Lattice dynamics across the ferroelastic phase transition in Ba$_2$ZnTeO$_6$: A Raman study

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ABSTRACT: Structural phase transitions drive several unconventional phenomena including some illustrious ferroic attributes which are relevant for technological advancements. With this note, we have investigated the structural transition of perovskite-type trigonal Ba$_2$ZnTeO$_6$ using Raman spectroscopy, across $T_c \sim 150$ K, which is also accompanied by a para- to ferroelastic transition. We have observed the presence of central peak (quasi-elastic Rayleigh profile), strong anharmonicity in the soft mode, hysteretic phonon behavior, and signatures of coexistent phases. The existence of central peak in Ba$_2$ZnTeO$_6$ is manifested by a sharp rise in the intensity of the Rayleigh profile in concomitant with the damping of the soft mode near $T_c$, shedding light on the lattice dynamics during the phase transition. While most of the phonons show splitting below $T_c$ confirming the phase transition, we have observed thermal hysteretic behavior of phonon modes that signifies the first-order nature of the transition and presence of coexisting phases, which are corroborated by our temperature-dependent x-ray diffraction and specific heat measurements. Further, an evidence of the concomitant ferroelastic transition appears in the form of a very strong anharmonicity in the thermal response of the soft phonon mode at $\sim 31$ cm$^{-1}$ which is remarkable compared to the hitherto known behavior of soft modes in well-known ferroelectrics.

1. INTRODUCTION

The investigation of phase transition witnessed a surging interest in the last few decades not only from technological but fundamental viewpoint as well. Structural phase transitions possessing strong coupling to the magnetic, electric, and elastic degrees of freedom are of immense
importance as they demonstrate remarkable effects like magneto-structural transition [1,2], metal-insulator transition [3,4], and sometimes, ferro orders as well [5]. While ferro orders like ferroelectricity and ferromagnetism are frequently encountered, occurrence of ferroelasticity is comparatively rare and restricted to selected class of structures that follow certain symmetry rules upon transition. Notably, Aizu listed down 94 active ferroelastic species associated with the symmetry lowering para-to ferro-elastic transition (that create lattice distortion) thus significantly influencing the phonon properties [6,7]. Of particular interest in this context are the low-frequency phonons that shed light on the dynamics of the lattice where soft modes and lattice relaxation processes play vital roles in the phase transition.

The concept of “soft phonon” or “soft mode” offers a powerful tool to establish a fair understanding of the mechanisms (displacive and/or order-disorder) responsible for a phase transition. Reportedly, the involvement of underdamped or overdamped phonons entitles such classification, as noted in case of PbTiO$_3$ and BaTiO$_3$ [8-12]. Crucial details of the nature (order) of the phase transition, associated crystal symmetries, and underlying lattice instabilities can also be understood from soft phonons [13,14]. It is important to note that the soft mode driven phase transition in ferroic systems is often accompanied by dynamical effects, which are manifested as central peak (quasi-elastic Rayleigh peak) thus shedding light on the evolution and dynamics of the lattice during the phase transition. The central peak originates from the phonon density and entropy fluctuations [15, 16], lattice defects [17], ion displacements [18], domain wall motion [19] and, therefore, it needs a careful investigation to elucidate the dynamics and the association with the soft mode. Soft phonons characteristically vanish across the phase transition temperature ($T_c$) and exhibit a pronounced decrement in frequency due to lattice anharmonicity which can be estimated as $\frac{\Delta \omega}{\omega} = \frac{\omega(T) - \omega(T_c)}{\omega(T_c)} \%$ if the quasi-harmonic contribution is negligible. Some of the
examples of the classic perovskite systems where a strong anharmonicity is associated with the soft phonon driving the phase transition are SrTiO$_3$ [20], KNbO$_3$ [21], and SrZrO$_3$ [22]. Notably, most of the systems cited above belong to the usual cubic/tetragonal/orthorhombic perovskite structures (phases) at ambient conditions, with a tolerance factor ($t = \frac{r_A+r_O}{\sqrt{2}(r_B+r_O)}$, where $r_A$ and $r_B$ represent the cationic and $r_O$ represents the anionic radii) close to unity. For $t > 1$, hexagonal variants of perovskites get stabilized possessing large extended unit cells with strong structural anisotropy (large $c/a$ ratio). As a result, the phonon anharmonicity in the hexagonal isomorphs can be really remarkable as compared to their cubic or tetragonal counterparts. One such hexagonal variant belonging to the double-perovskite type Ba$_2$BTeO$_6$ class of systems is Ba$_2$ZnTeO$_6$ (BZT) which crystallizes into a trigonal symmetry (R-3m space group) at ambient conditions [23] and cubic phase at high pressure [24]. Recently, Moreira et al. have shown that BZT undergoes a structural phase transition from trigonal to monoclinic phase at 140 K upon cooling, satisfying the symmetry requirements for ferroelasticity [25]. However, the evolution of lattice and its dynamics across the transition is still not well understood.

Inelastic light scattering is a robust and simple technique to probe phonon dynamics. Here, with a systematic temperature-dependent Raman investigation, we present some remarkable aspects of the phase transition in Ba$_2$ZnTeO$_6$ which are crucial to elucidate the lattice dynamics across the transition. We have discussed (a) the signatures of the ‘central peak’ near T$_c$ indicating involvement of lattice relaxation processes, (b) the hysteretic behavior of phonon modes across the phase transition, thus, identifying it to be of first-order in nature, (c) the presence of coexistent high temperature trigonal and low temperature monoclinic phases in the hysteretic region, and (d) a very strong anharmonicity of the soft phonon mode (at $\sim 31$ cm$^{-1}$) in comparison to the commonly studied perovskite-based ferroelectrics like BaTiO$_3$ and PbTiO$_3$. We have quantitatively analyzed
the quasi-harmonic and anharmonic contributions to invoke the role of anharmonicity in the observed phase transition. We have analyzed these observations with the lowering of the crystallographic symmetry across the phase transition and corroborated our results with temperature-dependent specific heat and x-ray diffraction measurements.

