field, external pressure, and so on.

It is widely recognized that AgNbO₃ will undergo six sequential phase transitions under the action of temperature: M₁^{340 K} → M₂^{540 K} → M₃^{626 K} → O₁^{634 K} → O₂^{660 K} → T^{852 K} → C [11]. Being similar to the thermal-induced behavior, the high-pressure technique is considered as a continuous and reversible means to modulate the electrical, optical and dielectric properties. The structural transition by pressure engineering is a significant category in condensed

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matter physics [12,13]. Meanwhile, K-doped AgNbO₃ (ANK65) has been demonstrated to have superb energy conversion properties under the modulation of pressure, which is the initial discovery of a pressure-driven FE-AFE phase transition in lead-free ferroelectrics [8]. However, the investigation of the pressure-induced structure transitions for pure AgNbO₃ is absent. It hinders the exploration of structural stability for the AFE phase and the understanding of the underlying mechanism for structure transition in AgNbO₃ family.

In the Paper, we studied the external pressure induced evolution of lattice and structural symmetry of AgNbO₃, whose phase transition process of M (*Pbcm*)-HP I (*C222₁*)-HP II (*P2₁*) was firstly discovered. The structural transition was confirmed relating to the rearrangement of cationic and oxygen octahedral distortion, respectively. Correspondingly, the phase boundary shifts to lower pressure points with the doping of KNbO₃, and belongs to the displacive-type observed by Raman active soft-mode behavior. In addition, we found that the paraelectric (PE) phase cannot be achieved at ambient temperature and any moderate pressure. Finally, the balance between the long-range Coulomb forces and short-range interatomic interactions would be broken by covalent interactions at high pressure. This work fills the blank in the pressure-induced phase structure of AgNbO₃. It is closely related to the critical AFE structure properties and the high-performance energy-conversion applications under extreme conditions.

2. Experimental section

AgNbO₃ and ANK65 ceramics were prepared by the solid-state reaction method. Details of sample fabrication can be referred to in the previous work [8]. Raman spectra were carried out by a micro-Raman spectrometer equipped with an Ultra-low frequency accessory (Jobin-Yvon LabRAM HR Evolution) in the frequency range of 5–1000 cm⁻¹, where the laser with a wavelength of 532 nm was used as the excitation source. The pure AgNbO₃ and ANK65 ceramics were crushed into powders with a few micrometers for *in situ* high-pressure experiments. The sample powders and ruby particles were inserted into a 120 μm diameter hole drilled in a 200 μm-thick tungsten gasket, which was preshrunk by a Mao Bell diamond anvil cell (DAC). The mixture of 4:1 methanol-ethanol was used as the pressure-transmitting medium. The calculation of sample pressure in the DAC was calculated from the ruby fluorescence spectra (R1 line position) [14,15]. The pressure at room temperature was fixed at 2/4 GPa in the variable temperature and pressure experiments. Considering the effect of temperature, the pressure was kept as close to 2/4 GPa as possible by adjusting the tightness of the DAC screw during the temperature rise. The temperature-dependent Raman experiment was performed in a Linkam THMSE 600 heating/cooling stage. All scattering spectra were modified by the Bose-Einstein factor coefficient: [16] $n(\omega, T) = [\exp(\hbar\omega/kT) - 1]^{-1}$, where \hbar , ω , k , and T are represented as Planck constant, phonon wavenumber, Boltzmann constant and temperature, respectively. *In situ* high-pressure angle-dispersive X-ray diffraction (XRD) experiment was performed on the BL15U1 beamline, Shanghai Synchrotron Radiation Center (SSRF), where the beam wavelength was 0.6199 Å. The CeO₂ was used as the standard sample for calibration. The XRD data were documented by the imaging plate detector and transformed into one-dimensional XRD patterns utilizing the DIOPTAS program.

3. Results and discussion

AgNbO₃ is the AFE-dominated ferrielectric phase at ambient temperature and pressure, in which the average structure can be described as the *Pbcm* space group [17]. Based on group theory

prediction, the lattice-vibrational irreducible modes in the orthorhombic *Pbcm* space group can be generalized to $\Gamma_{Pbcm} = 15A_g + 13A_u + 17B_{1g} + 15B_{1u} + 15B_{2g} + 17B_{2u} + 13B_{3g} + 15B_{3u}$, in which the acoustic modes are $B_{1u} + B_{2u} + B_{3u}$, A_u is silent, the rest are optical modes, $A_g, B_{1g}, B_{2g}, B_{3g}$ are Raman-active modes [18–20]. Raman spectra of AgNbO₃ under pressure can be seen in Fig. 1(a), where the fitting process and the assignments of the phonon modes are shown at the bottom. Fourteen peaks have been distinguished at ambient pressure, which can be divided into three regions by the origin of the vibration modes. Raman-active modes at low frequency (< 90 cm⁻¹) and high frequency (> 200 cm⁻¹) are derived from the vibrations from the A-site (Ag⁺) cationic and oxygen octahedron, respectively. Two peaks at 94 cm⁻¹ and 108 cm⁻¹ are assigned to librational modes of NbO₆⁻ [23]. The phonon vibrational modes of octahedral rotations in the high frequency range present a high sensitivity for the lattice volume or pressure evolution. The spectra exhibit a continuous variation below 10.7 GPa, in which the lower intensity peaks of the $F_{2g}(\nu_5)$ phonon modes merge into major broadening peaks as the pressure increases. When the pressure exceeds 10.7 GPa, the $A_{1g}(\nu_1)$, $E_g(\nu_2)$ and $F_{1u}(\nu_3)$ also gradually merge into one peak, yet the A-site cationic phonon does not exhibit significant anomalies. At pressures above 20.2 and 24.2 GPa, the ν_5 modes display an apparent splitting phenomenon, signifying the structural transition.

