Temperature- and pressure-induced structural transformations in PbTiO₃-Bi*Me*O₃ ferroelectric single crystals

Dissertation

Zur Erlangung des Doktorgrades an der Fakultät für Mathematik, Informatik und Naturwissenschaften Fachbereich Erdsystemwissenschaften der Universität Hamburg

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Hamburg, 2024

Fachbereich Erdsystemwissenschaften

Datum der Disputation:

04.09.2024

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Abstract

Perovskite-type ferroelectric materials with the general formula ABO₃ are essential for a wide range of technological applications. Several industries, including aerospace, automotive, and energy sectors, are experiencing a rising demand for ferroelectric materials that exhibit high piezoelectricity and maintain their stability under extreme conditions.

PbTiO₃-Bi*Me*O₃ ferroelectric systems, where *Me* can be either a single trivalent cation or a mixture of cations with an average valence of 3+, have attracted increasing attention over the past years due to their outstanding piezoelectric properties and high Curie temperatures. However, the influence of the substitutional disorder on the processes occurring at different length scales in PbTiO₃-Bi*Me*O₃ solid solutions is still not fully understood. Particularly high-pressure studies, which can provide a more comprehensive insight into the chemically-induced local elastic strains and the associated ferroic distortions, are very limited for these systems.

To better understand the effect of partial substitution at the A and B sites on the crystal structure and atomic dynamics of the PbTiO₃-Bi*Me*O₃ systems, two single-crystal compounds, $0.92PbTiO_3$ - $0.08Bi(Zn_{0.5}Ti_{0.5})O_3$ and $0.83PbTiO_3$ - $0.17Bi(Mg_{0.5}Ti_{0.5})O_3$, were thoroughly analyzed by temperature- and pressure-dependent polarized Raman scattering experiments as well as by synchrotron x-ray diffraction experiments conducted at ambient conditions. PbTiO₃ was used as a reference end-member material.

This thesis demonstrates for the first time that local non-tetragonal polar distortions play a major role in both the pressure- and temperature-induced phase transitions of PbTiO₃-Bi*Me*O₃ compounds. Furthermore, the Raman scattering data reveal that the chemical nature of the *Me* cation significantly influences the structural transformations induced by variations in temperature and pressure.

For $0.92PbTiO_3$ - $0.08Bi(Zn_{0.5}Ti_{0.5})O_3$, the partial substitution of Zn^{2+} for Ti^{4+} increases the resistance of the tetragonal matrix to rising pressure and temperature, preserving the tetragonal phase over a broader pressure and temperature range relative to PbTiO_3. In contrast, for $0.83PbTiO_3$ - $0.17Bi(Mg_{0.5}Ti_{0.5})O_3$, Mg^{2+} disturbs the coupling of the tetragonally distorted TiO_6 octahedra and promotes the expansion of local non-tetragonal polar distortions in the tetragonal matrix. The partial substitution of $0.17Bi(Mg_{0.5}Ti_{0.5})O_3$ for PbTiO_3 induces a structural instability at lower pressures relative to PbTiO_3. In addition, both the temperature and pressure dependences of the Raman modes reveal an enhancement of order-disorder phenomena for this compound.

Both solid solutions exhibit a local-scale doubling of the perovskite structure, which is enhanced with increasing pressure and temperature.

Zusammenfassung

Ferroelektrische Werkstoffe mit Perowskitstruktur (ABO₃) sind heutzutage unerlässlich für die Automobil-, Luft- und Raumfahrt-, und die Energieindustrie. Der Bedarf an ferroelektrischen Stoffen, die hohe Piezoelektrizität aufweisen und unter extremen Bedingungen stabil bleiben, nimmt stetig zu.

Dabei wird das Interesse an den ferroelektrischen Mischkristallsystemen mit der Zusammensetzung PbTiO₃-Bi*Me*O₃, wobei *Me* ein einzelnes dreiwertiges Kation oder eine Mischung von Kationen mit einer durchschnittlichen Wertigkeit von 3+ sein kann, aufgrund ihrer herausragenden piezoelektrischen Eigenschaften und hohen Curie Temperaturen immer größer. Jedoch ist der Einfluss der chemischen Substitution auf die Prozesse, die in PbTiO₃-Bi*Me*O₃-Mischkristallen auf verschiedenen Längenskalen auftreten, trotz intensiver Forschung noch nicht hinreichend verstanden. Insbesondere fehlen für diese Mischkristalle Hochdruckstudien, die einen umfassenderen Einblick in die lokalen elastischen Spannungen und die damit verbundenen ferroischen Verzerrungen ermöglichen können.

Um den Einfluss der chemischen Substitution an den A- und B-Plätzen auf die Kristallstruktur und auf die atomare Dynamik der PbTiO₃-Bi*Me*O₃ Mischkristalle besser zu verstehen, wurden temperatur- und druckabhängige Ramanstreuungsmessungen sowie Einkristall-Röntgenbeugungsmessungen unter Raumtemperaturbedingungen an den ferroelektrischen Einkristallen 0.92PbTiO₃-0.08Bi(Zn_{0.5}Ti_{0.5})O₃ und 0.83PbTiO₃-0.17Bi(Mg_{0.5}Ti_{0.5})O₃ durchgeführt. Dabei diente PbTiO₃ als Referenzmaterial.

Diese Dissertation zeigt zum ersten Mal, dass lokale, nicht-tetragonale polare Verzerrungen eine wesentliche Rolle bei den durch Druck und Temperatur induzierten Phasenübergängen von PbTiO₃-Bi*Me*O₃-Mischkristallen spielen. Darüber hinaus wird nachgewiesen, dass die chemischen Eigenschaften des *Me*-Kations einen starken Einfluss auf die temperatur- und druckabhängige Strukturumwandlungen in PbTiO₃-Bi*Me*O₃ Mischkristallsystemen haben. Die Substitution von Zn²⁺ für Ti⁴⁺ in 0.92PbTiO₃-0.08Bi (Zn_{0.5}Ti_{0.5})O₃ erhöht den Widerstand der tetragonalen Matrix gegen steigenden Druck und steigende Temperatur, wodurch die tetragonale Phase über einen breiteren Druckund Temperaturbereich im Vergleich zu PbTiO₃ erhalten bleibt. Im Gegensatz dazu, stört Mg²⁺ die Kopplung der tetragonal verzerrten TiO₆-Oktaeder und fördert lokale, nicht-tetragonale Verzerrungen in der tetragonalen Matrix von 0.83PbTiO₃-0.17Bi(Mg_{0.5} Ti_{0.5})O₃. Die Substitution von 0.17Bi(Mg_{0.5}Ti_{0.5})O₃ für PbTiO₃ führt, im Vergleich zu PbTiO₃, bereits bei einem niedrigeren Druck zu einer strukturellen Instabilität. Darüber hinaus zeigen sowohl die Temperatur- als auch die Druckabhängigkeiten der Raman-Moden dieses Mischkristalls eine Zunahme der Ordnungs-Unordnungsprozesse. Beide Mischkristalle zeigen eine Verdopplung der Perowskitstruktur auf lokaler Ebene, die sowohl mit steigendem Druck als auch mit steigender Temperatur verstärkt wird.

Motivation

Ferroelectrics are a fundamental class of functional materials characterized by a spontaneous electric polarization, switchable through the application of an external electric field (Jaffe et al., 1971). Ferroelectric materials are a subset of piezoelectrics, meaning they can transform mechanical stress into electrical energy, as well as of pyroelectrics, meaning they can convert temperature variations into electrical energy. Ferroelectrics are key components for functional devices, such as sensors, energy harvesting systems, medical instruments, and ferroelectric RAM (Moulson and Herbert, 1990; Scott, 2000; Callister and Rethwisch, 2007; Zhang et al., 2017; Yang et al., 2018; Wang et al., 2021; Tsikriteas et al., 2021).

Over the last few decades, the most popular ferroelectric has been $Pb(Zr_{1-x}Ti_x)O_3$ (PZT), a perovskite-type solid solution with exceptional dielectric and electromechanical properties (Jaffe et al., 1971; Guo et al., 2000; Shrout and Zhang, 2007). However, increasing environmental and safety concerns regarding the use of lead, along with a rising demand for piezoelectric materials able to withstand high temperatures and pressures, have motivated the search for a new generation of non-toxic lead-free or low-lead ferroelectrics (Eitel et al., 2001; Baettig et al., 2005; Grinberg et al., 2005; Shrout and Zhang, 2007; Damjanovic et al., 2010; Datta et al., 2015; Acosta et al., 2017).

Recently, there has been a growing interest in the bismuth-based PbTiO₃-Bi*Me*O₃ ferroelectric solid solutions, which can maintain superior dielectric and piezoelectric properties up to high operating temperatures (Eitel et al., 2001; Eitel et al., 2002; Grinberg and Rappe, 2007; Chen et al., 2012; Datta et al., 2017a: Datta et al., 2017b; Margaritescu et al., 2020). The PbTiO₃-Bi*Me*O₃ binary systems belong to the perovskite-type complex oxides with the general formula ABO₃. Their structure is characterized by a three-dimensional framework of corner-sharing BO₆ octahedra forming a cavity for the A cation and can accommodate a wide variety of cations at both the A and B sites, facilitating the optimization of specific properties (Scott, 2007). At the B site, *Me* can be a single trivalent cation (e.g. In^{3+} , Sc³⁺, Fe³⁺) or a combination of cations with an average valence of 3+ (e.g. Mg_{0.5}Ti_{0.5}, Zn_{0.5}Zr_{0.5}, Ni_{0.5}Ti_{0.5}). The nature of the *Me* element significantly influences physical characteristics such as Curie temperature, tetragonal strain, magnetic properties, thermal expansion, net polarization, and struc-

tural stability (Eitel et al., 2001; Grinberg et al., 2002; Kreisel et al., 2009). Furthermore, PbTiO₃-Bi*Me*O₃ solid solutions often possess a morphotropic phase boundary, which is a bridging region between the two end-member phases characterized by enhanced piezoelectric properties (Ahart et al., 2008).

Variations in the three main external thermodynamic parameters, temperature (T), pressure (*p*), and electric field (**E**), can induce substantial changes to the structure and properties of a ferroelectric material. A category of transformation processes with significant scientific and technological importance are ferroelectric-to-paraelectric phase transitions, which result in the loss of the ferroelectric properties of the material (Jaffe et al., 1971). So far, most studies concerning PbTiO₃-BiMeO₃ ferroelectrics focus on the structural modifications induced by the chemical substitution and/or the influence of temperature and electric field. However, high-pressure studies on lead-based relaxor ferroelectrics have shown that elastic stress can also alter the energetic balance between different phases in ferroelectric materials by disturbing the equilibrium between the short-range repulsive and the long-range attractive forces required for polar order (Cohen, 1992; Samara et al., 1975). In situ high-pressure analyses can also provide a deeper insight into the nature of the local elastic strains induced by substitutional disorder in perovskite-related materials (Welsch et al., 2011; Mihailova et al., 2008; Angel et al., 2005; Kreisel et al., 2009; Hemley and Ashcroft, 1998). Despite this, high-pressure studies of the PbTiO₃-BiMeO₃ systems are scarce and limited only to compounds with a magnetically active B-site cation ($Me = Fe^{3+}$) and multiferroic properties (Comyn et al., 2013; Basu et al., 2016), whereas the high-pressure behavior of 'pure' ferroelectric PbTiO₃-Bi*Me*O₃ compounds is still unexplored.

To better understand the mechanisms of substitution-triggered local structural transformations in PbTiO₃-Bi*Me*O₃ materials, the influence of pressure and temperature on ferroelectric single crystals of (1-x)PbTiO₃-xBiMg_{0.5}Ti_{0.5}O₃ (PT-xBMT) and (1-x)PbTiO₃xBiZn_{0.5}Ti_{0.5}O₃ (PT-xBZT) was comprehensively studied by in situ Raman spectroscopy. So far, most of the experiments on compounds belonging to these systems were conducted on polycrystalline samples (e.g. Randall et al., 2004; Grinberg et al., 2007; Datta et al., 2017a; Jeong and Kim, 2019), which are easier to synthesize than single crystals. However, the study of single crystals has several advantages compared to the study of the corresponding ceramics, as it provides a better understanding of the compositioninduced nanoscale structural inhomogeneities responsible for the macroscopic properties (Schneider et al., 2014; Matsuo and Noguchi, 2022). The choice of the PT-*x*BMT and PT-*x*BZT systems for this study was motivated by their scientific and technological significance. PT-*x*BMT exhibits stable piezoelectric and mechanical properties at elevated temperatures, with a high piezoelectric d₃₃ coefficient (Hu et al., 2009; Chen et al., 2009) and a morphotropic phase boundary in the range $0.60 \le x \le 0.67$, where a composition-induced P4mm - Pm phase transition occurs (Upadhyay and Singh, 2015). For low levels of *x*, PT-*x*BMT exhibits near-zero volume thermal expansion (Hu et al., 2009), which makes this system attractive for high-temperature devices, as it maintains its structural stability with increasing temperature. On the other hand, PT-*x*BZT is one of the very few ferroelectric solid solutions which exhibits enhanced tetragonality (*c*/*a*-ratio) and Curie temperature with increasing *x* (Suchomel and Davies, 2005; Grinberg et al., 2007), attracting interest from both theoretical and technological perspectives (Liu et al., 2022a).

Objectives

Many of the excellent properties exhibited by ferroelectric materials, such as high electromechanical coupling, very high Curie temperatures, and large coercive fields, are related to local-scale processes (Liu et al., 2020; Datta et al., 2018; Liu et al., 2022b). Thus, a central topic in the field of material science is to elucidate how the atomic-level behavior of a material influences its macroscopic properties.

The aim of this doctoral thesis is to provide a better understanding of the competing processes that take place at different time and length scales in solid solution compounds of the PbTiO₃-Bi*Me*O₃ system. For this, the effect of the chemical substitution at the A and B sites in the 0.83PbTiO₃-0.17Bi(Mg_{0.5}Ti_{0.5})O₃ and 0.92PbTiO₃-0.08Bi(Zn_{0.5}Ti_{0.5})O₃ ferroelectric single crystals is investigated by using the prototype ferroelectric PbTiO₃ as a reference end-member compound. The room-temperature crystal structure of the three compounds is studied by synchrotron single-crystal x-ray diffraction. Since phonons act as microscopic driving forces of phase transitions, the temperature and pressure dependence of the atomic dynamics is analyzed in detail by polarized Raman spectroscopy. The in situ Raman scattering experiments facilitate the study of dynamic ferroic structural species and coupling between different cation subsystems (Mihailova et al., 2008; Husson, 1998), revealing local- and mesoscopic-scale processes that precede the temperature- and pressure-induced phase transitions.

Results and Discussion

This section is based on the following articles:

a. I. Margaritescu, Z. Liu, Z.-G. Ye, and B. Mihailova. The role of local non-tetragonal polar displacements in the temperature- and pressure-induced phase transitions in PbTiO₃-Bi*MeO*₃ ferroelectrics. *Scientific Reports* 14, 7106 (2024).
I.M., Z.-G.Y., and B.M. developed the original project. Z.L. and Z.-G.Y. provided the single crystals. I.M. carried out the Raman measurements and analyzed the Raman data.

I.M. and B.M. wrote the manuscript. All authors reviewed and edited the manuscript.

b. **I. Margaritescu**, Z. Liu, T. Malcherek, C. Paulmann, Z.-G. Ye, and B. Mihailova. Pressure- and temperature-induced transformation processes in PbTiO₃-Bi*Me*O₃ ferroelectrics. *Physical Review B* **111**, 144101 (2025).

I.M., Z.-G.Y., and B.M. developed the original project. Z.L. and Z.-G.Y. provided the single crystals. **I.M.** carried out the Raman measurements and analyzed the Raman data. **I.M.**, T.M., C.P., and B.M. carried out the synchrotron XRD experiments. T.M. analyzed the XRD data. **I.M.** wrote the manuscript. All authors reviewed and edited the manuscript.

The PbTiO₃, 0.92PbTiO₃-0.08Bi(Zn_{0.5}Ti_{0.5})O₃ (PT-0.08BZT), and 0.83PbTiO₃-0.17Bi(Mg_{0.5} Ti_{0.5})O₃ (PT-0.17BMT) crystals investigated in this work were synthesized by the flux and the top-cooled solution growth methods (Liu et al., 2017; Liu et al., 2022b). The chemical composition and the homogeneity of the samples were verified by wavelength-dispersive electron microprobe analysis (Margaritescu et al., 2024).

The candidate for the doctoral title (I.M.) has considerably contributed to the development of both the project's concept as well as the strategy for the necessary analyses. I.M performed all in situ high-pressure and high-temperature Raman scattering analyses and was involved in the XRD experiments and their analysis. The papers underlying this cumulative doctoral thesis were prepared by I.M., while the co-authors only revised the text.