2. SYNTHESIS AND EXPERIMENTAL DETAILS

Solid state reaction method was used to synthesize polycrystalline Ba₂ZnTeO₆ with high purity (99.995%) oxide precursors such as BaCO₃, ZnO, and TeO₂ obtained from Sigma Aldrich. These precursors were mixed in stoichiometric ratio and later treated sequentially at 750°C, 900°C, and 1050°C for 4, 6, and 4 hours, respectively. X-ray diffraction (XRD) measurements were performed employing PANalytical diffractometer with Cu-Κα radiation (λ = 1.5406 Å) and the temperature was varied using Anton Paar 450 low-temperature stage. A Rietveld phase analysis detected a minor fraction of Ba₃TeO₆ (~ 2.1 %) as secondary phase besides the trigonal phase of Ba₂ZnTeO₆ (97.9 %). Further, compositional analysis of the BZT was obtained using the Energy Dispersive X-Ray spectrometer (EDAX) of a High-Resolution field emission scanning electron microscope (HR FESEM) from Zeiss (Model: ULTRA plus). Temperature-dependent Raman measurements were performed using LabRAM-HR Evolution Raman spectrometer combined with Linkam heating stage (Model: HFS600E-PB4) and Peltier-cooled charge coupled device (CCD) detector. Raman spectra were acquired in the backscattering geometry with a laser excitation source of wavelength 532 nm (Nd:YAG). The phase transition was further confirmed by measuring specific heat using Physical Property Measurement System (PPMS Re-Liquefier, Quantum Design).
3. RESULTS AND DISCUSSIONS

A. Phase determination and phonon assignments at Room-temperature

At room temperature, BZT crystallizes in the trigonal R-3m symmetry. Fig. 1(a) shows the Rietveld refined XRD pattern of BZT at room temperature [26]. The lattice parameters of the trigonal phase are found to be $a_t = b_t = 5.8236 \, \text{Å}$ and $c_t = 28.692 \, \text{Å}$, which are in agreement with earlier reports [24, 25]. The trigonal crystal structure of BZT comprises of corner- and face-shared ZnO$_6$ and TeO$_6$ octahedral units as shown in Fig. 1(b), giving rise to a unit cell of 12-layer (12R) type thus, possessing a strong structural anisotropy (large $c/a$-ratio). For a detailed analysis of the structure, the various interatomic distances associated with Ba-O, Zn-O, and Te-O bonds are extracted using the VESTA (Visualization of Electronic and STructural Analysis) software [27]. The interatomic bond distances are given in the supplementary material [28] and compared with the other reports [29-31]. Elemental analysis by EDAX measurement of BZT, shown in Fig. 1(c), suggests a stoichiometric composition within the instrumental resolution. Further details of the structure and crystal symmetry of BZT were obtained by Raman spectroscopic measurements which are discussed below.

Figure 2 shows the Raman spectrum of BZT at room temperature which is deconvoluted into 15 phonon modes (labelled as Z1 to Z15) by fitting with the Lorentzian function. The factor group analysis predicts a total of 16 Raman active phonons for the R-3m space group (trigonal structure) of BZT that comprise of 7 $A_{1g}$ and 9 $E_g$ symmetric modes (along with 2 $A_{2g}$ silent Raman modes). We, however, could clearly detect 9 $E_g$ and 6 $A_{1g}$ phonons in our measurements. A peak marked with asterisk (*) in Fig. 2 (at around ~ 135 cm$^{-1}$) could possibly be the seventh $A_{1g}$ mode which is weak in intensity and, therefore, its thermal behavior could not be studied. For identification of the mode symmetries and the atoms involved
in the lattice vibrations, the spectrum of BZT is compared with isostructural compound Ba₂NiTeO₆ as shown in the supplementary material [28]. The observed modes and their symmetries are listed in Table I based on earlier reports [25, 32-34] and our analysis.

**B. Temperature dependence of phonons**

Raman measurements were performed as a function of temperature in the range of 80 – 300 K in the heating and cooling cycles (and in the extended temperature range of 80 to 400 K in the heating cycle, shown in supplementary material [28]). As several of the modes split below ~150 K, the Raman spectrum was resolved with 25 Lorentzian peaks at lower temperatures. The increase in the number of modes at lower temperatures is an indicative of lowering of the crystal symmetry (a structural transition) associated with the para- to ferroelastic transition at ~ 150 K. Figure 3 presents the evolution of the Raman bands with temperature from which it is evident that 9 phonon bands (Z1, Z3, Z5, Z6, Z7, Z8, Z11, Z12, and Z15) split below the transition temperature lifting the degeneracy of the $E_g$ modes into $A_g$ and $B_g$ symmetries in the low symmetry monoclinic phase. Further, Z2 and Z4 show an unusual blue-shift in frequency upon cooling below 150 K as discussed later. Figure 4 presents the temperature response of the frequencies of all the phonon modes of BZT, a complete description of which is provided in the supplementary material [28]. While the thermal response of most of the phonons is in agreement with the earlier report [25], we notice a disagreement in the symmetry assignment based on thermal behavior of some of the modes like Z3, Z6, Z9 and Z13, as discussed in the supplementary material [28]. It may be noted that some of the phonons exhibit unusually large shifts in frequency over temperature besides splitting of the bands. The origin of such large shifts and its effects on the ground state properties are discussed below.
C. Signatures of strong anharmonicity and central peak