Fig. 1(b)–(c) depict the phonon frequency evolution of AgNbO₃ with the pressure. Raman-active phonon frequency is highly sensitive to the structural variation of lattice, such as the internal stress, lattice volume, and phase transition [21,22]. The anomalous evolution of phonon frequency can be considered as an essential symbol for determining the lattice transition, in which the phonon frequency under pressure always depends on the interatomic distances. When the pressure is below 10.7 GPa, phonon modes except for the Ag⁺ cationic vibration around the 50 cm⁻¹ show a blue shift, reflecting the reduction of the lattice parameters under pressure. Accompanying with the observed merging behavior of ν_1, ν_2 and ν_3 modes, the Ag⁺ cationic vibration around the 50 cm⁻¹ also exhibits significant anomalies over 10.7 GPa.

In addition, the frequency variation with the pressure exhibit different slopes over different pressure regions, listed in Table 1. The pressure-dependent slopes of the main phonon modes in AgNbO₃ undergo abrupt shift phenomena around 10.7 and 20.2 GPa, which is related to the rearrangement of the cation and the rotational reorientation of the oxygen octahedron. Simultaneously, the full width at half maximum (FWHM) values shown in Fig. 1(d) also present a monotonical relationship over a specific region, in which the distinct change from the slope occurred in the structure transition region. Three pressure-induced lattice transitions of AgNbO₃ were initially discerned by judging the anomalies of the frequency shift and the FWHM, which were labeled as M, HP I, and HP II regions, respectively. It is worth noting that the frequency of the Ag⁺ cationic vibration around the 50 cm⁻¹ presented a blue shift at 10.7 GPa, whereas the FWHM exhibited a significant anomaly until the pressure over 15.3 GPa. Therefore, we deduce the fact that there are a two-phase-coexistence state in the pressure range of 10.7–15.3 GPa, thus belonging to the first-order phase transition between the M to the HP I phase. The pressure-dependent Raman spectra of ANK65 also displayed similar trends, indicating that the critical pressure is around 9.0, 14.7, and 18.2 GPa, respectively, as displayed in Fig. 2. Nevertheless, some weak peaks of cations vibrational modes cannot be observed for ANK65 due to the doping of K⁺ ions. To highlight the evolution of the Raman spectra during the structural transformation, the representative fitting of Raman spectra peak profiles at critical pressure for AgNbO₃ and ANK65 were depicted in Fig. 3.

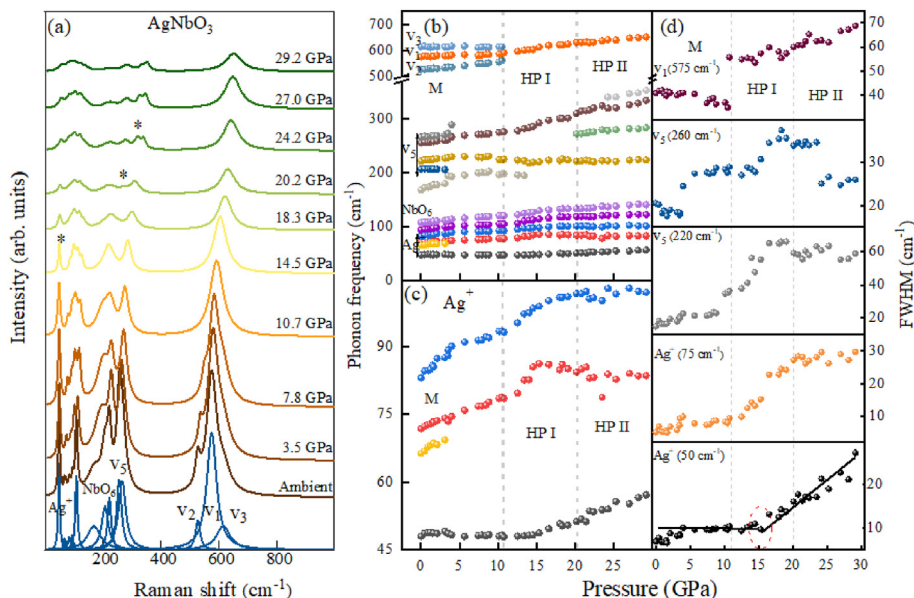


Fig. 1. (a) Pressure-dependent Raman spectra of AgNbO₃, where the phonon assignment at atmospheric pressure are shown on the bottom. The obvious phonon anomalies are indicated by (*). (b)–(c) The frequency evolution of the phonon modes under external stress field (0–29.2 GPa) for AgNbO₃, and the enlarged frequency range on 45–105 cm⁻¹. The dashed lines represent the potential phase boundary. (d) Pressure dependent FWHM of the representative phonon modes of AgNbO₃.

Table 1

Pressure coefficient of main phonon modes for AgNbO₃ ceramics in different high-pressure phases, where the center frequency (cm⁻¹) is confined at the ambient pressure condition.