3.1 Crystal structure and atomic dynamics at ambient conditions

Single-crystal x-ray diffraction (XRD)

At ambient conditions, PT, PT-0.08BZT, and PT-0.17BMT adopt a perovskite-type ABO₃ structure (Figure 1a) with *P4mm* symmetry. The lattice parameters obtained by single-crystal XRD experiments are given in Figure 1c. The off-centering of the A- and B-site cations from their ideal perovskite positions (Figure 1b) is driven by the hybridization of the Pb²⁺ and Bi³⁺ 6*s* orbitals and the 2*p* orbitals of the surrounding oxygen anions, as well as the coupling of the Ti⁴⁺ 3*d* orbitals with the O²⁻ 2*p* orbitals (Cohen, 1992; Baettig et al., 2005; Grinberg and Rappe, 2007). Furthermore, the nature of the additional *Me* element strongly influences the cationic displacements and coupling processes at both A and B sites.

For PT-0.08BZT, the Zn-O bonding has a strong covalent character due to the hybridization of the 4*s* and 4*p* orbitals of zinc with the 2*p* orbitals of oxygen, which leads to a significant off-centering of the Zn²⁺ cation and further facilitates the coupling between the A- and B-site off-center displacements (Suchomel and Davies, 2005; Grinberg et al., 2007). This is reflected by a slight increase in the tetragonal strain (*c*/*a* -ratio, Figure 1c), as well as in the magnitude of the A- and B-site cation displacements from the corresponding planar oxygen atoms (δ_{Z_A} and δ_{Z_B} , respectively, Figure 1d) of PT-0.08BZT relative to PT. In contrast, for PT-0.17BMT, the Mg-O bonding has an ionic character, and thus, the substitution of Mg²⁺ for Ti⁴⁺ at the B site disturbs the coupling processes between the tetragonally distorted TiO₆ octahedra, modifying the BO₆-network connectivity (Datta et al., 2017a; Margaritescu et al., 2024; Margaritescu et al., 2025). Therefore, the substitution of 0.17BMT results in a reduction of the unit-cell tetragonality, along with a slight decrease in the δ_{Z_A} and δ_{Z_B} values compared to pure PT.



Figure 1: a) Aristotype ABO₃ structure, plotted using VESTA (Momma and Izumi, 2011). The A-site cations (Pb²⁺/Bi³⁺) are 12-fold coordinated by O²⁻ anions, whereas the B-site cations (Ti⁴⁺/Zn²⁺/Mg²⁺) are 6-fold coordinated by O²⁻ anions. b) Sketch of the [001]-displacements of the A- and B-site cations relative to the corresponding oxygen plane (δ_{Z_A} and δ_{Z_B} , respectively). c) Unit-cell parameters and tetragonality (*c/a*-ratio) for PT, PT-0.08BZT, and PT-0.17BMT. d) δ_{Z_A} and δ_{Z_B} for PT, PT-0.08BZT, and PT-0.17BMT.

Raman Spectroscopy

The optical phonon modes at the Brillouin-zone center Γ of the cubic $Pm\bar{3}m$ and the corresponding tetragonal P4mm ABO₃ structures predicted by group theory (Kroumova et al., 2003; Aroyo et al., 2006) are given in Table I. In the ferroelectric P4mm phase, long-range electrostatic forces further split the A₁ and E modes into transverse (TO) and longitudinal (LO) components (Burns and Scott, 1973; Foster et al., 1993). None of the optical modes of the cubic, paraelectric phase is Raman active, whereas all the optical modes of the tetragonal, ferroelectric phase are Raman active. The scattering geometries which allow the observation of the $\Gamma_{Optical}^{P4mm}$ modes in a single crystal, as well as additional information on group-theoretical analysis, are given in Margaritescu et al., 2025.

Table I: Phonon modes at the Γ point of the Brillouin zone in the cubic $Pm\bar{3}m$ and the tetragonal P4mm phases. The irreducible representations of the modes are labeled using the Mulliken symbols (Mulliken, 1955).

Pm3m			P4mm		
Site	Wyckoff position	Phonons	Site	Wyckoff position	Phonons
A	1a	T _{1u}	А	1a	$A_1 + E$
В	1b	T_{1u}	В	1b	$A_1 + E$
0	3c	$2T_{1u} + T_{2u}$	O1	1b	$A_1 + E$
			O2	2c	$A_1 + B_1 + 2E$
Γ _{Total}		$4T_{1u} + T_{2u}$			$4A_1 + 5E + B_1$
$\Gamma_{Acoustic}$		T_{1u}			$A_1 + E$
$\Gamma_{Optical}$		$3T_{1u} + T_{2u}$			$3A_1 + 4E + B_1$

Polarized Raman spectra of PT, PT-0.08BZT, and PT-0.17BMT collected at ambient conditions in the $\bar{x}(yy)x$, $\bar{x}(zy)x$, and $\bar{z}(yy)z$ scattering geometries, where x, y, and z are parallel to the tetragonal [100], [010], and [001] directions, respectively, are shown in Figure 2a. The observed Raman peaks can be classified into three categories:



Figure 2: a) Raman spectra of PT, PT-0.08BZT, and PT-0.17BMT collected at ambient conditions in the $\bar{x}(yy)x$, $\bar{x}(zy)x$, and $\bar{z}(yy)z$ scattering geometries. b) Δ_{nTO} for PT, PT-0.08BZT, and PT-0.17BMT. c) Multicomponent line shape of the A₁(1TO) mode of PbTiO₃ measured in the $\bar{x}(yy)x$ scattering geometry at room temperature.

1. Fundamental P4mm modes.

The assignment of the fundamental $\Gamma_{optical}^{P4mm}$ modes was done in agreement with previous studies on PbTiO₃ (Fontana et al., 1991; Foster et al., 1993). The Raman peaks detected below 200 cm⁻¹ arise from vibrations of the A-site cations against the BO₆ octahedra, the peaks between 200 cm⁻¹ and 480 cm⁻¹ originate mainly from vibrations of the B-site cations, and the peaks above 480 cm⁻¹ are related to internal BO₆ modes involving stretching and bending of the octahedra (Frey and Silberman, 1976; Freire and Katiyar, 1988; Buixaderas et al., 2015; Welsch et al., 2011).

The splitting of the cubic T_{1u}(nTO) modes in the tetragonal phase, described by $\Delta_{nTO} = \omega_{A_1(nTO)} - \omega_{E(nTO)}$, where ω represents the wavenumber and n ranges from 1 to 3, can be used to evaluate the local anisotropy of the AO₁₂ cuboctahedra, the non-centrosymmetry of the BO₆ octahedra and the B-O bond length anisotropy, respectively. The Δ_{1TO} , Δ_{2TO} , and Δ_{3TO} values of PT and PT-0.08BZT (Figure 2b) are comparable, suggesting that the substitution of 0.08BZT does not significantly alter the local anisotropy of the AO₁₂ and BO₆ polyhedra compared to pure PT. On the other hand, the lower values of Δ_{2TO} and Δ_{3TO} for PT-0.17BMT indicate that the substitution of 0.17BMT suppresses the cationic off-centering at the B site and reduces the bond length anisotropy of the BO₆ octahedra. Within the errors, the obtained values are in good agreement with the results yielded by the XRD experiments.

2. Additional Raman peaks observed only in the mixed compounds.

Three additional peaks, labeled as X_1 , X_2 , and X_3 , are observed in the Raman spectrum of PT-0.17BMT near 52 cm⁻¹, 173 cm⁻¹, and 490 cm⁻¹, respectively. For PT-0.08BZT, X_2 has not been detected, whereas X_3 can be resolved only at pressures above 1 GPa. For other PbTiO₃-Bi*Me*O₃ solid solutions, X_1 has been previously ascribed to a new structural state of the A-site cations (Datta et al., 2017a; Margaritescu et al., 2020), whereas X_2 and X_3 have not been reported yet. In analogy to other Pb-based relaxor ferroelectrics (Mihailova et al., 2002; Welsch et al., 2011) and due to their enhancement with x, in this study the X_{1-3} peaks have been assigned to a composition-induced doubling of the perovskite structure, which can be triggered by chemical B-site ordering and/or compatible antiferrodistortive order on the local scale (Mihailova et al., 2002; Maier et al., 2011).

3. Additional Raman peaks observed in all compounds.

For all compounds, the A₁(1TO) phonon mode near ~ 150 cm⁻¹ has an asymmetric multicomponent line shape. In the lowest-energy region of the $\bar{x}(yy)x$ Raman spectrum of PT, four subpeaks can be distinguished (Figure 2c): (i) the highest energy subpeak corresponds to the fundamental A₁ mode, (ii) the two adjacent subpeaks, labeled as P'_{anh} and $P''_{anh'}$ are related to the anharmonic nature of the interatomic potential and have been assigned to transitions between neighboring excited phonon states in the double-well potential (Foster et al., 1993; Cho et al., 2001), and (iii) the lowest energy-subpeak, P_{nonT}, has been ascribed to local non-tetragonal polar distortions, confined to thermodynamically unavoidable crystal-lattice defects (Cho et al., 2001; Margaritescu et al., 2024).

Furthermore, three additional Raman peaks are observed in the highest-energy region of the spectrum, most pronounced in the $\bar{x}(yy)x$ configuration: Y₁, Y₂, and Y₃, near 614 cm⁻¹, 700 cm⁻¹, and 735 cm⁻¹, respectively. For PT and PT-0.0BZT, Y₁ is observed only at higher pressures. The Y₂ and Y₃ peaks have been previously attributed to the symmetrical BO₆ stretching in a doubled perovskite structure (Welsch et al., 2011; Mihailova et al., 2002; Siny and Katiyar, 1998). The presence of these peaks in all compounds, along with their enhancement with increasing *x*, suggest that the partial unit-cell doubling of the three compounds is induced by local-scale antiferrodistortive structural order.

3.2 Pressure-induced structural transformations

The high-pressure Raman experiments were conducted at room temperature using a diamond anvil cell. Polarized Raman spectra were collected in $\bar{x}(yy)x$ and $\bar{x}(zy)x$ scattering geometries up to 12 GPa. A detailed description of the experimental setup is given in Margaritescu et al., 2024 and Margaritescu et al., 2025.

At room temperature, PT undergoes a sequence of pressure-driven phase transitions: $P4mm \xrightarrow{13GPa} R3c \xrightarrow{27GPa} R\bar{3}c$ (Frantti et al., 2018). So far, the high-pressure phases of the mixed compounds have not been determined by XRD.

The pressure evolution of the wavenumber ω , fractional intensity *In*, and full width at half maximum (FWHM) Γ of the Raman modes suggests that for all compounds, multiple structural transformations occur within a wide pressure range, well before

the transition pressure. Moreover, the characteristic pressures at which these structural alterations emerge vary with the type of B-site cation.

The pressure dependence of Δ_{1TO} , which is defined as the wavenumber difference of the A-site localized A₁(1TO) and E(1TO) phonon modes, reveals that the anisotropy of the AO₁₂ polyhedra increases upon hydrostatic compression for all compounds (Figure 5 in Margaritescu et al., 2025). Moreover, for PT-0.17BMT, the effect of the internal elastic fields induced by the partial substitution of 0.17BMT corresponds to the effect of ~2.0 GPa external hydrostatic pressure on the local AO₁₂ anisotropy for PT (Figure 6c in Margaritescu et al., 2025).

The enhancement of P_{nonT} with pressure for all compounds, along with the suppression of the A₁(1TO), P'_{anh} and P''_{anh} modes (Figure 2 and Figure 4 in Margaritescu et al., 2024), indicate that pressure enhances the intrinsic local non-tetragonal polar distortions and suppresses the polar tetragonal displacements, which is consistent with the *P4mm*-to-*R3c* pressure-driven phase transition of PT. Furthermore, for PT-0.08BZT, the substitution of 0.08BZT slows down the development of the non-tetragonal distortions under pressure compared to pure PT. Conversely, for PT-0.17BMT the non-tetragonal distortions become dominant at a lower pressure.

With increasing pressure, P_{nonT} softens and for PT it exhibits a plateau-like minimum between 10.4-11.7 GPa. This, along with the minimum of $\omega_{E(1TO)}(p)$ observed at 10.4 GPa, reveal that significant pressure-induced structural rearrangements take place before the *P4mm*-to-*R3c* phase transition. For PT-0.08BZT, the minimum of E(1TO) shifts to 11.6 GPa and P_{nonT} does not show a minimum in the measured range, whereas for PT-0.17BMT the minimum of E(1TO) is observed already at 6.2 GPa. Furthermore, the composition-induced peak X₁ observed in PT-0.08BZT and PT-0.17BMT is enhanced with pressure and begins to soften around 8 GPa, which indicates that the related structural distortions evolve with pressure and are significantly involved into the pressureinduced transformation processes.

The evolution of the phonon modes related mainly to the B-site cation subsystem, E(2TO) and A₁(2TO), involving the decrease of Δ_{2TO} and $ln_{E(2TO)}$ with increasing pressure, reveal a gradual reduction of the off-centering of the B-site cations upon hydrostatic compression (Figure 7a and S3 in Margaritescu et al., 2025). An increased structural instability of the B-site cation subsystem is observed at 5.4 GPa and 6.3 GPa for PT and PT-0.08BZT, respectively. For PT-0.08BZT, a minimum in $\omega_{2(TO)}(p)$ occurs at 11 GPa, at a higher pressure than for pure PT (10.4 GPa), which suggests that the presence

of Zn²⁺ hardens the tetragonal cationic off-centering at the B site, enhancing the resistance of the tetragonal matrix to external pressure. Moreover, the values of $\Delta_{2(TO)}(p)$ for PT and PT-0.17BMT reveal that on a local scale, the substitution of Mg²⁺ for Ti⁴⁺ suppresses the tetragonal off-centering of the B-site cations to a degree comparable to an external pressure of ~4 GPa (Figure 7c in Margaritescu et al., 2025).

In the highest energy range of the spectrum, the pressure-induced decrease in $\Delta_{3(TO)}$, which describes the local octahedral anisotropy related to different B-O lengths, indicates that hydrostatic compression gradually reduces the differences in the B-O lengths for all three compounds. However, $\Delta_{3(TO)}(p)$ of PT and PT-0.08BZT are similar in the entire pressure range, whereas the effect of the internal chemical pressure introduced by the substitution of 0.17BMT at atmospheric conditions corresponds to that of an external pressure of ~1.0 GPa for PT (Figure 8c in Margaritescu et al., 2025).

With pressure, the composition-induced peak X_3 observed in PT-0.08BZT and PT-0.17BMT is enhanced, whereas the additional Raman peaks Y_2 and Y_3 , which are observed for all compounds and have been ascribed to a local-scale doubling of the unit cell, do not gain significant fractional intensity throughout the measured pressure range (Figure 8d and S4 in Margaritescu et al., 2025). This suggests that the intrinsic structural defects within the PT matrix are more susceptible to chemically induced internal local elastic stress fields than to external pressure.

3.3 Temperature-induced structural transformations

At atmospheric pressure, PT, PT-0.08BZT, and PT-0.17BMT undergo a ferroelectric-toparaelectric temperature-driven phase transition from P4mm to $Pm\bar{3}m$ at ~ 763 K (Burns and Scott, 1970), 805 K (Suchomel and Davies, 2005), and 810 K (Randall et al., 2004), respectively.

Polarized Raman spectra of PT, PT-0.08BZT, and PT-0.17BMT were collected in the $\bar{x}(yy)x$, $\bar{x}(zy)x$, and $\bar{z}(xx)z$ scattering geometries between 200 K and 1000 K. The experimental setup is described in Margaritescu et al., 2024.

Similar to other ferroelectric perovskite-type oxides, all three compounds show forbidden Raman scattering above the Curie temperature (T_C) (Figures 3-6) revealing the presence of local polar distortions and order-disorder phenomena in the cubic, paraelectric phase (Sicron et al., 1994; Colomban and Slodczyk, 2009; Margaritescu et al., 2018; Margaritescu et al., 2020). Moreover, above T_C , the parallel-polarized ($\bar{x}(yy)x$)



Figure 3: a) Raman spectra of PT, PT-0.08BZT, and PT-0.17BMT collected in the $\bar{x}(yy)x$ scattering geometry at selected temperatures. The spectra are vertically offset for clarity. The insets show the enlarged Raman spectra of PT and PT-0.08BZT at 1000 K, respectively. The red arrows mark the Curie temperature of each compound. b) Depolarization ratio for PT, PT-0.08BZT, and PT-0.17BMT. The dashed vertical lines mark the Curie temperature. The blue lines represent Boltzmann function fits to the experimental data points. Because of minor variations in the saturation values of I_{depol} obtained from different temperature control stages, only points above 360 K were considered in the Boltzmann fits for PT-0.08BZT and PT-0.17BMT.

Raman scattering is much stronger than the crossed-polarized ($\bar{x}(yz)x$) Raman scattering, as can be seen from the depolarization ratio shown in Figure 3b. This could be an indication that the system behaves as a dipole-glass (Datta et al., 2020).