The variation of phonon frequency as a function of temperature is usually described as \[35, 36\]

\[
\omega(T) = \omega(0) + \Delta\omega_{qh}(T) + \Delta\omega_{anh}(T) + \Delta\omega_{el-ph}(T) + \Delta\omega_{sp-ph}(T). \tag{1}
\]

where, \(\omega(0)\) is the phonon frequency at 0 K while the quasi-harmonic term, \(\Delta\omega_{qh}(T)\), represents the volume contribution arising from thermal expansion of the lattice. The term \(\Delta\omega_{anh}(T)\) refers to the change in frequency due to intrinsic anharmonic correction in self-energy arising from phonon-phonon interactions. On the other hand, \(\Delta\omega_{sp-ph}(T)\) is the contribution due to spin-phonon interaction renormalizing the phonon frequencies, which can be neglected in BZT due to its non-magnetic nature. The term, \(\Delta\omega_{el-ph}(T)\), takes into account the renormalization in phonon frequency due to electron-phonon interaction, which is also absent in the case of electrically insulating BZT. Therefore, it can be inferred that the renormalization of the phonon frequencies upon varying temperature in BZT occurs mainly due to the contribution from the quasi-harmonic (lattice expansion) and the intrinsic phonon-phonon anharmonic interactions. On analyzing the volume change of the trigonal phase from XRD data (refer to supplementary material for details [28]), we infer that the major contribution to the unusual shift in the soft mode (Z1) frequency is rendered by phonon-phonon anharmonic interactions as compared to a negligibly small quasi-harmonic contribution.

The mode Z1 exhibits a change in phonon frequency similar to soft phonons. In general, the behavior of soft modes as a function of temperature can be captured by Cochran’s relation which suggests that \[37, 38\]

\[
\omega(T) = A \, (T - T_c)^{1/2}, \tag{2}
\]

where, \(\omega(T)\) denotes the phonon frequency at a temperature \(T\), \(T_c\) refers to the phase transition
temperature, while $A$ represents the fitting parameter. The frequency response of the Z1 mode agrees well with Cochran’s relation (Eq. 2) with $T_c \sim 150$ K, shown in Fig. 4, suggesting the displacive-nature [13, 39] of the phase transition in BZT, as also reported earlier [25]. Since the frequency ($\omega$) of the soft mode (Z1) is larger than its linewidth ($\Gamma$) in the entire temperature range (see Fig. S4(a) in supplementary material [28]), the phonon mode can be interpreted as underdamped which further suggests a dominant displacive-type mechanism for the phase transition in BZT [8, 40]. However, it should be noted that the damping of the soft mode increases close to the transition temperature (with $\frac{\Gamma}{\omega}$ tending to unity) which may lead to the presence of central peak (Rayleigh quasi-elastic scattering profile) as discussed later. It is worth mentioning here that such an approach to identify the dominant displacive-type mechanism of the phase transition was not established before in BZT. More importantly, the mode Z1 splits below the transition and the shift in the frequency of Z1 over the temperature is unusually large in both the phases across the transition. However, a complete softening (i.e. phonon frequency going to zero) could not be observed for Z1 and the mode disappeared (near 170 K upon cooling) before the transition, suggesting it to be first-order in nature [13]. The Raman spectra recorded in the extended temperature range of 80 - 400 K (see Fig. S2 in supplementary material [28]) were employed to estimate the phonon anharmonicity in the soft mode. Strikingly, for the Z1 mode, the high-temperature phonon branch with $E_g$ symmetry shows a change in frequency by $\sim 120 \%$ upon cooling from 400 K to 170 K (refer supplementary material for more details [28]). Further, Z1 mode ($E_g$ symmetry) splits into two phonons with $A_g$ and $B_g$ symmetry at lower temperatures below the structural transition. The $A_g$ phonon branch is found to demonstrate another unusually large shift of about 145 % below $T_c$ down to 80 K. In absence of any significant quasi-
harmonic contribution, these unusually large phonon shifts of the soft mode can be attributed to a very strong anharmonicity. A quantitative analysis of the quasi-harmonic and anharmonic contributions to the phonon shifts is provided in the supplementary material [28, 41]. It is important to note that the values of shifts in frequencies are remarkably large as compared to the typically observed values (1-2 %) in most of the anharmonic systems. Further, the anharmonicity in the soft mode of BZT is much higher than those in the well-known strongly anharmonic systems like KNbO$_3$ [21], SrZrO$_3$ [19], Gd$_2$(MoO$_4$)$_3$ [42], and hexagonal BaTiO$_3$ [43], where the anharmonicity ranges in between 15 – 100 %. Therefore, it is important to contemplate the origin of such a strong anharmonicity that leads to unusually large frequency shifts ($\frac{\Delta \omega}{\omega}$ %) in BZT. We have made an estimate of $\frac{\Delta \omega}{\omega}$ % (a measure of anharmonicity) for the soft mode of some of the classic ferroelectric perovskite systems like BaTiO$_3$ and PbTiO$_3$ to compare with BZT. As shown in Fig. 5(a), BZT demonstrates anharmonicity comparable to BaTiO$_3$ [44] while that of PbTiO$_3$ [45] surpass the $\frac{\Delta \omega}{\omega}$ % values known for both BaTiO$_3$ and BZT at all normalized temperatures ($\frac{T}{T_c}$). It should be particularly noted that the temperature ranges (i.e. temperature of the sample) in which the $\frac{\Delta \omega}{\omega}$ % values are estimated for PbTiO$_3$ and BaTiO$_3$ are far higher (than that for BZT) where the anharmonic effects are supposed to be more pronounced owing to higher temperatures. Moreover, PbTiO$_3$ exhibits a negative thermal expansion coefficient from room temperature to ~ 763 K [46]. Therefore, one may expect a large anharmonicity for such (i.e. BaTiO$_3$ and PbTiO$_3$) systems. On the contrary, the estimated anharmonicity for BZT exists even at much lower temperatures with a positive thermal expansion coefficient as observed in our temperature-dependent x-ray diffraction data (refer Fig. S3 of supplementary material [28]). Therefore, we believe that the unusually large
value of $\frac{\Delta \omega}{\omega}$ % (anharmonicity) in BZT originates from the high structural anisotropy and long Ba-O bond lengths (see supplementary material (Table SII)), leading to the lattice instabilities and eventually to the ferroelastic phase transition. The large frequency-shift is seen not only for the mode Z1 but for other modes as well. Namely, the modes Z2 and Z4 display an increase in their phonon frequencies by $\sim 3$ % and 4 %, respectively, below the phase transition (between 150 – 80 K). These large shifts in Z2 and Z4 may be attributed to lattice renormalization at low temperatures below $T_c$ and associated anharmonicities.