Mode	$\omega_0(\text{cm}^{-1})$	$\frac{\partial\omega}{\partial p}(\text{cm}^{-1}\cdot\text{GPa}^{-1})$		
	M Phase	M phase	HP I phase	HP II phase
soft mode	49	-0.06	0.47	0.62
ν_5	256	2.00	3.61	2.10
ν_2	526	3.06		
ν_1	577	0.92	4.20	2.59
ν_3	615	-0.10		

Fig. 4 demonstrates the pressure-induced XRD patterns of AgNbO₃ measured at 300 K. The blue shift of diffraction peak and phonon with increasing the pressure, which indicates that the lattice volume can be compressed. Nevertheless, the grain size becomes smaller with the stronger stress control, where the dispersion effect of X-rays is apparent, leading to a decrease in the intensity of the diffraction peaks. Therefore, some peaks cannot be distinguished clearly by *in situ* high-pressure X-ray data, yet the overall structural evolution is distinct. As shown in Fig. 4(a), there is no significant anomaly for AgNbO₃ below 8.5 GPa, in which the (020/200), (220/008) and (134/038) diffraction peaks gradually

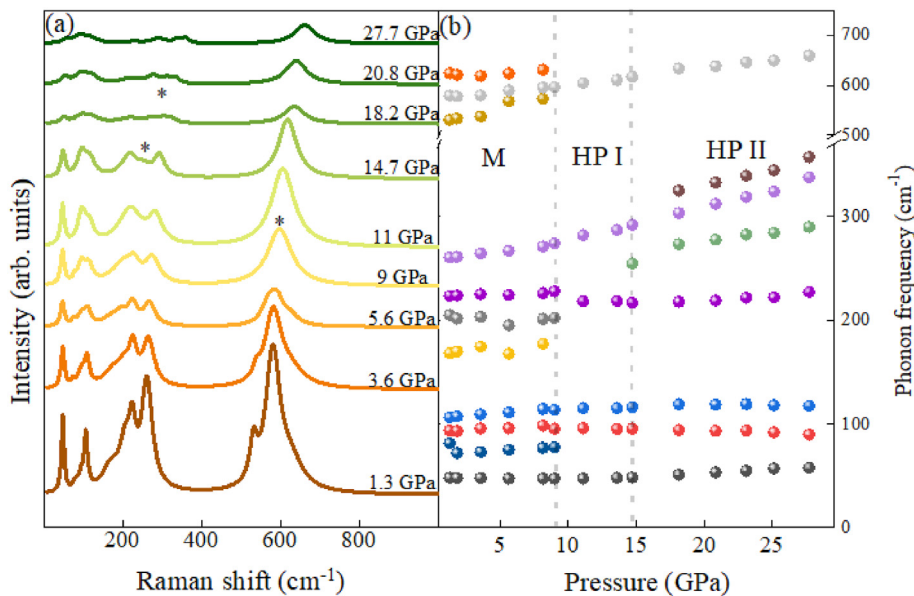


Fig. 2. (a) Pressure-dependent Raman spectra of ANK65. The obvious phonon anomalies are indicated by (*). (b) Frequency evolution of the phonon modes under external stress field (0–27.7 GPa) for ANK65, while the dashed lines represent the potential phase boundary.