The temperature dependence of the depolarization ratio $I_{depol} = I_{\bar{x}(yz)x} / I_{\bar{x}(yy)x}$ (Figure 3b), where $I_{\bar{x}(yz)x}$ and $I_{\bar{x}(yz)x}$ are the integrated intensities of the Raman peaks measured in the corresponding scattering geometries, was fitted with a Boltzmann growth function $I_{depol} = (A_1 - A_2)/(1 + e^{(T - T_0)/\delta T})$, which describes the evolution of incipient polar displacements into ferroelectric domains (Mihailova et al., 2020). A1 and A2 represent the saturation values before and after the phase transition, respectively, T_0 is the inflection point, and δT represents the rate of the growth process from A₂ to A₁. The T₀ values obtained for PT and PT-0.08BZT, 766(12) K and 808(5) K, respectively, closely match the previously reported Curie temperatures (Shirane et al., 1970, Suchomel and Davies, 2005). For PT-0.17BMT, the obtained T_0 value is 774(4) K. This deviation of T_0 from the $T_C = 810$ K derived from dielectric measurements (Randall et al., 2004) suggests a relaxor-type behavior. A relaxor behavior has been previously reported for PT-0.62BMT (Zhang et al., 2010). This is further supported by the gradual decrease in the overall Raman intensity of PT-0.17BMT while crossing the T_C , in contrast to the abrupt drop observed for PT and PT-0.08BZT (Figure 9 in Margaritescu et al., 2025 and Figure 3a). The slope of the Boltzmann function, $s = (A_1-A_2)/(4\delta T)$, is lower for PT-0.17BMT compared to pure PT and PT-0.08BZT (0.0013(1) versus 0.0024(6) and 0.0025(4), respectively), suggesting that, upon cooling, the development rate of the polar nanoregions is slowed down by the substitution of 0.17BMT.

Similar to the behavior observed under pressure, the $A_1(1TO)$, P'_{anh} and P''_{anh} modes are suppressed upon heating for all compounds, whereas P_{nonT} is enhanced (Figure 2a in Margaritescu et al., 2024). For PT and PT-0.08BZT, the maximum of $l_{P_{nonT}}$ occurs at 85 K lower than the Curie temperature of each compound (Figure 3d and 3e in Margaritescu et al., 2024), which implies significant alterations in the correlation length and/or magnitude of the non-tetragonal polar distortions within the tetragonal matrix already below the phase transition temperature. Moreover, when using $\omega_{P_{nonT}}$ as a microscopic order parameter, the substitution of 0.08BZT changes the character of the developing non-tetrahedral distortions from second-order (PT) towards tricritical (Margaritescu et al., 2024). Conversely, for PT-0.17BMT, the softening rate of P_{nonT} is reduced compared to the other compounds and an even fraction of tetragonal and non-tetragonal polar distortions is observed above 400 K (Figure 3c in Mar-



Figure 4: a) Temperature dependence of the wavenumber and FWHM of X₁, E(1TO), P_{nonT} and A₁(1TO) for PT, PT-0.08BZT, and PT-0.17BMT. The dashed vertical lines mark the Curie temperature of each compound. b) Fractional intensity of the X₁ mode for PT-0.08BZT and PT-0.17BMT. c) Temperature dependence of $\Delta_{1TO} = \omega_{A_1(1TO)} - \omega_{E(1TO)}$.

garitescu et al., 2024), which suggests an enhancement of the order-disorder character of the phase transition. This can be explained by the ionic nature of the Mg-O bond. The B-site $Mg^{2+} \rightarrow Ti^{4+}$ substitution disrupts the correlation between the tetrahedrally distorted TiO_6 octahedra, which facilitates the non-tetragonal local distortions of the A-BO₃ species over a broader temperature range.

The temperature dependence of Δ_{1TO} for PT and PT-0.08BZT (Figure 10c in Margaritescu et al., 2025 and Figure 4c) reveals an abrupt increase in the local anisotropy of the AO₁₂ cuboctahedra around the transition temperature, with a maximum at T_C , suggesting that the incoherent distortions of the AO₁₂ cuboctahedra rearrange to become coherent and evolve into long-range order. On cooling, preexisting off-center displacements within the A-site sublattice of PT begin to couple at ~ 880 K (Margaritescu et al., 2018), as indicated by the minimum of Δ_{1TO} (Figure 4c). For PT-0.08BZT and PT-0.17BMT, Δ_{1TO} gradually decreases upon heating up to 1000 K, indicating that the substitution of Bi³⁺ for Pb²⁺ shifts the beginning of the coupling process of the local A-site cationic displacements towards higher temperatures. For PT-0.08BMT, the maximum of $\Delta_{1TO}(T)$ is smeared out, indicating that the rearrangement of the A-site local dipoles takes place in a wide temperature range below T_C .

Similar to the effect of pressure increase, the composition-induced X₁ mode is enhanced upon heating (Figure 10b in Margaritescu et al., 2025 and Figure 4b), indicating that the corresponding structural distortions evolve with both hydrostatic compression and temperature. Moreover, the behavior of ω_{X_1} changes with *x*. For PT-0.08BZT, the wavenumber of X₁ is constant in a wide temperature range and merges with E(1TO) at T_C . Conversely, for PT-0.17BMT, ω_{X_1} exhibits a soft-mode behavior, with $\omega_{X_1}(T) \propto (T_C - T)^n$, where n =0.41 ± 0.02, which indicates a displacive component involved in the mechanism of the phase transition (Mihailova et al., 2020).

In the second spectral region, the E(2TO) and E(T_{2u}) modes (Figure 11 in Margaritescu et al., 2025 and Figure 5a) arise from off-center displacements of the B-site cations. For PT and PT-0.08BZT, $\Delta_{2TO}(T)$ and $ln_{E(2TO)}(T)$ decrease abruptly when approaching T_C from below (Figure 11 in Margaritescu et al., 2025 and Figure 5b), indicating a reduction of the BO₆ anisotropy due to the suppression of the B cation off-centering. The fitting of $\Delta_{2TO}(T)$ with a Boltzmann function has yielded comparable slopes *s* for PT and PT-0.08BZT ($s_{PT} = 0.29(1)$, with $T_0^{PT} = 734(4)$ K and $s_{PT-0.08BZT} = 0.25(2)$ with $T_0^{PT-0.08BZT} = 797(3)$ K) and a lower value of *s* for PT-0.17BMT ($s_{PT-0.17BMT} = 0.14(3)$, $T_0^{PT-0.17BMT} = 710(20)$ K). This suggests that for PT-0.17BMT, the preexisting off-centered shifts of the



Figure 5: a) Temperature dependence of the wavenumber, FWHM, and fractional intensity for E(2TO), E(T_{2u}), B₁, A₁(2TO), and P_{tilt} for PT, PT-0.08BZT, and PT-0.17BMT. The vertical dashed lines mark the Curie temperature of each compound. b) Temperature dependence of $\Delta_{2TO} = \omega_{A_1(2TO)} - \omega_{E(2TO)}$. The orange lines represent Boltzmann function fits to the data points. Note that above *T_C* (open symbols), the A₁(2TO) mode merges with the E(T_{2u}) mode.



Figure 6: a) Temperature dependence of the wavenumber and FWHM of E(3TO), A₁(3TO), A₁(3LO), Y₁, Y₂, and Y₃ for PT, PT-0.08BZT, and PT-0.17BMT. The vertical dashed lines mark the Curie temperature of each compound. b) Temperature dependence of $\Delta_{3TO} = \omega_{A_1(3TO)} - \omega_{E(3TO)}$.

B-site cations evolve into ferroelectric long-range order at a slower rate compared to the other compounds. For PT-0.17BMT, the E(2TO) and E(T_{2u}) modes could not be resolved above T_C due to their broadening and subsequent overlapping.

In the highest-energy spectral range, the decrease of Δ_{3TO} with increasing temperature (Figure 12 in Margaritescu et al., 2025 and Figure 6b) indicates that temperature gradually reduces the local BO₆ anisotropy caused by variations in B-O bond lengths. The minima of Δ_{3TO} observed for PT and PT-0.08BZT at 800 K and 900 K, respectively, indicate that the distortion of the BO₆ octahedra begins already well above T_C . In the case of PT-0.08BZT, this distortion process shifts to higher temperatures compared to PT, likely due to the strong hybridization between Zn²⁺ and the surrounding oxygen atoms, which consequently affects the entire octahedral framework. In contrast, for PT-0.17BMT, Δ_{3TO} exhibits a minimum exactly at T_C . Simultaneously, the values of Δ_{3TO} for PT-0.17BMT are higher in the paraelectric phase than for the other two compounds, suggesting a higher B-O bond length anisotropy, probably due to a size mismatch of the Ti-O and Mg-O bonds.

Similar to their behavior under increasing pressure, the Y₂ and Y₃ Raman peaks show little temperature dependence, as both ω_{Y_2,Y_3} (Figure 6a) and In_{Y_2,Y_3} remain almost constant in the whole measured range, indicating that the related structural de-

fects are also not sensitive to temperature.

Conclusions

This thesis demonstrates for the first time that local non-tetragonal polar distortions play a key role in both the pressure- and temperature-induced phase transitions of PbTiO₃-Bi*Me*O₃ compounds. Furthermore, it shows that the partial substitution of Bi*Me*O₃ for PbTiO₃ promotes the local-scale doubling of the perovskite structure. This process is enhanced at higher pressures and temperatures. Since B-site chemical order cannot be induced by external factors, this composition-induced local scale doubling of the perovskite structure likely arises from antiferrodistortive order.

Furthermore, the temperature and pressure dependence of the atomic dynamics of PbTiO₃-Bi*Me*O₃ is significantly influenced by the chemical characteristics of the *Me* cation. In case of PT-0.08BZT and PT-0.17BMT, opposite behavior are observed in response to changes in pressure and temperature.

For PT-0.08BZT, the partial substitution of Zn^{2+} for Ti⁴⁺ hardens the tetragonal displacements of the A- and B-site cations, which in turn increases the resistance of the tetragonal matrix to pressure and temperature. As a consequence, the phase transitions from the tetragonal *P*4*mm* to the high-temperature and high-pressure phases are shifted to higher critical values.

In contrast, for PT-0.17BMT, the presence of Mg^{2+} at the B site disturbs the correlation of the tetragonally distorted TiO₆ octahedra and reduces the global tetragonal anisotropy of the mixed compound compared to pure PT. Furthermore, Mg favors the expansion of local non-tetragonal polar distortions in the tetragonal matrix, which might account for the composition-induced phase transition from the tetragonal to a rhombohedral phase with increasing *x*. The analysis of the Raman data suggests that the pressure-induced phase transition of PT-0.17BMT is shifted towards lower values relative to PT. Moreover, both the temperature and pressure evolution of the Raman modes reveal an enhancement of order-disorder phenomena.

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Acknowledgments

First, I would like to thank my supervisors Prof. Dr. Boriana Mihailova and Dr. Thomas Malcherek for their guidance, patience, support, and the time devoted to reviewing this work.

I am grateful to Prof. Zuo-Guang Ye and Dr. Zenghui Liu for synthesizing the single crystals that were investigated in this study and for their insightful comments and suggestions. I would also like to thank Peter Stutz for the precise sample preparation, Dipl.-Min. Stefanie Heindrich for the chemical analysis of the samples by electron microprobe analysis, and Dr. Carsten Paulmann for the technical assistance during the synchrotron XRD experiments at the P24 beamline, PETRA III (DESY).

Many thanks to both current and former members of our department for their support and for the fruitful discussions during our Crystal Coffee meetings. Special thanks to Constanze Rösche, with whom I have been sharing the office for the past few years.

The financial support provided by Universität Hamburg through a scholarship (Stipendium der Landesgraduiertenförderung nach dem HmbNFG) is gratefully acknowledged.

And finally, I am very thankful to my husband, my daughter, and my parents for their unconditional support and encouragement, which were a constant source of motivation throughout my doctoral studies.
List of publications

- Margaritescu, I., Malcherek, T., Paulman, C., Liu, Z., Ye, Z.-G., and Mihailova, B. Pressure- and temperature-induced transformation processes in PbTiO₃-Bi*Me*O₃ ferroelectrics. *Physical Review B* **111**, 144101 (2025).
- **Margaritescu, I.**, Liu, Z., Ye, Z.-G., and Mihailova, B. The role of local non-tetragonal polar displacements in the temperature- and pressure-induced phase transitions in PbTiO₃-Bi*Me*O₃ ferroelectrics. *Scientific Reports* **14**, 7106 (2024).
- **Margaritescu, I.**, Datta, K., Chen, J., and Mihailova, B. Distinct temperature behavior of the local structure of (1-x)PbTiO₃-xBiNi_{0.5}Ti_{0.5}O₃ at the morphotropic phase boundary. *Journal of Raman Spectroscopy* **51**, 1200 (2020).
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OPEN The role of local non-tetragonal polar displacements in the temperatureand pressure-induced phase transitions in PbTiO₃-Bi*Me*O₃ ferroelectrics

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In situ high-pressure/high-temperature Raman-scattering analyses on PbTiO₃, 0.92PbTiO₃ – 0.08Bi(Zn_{0.5}Ti_{0.5})O₃ and 0.83PbTiO₃ – 0.17Bi(Mg_{0.5}Ti_{0.5})O₃ single crystals reveal an intensity transfer between the fine-structure components of the A₁(TO) soft mode. The enhancement of the lowest-energy subpeak, which stems from intrinsic local non-tetragonal polar distortions, along with the suppression of the tetragonal A₁(1TO) fundamental mode with increasing pressure and temperature indicates the key role of the local polarization fluctuations in transformation processes and emphasizes the significance of the order-disorder phenomena in both the pressure- and temperature-induced phase transitions of pure PbTiO₃ and its solid solutions with complex perovskites. Moreover, the temperature and pressure evolution of the fraction of the local non-tetragonal polar distortions is highly sensitive to the type of B-site substituent.

Many of the outstanding macroscopic properties observed in ferroelectric materials, including high electromechanical coupling, very high Curie temperatures, enhanced thermal stability, and large coercive fields, are closely linked to local-scale structural phenomena¹⁻⁵. Therefore, a fundamental requirement for engineering novel ferroelectrics capable of withstanding extreme conditions is to understand how the nature of the processes and competing interactions that take place at different length-scales in a material affect its macroscopic properties.

Lead titanate (PbTiO₃) is one of the most studied ferroelectric materials. PbTiO₃ has a simple, highly polar ABO₃ perovskite-type structure and it is an end member of technologically important ferroelectric solid solutions such as $PbZr_{(1-x)}Ti_xO_3$, $(1-x)PbTiO_3 - xBiMeO_3$ and $(1-x)PbTiO_3 - xPbMe_{1/3}^{2+}Me_{2/3}^{5-11}O_3^{6-11}$.

Upon heating, PbTiO₃ undergoes a ferroelectric-to-paraelectric phase transition at 763 K from a tetragonal *P4mm* to a cubic *Pm3m* phase⁶, whereas two pressure-induced structural phase transitions occur at room temperature: $P4mm \xrightarrow{13 \text{ GPa}} R3c \xrightarrow{27 \text{ GPa}} R3c^{12}$. For a long time, the temperature-driven phase transition in PbTiO₃ had been considered to be a typical soft-mode-driven displacive transition¹³, until several studies revealed a significant contribution of order-disorder processes around the Curie temperature T_C^{14-18} . Particularly the lowest-energy non-degenerate transverse-optical mode A₁(1TO) near 148 cm⁻¹, which involves vibrations of the A-site cations against the BO₆ octahedra parallel to the direction of the spontaneous polarization¹⁹ (Figure 1), has attracted significant interest due to its anomalous asymmetric multicomponent Raman-peak shape consisting of four subpeaks²⁰⁻²⁴.

The first model to explain the anomalous peak shape of $A_1(1TO)$ in PbTiO₃ was proposed by Foster et al.^{20,21}, who ascribed the asymmetry of the soft mode to the anharmonic nature of the interatomic potential and assigned the three additional lower-energy subpeaks to the transitions between adjacent excited phonon states in the

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Figure 1. Sketch of the atomic vibrations associated with the optical $A_1(1TO)$ mode, plotted using VESTA²⁵.

double-well potential. However, further studies of the Raman scattering at elevated temperatures^{22,23} showed that the suppression of the higher-energy subpeaks (here labeled P_1 - P_3 , in agreement with another study²³) and the enhancement of the lowest-energy subpeak (labeled P_4) with increasing temperature were inconsistent with the phonon anharmonicity theory. Hence, a modified model has been proposed by Cho et al.²³, in which P_4 arises from frozen local polarization fluctuations from the direction of the macroscopic polarization, which are confined around thermodynamically unavoidable crystal-lattice defects. These "defect" local polar dipoles have been assumed to have a critical temperature lower than the inherent critical temperature of the matrix, and, as the temperature approaches T_C , the correlation between the "defect" polar regions increases and influences the high-temperature behavior of the whole crystal²³. However, the contribution of these intrinsic non-tetragonal local polar distortion to the pressure-induced phase transitions of PbTiO₃ has been neglected, as the Raman scattering near 148 cm⁻¹ has been regarded as a single peak to date^{26–28}. In addition, studies of the effect of co-substitutions at A and B sites on the subpeak structure of $A_1(1TO)$ are scarce^{23,24,29}.

Recently, compounds of the complex perovskite PbTiO₃–Bi*Me*O₃ binary system (Me = Sc, In, $Zn_{0.5}Zr_{0.5}$, Ni_{0.5} Ti_{0.5},...) have attracted significant attention due to their potential applications in high-temperature electromechanical devices^{4,30,31}. Of notable technological significance are the (1–*x*)PbTiO₃ – *x*Bi($Zn_{0.5}Ti_{0.5}$)O₃ and (1–*x*) PbTiO₃ – *x*Bi(Mg_{0.5}Ti_{0.5})O₃ solid solutions, which exhibit stable piezoelectric and mechanical properties at high temperatures^{9,32-34} and show a near-zero volume thermal expansion for low levels of *x*³⁵. Furthermore, (1–*x*) PbTiO₃–*x*Bi($Zn_{0.5}Ti_{0.5}$)O₃ is one of the very few ferroelectric solid solutions which exhibit enhanced tetragonality with increasing *x*³⁴.