Our Raman investigation of the low-frequency region of BZT further shows an important and new observation. It is observed that as we approach close to the transition temperature, the intensity of the central peak, that is the Rayleigh profile, grows rapidly and then falls off again away from the $T_c$, as shown in Fig. 5(b). Simultaneously, the intensity of the soft phonon band (see inset of Fig. 5(b)) weakens close to the $T_c$ suggesting a possible coupling between the two modes (i.e. the central peak and the soft phonon) that results in the spectral weight (intensity) transfer between the modes [42]. This is an important observation that resembles closely with the reported behavior and phonon dynamics in Pb$_5$Ge$_3$O$_{11}$ [47], Li$_2$RuO$_3$ [48], AgNbO$_3$ [49], and Gd$_2$(MoO$_3$)$_4$ [42] in the low-frequency region. Such a behavior of the central peak is often connected with the internal relaxation processes of the crystal which are activated due to an interaction with the dynamical lattice defects [17], phonon density as well as entropy fluctuations [15, 16], and movement of the domain walls [19]. This is evident from the behavior of the linewidth of the central peak (see Fig. S4(b) in supplementary material [28]) which decreases as we approach the $T_c$. To recall that the linewidth ($\Gamma$) of a mode provides the information about its lifetime ($\tau$) because $\Gamma \propto 1/\tau$. Although a detailed quantitative analysis of the linewidth and intensity of the central (Rayleigh) peak cannot be fully achieved as our Raman spectra are limited
by the lowest frequency measurable near to the excitation wavelength (~ 8 cm\(^{-1}\) in our case due to the optical filter used), their behavior can still be qualitatively examined to develop an understanding of the dynamics during the phase transition [48,50]. As shown in the supplementary material (Fig. S4(b) [28]), an increase in the relaxation time of the central peak near \(T_c\) is an indicative of slowing down of the lattice dynamics which implies the presence of additional relaxation mechanisms involving dynamical lattice defects, phonon density, and possible domain wall motion during the transition (to be discussed further later).

### D. Hysteretic phonon behavior and its origin

The thermal response of the soft phonon (Z1), discussed above, is suggestive of a first-order phase transition. In order to verify the nature (order) of the phase transition, Raman spectra were recorded both in the heating as well as cooling cycles to examine the response of the phonons to thermal cycle. Upon careful observation, it can be noted that the modes Z7, Z9, Z10, and Z11 show hysteretic behavior in their temperature-dependent frequencies, as presented in Fig. 6, in the temperature range of 150 K to about 230 K. Since thermal hysteresis is an inherent property of first-order phase transition [51], it thereby verifies the order of the transition. Moreover, the appearance of thermal hysteresis with temperature is associated with co-existence of both the phases (due to nucleation of one phase in the other) in this temperature range. Therefore, we believe that the monoclinic phase coexists with the trigonal phase in the temperature range 150 K < \(T\) < 230 K thus leading to the observed thermal hysteresis, as also evidenced by our XRD measurements (discussed in the next section). The thermally induced motion of the domain walls, mentioned earlier, in this coexisting phase likely contributes to the central peak discussed above.

### E. Specific heat and temperature-dependent X-Ray Diffraction

Our Raman data, discussed above, confirm the structural transition of BZT to be first-order in
nature. In order to gain further insights, specific heat measurements were carried out in the temperature range of 80 to 200 K. We observe a broad anomaly in the specific heat near 150 K, as shown in Fig. 7(a), which is an indicative of the evolution of the lattice dynamics around that temperature range discussed above. The observed anomaly in specific heat is a manifestation of the phase transition in BZT, thus corroborating our Raman data. The total specific heat \( C_p \) can be represented as a sum of the lattice \( C_{\text{latt}} \), magnetic \( C_{\text{mag}} \), and electronic specific heat \( C_{\text{el}} \) i.e. \( C_p = C_{\text{latt}} + C_{\text{mag}} + C_{\text{el}} \) [52, 53]. In the present case, the insulating and non-magnetic nature of BZT eliminates the contribution from the electronic and magnetic terms, respectively. As a result, the total specific heat can be ascribed to the lattice contributions arising from the anharmonic and the lattice dynamical effects. To be noted that we do not observe a sharp feature in the specific heat at the transition but a smeared broad peak feature which is likely due to the coexistence of both the low and high temperature phases near the \( T_c \) (additional details are provided in the supplementary material [28]), thus corroborating our Raman data discussed above.