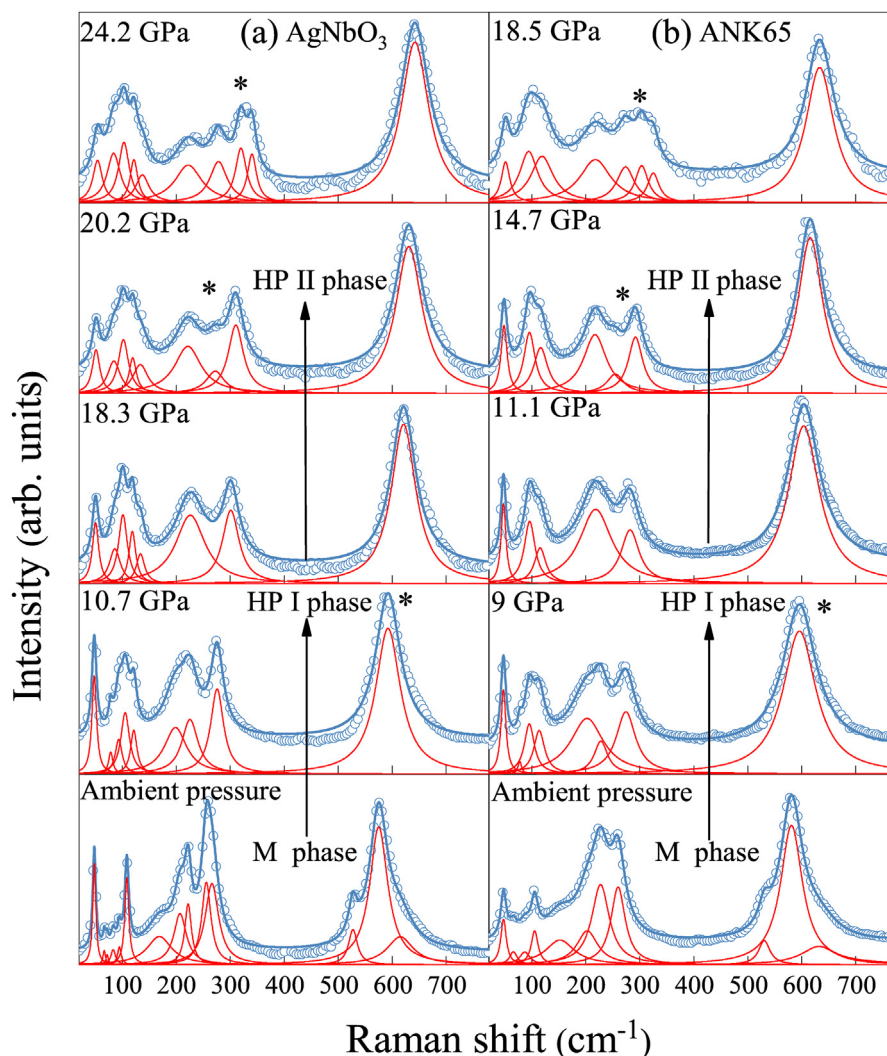


Fig. 3. Representative fitting of Raman spectra peak profiles at five critical pressure for (a) AgNbO_3 and (b) ANK65, respectively, while the obvious phonon anomalies are indicated by (*).

broaden and finally merge into a single peak at 14.7 GPa. It is worth noting that the (220/008) diffraction peak appears a clear splitting phenomenon above 19.9 GPa, which indicates a decrease in structural symmetry. Therefore, the XRD results can provide direct evidence for the pressure-induced lattice transformation, whose critical pressure points were consistent with that obtained by pressure-induced Raman spectra.

In order to determine the unknown crystal structure of AgNbO_3 in theory, the unbiased crystal structure search technique is implemented in the CALYPSO [24], which has succeeded in solving the crystal structures of numerous and diverse materials under high pressure [25]. We have performed an extensive structure search for AgNbO_3 at the pressure of 10 and 20 GPa, while the most stable or metastable structures were determined based on the global minimization of the free energy surface. Besides the known experimental structures, the orthorhombic structure with the $C222_1$ space group and the monoclinic structure with the $P2_1$ space group was successfully observed at 10 and 20 GPa. To verify the theoretical predictions, we performed a Rietveld fit with the Le Bail method to the XRD data. The experimental results are in good agreement with the predicted $C222_1$ space group as well as the $P2_1$ space group, as shown in Fig. 4(b). Therefore, the HP I and HP II

phase may belong to $C222_1$ and $P2_1$ space group, respectively, which were obtained by a joint theoretical prediction and experimental exploration of AgNbO_3 under high pressure. The lattice parameters of refined $C222_1$ and $P2_1$ structure were summarized in Table 2.

The structural transformation of the AFE/FE phase has been focused on two main aspects: (a) whether the continuous structure transitions are related to the displacive-type characterized by soft mode or an order-disorder type with a central peak; (b) whether the PE phase can be realized at ambient temperature under the control of high pressure. It has been proven that AgNbO_3 will undergo a sequential structure transformation of $M_1 \xrightarrow{340\text{K}} M_2 \xrightarrow{540\text{K}} M_3 \xrightarrow{626\text{K}} O_1 \xrightarrow{634\text{K}} O_2 \xrightarrow{660\text{K}} T \xrightarrow{852\text{K}} C$ under the action of the thermodynamic field [11]. The M_2 and M_3 phases are the AFE ones, while the O, T, and C phases belong to the PE ones. There still exist controversy on the structure of M_1 phase, the M_1 is generally considered to possess weak ferroelectricity [17,26,27]. In addition, a sharp dielectric response appears due to partial freezing of the polar Nb^{5+} shift when approaching freezing temperature (T_f) on 440 K, while the T_f transition actually originates from a structure transformation between a nonpolar phase and a weakly polar phase reported by Tian *et al.* [28] It is well known that