In order to to elucidate the behavior of the $A_1(1TO)$ fine structure near and above T_C , we performed temperature-dependent Raman experiments with small temperature increments up to 1000 K on single crystals of PbTiO₃ (PT), as well as on two complex PbTiO₃-based oxide solid solutions, $0.92PbTiO_3-0.08Bi(Zn_{0.5}Ti_{0.5})O_3$ (PT-0.08BZT) and $0.83PbTiO_3-0.17Bi(Mg_{0.5}Ti_{0.5})O_3$ (PT-0.17BMT), which undergo a ferroelectric (*P4mm*)-to-paraelectric(*Pm3m*) phase transition at 805 K³⁴ and 810 K⁹, respectively. Furthermore, we report the pressure dependence of the $A_1(1TO)$ -subpeaks for the same materials up to 10 GPa. Our experimental results show that for all three compounds, the "defect" mode P₄ is the dominant excitation that softens upon pressure or temperature increase, that is, the intrinsic non-tetragonal polar fluctuations within the tetragonal polar matrix contribute significantly to both the pressure- and temperature-driven phase transitions. Furthermore, we show that the temperature range of the ongoing processes involving the polarization fluctuations is heavily influenced by the type of chemical bonding between the B²⁺ cation and the oxygen anions.

Results

Figure 2a and b show the A1(1TO)-related Raman scattering of PT, PT-0.08BZT and PT-0.17BMT single crystals at selected temperatures and pressures, respectively. The entire Raman spectrum of PbTiO₃ measured under ambient conditions is presented in Fig. S2 (Supplementary Material). The anomalous line shape of $A_1(1TO)$ can be observed for all three compounds, but all four previously reported subpeaks²⁰⁻²² could only be resolved for pure PT. Due to the substitution disorder, an increase in the width of the Raman peaks is observed for PT-0.08BZT and PT-0.17BMT. Consequently, for PT-0.08BZT the anharmonicity-related subpeak P2 could not be resolved from the fundamental A₁(1TO) (peak P₁), whereas for PT-0.17BMT none of anharmonicity-related subpeaks P2 and P3 can be resolved. However, for both PT-0.08BZT and PT-0.17BMT the defect-related, nontetragonal subpeak P_4 can be separated from the Raman scattering related to the $A_1(1TO)$ mode of the tetragonal matrix and the relative errors of the fitted spectral parameters are within the commonly accepted mathematical criteria (see also Supplementary Material, Fig. S3, and Fig. S4). The suppression of the fundamental phonon mode P_1 and the two subpeaks related to the anharmonicity of the interatomic potential (P_2 and P_3), as well as the enhancement of the "defect" peak P₄ upon temperature and pressure increase, can be observed for all samples. Figure 3a-f show the temperature dependences of the wavenumber ω of all subpeaks as well as the Raman intensity I₄ of the lowest-energy subpeak for PT, PT-0.08BZT, and PT-0.17BMT, respectively. As in other perovskite-type ferroelectric materials, forbidden Raman scattering is observed above the Curie temperatures of all three compounds, revealing the existence of local polar distortions within the cubic matrix^{15,18,3}

As can be seen in Fig. 3a, for PT $\omega_4(T)$ has a much more pronounced non-linear character than $\omega_1(T)$, $\omega_2(T)$ and $\omega_3(T)$. A power function $\omega(T) \propto (T_C - T)^n$ was used to fit $\omega_4(T)$, with $\omega_4^{PT}(T) \propto (765 - T)^{0.40 \pm 0.03}$. The 37



Figure 2. Raman spectra of the A₁(1TO) phonon as a function of (**a**) temperature and composition and (**b**) pressure and composition. The fitting peak functions are labeled from P₁ to P₄, from the highest to the lowest energy. All spectra were collected in the $\bar{x}(yy)x$ backscattering geometry (Porto's notation³⁶, *x* and *y* parallel to the tetragonal [100] and [010] directions, respectively) and were normalized to the intensity of the highest peak. The presence of the E(1TO)-peak in the spectra is related to a slight deviation from the ideal orientation of the single crystals and, in the case of experiments in DAC, the depolarization effects of the diamond anvils.

value of $n \approx 0.40$ indicates that the thermal evolution of non-tetragonal local defects is relatively gradual, exhibiting second-order-transition behavior^{40,41}, although the PT matrix undergoes a first-order phase transition as revealed by the fundamental E(1TO) phonon mode and macroscopic spontaneous polarization^{13,42}. One can speculate that upon heating, the "defect" P₄ mode, which behaves as a non-degenerate A-type excitation, disturbs the correlation length of the tetragonal distortion along the direction of the macroscopic spontaneous polarization, while the softening of the fundamental doubly degenerated E(1TO) mode^{13,18} ensures the destabilization of the correlated tetragonal distortions within the plane perpendicular to the direction of macroscopic polarization. As a result, above T_C an ergodic state of dynamic local ferroic distortions is established, which only on average appears as having a primitive cubic symmetry^{17,18}.

The gradual suppression of the fundamental mode P_1 and the anharmonic subpeaks P_2 and P_3 upon heating observed in Fig. 2a is a consequence of the reduction of the magnitude of polar tetragonal distortions while approaching T_C from below¹⁷. In contrast, $I_4(T)$ exhibits an increase up to ~680 K, followed by a decrease (Fig. 3d). However, the full width at half maximum (FWHM) of P_4 does not show any anomalous increase near 680 K (Supplementary Material, Fig. S5), therefore the maximum in $I_4(T)$ cannot be related to local-scale transformations involving the existing non-tetragonal polar distortions. Thus, we assume that $I_4(T)$ mirrors the $\mathbf{28}$



Figure 3. (**a**–**c**) Wavenumber ω of the A₁(1TO) phonon-subpeaks as a function of temperature and composition. The red dashed lines mark the Curie temperature of each compound. (**d**–**f**) Raman intensity I_4 of the lowest-energy peak as a function of temperature and composition. I_4 of each compound was normalized to the total integrated intensity of the Raman spectrum measured at 300 K. I_4^{PT} and $I_4^{PT-0.08BZT}$ were fitted with an asymmetric double Sigmoidal function. The insets show the intensity ratios $\frac{I_1+I_2+I_3}{I_1+I_2+I_3+I_4}$ (black symbols) and $\frac{I_4}{I_1+I_2+I_3+I_4}$ (gray symbols).

temperature evolution of the average of the non-tetragonal polar distortions, which may include a change in the magnitude and/or correlation length of the existing distortions as well as the nucleation of new distortions. Above 580 K the fractional intensity of P₄, $I_{n4} = \frac{I_4}{\sum_{i=1}^{l}(I_i)}$, surpasses 0.5 (Fig. 3d, inset), indicating that the fraction of non-tetragonal displacements becomes dominant over the fraction of tetragonal distortions well below T_C . Moreover, both P₄ and P₁ persist well above T_C (Fig. 3a and Fig. S6, Supplementary Material), that is, both tetragonal and non-tetragonal polar distortions exist in the paraelectric phase, which is in full accordance with a total neutron scattering analysis revealing non-zero polar displacements across T_C and a high degree of local orientation disorder¹⁷. Both $I_{n4}(T)$ and $\omega_4(T)$ trends as well as the reversibility of the spectral changes on cooling down clearly demonstrate the key role of the non-tetragonal polar entities in the occurrence of ferroelectric-paraelectric phase transition in PT and emphasize the importance of order-disorder processes.

Thus, the Raman data presented here and the previously reported results from pair-distribution-function analysis¹⁷ are consistent with the model of Cho et al.²³, according to which the non-tetragonal polar displacements confined around crystal-lattice defects influence the behavior of the whole system above a certain critical temperature corresponding to a critical correlation length. However, it should be mentioned that an increase in the Raman intensity might reflect not only an increase in the correlation length, but also an increase in the magnitude of the individual polar distortions and/or further nucleation of non-polar distortions.

We now consider the effects of substitutions. Similar to PT, the higher-energy subpeaks in the spectra of both PT-0.08BZT and PT-0.17BMT are suppressed with increasing temperature, while P₄ is enhanced (Fig. 2a and Fig. S6, Supplementary Material) and begins to dominate over P₁-P₃ already below T_C (see the insets in Fig. 3e and f). However, PT-0.08BZT and PT-0.17BMT significantly differ from each other in the temperature dependences of ω_4 and I_4 . For PT-0.08BZT, $\omega_4(T)$ shows a typical soft-mode behavior (Fig. 3b) and a power-function fit reveals $\omega_4(T) \propto (805 - T)^{0.29\pm0.02}$. The *n* value suggests that the BZT substitution changes the character of developing non-tetrahedral distortions from second-order (PT) towards tricritical (PT-0.08BZT)^{40,41}. Moreover, for PT-0.08BZT $I_4(T)$ shows a clear maximum at a temperature that is ~85 K below T_C (Fig. 3e), as in the case of PT, and the FWHM of the asymmetric Sigmoidal function fitting the $I_4(T)$ data points is even smaller than that for PT-0.17BMT (Fig. 3c), the softening rate of the lowest-energy subpeak is less pronounced compared to the other solid solutions, which suggests a significant contribution of the order-disorder phenomena across T_C for PT-0.17BMT and is consistent with the results from a second-harmonic-generation analysis on a similar composition⁴³. Furthermore, I₄ shows a maximum around 400 K (Fig. 3f), followed by a gradual decrease over a broad temperature range. Within this temperature range, the intensity ratios of the two peaks are comparable, suggesting an even fraction of tetragonal and non-tetragonal polar distortions.

We assume that the main reason for the different temperature behavior of the two solid solution compounds is the character of the B-O interactions: both Ti^{4+} and Zn^{2+} have a covalent bonding with oxygen through the

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hybridization of the Ti 3*d* orbitals with the O 2*p* orbitals and the hybridization of the Zn 4*s* and 4*p* orbitals with the 2*p* orbitals of oxygen, respectively, whereas the interaction between Mg^{2+} and oxygen anions is predominantly ionic^{44,45}. Thus, Mg^{2+} cations act as "modifiers" of the BO₆-network connectivity, disturbing the correlation between the tetrahedrally distorted TiO₆ octahedra. This in turn indirectly promotes the non-tetragonal local distortions of the A-BO₃ species in a wide temperature range and enhances the order-disorder character of the phase transition.

Figure 2b shows that P_4 is also significantly enhanced under hydrostatic pressure, whereas P_1-P_3 are gradually suppressed. This indicates that pressure, like temperature, suppresses the polar tetragonal distortions and enhances the preexisting local polar non-tetragonal distortions, which is consistent with the previously reported *P4mm*-to-*R3c* phase transition of PT¹². So far, the mixed compounds have not been analyzed by in situ high-pressure XRD.

Figure 4a-c show the pressure dependences of the wavenumber ω of the A₁(1TO)-mode subpeaks of the studied compounds. For PT (Fig. 4a), a slight decrease in the peak positions of the higher-energy subpeaks is observed up to 2 GPa. Upon further pressure increase, $\omega_1 - \omega_3$ remain nearly constant. In contrast, $\omega_4(p)$ clearly softens upon compression. Several factors could account for the constant value of the wavenumber with increasing pressure: (1) the phonon compressibility is close to $zero^{46}$, (2) the increase in ω due to the shrinking atomic distances is compensated by a mode softening at the same rate, or (3) the anharmonicity of the potential does not change with pressure in the corresponding range (for P2 and P3). A similar trend can be observed for PT-0.08BZT (Fig. 4b). Although the analysis of the pressure evolution of the peaks is complicated by the overlapping of P_1 and P_2 , it is apparent that the wavenumbers of P_1+P_2 and P_3 are not sensitive to changes in pressure. Above 7.4 GPa an additional peak near 99 cm⁻¹, labeled P* in Fig. 2b, can be resolved for PT-0.08BZT (see Fig. S4 in the Supplementary Material for more details on the fitting procedure). Since the wavenumber of P* remains nearly constant with pressure, as P₁, P₂, and P₃ do for both PT and PT-0.08BZT, we assume that P* also originates from the anharmonicity of the interatomic potential, and it could not be observed at lower pressures as a result of overlapping with P4. For PT-0.17BMT (Fig. 4c), the wavenumber of the higher-energy peak hardens on compression, whereas the wavenumber of the lower energy peak decreases almost linearly with the increase in pressure. The composition dependence of $\omega(p)$ indicates that the rate of softening decreases through increasing the concentration of the substitution.

The pressure dependencies of the fractional intensity $I_{n4} = \frac{I_4}{\sum_{i=1}^4 (I_i)}$ (Fig. 4d–f) reveal that the non-tetragonal distortions prevail over the polar tetragonal distortion above 2.2 GPa for PT, 3.8 GPa for PT-0.08BZT, which suggests that B-site Zn²⁺ slows down the progressive development of non-tetragonal distortions under pressure. For PT-0.17BMT, it is apparent that B-site Mg²⁺ favors the non-tetragonal distortions already at relatively low pressures. However, the peak broadness and possible overlapping hinders the precise determination of the pressure above which the non-tetragonal distortions become dominant. Due to potential artifacts related to the depolarization of the diamond anvils, the pressure dependence of the absolute intensity I_4 (Supplementary Material, Figure S7) will not be discussed in detail.



Figure 4. (a-c) Wavenumber ω of the A₁(1TO) phonon-subpeaks as a function of pressure and composition. (d-f) Intensity ratios $\frac{I_1+I_2+I_3}{I_1+I_2+I_3+I_4}$ (black symbols) and $\frac{I_4}{I_1+I_2+I_3+I_4}$ (gray symbols) for PT and PT-0.17BMT, $\frac{I_1+I_2+I_3+I_4+P*}{I_1+I_2+I_3+I_4+P*}$ and $\frac{I_1+I_2+I_3+I_4+P*}{I_1+I_2+I_3+I_4+P*}$ for PT-0.08BZT.

Conclusions

In conclusion, we demonstrate that above a certain characteristic temperature or pressure, the *atomic dynamics* of polar A-BO₃ entities distorted in a non-tetragonal way become dominant, even though the symmetry of the average structure is still polar tetragonal. Given that the A₁-mode polarization is along the tetragonal [001] direction (see Fig. 1), the "defect" A-type excitations violate the polar tetragonal long-range order along the direction of the macroscopic polarization. Consequently, these excitations significantly contribute to the temperature/ pressure-induced phase transitions of pure PT and its solid solutions with complex perovskites. Moreover, we show that Zn improves the resistivity of the polar tetragonal distortions to increasing pressure or temperature, whereas Mg favors the expansion of non-tetragonal distortions. This might explain the decrease in the unit-cell tetragonality of PbTiO₃-*x*Bi(Mg_{0.5}Ti_{0.5})O₃ with increasing *x* and the existence of a tetragonal-to-rhombohedral composition-induced phase transition P4mm $\frac{x = 0.63}{R3c^9}$. In contrast, the substitution of Bi(Zn_{0.5}Ti_{0.5})O₃ only enhances the tetragonality of the unit cell³⁴, without leading to a composition-driven phase transition.

Methods

Single crystals of PbTiO₃, 0.92PbTiO₃–0.08Bi(Zn_{0.5}Ti_{0.5})O₃, and 0.83PbTiO₃–0.17Bi(Mg_{0.5}Ti_{0.5})O₃ were grown using the flux method and the top-cooled solution growth method^{4,47}. The chemical composition and homogeneity of the samples were verified by wavelength-dispersive spectroscopy using a Cameca SX100 electron microprobe. Polarized Raman spectra were collected in the $\bar{x}(yy)x$ backscattering geometry with a Horiba Jobin-Yvon T64000 triple-grating spectrometer, using the 514.532-nm line of an Ar⁺ laser. The spectral resolution was 2 cm⁻¹ and the peak position accuracy was ~0.35 cm⁻¹. A detailed description of the experimental conditions and data evaluation is given in the Supplementary Material.

Data availibility

All data analysed during this study are included in this published article and its Supplementary Material.

Received: 24 January 2024; Accepted: 21 March 2024 Published online: 26 March 2024

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Acknowledgements

I. M. thanks Universität Hamburg for financial support through a scholarship (Stipendium der Landesgraduiertenförderung nach dem HmbNFG). Z. L. acknowledges the support of the National Natural Science Foundation of China through Grant No. 52372124. Z.-G. Y. acknowledges the support from the Natural Sciences and Engineering Research Council of Canada (NSERC, Discovery Grants No. RGPIN-2017-06915 & No. RGPIN-2023-04416).

Author contributions

I.M., Z.-G.Y. and B.M. developed the original project. Z.L. and Z.-G.Y. provided the single crystals. I.M. carried out the Raman measurements and analyzed the Raman data. I.M. and B.M. wrote the manuscript. All authors reviewed and edited the manuscript.

Funding

Open Access funding enabled and organized by Projekt DEAL.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1038/s41598-024-57765-w.