Further, we have performed temperature-dependent x-ray diffraction measurements to examine the crystallographic structure across the transition while heating. Figure 7(b) displays the evolution of the XRD patterns of BZT at a few typical temperatures that reveal the presence of additional reflection peaks at \( 2\theta = 22.7^\circ \) and \( 24.2^\circ \) in the low temperature regime (below \( \sim 230 \) K) which is a clear evidence of the structural transition from the (low temperature) monoclinic phase having a reduced rotational symmetry to the (high temperature) trigonal phase. We observe that the new reflection at \( 24.2^\circ \), inherent to the low temperature phase, prevails even above the \( T_c \) (\( \sim 150 \) K) with significant intensity upon heating. Notably, the complete transition takes place above \( \sim 230 \) K, as also suggested by our hysteretic Raman modes (see Fig. 6) thus further corroborating the proposition of coexistence of the phases across the transition. We conjecture that
the nucleation for the phase transition takes place locally within the host crystal leading to the formation of micro-domains bounded by domain walls (i.e. a coexistence of both the phases) and, therefore, the complete transition occurs eventually at temperatures much above the $T_c \sim 150$ K. It is to be noted that a similar indication of coexistence of phases in perovskite SrTiO$_3$ even above its structural phase transition temperature ($\sim 105$ K) was reported by various groups [54-56]. Our observations on BZT based on Raman, specific heat, and XRD measurements are suggestive of such phase-coexistence across the transition temperature ($T_c$). Therefore, based on the Landau theory of phase transition, it can be proposed that a non-zero order parameter, which depends on the atomic displacement associated with the soft phonon, triggers the structural phase transition in concomitant with the para- to ferroelastic transition [57]. However, a comprehensive theoretical analysis is necessary to understand the lattice dynamics and the order parameter which is beyond the scope of this work and may be left for future studies.

F. Phase transition and phonon band splitting: A Group-subgroup transformation

To recall that BZT crystallizes into trigonal structure at room-temperature (with R-3m space group). It undergoes a transition to the monoclinic phase below $\sim 150$ K. According to Aizu’s notation ‘-3mF2/m’, the structural transformation from the trigonal R-3m to the low temperature monoclinic C2/m phase can be categorized under the class of 94 possible ferroelastic phase transitions [6, 7]. This group-to-subgroup transformation leads to a loss of point group symmetry while preserving the translational symmetry with respect to the prototypical trigonal phase [58]. An estimation of the low temperature monoclinic phase lattice parameters of BZT can be made in terms of the room temperature trigonal phase parameters using the following relations [59]

$$a_m = \sqrt{3}a_t,$$  \hspace{1cm} (4)

$$b_m = a_t,$$  \hspace{1cm} (5)
\[
c_m = c_t/3 \sin \beta_m, \tag{6}
\]

\[
\beta = 180^\circ - \tan^{-1} \left( \frac{c_t}{\sqrt{3}a_t} \right), \tag{7}
\]

where, \( a_m, b_m, c_m, \) and \( \beta \) represent the lattice parameters in the low temperature monoclinic phase while \( a_t \) and \( c_t \) are the high temperature trigonal lattice parameters in the hexagonal setting. As obtained from our XRD results, the lattice parameters of the trigonal phase at room temperature are \( a_t = 5.8236 \) Å and \( c_t = 28.692 \) Å. Therefore, the above set of equations yield the monoclinic lattice parameters as \( a_m = 10.086 \) Å, \( b_m = 5.8236 \) Å, \( c_m = 9.0228 \) Å, and \( \beta = 109.36^\circ \). It is evident that the estimated monoclinic lattice parameters suggest a reduced symmetry in the ab-plane as compared to that in the R-3m (trigonal) phase where \( a_t = b_t = 5.8236 \) Å. This justifies the observed splitting of most of the phonon modes with \( E_g \) symmetry below the transition temperature \( \sim 150 \) K, as shown in Fig. 4. Moreover, an increase in the lattice constant along the ‘a’ direction would modify the interatomic potential such that the atoms displace with larger amplitudes during the lattice vibration, resulting in an increased anharmonicity for a few phonon modes (e.g. \( Z2 \) and \( Z4 \)) at low temperatures below the structural phase transition. This also suggests that the phonon modes \( Z2 \) and \( Z4 \) may predominantly involve displacements of the associated atoms along the ‘a’ direction. The lowering of symmetry upon transition and increase in the number of phonons can be further understood by considering the symmetry elements and Wyckoff-site splitting scheme, respectively, as described in the supplementary material [28].

4. SUMMARY AND CONCLUSION

To summarize, we have investigated the lattice dynamics of polycrystalline trigonal \( \text{Ba}_2\text{ZnTeO}_6 \) across its ferroelastic phase transition at \( \sim 150 \) K using temperature-dependent Raman, XRD, and specific heat measurements. While our extensive Raman study reveals various important observations related to the phase transition such as the presence of the central peak, hysteretic
phonon behavior, coexistence of both high and low temperature phases in the hysteretic region, and phonon anomalies arising due to very strong anharmonicity, the specific heat and temperature-dependent XRD measurements provide further evidences for the observed phase transition. We have quantified the anharmonicity of the soft mode (Z1 mode at ~ 31 cm\(^{-1}\)) that plays an important role in the phase transition. The evolution of the soft mode is accompanied with a rise in the intensity of the central peak (quasi-elastic Rayleigh profile) near \(T_{c}\) and a decrease in its linewidth, suggesting the presence of additional relaxation processes associated with the lattice and its dynamical effects. In addition, we have shown that phonons display a hysteretic behavior with temperature which not only indicates the first-order nature of the phase transition but also the presence of coexistent phases above \(T_{c}\), as corroborated by our x-ray diffraction data and specific heat data. Thus, we believe that our findings in Ba\(_2\)ZnTeO\(_6\) not only shed light on its lattice dynamics across the ferroelastic phase transition but will also motivate further investigations on similar hexagonal systems to explore their fundamentals and potential applications.