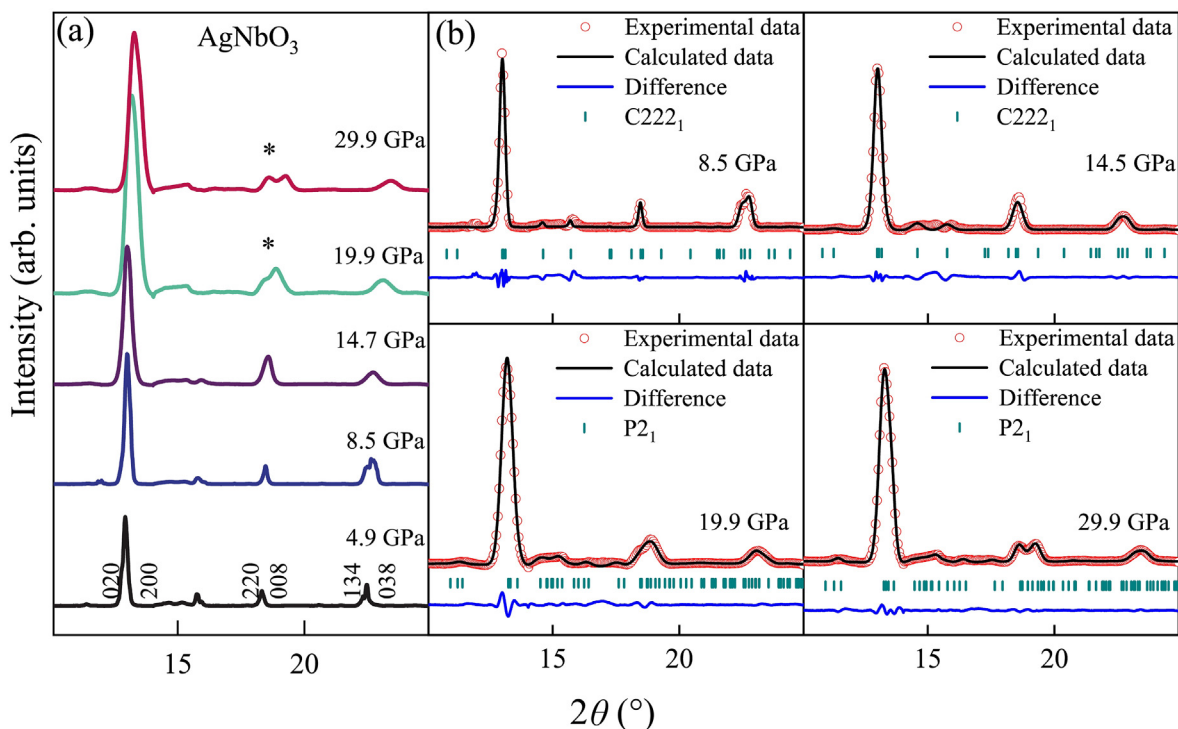


Fig. 4. (a) Pressure dependence of angle-dispersive XRD spectra for AgNbO_3 at ambient temperature, while the obvious anomaly behavior are indicated by (*). The Rietveld refinement patterns via the Le Bail method in terms of the $C222_1$ mode and the $P2_1$ mode under pressure.

Table 2

Lattice parameters of refined $C222_1$ and $P2_1$ structure.

Space group	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$
$C222_1$	5.451	6.336	5.419
$P2_1$	5.343	6.218	5.233

the transformation of the lattice structure under external fields is highly likely to exhibit the anomalous lattice phonon behavior, while the temperature-dependent phonon evolution behavior of AgNbO_3 can be considered as a reference to reveal the pressure-induced phase transitions. The temperature-dependent Raman spectra of AgNbO_3 were displayed in Fig. 5(a). Due to the anharmonic effect on the thermal expansion of the lattice, the phonon frequency gradually decreases with increasing the temperature. The phonon frequencies of main phonon modes shown in Fig. 5(b) exhibit different slopes in different temperature regions, which are related to lattice transitions between M_1 - M_2 - M_3 -O phases. Otherwise, there also exist anomalous shifts in ν_1 and ν_5 phonon near the T_f transition temperature in our temperature-dependence Raman spectra, which may be caused by the transformation between the weakly ferroelectric and antiferroelectric phases. The representative fitting of Raman spectra peak profiles at critical temperature for AgNbO_3 were shown in Fig. 5(c)–(h). It is noteworthy that the phonon mode around 50 cm^{-1} was identified as the soft mode under temperature changes [23]. The soft mode has disappeared at 640 K, which has been considered to be a significant mark of structural transitions. The evolution of Raman spectra during the structure transition from the M_3 to O is depicted in Fig. 5(f)–(h), while the annihilation of soft mode has been revealed clearly, originated from the behavior of the phonon mode at the Brillouin zone boundary. However, the frequency of soft mode is still not zero at the critical temperature, which is typical of a first-order phase transition. The order parameter will jump from zero to a finite

value, which is the sudden appearance of the atomic static displacement. The structure of AgNbO_3 undergoes an AFE ($a^-b^-c^+$ / $a^-b^-c^-$) – PE ($a^0b^-c^+$) transition under the modulation of the temperature field, in which the Nb ions are displaced to form a dipole moment and the antiferroelectric state appears during the transition. The strong structural disorder by oxygen octahedra is dominated in the PE phase, while the displacement of Nb is proposed to be responsible for the antipolar characteristics of the AFE phase [29,30]. The significant annihilation of several phonon modes exhibits an improvement in structural symmetry during the structural transition, while a similar phenomenon does not occur during the pressure-induced process. A successive phase transition ordering [M – HP I – HP II] has been observed in the pressure range of 0–30 GPa, yet the intrinsic structural transition mechanism is still unknown. The successive structure transitions of AgNbO_3 under the thermodynamic field were associated with the displacive-type characterized, whereas the appearance of the PE one was accompanied by the annihilation of the soft mode. Despite the fact that Raman spectra of high-pressure phase are not analogous to those of the high-temperature or low-temperature phases, the mechanisms of lattice transformation are comparable. The distance between atoms decreases with compression, a slight contraction in volume necessarily involves a relative movement of atomic positions. It is worth noting that the structural transitions of AgNbO_3 under the stress field are also related to the behavior of the soft mode despite the absence of phonon annihilation at 50 cm^{-1} . Moreover, we also inferred the existence of two mechanisms for the pressure-induced phase transitions of AgNbO_3 . The structure transformation from M to HP I phase is mainly reflected in the abnormal frequency shift of cations and the merging of ν_1 , ν_2 and ν_3 vibrational modes, while the transition from HP I to HP II phase is accompanied by the splitting of ν_5 phonons. Therefore, the effect of pressure on lattice structure is a joint effect of cation and oxygen octahedron at low pressure zone, while the distortion of oxygen