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The role of local non-tetragonal polar displacements in the temperature- and pressure-induced phase transitions in PbTiO₃-Bi*Me*O₃ ferroelectrics

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Supplementary Material

Experimental details

Polarized Raman spectra were collected in the $\bar{x}(yy)x$ scattering geometry (x and y parallel to the tetragonal [100] and [010] directions, respectively) with a Horiba Jobin-Yvon T64000 triple-grating spectrometer equipped with an Olympus BH41 microscope. The 514.532-nm line of an Ar⁺-laser was focused on the sample surface through a 50× long-working distance objective to a spot with a diameter of ~2 µm. The spectrometer was calibrated to the Raman peak at 520.5 cm⁻¹ of a Si wafer. The spectral resolution was 2 cm⁻¹ and the accuracy of the peak position was ~0.35 cm⁻¹.

The temperature-dependent measurements were carried out on (100)-oriented platelets with a size of \sim 1×1×0.5 mm³, using a Linkam THMS-E600 stage on cooling between 300 K and 150 K and a Linkam TS1200 EV-1015 stage on heating between 300 K and 1000 K with a temperature step of 20 K.

The *in situ* high-pressure Raman measurements up to 10 GPa were conducted at room temperature on (100)-oriented platelets with a size of $\sim 100 \times 70 \times 50 \ \mu\text{m}^3$, using a Boehler-Almax diamond anvil cell (DAC) with diamond culets of 600 μm in diameter. Stainless steel gaskets were preindented to $\sim 90 \ \mu\text{m}$ thickness and a gasket hole with a diameter of 300 μm was drilled using a spark eroder. A 16:3:1 methanol-ethanol-water mixture was used as a hydrostatic pressure transmitting medium and the R1 florescence line of a ruby crystal placed near the sample was used to determine the pressure. The spectra were collected with a pressure step of ~ 0.3 GPa and a pressure accuracy of ~ 0.1 GPa.



Figure S1: Graphical representation of the experimental setup used for the high-pressure Raman measurements (a) Lateral view of the diamond anvil cell (b) Schematic view of the diamond anvil cell. By simultaneously tightening the three pressure screws seen in (a) using a gear tool, the diamond anvils apply uniaxial pressure (gray arrows) to the gasket. The pressure medium transforms the uniaxial stress into hydrostatic pressure (green arrows). The pressure transmitting medium used in this study, 16:3:1 methanol-ethanol-water, ensures hydrostatic conditions up to 10.4 GPa¹. (c) Sample and ruby crystal in the high-pressure chamber viewed from above. The direction of propagation of the incident and Acattered light is along [100]. The polarization direction of the incident and scattered light (\mathbf{e}_i and \mathbf{e}_s , respectively) is parallel to [010].

Fitting details

The experimental data were evaluated using the OriginPro 2019b software package². To eliminate the trivial temperature dependence of the peak intensities due to the alteration in energy-level population, the measured Raman spectra were first corrected by the Bose-Einstein phonon occupation factor $I = I_{measured} / \left[\left(e^{\hbar \omega / k_B T} - 1 \right)^{-1} + 1 \right]$, where \hbar , ω , k_B , and T are the reduced Planck constant, phonon wavenumber (in s⁻¹), Boltzmann constant, and temperature, respectively. The temperaturereduced spectra were fitted with pseudo-Voigt functions PV = μL + (1- μ)G, where L and G are Lorentzian and Gaussian peak-shape functions of equal width and μ is a weight coefficient. Thus for each peak four parameters were refined: the peak positions ω , full widths at half maximum (FWHMs) Γ, integrated intensities I and coefficients μ , where μ varies between 0 and 1. μ =1 corresponds to a pure Lorentzian peak-shape function, which is the natural peak shape of any damped harmonic oscillator, whereas $\mu < 1$ represents the Gaussian contribution to the peak shape related to the statistical dispersion over phonon energy, which can be inspected in materials with structural and/or compositional disorder³. It should be emphasized that Lorentzian or Voigtian peak-shape functions are routinely applied to ferroelectric materials⁴⁻¹⁵, including solid solutions. An asymmetric peak-shape function related to the chemically induced folding of the Brillouin zone (e.g. Bergmann et al.¹⁶) is not necessary to be introduced for perovskite-type ferroelectrics (as the materials studied here), because they are wide-bandgap insulators and such effects are negligible⁸.

The fittings were performed without putting any constraints on the variable parameters, apart from the μ coefficients, which were initially released to vary between 0 and 1 and then fixed to the resultant value only at the final step of fitting, after reaching the final values of all fitting parameters. In the case of PT the μ coefficients converged to 1, corresponding to a Lorentzian peak-shape function, whereas for PT-0.08BZT and PT-0.17BMT, the μ values varied in the range [0, 1]. In order to check the effect of the peak shape we have tested different fitting models, using pure Lorentzians, pure Gaussians or pseudo-Voigt functions with intermediate μ values and observed that the temperature and pressure trends of ω , I and Γ remain consistent regardless of the fitting peak-shape functions chosen.

The number of peak functions used to fit the spectra was based on the group-theory selection rules about the number of fundamental Raman-active phonon modes allowed to be observed in a certain scattering geometry. When the number of peaks deviated from the predictions of group theory, the number of used pseudo-Voigt peaks at each pressure or temperature step was justified by the standard criteria for goodness-of-fit: adjusted R², reduced χ^2 , the relative uncertainties of each fitted parameter as well as the statistical t and prob>|t| values⁷. The t and prob>|t| values describe the fitted value divided by the error and the probability of a certain parameter to exist, respectively. The decision to keep or exclude a peak was based on the requirement the relative error in intensity $\Delta I/I$ to be smaller than 0.5 and the corresponding prob>|t| value to be smaller than 0.05. According to the null-hypothesis significance testing, a prob>|t| value below 0.05 supports the presence of the parameter, whereas a value higher than 0.05 indicates that the parameter should be removed. In the case where an additional peak was required, we have tried several fitting models while considering the R², reduced χ^2 and prob>|t| values. This procedure is shown below for PT-0.08BZT.

Group-theory analysis

The Γ -point optical phonon modes in the cubic $Pm\overline{3}m$ ABO₃ structure are $\Gamma_{optic} = 3T_{1u} + T_{2u}$. In the tetragonal *P4mm* phase, each T_{1u} mode splits as A_1+E , whereas the T_{2u} mode splits as B_1+E . Furthermore, long-range electrostatic forces further split the polar A_1 and E modes into TO (transverse) and LO (longitudinal) components [13]. The phonon modes in the cubic phase are not Raman active, whereas the phonon modes in the tetragonal phase are all Raman active. According to group-theory analysis, the E(TO), $A_1(TO) + B_1$, and $A_1(LO) + B_1$ modes can be observed in the $\bar{x}(zy)x$, $\bar{x}(yy)x$, and z(xx)z scattering geometries, respectively.

The peak assignment for pure PbTiO₃ is in a good agreement with previous studies [14, 15].



Figure S2: Raman spectra of PbTiO₃, PT-0.08BZT and PT-0.17BMT measured under ambient conditions in the $\bar{x}(zy)x$ and $\bar{x}(yy)x$ scattering geometries. Small intensity leakage of phonon modes in forbidden scattering geometries is due to unavoidable experimental imperfections.

Chemical analysis

The chemical composition and homogeneity of the mixed samples were determined by wavelengthdispersive electron microprobe analysis. Sections with a thickness of ~200 µm were cut from each sample and mounted in an epoxy disk. The experiments were carried out with a Cameca Microbeam SX100 equipped with a wavelength-dispersive detector. An accelerating voltage of 15 keV and a beam current of 20 nA were used. The beam diameter on the sample surface was ~10 µm. The following standards were used for the calibration: MgO for Mg, TiO₂ for Ti, complex silicate glass for Pb and Zn, and Bi₄Ge₃O₁₂ for Bi. The chemical composition of each sample was obtained by averaging over 60-130 spatial points collected along several lines set across the crystals. The obtained chemical compositions are given in Table S1.

	Pb ²⁺	Bi ³⁺	Ti ⁴⁺	Zn ²⁺	Mg ²⁺	0 ²⁻	Chemical formula	
DT-B7T	17 /0(15)	1 66(6)	10 5/(11)	0 03(1)	0 03(1)	_	60 33(5)	0.92PbTiO ₃ -
FI-DZI	17.40(13)	1.00(0)	19.34(11)	0.93(4)	_	00.55(5)	0.08Bi(Zn _{0.5} Ti _{0.5})O ₃	
	1 - 9 - (1 4)	2 20/01	19 60(11)		1 71/5)	60 20(6)	0.83PbTiO ₃ -	
PT-DIVIT	15.85(14)	5.50(0)	10.00(11)	-	1.71(5)	00.28(0)	0.17Bi(Mg _{0.5} Ti _{0.5})O ₃	

Table S1: Chemical composition in atomic percentage and chemical formulae of the studied samples. The statistical standard deviations are given in brackets.



Figure S3: Raman spectra of PT-0.17BMT collected at 400K, 500 K, 600 K, and 700 K. The Raman peak positions ω , FWHMs Γ , integrated intensities I, and the Lorentzian contribution μ , along with their corresponding errors and prob>|t| values are shown in the tables next to the figures. The prob>|t| values of I₁ and I₄ are below 0.05, as required by the null-hypothesis significance testing, which indicates that two peaks should be used to fit this spectral region.



Figure S4: a) Raman spectra of PT-0.08BZT collected between 7 and 10.2 GPa. Above 7.4 GPa a new peak (P*) is observed; the dashed lines trace peaks P_{1+2} near 140 cm⁻¹, P_4 near 80 cm⁻¹, and P* near 100 cm⁻¹. Figures b) and c) show the fitting of the Raman spectra collected at 9 GPa using pseudo-Voigt functions and two different models with 3 (b) and 4 (c) peaks. The values of the Raman peak positions ω , FWHMs Γ , integrated intensities I, and the Lorentzian contribution μ , as well as the corresponding errors and prob>|t| values are given in the tables below the figures. In the pressure range 7.4-10.2 GPa, the prob>|t| value of I₃ (the intensity of peak P₃) starts oscillating and at some pressures it exceeds 0.05. For example, for P₃, at 9 GPa, $\Delta I/I > 0.5$ and prob>|t| ~ 0.1. Therefore, we have removed this weak peak from the fitting model in the pressure range 7.4-10.2 GPa.



Figure S5: Full width at half maximum (FWHM) of the lowest energy subpeak P₄ as a function of temperature for PT, PT-0.08BZT and PT-0.17BMT.



Figure S6: Raman intensity of the lowest-energy subpeak P_4 and sum of the Raman intensities of the highest-energy subpeaks P_1 - P_3 as a function of temperature for PT, PT-0.08BZT and PT-0.17BMT.



Figure S7: Raman intensity of the lowest-energy subpeak P_4 and sum of the Raman intensities of the highest-energy subpeaks P_1 - P_3 as a function of pressure for PT, PT-0.08BZT and PT-0.17BMT.



Figure S8: Weight coefficient μ as a function of temperature and pressure for PT-0.08BZT and PT-0.17BMT. For pure PT, unconstrained fits yielded weight coefficients ~1, and therefore pure Lorentzian peak shape functions were used in the final fits.

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Pressure- and temperature-induced transformation processes in PbTiO₃-BiMeO₃ ferroelectrics

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(Received 4 April 2024; revised 19 July 2024; accepted 20 March 2025; published 1 April 2025)

The structural response to high pressures as well as to high temperatures of $(1-x)PbTiO_3-xBi(Zn_{0.5}Ti_{0.5})O_3$ with x = 0.08, $(1-x)PbTiO_3-xBi(Mg_{0.5}Ti_{0.5})O_3$ with x = 0.17, and PbTiO_3 single crystals was studied by *in situ* pressure-/temperature-dependent polarized Raman spectroscopy, complemented by synchrotron x-ray diffraction analysis at ambient pressure and different temperatures. The compositional and pressure dependencies of phonon anomalies indicate the existence of local-scale antiferrodistortive structural entities inside the perovskite (ABO₃) polar tetragonal matrix, the fraction of which is enhanced by the substitution of Bi*Me*O₃ for PbTiO₃. The type of cation (Zn²⁺ versus Mg²⁺) replacing Ti⁴⁺ at the B site affects the coherence within the dominant singleperovskite polar tetragonal matrix and the coupling between the "defect" double-perovskite antiferrodistortive entities. As a result, on increasing pressure, the partial substitution of Bi(Mg_{0.5}Ti_{0.5})O₃ triggers a structural instability at lower pressure values as compared to pure PbTiO₃, whereas that of Bi(Zn_{0.5}Ti_{0.5})O₃ preserves the polar tetragonal phase over a wider pressure range. Furthermore, at ambient pressure B-site Zn²⁺ favors the coherence between local BO₆ tetragonal distortions already above the Curie temperature T_C , causing a larger unit-cell tetragonality below T_C ; in contrast, B-site Mg²⁺ reduces the local BO₆ anisotropy and disturbs the correlation between polar AO₁₂ tetragonal distortions below T_C , which results in a considerable reduction of both the unit-cell tetragonality and accumulated volume strain on cooling between T_C and room temperature.

DOI: 10.1103/PhysRevB.111.144101

I. INTRODUCTION

Ferroelectrics of the perovskite (ABO₃) structure type are used in a wide range of applications, such as energy harvesting, medical instruments, electro-optic devices, as well as in the automotive industry [1–3]. Therefore, the fundamental understanding of the structural transformations occurring in these compounds as a result of varying external thermodynamic parameters such as temperature (*T*), pressure (*p*), electric field (**E**), or chemical composition (*x*), is of major significance for the further development of technologically important materials.

Recently, there has been a growing interest in $(1-x)PbTiO_3-xBiMeO_3$ binary ferroelectric systems, where Me can be a single trivalent cation (e.g., Sc^{3+} and Fe^{3+}) or a combination of cations with an average valence of 3+, such as $Zn_{0.5}Ti_{0.5}$, $Ni_{0.5}Zr_{0.5}$, $Mg_{0.5}Ti_{0.5}$, etc. These solid solutions exhibit excellent piezoelectric and dielectric properties up to high operating temperatures and usually possess a mor-

photropic phase boundary (MPB): a composition at which the properties reach a peak while the structure switches between the two end-member phases [4-11]. Figure 1 shows the aristotype ABO₃ perovskite structure. For (1-x)PbTiO₃-*x*BiMeO₃, both types of A-site cations, Pb^{2+} and Bi^{3+} , have stereochemically active $6s^2$ lone pair electrons [4]. This promotes A-site cationic off-center displacements due to the coupling of the 6s orbitals of the Pb^{2+}/Bi^{3+} cations with the 2p orbitals of the oxygen anions [4,13], in addition to the well-known hybridization of the oxygen 2p orbitals with the B-site Ti⁴⁺ 3dorbitals and the pseudo-Jahn-Teller effect [8,14,15]. Depending on the chemical characteristics of the Me cations, the tetragonality (c/a), Curie temperature T_C , net polarization and other related properties may vary [5-7,9,16] and even new properties, such as magnetic activity, can be induced in the (1-x)PbTiO₃-*x*Bi*Me*O₃ systems [9,17].

The chemistry-structure-property relationship in complex ferroelectrics is commonly studied at ambient pressure by varying T, E, and x [10,18–20]. However, over the past few years there has been an increased interest in the behavior of ferroelectric solid solutions at high pressure (HP), because several studies on relaxor ferroelectrics have demonstrated that pressure can trigger the development of long-range nonpolar ferroic order and thus it can reveal the existence of additional incipient local-scale order at ambient conditions [18,21–23]. Moreover, high-pressure studies can 53 provide a more comprehensive view of the nature of the

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FIG. 1. Aristotype ABO₃ perovskite structure with space group symmetry $Pm\bar{3}m$, plotted using VESTA [12]

substitution-induced local elastic strains and associated ferroic distortions in solid solutions, especially when combined with high-temperature (HT) analyses. Particularly, in situ HP/HT Raman spectroscopy, which is extremely sensitive to local-scale ferroic structural entities in ABO₃-type materials, is a powerful method to shed light on the competing interactions and nanoscale processes that can take place in complex ferroelectric systems [22,24].

At room temperature, PbTiO₃ (PT) undergoes a series of pressure-induced phase transitions: $P4mm \xrightarrow{13 \text{ GPa}} R3c \xrightarrow{27 \text{ GPa}}$ $R\bar{3}c$, where the $R\bar{3}c$ and $R\bar{3}c$ phases feature a compression mechanism involving antiphase rotation of the octahedra about the threefold axis of symmetry [25]. While the pressuredependent behavior of PT has been extensively studied, there are only few HP studies on PbTiO₃-BiMeO₃ systems, focusing on compounds with a magnetically active B-site cation ($Me = Fe^{3+}$) and multiferroic properties [26,27]. So far, "purely ferroelectric" PbTiO₃-BiMeO₃ materials have not been studied at elevated pressures, except for our pilot study, focusing on the fine-structure components of the $A_1(1TO)$ soft mode near 148 cm⁻¹ [28]. Previous studies of pure PT at ambient pressure and different temperatures have demonstrated that the lowest-energy subpeak (designated hereafter as P_{nonT}) of this A₁(1TO) mode arises from inherent local-scale nontetragonal cationic displacements, i.e., from thermodynamically unavoidable defects in the polar tetragonal matrix [29,30]. The use of single crystals allowed us to detect the fine structure of $A_1(1TO)$ at both elevated temperatures and pressures also in solid-solution systems, namely, $0.92PbTiO_3$ - $0.08Bi(Zn_{0.5}Ti_{0.5})O_3$ (PT-0.08BZT) and $0.83PbTiO_3-0.17Bi(Mg_{0.5}Ti_{0.5})O_3$ (PT-0.17BMT) [28]. We have shown that the atomic dynamics of the nontetragonal ferroic entities destabilize the tetragonal matrix at both high temperatures and pressures, driving the system to a phase transition; however, the type of B-site substituent affects the fraction of A-BO₃ entities distorted in a nontetragonal way and thus enhances (Zn^{2+}) or reduces (Mg^{2+}) the resistivity of the tetragonal structural polarity to external stimuli.