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Table I. Room-temperature phonon frequencies, symmetry assignments and atoms involved in the phonon vibration of the hexagonal perovskite Ba$_2$ZnTeO$_6$. Phonon symmetries are compared with previous report [25].

| Phonon | Frequency (cm$^{-1}$) | Symmetry | This work | Earlier report Ref[25] | Atoms involved in vibration |
|--------|-----------------------|----------|-----------|------------------------|----------------------------|
| Z1     | 31                    | $E_g$    | $E_g$     | Ba                     |
| Z2     | 87                    | $A_{1g}$ | $A_{1g}$  | Ba                     |
| Z3     | 103                   | $E_g$    | $A_{1g}$  | Ba                     |
| Z4     | 110                   | $A_{1g}$ | $A_{1g}$  | Ba                     |
| Z5     | 120                   | $E_g$    | $E_g$     | Zn-O                   |
| Z6     | 153*                  | $E_g$    | $A_{1g}$  | Zn-O                   |
| Z6'    | Absent (185 at 80 K)  | $A_{2g}(B_g)$ | $A_{2g}(B_g)$ | O                      |
| Z7     | 382                   | $E_g$    | $E_g$     | O                      |
| Z8     | 394                   | $E_g$    | $E_g$     | O                      |
| Z9     | 405                   | $A_{1g}$ | $E_g$     | O                      |
| Z10    | 470                   | $A_{1g}$ | $A_{1g}$  | O                      |
| Z11    | 573                   | $E_g$    | $E_g$     | O                      |
| Z12    | 616                   | $E_g$    | $E_g$     | O                      |
| Z13    | 689                   | $A_{1g}$ | $E_g$     | O                      |
| Z14    | 736                   | $A_{1g}$ | $A_{1g}$  | O                      |
| Z15    | 766                   | $E_g$    | $E_g$     | O                      |

An earlier report [25] showed the presence of two modes at ~ 142 cm$^{-1}$ and 154 cm$^{-1}$ whereas we have observed only one mode clearly. However, we have observed an additional weak mode at ~ 135 cm$^{-1}$ whose thermal evolution could not be studied due to its low intensity. The mode at ~ 135 cm$^{-1}$ may possibly be the missing $A_{1g}$ phonon giving a total of $9 E_g + 7 A_{1g}$ modes, predicted by group theory.
Figure 1 (Color online): (a) Room-temperature x-ray diffraction pattern of Ba$_2$ZnTeO$_6$ showing the lattice parameters derived from the refined diffraction profile where $I_{\text{obs}}$ is the observed experimental data (black open circles), $I_{\text{cal}}$ is the fitted (calculated) x-ray profile (red solid line), and their difference, i.e. $I_{\text{obs}} - I_{\text{cal}}$ is represented with the blue solid line. The reflection peak due to the presence of a secondary phase of Ba$_3$TeO$_6$ (of ~ 2.1 %) is encircled with a green circle. (b) Trigonal crystal structure of BZT showing the face shared ZnO$_6$-TeO$_6$ octahedra. (c) EDAX analysis showing the atomic and weight percentage of the elements present in BZT.
Figure 2 (Color online): Room-temperature Raman spectrum of Ba$_2$ZnTeO$_6$ with modes labelled as Z1 to Z15. Modes below ~ 650 cm$^{-1}$ are scaled for clarity. The weak peak at 135 cm$^{-1}$ labelled with asterisk (*) is probably the missing (seventh) A$_{1g}$ mode discussed in the main text.
Figure 3 (Color online): Raman spectra of Ba$_2$ZnTeO$_6$ shown at a few temperatures across the phase transition (at $T_c \sim 150$ K). Dashed arrows are guide to the eye representing phonon splitting and shift of the modes.
Figure 4 (Color online): Evolution of the phonon frequencies as a function of temperature exhibiting splitting of the modes upon cooling below the transition as well as signatures of strong anharmonicity, as discussed in the text. Vertical dashed lines represent the transition temperature ($T_c \sim 150$ K). The solid lines for the mode Z1 show the fitting by Cochran relation (Eqn. 2).
Figure 5 (Color online): (a) Comparison of the soft mode (Z1) frequency-shift \( \left( \frac{\Delta \omega}{\omega} \right) \) of \( \text{Ba}_2\text{ZnTeO}_6 \) with classic perovskite systems \( \text{BaTiO}_3 \) [44] and \( \text{PbTiO}_3 \) [45] as a function of temperature normalized with respect to the respective \( T_c \). (b) Variation of the intensity of the central peak as a function of temperature where the vertical dashed line represents the transition temperature. The inset shows the variation of the intensity of the soft mode (Z1) with temperature where solid lines (in blue color) represent guide to eye for the decreasing intensity near \( T_c \).
Figure 6 (Color online): Hysteretic shift in the phonon frequencies of Z7, Z9, Z10, and Z11 during cooling (blue open circles) and heating (red filled circles) cycles. Insets are shown for visual clarity of the hysteresis. Error bars represent the standard deviation in the phonon frequencies which are smaller than or comparable to the symbol size.
Figure 7 (Color online): (a) Specific heat of Ba$_2$ZnTeO$_6$ displaying a weak anomaly (magnified in the inset) near the phase transition (b) X-Ray diffraction profiles of Ba$_2$ZnTeO$_6$ at a few temperatures showing emergence of new reflections in the low-temperature monoclinic phase.
Supplementary Material

Lattice dynamics across the ferroelastic phase transition in Ba$_2$ZnTeO$_6$: A Raman study

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This supplementary material contains details of comparative room temperature Raman analysis of Ba$_2$ZnTeO$_6$ and Ba$_2$NiTeO$_6$, mode symmetry assignments, high temperature Raman data, thermal response of lattice constants, linewidth of soft mode and central peak, specific heat data and Wyckoff-site splitting scheme.
SM1. Comparison between isostructural $\text{Ba}_2\text{ZnTeO}_6$ and $\text{Ba}_2\text{NiTeO}_6$

$\text{Ba}_2\text{ZnTeO}_6$ (BZT) and $\text{Ba}_2\text{NiTeO}_6$ (BNT) are isostructural systems with 12-layer trigonal structure. Thus, a comparison is made between the Raman spectra of these two compounds at room temperature, as shown in Fig. S1, to better identify the atoms involved in the modes and their assignments. It is evident from Fig. S1 that the high frequency region ($> 300 \text{ cm}^{-1}$) of the spectrum of BZT matches well with that of BNT. However, we observe some differences in the low frequency region of the spectrum which are due to the involvement of heavier atoms (Ba/Te/Ni/Zn) in the vibrations. The difference in the two spectra below $300 \text{ cm}^{-1}$ are due to the differences in the mass and ionic radii of Zn and Ni atoms.