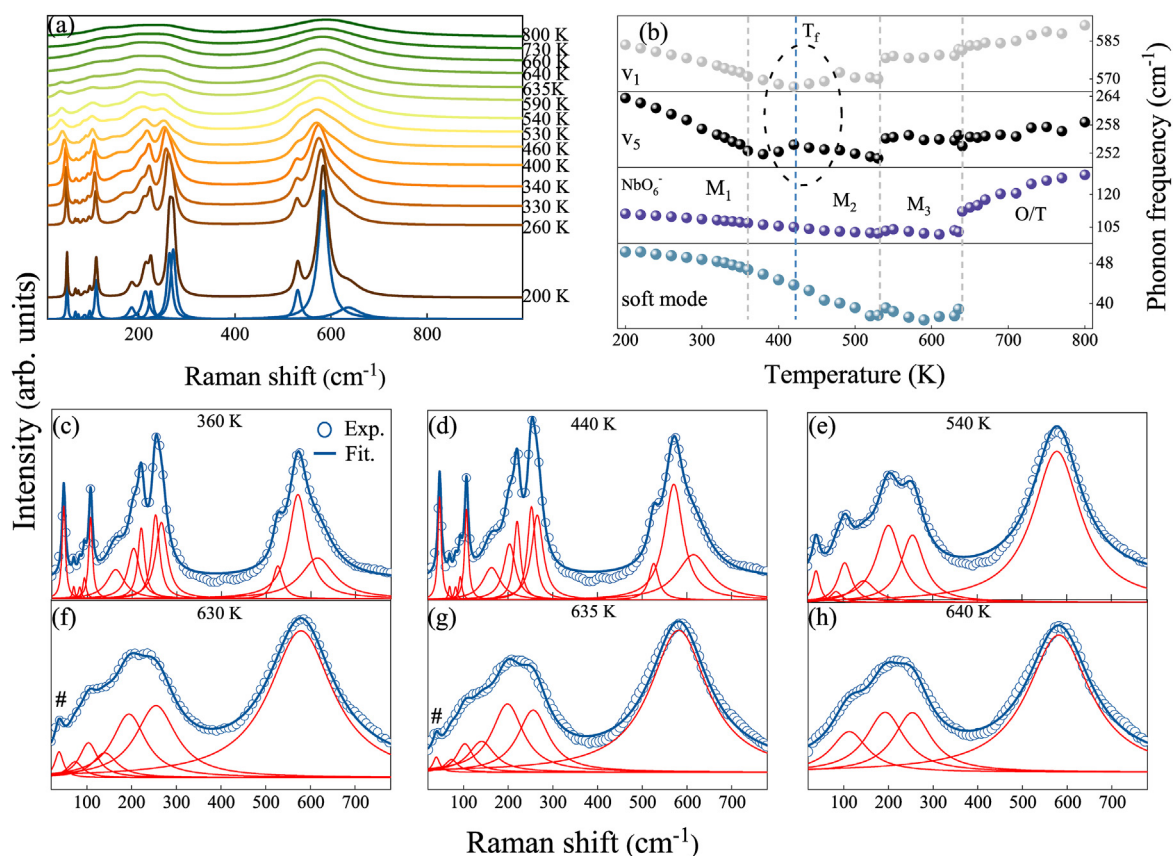


Fig. 5. (a) Temperature dependent Raman spectra of AgNbO₃. Bottom displays the fitting process for corresponding multi-Lorentz at 200 K. (b) The frequency evolution of the main phonon modes under thermodynamic field (200–800 K) for AgNbO₃. The dashed lines represent the potential phase transition boundary under the control of temperature, while the corresponding Raman experimental (dots) and the fitting (solid lines) spectra at critical temperature were displayed in (c)–(h), respectively. Note that the soft mode behavior are indicated by (#).

octahedron is dominated at high pressure.

Furthermore, whether can AgNbO₃ achieve the PE phase at ambient temperature under pressure? Combined with the temperature-dependent Raman spectra, we can reveal that the successive structural transitions of AgNbO₃ are displacive-type, while the soft mode of AgNbO₃ has no Raman-active in the PE phase. However, there was no annihilation of the soft mode during the pressure-induced structural transformation. Therefore, we believe that the PE phase of AgNbO₃ cannot be induced at ambient temperature under the control of high pressure. Moreover, the critical temperature T_c will decrease with the pressure in the displacement-type FE-PE transition, in which the disappearance of the soft mode at T_c was the consequence of the Coulomb force canceling out the short-range force. The frequencies of the soft modes in the center of the Brillouin zone can be obtained by the harmonic approximation: $\omega_{z,c}^2 \propto f_s - f_l$, where $\omega_{z,c}$, f_s , and f_l represent the frequencies of the soft modes in the center of the Brillouin zone, short-range interaction, and long-range interaction, respectively [12,31]. The long-range interactions occur at distances where the electron wave functions no longer overlap, while the short-range interactions only operate when the electron wave functions overlap. It is noteworthy that decreasing the inter ionic distance (r) by pressure will increase the short-range interaction ($\sim r^{-10}$) much more dramatically than the long-range interaction ($\sim r^{-3}$). The temperature dependence of ω can be summarized as the following expressions: $\omega^2 = K(T - T_c)$. Since K is a positive constant, T_c will decrease as the pressure increases at a constant temperature. However, the phonon behavior in the boundary of the Brillouin