To further elucidate the effect of the substitution disorder at the A and B sites on the local structure and transformation processes of PbTiO₃-BiMeO₃ ferroelectric systems, we have applied hard-mode Raman spectroscopy [24,31] to PT-0.08BZT, PT-0.17BMT, and PT as a reference end-member material, considering the entire spectral range of crystal normal phonons. In addition, the same compounds were studied $54\bar{x}(zy)x$, and $\bar{z}(xx)z$ scattering geometries, using a Linkam

by in situ high-temperature x-ray diffraction (XRD) with synchrotron radiation. We have selected these two solid solution compounds because both $(1-x)PbTiO_3-xBi(Mg_{0.5}Ti_{0.5})O_3$ (PT-*x*BZT) and (1-x)PbTiO₃-*x*Bi(Zn_{0.5}Ti_{0.5})O₃ (PT-*x*BMT) exhibit stable piezoelectric and ferroelectric properties at elevated temperatures [7,32-34] and for low levels of x show near-zero volume thermal expansion [35]. However, PT-*x*BMT has an MPB in the range $0.60 \leq x \leq 0.67$, with a composition-induced P4mm-Pm phase transition [36], whereas PT-*x*BZT exhibits enhanced tetragonality (c/a) with increasing x due to the covalent character of the Zn-O interactions and enhanced coupling between the A-site and B-site cationic displacements [5,8,34]. For PT-xBMT, the Curie temperature T_C initially increases with x and decreases when x exceeds 0.35 as it approaches the MPB. In contrast, for PT-xBZT, T_C continuously increases with x. At atmospheric pressure, PT, PT-0.08BZT and PT-0.17BMT undergo a temperature-induced ferroelectric-to-paraelectric phase transition from P4mm to $Pm\bar{3}m$ at T_C equal to 763 K [37], 805 K [5], and 810 K [7], respectively.

II. EXPERIMENTAL DETAILS

Single crystals of PbTiO₃, 0.92PbTiO₃-0.08Bi(Zn_{0.5}Ti_{0.5}) O₃, and 0.83PbTiO₃-0.17Bi(Mg_{0.5}Ti_{0.5})O₃ were synthesized using the flux and the top-cooled solution growth methods [10,38].

A wavelength-dispersive electron microprobe system Cameca SX100 was used to verify the composition and chemical homogeneity of the samples. Temperature-dependent single-crystal XRD patterns at ambient pressure were collected at the P24 beamline at PETRA III (DESY) using a PILATUS CdTe 1M detector, a wavelength $\lambda = 0.4959$ Å, and an N₂-gas-streaming heating device. The holding time at the desired temperature prior the measurement varied between 15 and 30 min, depending on the temperature step. The pixel intensities were integrated using the Eval15 program suite [39]. The structure refinements to the room-temperature data were performed with JANA2006 [40].

Raman spectra in the range $15-1200 \text{ cm}^{-1}$ were collected using a Horiba Jobin-Yvon T64000 triple grating spectrometer equipped with a liquid-nitrogen-cooled chargecoupled device camera. An Ar⁺ laser with a wavelength of 514.532 nm was focused on the sample surface through a 50×-long-working distance objective. Although optical transmission microscopy indicated that the samples were not single-domain, the ferroelectric domains were significantly larger than the laser spot on the sample surface. The diameter of the laser beam spot was $\sim 2 \,\mu m$, which allowed us to collect Raman scattering data from an individual domain. The spectral resolution was $\sim 2 \,\mathrm{cm}^{-1}$, while the accuracy of the peak position was ~ 0.35 cm⁻¹. Initial measurements were carried out at ambient conditions on (100)-oriented platelets in $\bar{x}(yy)x$ and $\bar{x}(zy)x$ scattering geometries as well as on (001)-oriented platelets in $\overline{z}(xx)z$ scattering geometry (Porto's notation [41], where x, y, and z are parallel to the tetragonal [100], [010], and [001] directions, respectively).

The HT experiments were performed on (100)-oriented platelets with dimensions of $\sim 1 \times 1 \times 0.5 \text{ mm}^3$ in the $\bar{x}(yy)x$,



FIG. 2. (a) Schematic representation of a diamond anvil cell setup. (b) A sample of PT-0.08BZT surrounded by chips of ruby in the high-pressure chamber of the diamond anvil cell.

THMS-E600 stage on cooling between 300 K and 150 K and a Linkam TS1200 EV-1015 stage on heating between 300 K and 1000 K, with a 20 K step and a heating/cooling rate of 10 K/min. The temperature accuracy was 0.1 K and 1 K below and above 300 K, respectively.

The HP experiments up to 12 GPa were conducted at room temperature in $\bar{x}(yy)x$ and $\bar{x}(zy)x$ scattering geometries on (100)-oriented platelets with a size of $\sim 100 \times 70 \times 50 \,\mu\text{m}^3$ using a Boehler-Almax diamond anvil cell equipped with 600um-diameter diamond anvils (Fig. 2). Each sample was loaded in a 300-µm-diameter chamber of a stainless-steel gasket preindented to ~90-µm thickness. The pressure-transmitting medium was a 16:3:1 methanol-ethanol-water mixture, which has a strict hydrostatic limit of 10.4 GPa [42], but the deviation of nonhydrostaticity between 10 and 12 GPa is negligibly small [43,44]. The pressure was determined by using the photoluminescence R1-line of a ruby crystal placed near the sample [45]. Raman spectra were collected with a pressure step of ~ 0.3 GPa and a pressure uncertainty of ~ 0.1 GPa. Measurements on decompression confirmed the reversibility of the pressure-induced changes. At each pressure step a background spectrum was collected aside from the sample and then subtracted from the sample spectrum to eliminate the artificial contribution from the upper anvil and pressure medium. In addition, Raman scattering of diamond was collected in the range 1050-1600 cm⁻¹ to trace the stress-induced change in the optical properties of the anvils, which might have slightly affected the depolarization ratio of the sample Raman scattering [46].

The measured spectra were temperature-reduced by the Bose-Einstein occupation factor and fitted with pseudo-Voigt peak-shape functions to determine the peak positions ω , full widths at half maximum (FWHMs) Γ , and integrated intensities *I* [47] using the OriginPro software package and following the procedure described in detail in the Supplemental Material of Ref. [48].

III. RESULTS AND DISCUSSION

A. Structure and atomic dynamics at ambient conditions

Table I provides the room-temperature lattice constants, FIG. 3. Ske tetragonality (c/a ratio), unit-cell volume, bond lengths, shifts of the A- and B-site cations from the planar55 (O^{I+} and O^{II-}).

TABLE I. Lattice parameters, tetragonality, volume, bond lengths, δ_{Z_A} , δ_{Z_B} and tolerance factors for PT, PT-0.08BZT, and PT-0.17BMT.

	РТ	PT-0.08BZT	PT-0.17BMT
a	3.8989(2) Å	3.8985(2) Å	3.9142(2) Å
С	4.1514(4) Å	4.1699(4) Å	4.1199(4) Å
c/a	1.0648(1)	1.0696(1)	1.0526(1)
Volume	63.107(7) Å ³	63.375(5) Å ³	63.120(7) Å ³
A-O ^I	2.7954(6) Å	2.7986(4) Å	2.8041(11) Å
$A-O^{II+}$	2.5132(14) Å	2.5051(11) Å	2.507(4) Å
$A-O^{II-}$	3.2220(17) Å	3.2467(14) Å	3.217(5) Å
B-O ^{I+}	1.773(3) Å	1.772(3) Å	1.798(7) Å
B-O ^{I-}	2.379(3) Å	2.398(3) Å	2.322(7) Å
B-O ^{II}	1.9773(4) Å	1.9789(4) Å	1.9808(9) Å
δ_{Z_A}	0.462(8) Å	0.482(5) Å	0.449(12) Å
δ_{Z_R}	0.330(6) Å	0.341(4) Å	0.305(11) Å
Tolerance factor	1.019	1.015	1.012

oxygen atoms (δ_{Z_A} and δ_{Z_B} , respectively, as depicted in Fig. 3), and the tolerance factors for PT, PT-0.08BZT, and PT-0.17BMT. Due to the relatively low x values, the tolerance factors of the mixed compounds only slightly reduce compared to PT, although both six-coordinated Zn²⁺ and Mg^{2+} have larger ionic radii than Ti^{4+} (0.74 Å, 0.72 Å, and 0.605 Å, respectively [49]) and the 12coordinated Bi³⁺ has a slightly smaller ionic radius than Pb²⁺ (see also the Supplemental Material [50]). In good agreement with previous results [5,7,51], PT-0.08BZT shows a larger unit-cell tetragonality than PT, whereas the c/a ratio is lower for PT-0.17BMT. Moreover, both δ_{Z_A} and δ_{Z_B} are larger for PT-0.08BZT than for PT. This is attributed to the covalent character of the Zn-O bonds due to the strong hybridization between the Zn 4s and 4p orbitals and the O 2p orbitals [52], leading to a significant off-centering of the Zn^{2+} cation, which in turn facilitates the coupling between the A- and B-site displacements [5,52,53]. In contrast, the Mg²⁺-O bonding has an ionic character, which leads to a smaller δ_{Z_B} . Within uncertainties, the values of δ_{Z_A} for PT-0.17BMT and PT are the same.



FIG. 3. Sketch of the [001] noncoplanarity of the A- and B-site cations (δ_{Z_A} and δ_{Z_B}) relative to the corresponding oxygen-atom plane (O^{I+} and O^{II-}).



FIG. 4. Raman spectra of PT, PT-0.08BZT, and PT-0.17BMT collected in different scattering geometries at ambient conditions. The gray-shaded peaks are allowed within the corresponding scattering configuration, whereas peaks depicted with dotted lines are group-theory forbidden but observed due to unavoidable experimental artifacts. The violet-shaded peaks (X_1-X_3) are activated only in the solid solutions, while the green-shaded peaks (Y1-Y3) are observed for all compounds (at atmospheric and/or at higher pressures). Vertical dashed lines mark the three basic spectral ranges as discussed in the text.

The optical phonon modes at the Brillouin-zone center Γ of the cubic $Pm\bar{3}m$ prototype ABO₃ structure are $\Gamma_{\text{optical}}^{Pm\bar{3}m} =$ $3T_{1u} + T_{2u}$, all Raman inactive. In the tetragonal *P4mm* phase, each T_{1u} mode splits into an A_1 and an E mode (both polar), whereas the T_{2u} mode splits into a B_1 nonpolar mode and an E mode, leading to $\Gamma_{\text{optical}}^{P4mm} = 3A_1 + B_1 +$ 4E, all Raman active. Long-range electrostatic forces further split the polar A_1 and E modes into transverse optical (TO) and longitudinal optical (LO) components [54]. Grouptheory analysis, specifying the Raman-scattering geometries in which the A₁(TO), A₁(LO), B₁, E(TO), and E(LO) phonon modes are symmetry allowed, is given in the Supplemental Material [50].

The Raman spectra of PT, PT-0.08BZT, and PT-0.17BMT measured at ambient conditions in the $\bar{x}(zy)x$, $\bar{x}(yy)x$, and $\overline{z}(xx)z$ experimental setups are shown in Fig. 4. The positions of the measured Raman peaks are given in Table II. The peak assignment to fundamental phonons in P4mm was done in accordance to earlier PT studies [55,56]. Similarly to other Pbbased ferroelectric systems [57,58], the Raman spectra shown in Fig. 4 can be divided into three main regions, corresponding to the energy ranges of the aristotype-structure fundamental 200 cm^{-1} , arising from vibrations of the heavier A-site cations against the BO₆ octahedra perpendicular and parallel to the direction of the spontaneous polarization; (2) between 200 and 480 cm^{-1} , related mainly to the vibrations of the B-site cations $[T_{1u}(2TO)]$ and the rotational BO₆ vibrations (T_{2u}) ; and (3) above 480 cm⁻¹, which is dominated by internal BO₆ modes [57-60].

The inspection of the P4mm-phonon wave numbers (Table II) reveals that the addition of $Bi(B'_{0.5}Ti_{0.5})O_3$ considerably hardens the nonpolar B1 mode, while slightly softening the E mode stemming from the nonpolar T_{2u} . This results in a nonzero $\Delta \omega_{T_{2u}} = \omega_{B_1} - \omega_E$ for both PT-Bi*Me*O₃ crystals (in contrast to pure PT); $\Delta \omega_{T_{2u}}$ increases with x from 12 cm⁻¹ for PT-0.08BZT to 22 cm⁻¹ for PT-0.17BMT. This implies that the cosubstitution of Bi^{3+} for Pb^{2+} and divalent B' for Ti^{4+} enhances the local anisotropy related to nonpolar structural fluctuations.

However, the effect of B-site Zn²⁺ and Mg²⁺ on the A₁-E splitting of the polar T_{1u} modes is different. The incorporation of Zn^{2+} negligibly changes this splitting for all three T_{1u} modes, although the tetragonality of the average structure increases (Table I). On the other hand, for PTmodes $T_{1u}(1TO)$, $T_{1u}(2TO) + T_{2u}$, and $T_{1u}(3TO)$: (1) below 560.17BMT, $\Delta \omega_{1TO} = \omega_{A_1(1TO)} - \omega_{E(1TO)}$, which describes the

TABLE II. Raman-peak wave numbers (in cm⁻¹) measured at ambient conditions. The fundamental phonon modes in *P4mm* are given in bold. The X_{1-3} peaks appear only in the solid solutions, whereas the Y_{1-3} peaks appear in all three compounds at ambient conditions and/or at higher pressures.

	PT, Ref. [59]	PT, Ref. [56]	PT, pres. work	PT-0.08BZT	PT-0.17BMT	Peak assignment
X ₁	_	_	_	53	52	<i>x</i> -ind. excitation in duc ^a
E(1TO)	88	87.5	88.5	87	78	P4mm fundamental mode
$P_{\rm nonT}$	_	110.5	112	113	125	Nontetragonal distortions
$P'_{\rm anh}$	_	126.5	125	129	144	Anharmonicity-related subpeak
$P_{\rm anh}^{\prime\prime}$	_	137.5	140	147	144	Anharmonicity-related subpeak
$A_1(1TO)$	147	148.5	150	147	144	P4mm fundamental mode
E(1LO)	128	128	_	_	_	P4mm fundamental mode
X ₂	_	-	_	_	173	x-induced excitation in duc
A ₁ (1LO)	189	194	189	192	191	P4mm fundamental mode
E(2TO)	220	218.5	220	229	239	P4mm fundamental mode
E(TO+LO)	289	289	289	286	281	P4mm fundamental mode
B ₁	289	289	289	298	303	P4mm fundamental mode
$A_1(2TO)$	359	359.5	358	363	353	P4mm fundamental mode
E(2LO)	439	440.5	_	_	_	P4mm fundamental mode
$A_1(2LO)$	465	465	465	463.5	451	P4mm fundamental mode
X ₃	-	-	-	>1 GPa	490	<i>x</i> -ind. excitation in duc
E(3TO)	505	505	506	513	518	P4mm fundamental mode
Y ₁	_	_	>1.8 GPa	>1 GPa	614	Antiferrodist. defects
$A_1(3TO)$	646	647	642	649	634	P4mm fundamental mode
E(3LO)	_	687	_	_	_	P4mm fundamental mode
Y ₂	_	_	699	696	714	Antiferrodist. defects
Y ₃	_	_	741	735	735	Antiferrodist. defects
A ₁ (3LO)	796	795	796.5	801.5	784	P4mm fundamental mode

^aduc, doubled unit cell.

local anisotropy of the AO₁₂ cuboctahedra, slightly increases by ~5 cm⁻¹. At the same time, both $\Delta\omega_{2TO} = \omega_{A_1(2TO)} - \omega_{E(2TO)}$ and $\Delta\omega_{3TO} = \omega_{A_1(3TO)} - \omega_{E(3TO)}$, which reflect the local BO₆ anisotropy in terms of noncentrosymmetry and bond lengths, respectively, strongly decrease from 137 ± 1 cm⁻¹ for PT to 115 ± 1 cm⁻¹ for PT-0.17BMT. The value of $\Delta\omega_{2TO}$ corroborates the decrease in δ_{Z_B} of the average structure (Table I).