![Raman Spectra of BZT and BNT](image)

**Figure S1:** Room-temperature Raman spectra of $\text{Ba}_2\text{ZnTeO}_6$ and $\text{Ba}_2\text{NiTeO}_6$ fitted with Lorentzian function presenting phonons designated as Z1 to Z15 and N1 to N15. The frequency region $< 640 \text{ cm}^{-1}$ is scaled for visual clarity.
Table SI. Comparison of the Room-temperature phonon frequencies of $\text{Ba}_2\text{ZnTeO}_6$ and $\text{Ba}_2\text{NiTeO}_6$.

|            | $\text{Ba}_2\text{NiTeO}_6$ | $\text{Ba}_2\text{ZnTeO}_6$ |
|------------|------------------------------|------------------------------|
| Phonon     | Frequency (cm$^{-1}$)         | Phonon                       | Frequency (cm$^{-1}$) |
| N1         | 56                           | Z1                           | 31                     |
| N2         | 94                           | Z2                           | 87                     |
| N3/N4      | 111                          | Z3                           | 103                    |
| N5         | 122                          | Z4                           | 110                    |
| N6         | 180                          | Z5                           | 120                    |
| N(a)       | 226                          | Z6                           | 153                    |
| N(b)       | 252                          | Z6'                          | Absent (185 at 80 K)   |
| N7         | 379                          | Z7                           | 382                    |
| N8         | 392                          | Z8                           | 394                    |
| N9         | 410                          | Z9                           | 405                    |
| N10        | 482                          | Z10                          | 470                    |
| N11        | 582                          | Z11                          | 573                    |
| N12        | 613                          | Z12                          | 616                    |
| N13        | 684                          | Z13                          | 689                    |
| N14        | 736                          | Z14                          | 736                    |
| N15        | 750                          | Z15                          | 766                    |

The phonon frequencies of the two compounds (BZT and BNT) are listed in Table SI. Almost all the modes, except N(a) and N(b), are present in both the compounds. For the sake of analysis, the Raman spectrum at room temperature can be divided into three regions: (i) Low-frequency region (10-180 cm$^{-1}$), (ii) Intermediate-frequency region (200-500 cm$^{-1}$), and (iii) High-frequency region (550-800 cm$^{-1}$). The information about the atoms associated with a particular phonon mode may be qualitatively deduced based on the relation $\omega \propto \sqrt{k/m}$, where $\omega$ denotes the phonon frequency, $k$ depicts the bond stiffness, and $m$ refers to the reduced atomic mass. Therefore, it can be proposed that the phonon modes at lower frequencies (Z1 to Z4) involve Ba-atoms (atomic mass ~ 137 amu). It is worth noting that all the Ba-O related interatomic bond lengths, especially, Ba(2)-O(2) (~ 3.1 Å), are larger than the similar Ba-O bond lengths in other Ba-based perovskite oxides [1-3] leading to weaker bond stiffness in BZT. Hence, the combined effect of mass and bond strength favors our conjecture that the Ba atoms contribute to the low-
frequency phonon modes. Similarly, the heavy Tellurium (Te) (~127 amu) atom may also be expected to contribute to the low-frequency phonon modes. However, group theory does not allow phonons associated with Te vibrations in BZT to be Raman active [4]. Hence, the participation of the Te-atom in the modes Z1 to Z4 can be safely ruled out. On the other hand, comparison of the Raman spectra of BZT and BNT suggests that the modes Z5 and Z6 involve vibrations of Zn atom associated with Zn-O bonds. All the intermediate and high-frequency phonons can be attributed to the vibrations of oxygen atoms. The modes Z7 (~ 382 cm\(^{-1}\)) and Z8 (~ 394 cm\(^{-1}\)) can be assigned to oxygen vibrations associated with Ba/Te – O bonds based on their thermal response (discussed in the main text). The modes Z9 (~ 405 cm\(^{-1}\)) and Z10 (~ 470 cm\(^{-1}\)) originate from Zn-O vibrations that predominantly involve the movement of oxygen atoms. On the other hand, the origin of the high-frequency modes Z11 to Z15 can be ascribed to the vibration of O-atoms in the face-shared and/or corner-shared TeO\(_6\) octahedral units [5, 6]. Our analysis based on the frequency-mass relation and earlier reports [5,6] suggest that the vibrational modes (Z13, Z14, and Z15) arise due to oxygen displacements where the lighter oxygen atoms form an integral part of face-shared and/or corner-shared TeO\(_6\) octahedral frameworks. It is evident from the list of bond distances (refer Table SII) that the Zn-O bond length in the face-shared ZnO\(_6\)-TeO\(_6\)-ZnO\(_6\) octahedral triplet is larger than that in the corner-shared TeO\(_6\)-ZnO\(_6\) linkages. This observation is found to be consistent with the previous report by Duyckaerts et al. [5] Therefore, the face-shared unit will give rise to a phonon at a relatively lower frequency than the corner-shared unit. Hence, the origin of Z13 and Z15 can be assigned to the face-shared and corner-shared TeO\(_6\) octahedral units, respectively, as also suggested previously [5]. Further, the symmetries of all the phonon modes
are assigned by understanding the temperature-dependent Raman data as discussed in the main text and below.