zone is significantly different. According to the analytical results of the rigid ion model and shell model calculations, Yoshimitsu *et al.* have found that the phonon in the boundary of the Brillouin zone was stable by long-range interactions and unstable by negative short-range interactions [32]. Therefore, the frequencies of the soft mode in the boundary of the Brillouin zone can be obtained by the harmonic approximation: $\omega_{z,b}^2 \propto f_l - f_s$. The f_l interaction exhibits a weak pressure dependence than the SR interaction. T_c will increase with increasing the pressure. Fig. 6 depicts the variable temperature dependent Raman spectra of AgNbO₃ under 2 GPa and 4 GPa pressure, respectively, while the evolution of the main phonons shows a similar trend to that at ambient pressure. However, the annihilation of the soft mode still does not occur under pressure as the temperature increased to 800 K, due to the increasing temperature of T_c . Accordingly, we give a pressure and temperature phase diagram of AgNbO₃ ceramics displayed in Fig. 7, which the pressure enhances the critical temperatures of structure transitions from AFE phase to PE phase. Therefore, the AFE-PE phase boundary induced by pressure-temperature should have a positive slope for AgNbO₃. The PE phase cannot exist at ambient temperature considering the evolution of soft mode and the decrease of structural symmetry, which also explains the fact that the pressure-induced annihilation behavior for soft mode on PbTiO₃ system [33] was not observed in AgNbO₃. It is worth noticing that the annihilation of soft modes does not mean that the structure enters the PE phase, for example, soft mode annihilation was also observed during the AFE/FE transition in AgNbO₃-LiTaO₃ ceramic [23]. The soft mode annihilation generally corresponds to a

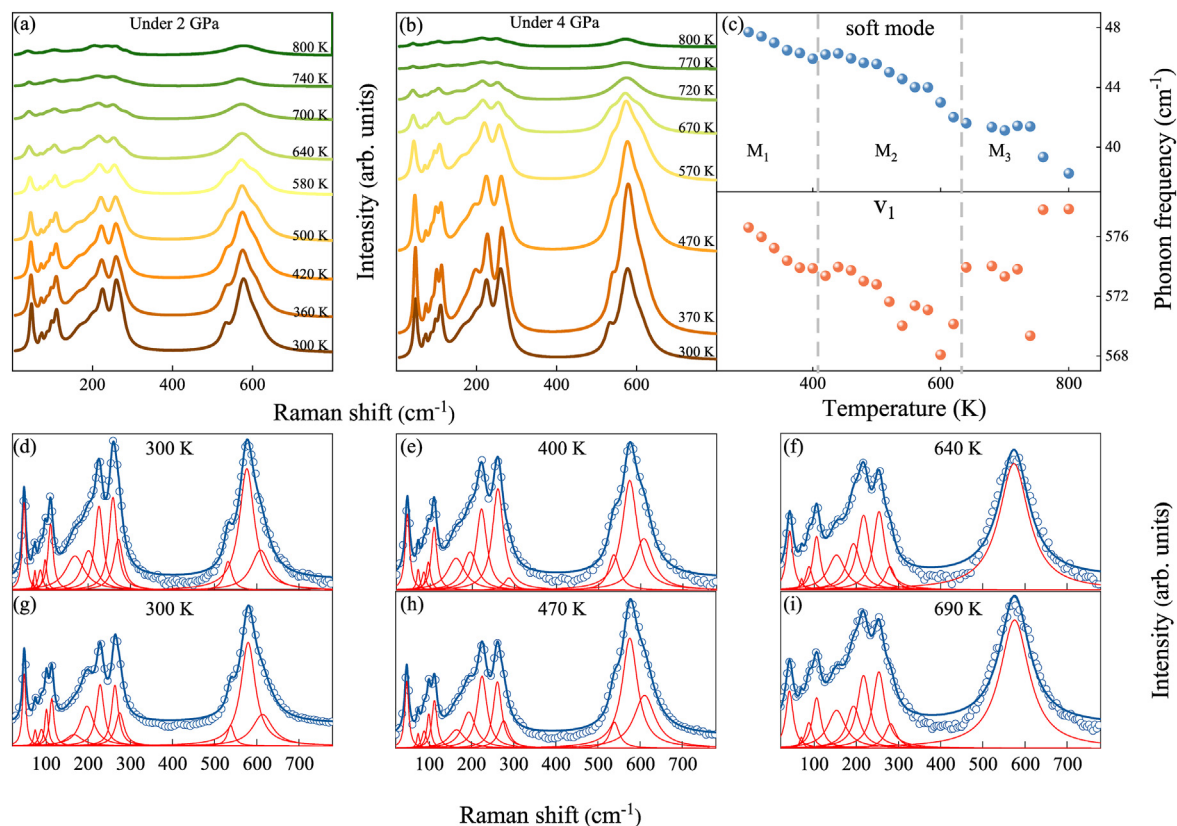


Fig. 6. Temperature dependent Raman spectra of AgNbO_3 under 2 GPa pressure (a), under 4 GPa pressure (b). (c) The frequency evolution of the phonon modes under temperature at 2 GPa for AgNbO_3 . Representative Lorentzian-shape convolutions of Raman spectra at three critical temperature under 2 GPa pressure (d–f) and 4 GPa pressure (g–i), respectively.

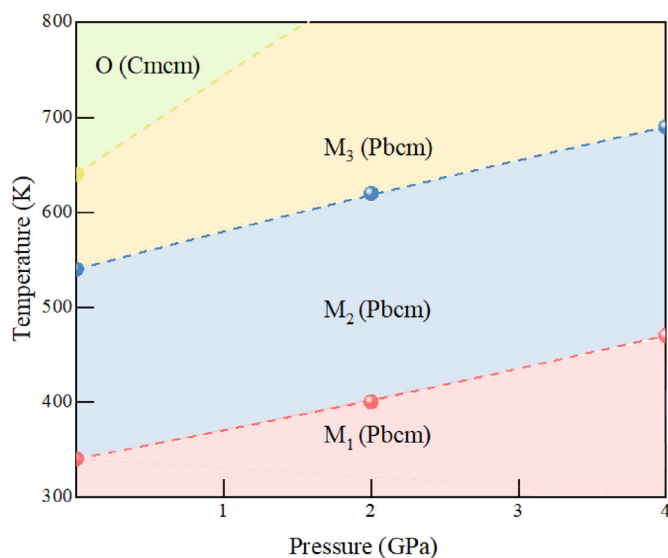


Fig. 7. A pressure and temperature phase diagram of pure AgNbO_3 ceramics.

structural symmetry transformation, while the details structure information needs to be determined in conjunction with other experimental and theoretical evidence.