In addition to the Raman peaks generated by the fundamental *P4mm* phonons, several extra Raman peaks are observed at ambient pressure. First, the A₁(1TO)-related Raman scattering near 150 cm⁻¹ has a multicomponent structure observed for all three compounds. For PT, its fine structure has been previously ascribed to the anharmonicity of the interatomic potential (extra subpeaks P'_{anh} and P''_{anh}) as well as to local-scale nontetragonal polar displacements in the tetragonal matrix (the lowest-energy subpeak P_{nonT}) [29,30,56,61]. Due to the substitution-induced inherent broadening of the Raman peaks, P'_{anh} and P''_{anh} cannot be resolved for the mixed compounds but P_{nonT} , which is considerably involved in the destabilization of the tetragonal phase at elevated temperatures and pressures [28], is clearly seen for both solid solutions.

Second, three additional peaks, X_1 at $\sim 52 \text{ cm}^{-1}$, X_2 at $\sim 173 \text{ cm}^{-1}$, and X_3 at $\sim 490 \text{ cm}^{-1}$, are exclusively observed in the mixed compounds, i.e., they are *x* induced. Note that for PT-0.08BZT X_3 is resolved only above 1 GPa, whereas X_2 could not be resolved at any pressure due to overlapping with neighboring peaks. Peak X_1 , which is enhanced with increasing *x*, has been previously ascribed to a different 57

structural state of the A-site cations in the PT-BiMeO₃ solid solutions [19,20,47,62]. It should be underlined that Pb-based B-site complex relaxor ferroelectrics also exhibit a strong peak near 50 cm⁻¹, due to the local-scale doubling of the unit cell of the aristotype perovskite structure associated with a NaCl-type B-site chemical order [58,63]. However, in ferroic perovskites a doubling of the unit cell may also be related to the presence of antiferrodistortive order such as antiphase BO_6 tilting and/or antipolar displacements of the A-site cations, which are typical of the high-pressure state of relaxor ferroelectriocs [63,64]. Moreover, local-scale antiphase octahedral tilts across the MPB were suggested to give rise to the extra Raman scattering near 60 cm⁻¹ in $PbZr_{1-x}Ti_xO_3$ with x = 0.25 - 0.65 [60]. Regardless of the origin of the unit-cell doubling, a reduction of the translational symmetry leads to a larger number of Raman-active phonon modes [63]. Given that the X_{1-3} peaks are enhanced with x, we have assigned them to a x-induced doubling of the perovskite structure, as the substitution of BiMeO₃ may trigger both chemical B-site order and compatible antiferrodistortive order on the local scale.

Finally, three extra peaks, Y_1 near 614 cm⁻¹, Y_2 near 700 cm⁻¹, and Y_3 near 735 cm⁻¹, are observed for all three compounds, although for PT and PT-0.08BZT Y_1 is resolved only above 1.8 and 1.0 GPa, respectively (see Sec. III B). A possible assignment to second-order Raman scattering is ruled out, since the peak positions do not match any combination of fundamental phonons. Y_2 and Y_3 , which are also typical to other PT-*x*Bi*Me*O₃ solid solutions and increase in intensity with *x* [47,62], have been previously ascribed to the



FIG. 5. Raman spectra of PT, PT-0.08BZ, and PT-0.17BMT at selected pressures measured in the $\bar{x}(yy)x$ scattering geometry. For clarity, the Raman spectra were normalized to the height of the strongest peak and vertically off shifted.

symmetrical BO₆ stretching in a doubled perovskite structure [58,62,63,65,66]. The presence of these peaks in pure PT suggests that the unit-cell doubling is a result of local-scale antiferrodistortive order. Moreover, these intrinsic structural defects in the polar tetragonal matrix of PT are enhanced by the cosubstitution at the A and B sites. Likewise, we have assigned Y_1 to BO₆ internal vibration in a locally distorted doubled perovskite structure.

B. Structural transformations under elevating pressures

The room-temperature Raman spectra of PT, PT-0.08BZT, and PT-0.17BMT collected at different pressures are shown in Fig. 5. The pressure evolution of the Raman peaks is discussed in detail below.

Figure 6(a) shows the Raman spectra below 200 cm⁻¹ at ambient conditions, 9.5 GPa, and 12 GPa. The pressure evolution of the wave number of E(1TO), $A_1(1TO)$, and P_{nonT} as well as that of the composition-induced X_1 and X_2 modes is shown in Fig. 6(b). For all compounds P_{nonT} and E(1TO) soften with pressure, while $\omega_{A_1(1TO)}$ remains almost constant in the measured range. This emphasizes that the atomic dynamics of the nontetragonal local distortions play a significant role in the development of a high-pressure phase and, along with the E(1TO) mode, ensure the flattening of the crystal potential across the P4mm-to-R3c transition. For pure PT, $\omega_{\rm E(1TO)}$ shows a minimum around 10.4 GPa, while $\omega_{\rm P_{nonT}}$ has a plateaulike minimum between 10.4 and 11.7 GPa, pointing to ongoing structural transformations within the A-site cationic subsystem across a pressure range of ~ 1.3 GPa, just before the change of the global structure from P4mm to R3c at 13 GPa [25].

For PT-0.08BZT, $\omega_{E(1TO)}(p)$ has a minimum at 11.6 GPa, higher than the corresponding pressure for PT, and $\omega_{P_{nonT}}(p)$ gradually decreases in the entire studied range, indicating that the substitution of Zn²⁺ extends the pressure range of the 58 instability in the B-cation subsystem.

tetragonal phase by ~1.0 GPa. In contrast, the substitution of Mg²⁺ at the B-site leads to a broad minimum of $\omega_{E(1TO)}(p)$ centered around 6.2 GPa (see also Fig. S2 in the Supplemental Material [50]), and a local minimum of $\omega_{P_{nonT}}$ at 7.6 GPa, indicating that the A-site sublattice undergoes rearrangements at lower pressures than PT. The opposite effects of Zn and Mg on the pressure-induced transformation processes are also revealed by the pressure dependence of the intensity of P_{nonT} relative to the A₁(1TO)-related Raman scattering [28].

For all three compounds, $\Delta \omega_{1TO}$ increases with pressure, as a results of the softening of the E(1TO) mode and the consequent destabilization of the AO₁₂ tetragonal distortion. This manifests as an increasing anisotropy of the AO₁₂ cuboctahedra, due to the incoherent lowering of their local symmetry [see Fig. 6(c)]. Notably, the effect of the "internal" chemical pressure introduced by the substitution of 0.17BMT corresponds to the effect of ~2.0 GPa external hydrostatic pressure on the local AO₁₂ anisotropy for PT [see the horizontal dotted line in Fig. 6(c)].

Figure 7(a) shows the pressure-induced changes in the wave number and FWHM of the Raman modes in the 200- to 480 cm^{-1} region. The three compounds behave very similarly in this spectral range:

(i) The wave numbers of the E and B_1 modes, which originate from the T_{2u} mode and involve mainly vibrations of the oxygen atoms, show a negligible pressure dependence.

(ii) With increasing pressure, the wave number of $A_1(2TO)$ decreases linearly and crosses that of $E(T_{2u})$ at 5.4 GPa, 6.3 GPa, and 5.6 GPa for PT, PT-0.08BZT, and PT-0.17BMT, respectively (Figs. 7(a) and 7(b) and Fig. S5 in the Supplemental Material [50]). At the crossing pressure, $In_{A_1(2TO)}$ is enhanced while $In_{E(T_{2u})}$ is reduced, and above the crossing pressure a strong increase in the FWHM of the $A_1(2TO)$ mode is observed (Fig. 7(a) and Fig. S3 in the Supplemental Material [50]), suggesting an increased structural instability in the B-cation subsystem.



FIG. 6. (a) $\bar{x}(yy)x$ Raman spectra of PT, PT-0.08BZT, and PT-0.17BMT measured under ambient conditions, at 9.5 GPa, and at 12 GPa. (b) Pressure dependencies of the wave number of X₁, E(1TO), A₁(1TO), P_{nonT}, and X₂; for clarity, P'_{anh} and P''_{anh} are not shown. The dotted line in (b) is a guide to the eye tracing the data between 8.5 and 10.8 GPa for PT-0.08BZN, where X₁ cannot be satisfactorily resolved from E(1TO). (c) Pressure dependence of $\Delta \omega_{1TO} = \omega_{A_1(1TO)} - \omega_{E(1TO)}$. The horizontal dashed line in (c) traces the position of Δ_{1TO} at ambient conditions for PT-0.17BMT. Error bars for most data points are smaller than the size of the symbols.

(iii) With increasing pressure, $\Delta \omega_{2TO}(p)$ strongly decreases [Fig. 7(c)], indicating a reduction of the BO₆ noncentrosymmetry for all compounds. This is also reflected by the decrease of the fractional intensity of the E(2TO) mode, In_{E(2TO)}(*p*) (Fig. S3 in the Supplemental Material [50]), which implies a reduction of the B-site cation off-centering, similar to other perovskite-type ferroelectrics [22,48,58].

For PT, $\Delta\omega_{2TO}(p)$ exhibits a minimum at 10.5 GPa, whereas for PT-0.08BZT, Zn²⁺ slightly shifts this minimum towards higher pressures, as $\Delta\omega_{2TO}(p)$ decreases up to 11 GPa and then remains constant up to 12 GPa. For PT-0.17BMT, the A₁(2TO) peak could not be clearly resolved between 6 and 8 GPa due to peak overlapping, but a simplified linear extrapolation of the data points $\omega(p)$ [see Fig. 7(a)] suggests that



FIG. 7. (a) Pressure dependencies of the wave number and FWHM of the E(2TO), $A_1(2TO)$, B_1 , and $E(T_2u)$ modes for all compositions; the dotted line is an extrapolation of the data points of $A_1(2TO)$ for PT-0.17BMT at high pressures, where this mode cannot be clearly separated from the E(2TO) mode. (b) Raman spectra of PT measured in $\bar{x}(yy)x$ scattering geometry at different pressures, showing the crossing of the $A_1(2TO)$ and $B_1 + E$ modes. (c) Pressure dependence of $\Delta \omega_{2TO} = \omega_{A_1(2TO)} - \omega_{E(2TO)}$. The dotted lines in (a) and (c) are guides for the eye; the horizontal dashed line in (c) traces the position of $\Delta \omega_{2TO}$ at ambient conditions for PT-0.17BMT. Error bars for most data points are smaller than the size of the symbols.



FIG. 8. (a) $\bar{x}(yy)x$ Raman spectra of the internal octahedral modes collected at 6 GPa for all compositions. (b) Pressure dependencies of the wave number of the E(3TO), A₁(3TO), Y₁₋₃, as well as the X₃ modes for all compositions. (c) Pressure dependence of $\Delta \omega_{3TO} = \omega_{A_1(3TO)} - \omega_{E(3TO)}$. (d) Fractional intensity of the X₃ peak for PT-0.08BZT and PT-0.17BMT. Error bars for most data points are smaller than the size of the symbols.

the A₁(2TO)-E(2TO) splitting disappears around 9 GPa, i.e., at a lower pressure than the minimum of $\Delta \omega_{2TO}$ for PT. The comparison of the $\Delta \omega_{2TO}(p)$ trends for PT and PT-0.17BMT reveals that on the local scale, the partial substitution of Mg²⁺ for Ti²⁺ suppresses the tetragonal off-centering of the B-site cations to the same degree as an external pressure of ~4 GPa [Fig. 7(c)].

Figure 8(b) illustrates the pressure dependence of the wave number of the internal octahedral modes observed in the highest-energy range of the spectrum. For all compounds, E(3TO) strongly hardens on compression, whereas $\omega_{A_1(3TO)}$ changes only slightly. As a result, $\Delta \omega_{3TO} = \omega_{A_1(3TO)} - \omega_{A_2(3TO)}$ $\omega_{\rm E(3TO)}$ decreases with pressure [Fig. 8(c)]. Since the parent $T_{1u}(3TO)$ consists of BO₆ stretching vibrations in the single perovskite structure [58], $\Delta \omega_{3TO}$ represent the local BO₆ anisotropy related to differences in the B-O lengths. Hence, hydrostatic pressure gradually reduces the difference in the B-O lengths. For PT and PT-0.08BZT, $\Delta \omega_{3TO}(p)$ is the same in the entire pressure range, whereas for PT-0.17BMT, $\Delta \omega_{\rm 3TO}(p)$ equals to that of PT only above ~2.0 GPa. Furthermore, the effect of 0.17BMT substitution at atmospheric pressure corresponds to that of an external pressure of ~ 1.0 GPa for PT [Fig. 8(c)].

Above 1 GPa, the composition-induced peak X₃ observed already at ambient conditions in PT-0.17BMT can be detected also in PT-0.08BZT [Fig. 8(a)]. For both compounds, $\omega_{X_3}(p)$ does not vary in the measured range, whereas In_{X3}(p) is enhanced on compression, especially for PT-0.017BMT [Fig. 8(d)], indicating that the related structural distortions evolve with pressure. This suggests that the *x*-induced local-scale doubling of the perovskite structure involves antiferrodistortive order, since pressure cannot trigger B-site chemical order.

Above 1 and 1.8 GPa, the additional peak Y_1 can be observed also for PT-0.08BZT and PT [Fig. 8(a)], respectively, and for pure PT its intensity slightly increases with pressure (Fig. S4a in the Supplemental Material [50]). The Y_2 and Y_3 peaks only trivially harden with pressure, without gaining significant fractional intensity throughout the measured pressure range (Fig. S4b in the Supplemental Material [50]). Therefore, the In(x, p) trends of the Y_{1-3} peaks indicate that the related intrinsic structural defects of the PT matrix are more sensitive to internal, chemically induced local elastic stress fields than to external hydrostatic pressure, because their fraction clearly increases with the increase of x but remains nearly the same with p.

C. Structural transformations under elevating temperature

Raman spectra of PT, PT-0.08BZT, and PT-0.17BMT collected in $\bar{x}(yy)x$ scattering geometry at selected temperatures are shown in Fig. 9. Similarly to other ferroelectric perovskite-type oxides, all three compounds show symmetry-forbidden first-order Raman scattering above T_C (Figs. 10–12), revealing the presence of local polar distortions in the paraelectric cubic phase [47,67–69]. The anomalous Raman scattering increases with x, indicating that cosubstution at the A and B sites enhances the local ferroic distortions in the globally cubic phase.

[Fig. 8(d)], indicating that the related structural distortions evolve with pressure. This suggests that the x-induced local-scale doubling of the perovskite structure involves an-60 vibrations of the A-site cations. For all three compounds P_{norT}



FIG. 9. (a) Raman spectra of PT, PT-0.08BZT, and PT-0.17BMT collected in $\bar{x}(yy)x$ scattering geometry at selected temperatures. The spectra are vertically offset for clarity. The insets show the enlarged Raman spectra of PT and PT-0.08BZT at 1000 K, respectively. The red arrows mark the Curie temperature of each compound.



FIG. 10. (a) Temperature dependence of the wave number of X₁, E(1TO), P_{nonT} , and A₁(1TO) for PT, PT-0.08BZT, and PT-0.17BMT. The dashed vertical lines mark the Curie temperature of each compound. (b) Fractional intensity of the X₁ mode for PT-0.08BZT and PT-0.17BMT. (c) Temperature dependence of $\Delta_{1TO} = \omega_{A_1(1TO)} - \omega_{E(1TO)}$. Note that the wave numbers of P_{nonT} and E(1TO) are independently derived from fitting the $\bar{x}(yy)x$ and $\bar{x}(zy)x$ polarized spectra, respectively.



FIG. 11. Temperature dependence of the wave number of E(2TO), E(T_{2u}), B₁, and A₁(2TO) as well as $\Delta_{2TO} = \omega_{A_1(2TO)} - \omega_{E(2TO)}$ for PT, PT-0.08BZT, and PT-0.17BMT. The vertical dashed lines mark the Curie temperature of each compound. The orange lines represent Boltzmann function fits to the $\Delta_{2TO}(T)$ data points.

experiences significant softening on the approach to T_C [28], along with the classical E(1TO) soft mode. This indicates that the E(1TO) ensures coupling of the local dipoles within the plane perpendicular to the crystallographic polar axis below T_C , while the alinement of the local dipoles along the polar axis is strongly influenced by the atomic dynamics of the inherent nontetragonal local distortions. Moreover, for the mixed compounds, the composition-induced X_1 mode is strongly enhanced in the approach to T_C from below [Fig. 10(b)] and for PT-0.17BMT it exhibits soft-mode



FIG. 12. Temperature dependence of the wave number and FWHM of E(3TO), A₁(3TO), A₁(3LO), Y₁, Y₂, and Y₃ as well as $\Delta \omega_{3TO} = \omega_{A_1(3TO)} - \omega_{E(3TO)}$ for PT, PT-0.08BZT, and PT-0.17BMT. The vertica $\omega_{A_1(3TO)} - \omega_{E(3TO)}$ for PT, PT-0.08BZT, and PT-0.17BMT. The vertica $\omega_{A_1(3TO)} - \omega_{E(3TO)}$ for PT, PT-0.08BZT, and PT-0.17BMT. The vertica $\omega_{A_1(3TO)} - \omega_{E(3TO)}$ for PT, PT-0.08BZT, and PT-0.17BMT.

behavior, with $\omega_{X_1}(T) \propto (T_C - T)^{0.41 \pm 0.02}$. This further reveals that "defect" excitations, particular those of local-scale doubled-perovskite structural entities, significantly participate in the temperature-induced transformation processes.

The temperature dependence of $\Delta \omega_{1TO} = \omega_{A_1(1TO)} - \omega_{E(1TO)}$ for PT and PT-0.08BZT [Fig. 10(c)] indicates an abrupt increase in the local anisotropy of the AO₁₂ cuboctahedra around the transition temperature, with a maximum at T_C , suggesting that the off-centered shifts of the A-site cations reorient to become coherent and evolve into long-range tetragonal polar order on cooling down. For PT-0.17BMT, $\Delta_{1TO}(T)$ is smeared out over a wide temperature range between T_C down to ~350 K, indicating that B-site Mg²⁺ impedes the rearrangement of the A-site local dipoles.

The temperature dependence of the wave numbers of phonon modes involving B-site cations is shown in Fig. 11. At T_C the A₁(2TO) and B₁ modes merge with the E(T_{2u}) mode. For PT and PT-0.08BZT the Curie temperature is also clearly marked by the minimum of $\omega_{E(2TO)}(T)$. For PT-0.17BMT E(2TO) could not be resolved from $E(T_{2u})$ above T_C , due to peak broadening and subsequent overlapping. On heating $\Delta \omega_{2TO}(T)$ as well as $In_{E(2TO)}(T)$ decreases abruptly when approaching T_C from below (Fig. 11), indicating a reduction of the BO₆ anisotropy due to the suppression of the B cation off-centering. The fitting of $\Delta \omega_{2TO}(T)$ with a Boltzmann function has yielded comparable slopes s for PT and PT-0.08BZT [$s_{PT} = 0.29(1)$, with $T_0^{PT} = 734(4)$ K and $s_{\text{PT}-0.08\text{BZT}} = 0.25(2)$ with $T_0^{\text{PT}-0.08\text{BZT}} = 797(3)$ K] and a lower value of *s* for PT-0.17BMT [$s_{PT-0.17BMT} = 0.14(3)$, $T_0^{\text{PT}-0.17\text{BMT}} = 710(20) \text{ K}$]. This suggests that on cooling the preexisting off-centered shifts of the B-site cations evolve into ferroelectric long-range order at a slower rate for PT-0.17BMT as compared to PT and PT-0.08PZT.

In the highest-energy spectral range, the decrease of $\Delta \omega_{3TO}$ on heating (Fig. 12) indicates that temperature gradually reduces the local BO₆ anisotropy arising from different B-O lengths. The minima of $\Delta \omega_{3TO}$ observed for PT and PT-0.08BZT at 800 K and 900 K, respectively, indicate that the coupling between distorted BO₆ octahedra begins already above T_C . For PT-0.08BZT, this process is shifted to higher temperatures compared to PT, probably as a result of the strong hybridization between Zn^{2+} and the surrounding oxygen atoms, which in turn influences the whole octahedral network. In contrast, for PT-0.17BMT, $\Delta \omega_{3TO}$ exhibits a minimum exactly at T_C . Simultaneously, the values of $\Delta \omega_{3TO}$ for PT-0.17BMT are higher in the paraelectric phase than for the other two compounds, suggesting a higher B-O bond length anisotropy, probably due to a size mismatch of the Ti-O and Mg-O bonds.

Similarly to the evolution with increasing pressure, the Y_2 and Y_3 Raman peaks show little temperature dependence, as ω_{Y_2,Y_3} (Fig. 12) and In_{Y_2,Y_3} remain almost constant in the whole measured range, indicating that the related structural defects are also not sensitive to temperature.

The high-temperature single-crystal XRD patterns of all three compounds did not show any diffuse-scattering features, contrary to the case of Pb-free ferroelectrics [70,71] or Pb-based relaxor ferroelectrics [72]. The absence of diffuse scattering in pure PT has been explained by the absence of



FIG. 13. Temperature dependence of the unit-cell volume (a), volume strain with respect to the paraelectric state (b), and unit-cell tetragonality c/a. Solid lines in (a) are linear fits to the corresponding data points above T_C , while dashed lines are just guides for the eye.

any intermediate-range correlations between the local $\langle 001 \rangle$ cationic displacements [73]. Hence, the absence of x-ray diffuse scattering for PT-0.08BZT and PT-0.17BMT indicates that at these x levels the cosubstitution at the A and B sites does not promote any correlations between the local dipoles above T_C . According to the maximum of dielectric permittivity, T_C shifts by ~40 K to high temperatures on the addition of 0.08BZT or 0.17BMT [5,7]. Our single-crystal XRD data show that for both mixed compounds the unit-cell volume V(T) has only a subtle deviation near 800 K (i.e., $\sim T_C$) from the linear trend of the corresponding paraelectric phase [Fig. 13(a)], while V(T) exhibits a minimum around the

Curie temperature of PT (763 K). However, there is a clear difference between PT-0.08BZT and PT-0.17BMT regarding the accumulated volume strain below the phase transition temperature. For PT-0.17BMT, V(T) barely changes between T_C and room temperature [Fig. 13(a)] and the volume strain is definitely smaller than that of PT [Fig. 13(b)]. In contrast, the V(T) trend for PT-0.08BZN resembles that for PT in Fig. 13(a), resulting in the same volume strain at room temperature as that of PT in Fig. 13(b). Moreover, the unit-cell anisotropy (c/a) is highest for PT-0.08BZT and smallest for PT-0.17BMT at any temperature below T_C [Fig. 13(c)]. The different effect of B-site Zn and Mg on the unit-cell volume strain and anisotropy further clarify why PT-xBZT solid solution does not exhibit MPB, while PT-xBMT does.

IV. CONCLUSIONS

Our results reveal the existence of local-scale doubling of the perovskite structure due to the presence of antiferrodistortive structural entities inside the polar tetragonal matrix even in pure PbTiO₃. The short-range antiferrodistortive order is most probably composed of antiphase BO₆ tilts and, in the case of PbTiO₃-Bi*Me*O₃ solid solutions, compatible antipolar A-site cation shifts. The coupling processes between the polar tetragonal distortions existing already above the Curie temperature and between the nontetragonal antiferrodistortive structural entities inside the polar tetragonal matrix below the Curie temperature can be tuned via the chemical characteristics of the B-site substituent. Thus, the incorporation of Zn²⁺ and Mg²⁺ into the perovskite structure results into opposite effects on the response of the structure to high pressure or temperature:

(i) The δ_{Z_A} and δ_{Z_B} values derived from the average structure, refined from XRD data, as well as the c/a ratio, indicate that the presence of Zn^{2+} at the B-site enhances the macroscopic tetragonal anisotropy (c/a). On the other hand, Raman

spectroscopy, which probes the ABO₃ structure at a much shorter length scale of only a few unit cells, reveals that locally, Zn^{2+} negligibly affects the anisotropy of the BO₆ and AO₁₂ polyhedra (at the level of x = 0.08). However, Zn^{2+} stiffens the tetragonal cationic off-centering at both A and B sites, making the polar tetragonal matrix more resistant to an increase in either pressure or temperature.

(ii) The incorporation of B-site Mg²⁺ reduces the global tetragonal anisotropy (c/a) and volume strain accumulated on cooling below the Curie temperature as well as the local BO₆ anisotropy, in terms of both B-site cationic offcentering and different B-O bonds. However, locally, B-site Mg^{2+} favors the anisotropy of the AO₁₂ polyhedra. The effects of the chemically induced local elastic-stress fields leading to an enhancement of AO12 off-centering and suppression of BO₆ off-centering correspond to that of a external hydrostatic pressure of ~ 2.0 and ~ 4.0 GPa, respectively. The Raman spectroscopic analysis suggest that the pressureinduced phase transition is shifted to lower pressures with the substitution of 0.17BMT. On the other hand, although the temperature-induced phase transition takes place at a higher value compared to PT, the A-site local dipole rearrangement takes place in a broader temperature range than for PT.

ACKNOWLEDGMENTS

I.M. acknowledges the support from Universität Hamburg (Stipendium der Landesgraduiertenförderung nach dem HmbNFG). Z.L. acknowledges the support of the National Natural Science Foundation of China through Grant No. 52372124. Z.-G.Y. acknowledges the support from the Natural Sciences and Engineering Research Council of Canada (NSERC, Discovery Grant No. RGPIN-2023-04416). We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities. Parts of this research were carried out at beamline P24, PETRA III. Beamtime was allocated for Proposal No. I-20191031.

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Pressure- and temperature-induced transformation processes in $PbTiO_3$ -BiMeO₃ ferroelectrics

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SUPPLEMENTARY MATERIAL

Group-theoretical analysis of phonons Α.

A phonon mode is Raman-active if it induces a change in the polarizability of the crystal. The polarizability tensors \mathbf{R} of the Raman active modes in a crystal with P4mm symmetry and 1a, 1b and 2c occupied Wyckoff positions are [1, 2]:

$$A_{1}(z) = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} E(x) = \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{pmatrix} E(y) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & e \\ 0 & e & 0 \end{pmatrix} B_{1} = \begin{pmatrix} c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

The Raman-scattering intensity I_S of a phonon depends on the orientation of the sample relative to the propagation and polarization directions of the incident and scattered light, respectively. I_S is given by the relation:

$$I_S \propto \left| e_i \cdot \mathbf{R} \cdot e_s \right|^2 \tag{1}$$

where e_i and e_s are the polarization direction of the incident and scattered light, respectively.

The phonon modes allowed in different scattering geometries were determined using Equation 1 and are given in Table SI. The experimental configuration is described in Porto's notation [3] $k_i(e_i e_s)k_s$, where k_i and k_s represent the propagation direction of the incident and scattered light, respectively.

Experimental configuration	$ A_1(LO) $	$A_1(TO)$	E(LO)	E(TO)	B_1
$ar{x}(yy)x$		x			x
$ar{x}(zy)x$				х	
$ar{x}(zz)x$		х			
$ar{y}(xx)y$		x			х
$ar{y}(zx)y$				х	
$ar{y}(zz)y$		x			
$\overline{z}(xx)z$	x				х
$\overline{z}(yx)z$					
$ar{z}(yy)z$	x				х

TABLE SI: Raman selection rules for (100)- and (001)-oriented single crystals measured in backscattering geometry. The laboratory coordinates x, y, and z coincide with the crystallographic axes [100], [010], and [001], respectively.

In our experimental configuration, the laboratory coordinate system (x, y, z) coincides with the crystallographic axes of the crystal structure. The results from Table SI show that, in order to study the phonons expected in the

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ferroelectric phase, at least three different experimental geometries are required: $\bar{x}(yy)x$, $\bar{x}(zy)x$, and $\bar{z}(xx)z$ (Figure S1). The E(LO) modes cannot be observed in (100)- and (001)-oriented single crystals measured in backscattering geometry.



FIG. S1: $\bar{x}(yy)x$, $\bar{x}(zy)x$ and $\bar{z}(xx)z$ scattering configurations. The vertical arrows represent the direction of the incoming and scattered light, whereas the horizontal arrows describe the orientation of the electric field of the incoming (dark red) and scattered (grey) light.

B. Tolerance factor t

The stability of a perovskite-structured material can be predicted using the tolerance factor t [4], defined as:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)},$$

where r_A is the ionic radius of the A-site cation, r_B is the ionic radius of the B-site cation, and r_O is the ionic radius of the oxygen anion. For t = 1, the compound adopts the ideal cubic perovskite structure. If t > 1, the B-site cation is too small to fill its surrounding oxygen cage, which promotes off-center displacements at the B site. If t < 1, the ionic radius of the A-site cation is smaller than the ideal value, which allows the rotation and tilting of the BO₆ octahedra [4–6].

The ionic radii of the oxygen anion and the A- and B-site cations for PT, PT-0.08BZT, and PT-0.17BMT are given in Table SII.

Cation/ Anion	Ionic radius (A)
Pb^{2+}	1.49
Bi^{3+}	1.45
Ti^{4+}	0.605
Zn^{2+}	0.74
Mg^{2+}	0.72
O^{2-}	1.4

TABLE SII: Ionic radii of the twelve-fold coordinated Pb^{2+} and Bi^{3+} cations, six-fold coordinated Ti^{4+} , Zn^{2+} , and Mg^{2+} cations, and the six-fold coordinated O^{2-} anion [7, 8].

The tolerance factors of PT, PT-0.08BZT and PZ-0.17BMT calculated using the ionic radii given in Table SII and the adjusted formula of the tolerance factor,

$$t = \frac{(1-x)r_{Pb} + xr_{Bi} + r_O}{\sqrt{2}((1-\frac{x}{2})r_{Ti} + \frac{x}{2}r_{Zn/Mg} + r_O)}$$

are given in Table SIII.

Compound	Tolerance factor
PT	1.019
PT-0.08BZT	1.015
$\operatorname{PT-0.17BMT}$	1.012

TABLE SIII: Tolerance factors of PT, PT-0.08BZT and PZ-0.17BMT.

C. Additional experimental data

Compound	Ions	x	y	z	Anisotropic displacement parameters	
PbTiO ₃	Pb	0	0	-0.000039(11)	$U_{11} = U_{22} = 0.00948(3)$	R-factor: 0.0140
					$U_{33} = 0.00778(3)$	Number of used reflections: 744
	Ti	0.5	0.5	0.53827(10)	$U_{11} = U_{22} = 0.00442(6)$	
					$U_{33} = 0.00487(17)$	
	O^{I}	0.5	0.5	0.1113(7)	$U_{11} = U_{22} = 0.0097(4)$	
					$U_{33} = 0.0054(5)$	
	$ O^{II}$	0	0.5	0.6179(5)	$U_{11} = 0.0042(3)$	
					$U_{22} = 0.0090(4)$	
					$U_{33} = 0.0093(4)$	
PT-0.08BZT	Pb/Bi	0	0	0.140350(17)	$U_{11} = U_{22} = 0.01003(2)$	R-factor: 0.0125
					$U_{33} = 0.01342(3)$	Number of used reflections: 790
	Ti/Zn	0.5	0.5	0.68112(8)	$U_{11} = U_{22} = 0.00441(7)$	
					$U_{33} = 0.00985(14)$	
	O^{I}	0.5	0.5	0.2561(5)	$U_{11} = U_{22} = 0.0104(3)$	
					$U_{33} = 0.0093(4)$	
	$ O^{II}$	0.5	1	0.7630(4)	$U_{11} = 0.0101(3)$	
					$U_{22} = 0.0041(2)$	
					$U_{33} = 0.0131(4)$	
PT-0.17BMT	Pb/Bi	0	0	-0.005970(16)	$U_{11} = U_{22} = 0.01685(8)$	R-factor: 0.0435
					$U_{33} = 0.02746(17)$	Number of used reflections: 614
	Ti/Mg	0.5	0.5	0.5396(3)	$U_{11} = U_{22} = 0.00752(13)$	
	_				$U_{33} = 0.0184(5)$	
	O^{I}	0.5	0.5	0.1032(16)	$U_{11} = U_{22} = 0.0135(9)$	
					$U_{33} = 0.0168(16)$	
	$ O^{II}$	0	0.5	0.6137(13)	$U_{11} = 0.0077(7)$	
				. ,	$U_{22} = 0.0142(11)$	
					$U_{33} = 0.0207(12)$	

TABLE SIV: Structural parameters for PT, PT-0.08BZT, and PZ-0.17BMT.



FIG. S2: Pressure dependence of the wavenumber of E(1TO) for PT, PT-0.08BZT and PT-0.17BMT. The y-axis scaling differs for the three compounds.



FIG. S3: Fractional intensity of the E(2TO), A₁(2TO) and E(TO+LO) phonon modes for PT, PT-0.08BZT and PT-0.17BMT.


0.15

0.10

0.05

0.00

 $\mathbf{5}$

4 6 8 10 12 2 6 8 10 12 2 6 8 10 12 2 0 4 4 0 0 Pressure (GPa) Pressure (GPa) Pressure (GPa)

0.15

0.10

0.05

0.00

a)

Fractional Intensity

b)

Fractional Intensity

0.30

0.25

0.20

0.15

0.10

0.05

0.00

0.30

0.25

0.20

0.15

0.10

0.05

0.00

0 2 4

PT

PT

FIG. S4: a) Fractional intensity of the A₁(3TO) and Y₁ peaks for PT, PT-0.08BZT, and PT-0.17BMT. b) Fractional intensity of the Y₂ and Y₃ peaks for PT, PT-0.08BZT, and PT-0.17BMT.



FIG. S5: Raman spectra of PT-0.08BZT and PT-0.17BMT measured in the $\bar{x}(yy)x$ scattering geometry at different pressures showing the crossing of the A₁(2TO) and E modes.



FIG. S6: Temperature dependence of the FWHM and fractional intensities of E(2TO), $E(T_{2u})$, and $A_1(2TO)$ for PT, PT-0.08BZT, and PT-0.17BMT. The vertical dashed lines mark the Curie temperature of each compound.



FIG. S7: Temperature dependence of the FWHM of E(3TO), $A_1(3TO)$, $A_1(3LO)$, Y_2 , and Y_3 for PT, PT-0.08BZT, and PT-0.17BMT. The vertical dashed lines mark the Curie temperature of each compound.

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Eidesstattliche Versicherung

Hiermit erkläre ich an Eides statt, dass ich die vorliegende Dissertation selbst verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

J. Schablack

Hamburg, den 06.05.2025

Unterschrift