The transition from the HP I to the HP II phase has been obtained by pressure-induced Raman spectra and XRD, while the origin of the HP I – HP II phase transition has not been discussed yet. The ν_5 phonon and the (200/020) diffraction peak exhibit splitting as the

pressure lifts, accompanying with the structure transformed from the $C222_1$ phase to the $P2_1$ phase. A similar phonon splitting phenomenon occurred in the component-dependent $\text{PbZr}_{1-x}\text{TiO}_3$ system, which the lattice structure was transitioned from rhombohedral to monoclinic phase as increasing the components of PbTiO_3 [34]. Furthermore, Y. Kobayashi *et al.* have discovered the peak-splitting phenomenon of (200) for AFE PbZrO_3 in the stress field [35], demonstrating the orthorhombic-monoclinic phase transition. These structural transitions from the high-symmetry to the low-symmetry phase could be caused by pressure-induced covalency, where structural instability is associated with non-classical short-range interactions. Kornev *et al.* pointed out that the d-state of the B-site atoms is responsible for comprehending the high-pressure structural instability [36]. The Nb 3d states under high pressure will hybridize with O 2s orbitals, which will lead to a local repulsion between overlapping charge densities. On one hand, this repulsive interaction will dissipate part of energy. On the other hand, the repulsive forces will be compensated by the hybridization in the generated bond state. Therefore, the atoms could be distorted under the competition of these two interactions, contributing to the lattice transition at high pressures. Cohen claims that the covalent interactions break the balance between Coulomb interactions supporting ferroelectric distortions and short-range interactions supporting undistorted high-symmetry structures [37,38]. Due to covalent interactions, for perovskite structures, either FE or AFE should be FE (not PE) ones at sufficiently high pressures, although high-pressure ferroelectricity may be intrinsically different from conventional ferroelectricity. Fig. 8 displays the overview of the structural evolution for AgNbO_3 with increasing the pressure. AgNbO_3 is an orthorhombic AFE-dominated

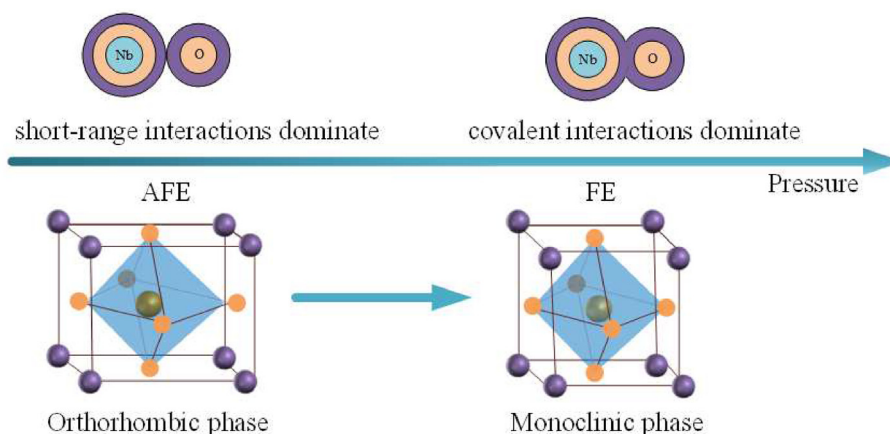


Fig. 8. Overview of the structural evolution for AgNbO_3 with increasing the pressure.

ferrielectric phase at room temperature and pressure with soft mode characteristics exhibiting displacive structural transitions. As the pressure increases, the distance between the atoms gradually decreases, resulting in the short-range interatomic forces acting much more than the long-range Coulomb forces. The increasing pressure also caused the blue shift for the soft mode phonon without the annihilation phenomenon, which signifies that the PE phase cannot exist at ambient temperature. The distance between atoms decreases further as increasing the pressure further. The Nb 3d and O 2s orbitals are hybridized leading to distortion of the lattice structure, inducing the structural transition from the AFE phase to the high-pressure FE phase.

4. Conclusion

In conclusion, we have firstly investigated the pressure dependent structural transformation and the lattice dynamics of AgNbO_3 ceramics. A sequential phase transition orderings $M - \text{HP I} - \text{HP II}$ have been obtained by studying pressure-induced phonon behavior, lattice symmetry evolution as well as the theoretic structure prediction, in which the HP I and HP II phases may belong to the orthorhombic ($C22_1$) and monoclinic ($P2_1$) ones, respectively. Moreover, the lattice transition of AgNbO_3 presents displacive-type characteristics, caused by the cationic and oxygen octahedral distortion. At the same time, the short-range interatomic interaction and long-range Coulomb forces in AgNbO_3 lattice under the external pressure control has been discussed. The structural instability is associated with the covalent interactions under the certain pressure. The work would provide new insight for understanding structure of AgNbO_3 , and gives a distinct guide for exploring more lattice dynamics behavior for AFE perovskites in the external stress fields.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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