**SM2. Temperature dependence of the Raman spectrum (80 – 400 K)**

(a) Mode symmetry assignments

Figure S2 depicts the evolution of the phonon bands as temperature progresses from 80 to 400 K. As it is evident from Fig. S2(a), Z1 initially demonstrates an anomalous trend (i.e. a decrease in the frequency with decreasing temperature) upon cooling and switches to a normal behavior (i.e. an increase in the frequency with lowering temperature) below 150 K. Besides, it splits into two phonon bands below the transition temperature (Tc ~ 150 K), thus lifting its in-plane Eg symmetry (double-degeneracy) to Ag and Bg symmetries at low temperatures. Such behavior (i.e. softening and vanishing of a mode) is a typical characteristic of soft phonon that plays an important role in driving a system to an ordered phase (ferroelectric/ferroelastic) of displacive-type [7, 8]. Notably, the disappearance of the soft mode (before splitting) upon cooling down to ~ 170 K (i.e. merging with the central peak) is an indicative of a first-order phase transition. We believe that the soft phonon (Z1 mode) involving the displacement of Ba-atoms in BZT gives rise to lattice instabilities leading to a transition from the high-temperature trigonal to low-temperature monoclinic phase.

Signatures of the phase transition are also evident in other phonon modes of BZT in the form of phonon splitting and unusually large shifts below Tc, as can be seen in Fig. S2(b). The modes Z2 and Z4 shift rapidly with temperature below ~ 150 K as compared to their shifts at higher temperatures (see Fig. S2(b) and Fig. 4 in main text), providing another indication of the phase transition. While the observed behavior for Z2 is in agreement with an earlier report by Moreira et al. [9], Z4 shows a disparity in its thermal behavior below the transition temperature where we observe a larger shift with temperature. The modes Z2 and Z4 can be assigned to Ag symmetries. The mode Z3 splits into two components at lower temperatures and, hence, at room temperature it can be assigned to Eg symmetry. Similarly, we observe splitting of the Z5, Z6, Z7, and Z8 phonon bands into two modes for each of them on approaching the transition temperature (~ 150 K). Therefore, all these modes (Z5 to Z8) at room temperature can be assigned to Eg symmetries. According to Moreira et al. [9], the modes observed at ~142 cm⁻¹ and ~163 cm⁻¹ (in our case these are split components of Z6) at 80 K distinctly exist up to room temperature without merging which is in contrast to our observation. We have observed that these modes persist till the
phase transition upon heating and merge into a single mode that is identified as Z6 (at ~153 cm\(^{-1}\)) above ~150 K, as shown in Fig. S2(b). Therefore, we assign Z6 to \(E_g\) symmetry contrary to the earlier assignment of \(A_{1g}\) symmetry [9]. As shown in Fig. 3 in the main text, the mode Z6' is clearly visible in the low temperature monoclinic phase possessing a normal shift in frequency with temperature. However, the intensity of Z6' becomes extremely weak to be deciphered at higher temperatures (in the trigonal phase). Therefore, based on its behavior and an earlier report [9], it can be assigned to \(B_g\) symmetry. Moreira et al. [9] observed a bifurcation of the mode Z9 (at ~405 cm\(^{-1}\)) near the phase transition and hence, assigned it to \(E_g\) symmetry. However, we note that Z9 displays a weak but anomalous temperature-dependent shift with a change in slope across the phase transition temperature without undergoing any splitting at lower temperatures. Importantly, the polarization-dependent Raman data by Moreira et al. demonstrate a considerable decrease in the mode intensity of Z9 in cross polarization, which is suggestive of its \(A_{1g}\) (\(A_g\) below \(T_c\)) symmetry counter to their assignment of \(E_g\) symmetry [9]. Therefore, we assign the Z9 to \(A_{1g}\) symmetry. A similar disagreement was again noticed with the symmetry assignment of the phonon mode Z13 which can again be resolved by considering their polarization-dependent Raman data that show a significant decrease in the Raman intensity upon changing the polarization from cross to parallel configuration. Thus, we assign the mode Z13 to \(A_{1g}\) symmetry. The mode Z10 exhibits an anomalous shift with temperature without undergoing splitting and, therefore, it is assigned to \(A_{1g}\) symmetry. The modes Z11, Z12, and Z15 split below the phase transition temperature. Therefore, we assign them (Z11, Z12, and Z15) as \(E_g\) symmetry modes. Notably, the mode Z14 (\(A_{1g}\)) shows a change in behavior (slope) at ~150 K without undergoing any splitting of the band, which is in agreement to the report by Moreira et al. [9]

(b) **Estimation of quasi-harmonic and phonon-phonon anharmonic interaction contributions**

As we notice the frequency response of the mode Z1 over temperature, remarkably large shift in frequency was observed than usually expected. An unusually large shift in the frequency of the mode over temperature can be attributed to the dominant phonon-phonon anharmonic interactions. The quasi-harmonic change in frequency can be obtained by estimating the change in lattice volume \(\left(\frac{\Delta V}{V}\right)\) over temperature, as given below. As discussed in the main text eliminating the contribution from spin-phonon and electron-phonon interaction in non-magnetic and insulating
BZT, the overall shift in phonon frequency ($\Delta \omega(T)$) as a function of temperature can be attributed to quasi-harmonic (volume-dependent) and intrinsic anharmonic (phonon-phonon) interactions.

![Figure S2](image.png)

**Figure S2:** (a) Evolution of soft phonon (Z1) as a function of temperature where dotted arrows represent guide to the eye and the shaded region in blue indicates signatures of central peak. (b) Raman spectra of Ba\textsubscript{2}ZnTeO\textsubscript{6} at temperatures up to 400 K. Dotted lines separate different regions of frequency which are scaled accordingly for showing the low intensity peaks and phonon splitting at low temperatures.

On examination of tellurium-based systems like Sr\textsubscript{2}ZnTeO\textsubscript{6}[10], the Grüneisen parameters ($\gamma$) for different modes were found to be typically in the range of $\sim 0.9 - 2$, suggesting a small contribution to the frequency shift from the quasi-harmonic term. Therefore, we can expect that the quasi-harmonic contribution of BZT may not be too different from Sr\textsubscript{2}ZnTeO\textsubscript{6}. An estimate of the frequency shift ($\Delta \omega^i \sim \Delta \omega_{qh}(T)$) produced by volume-dependent quasi-harmonic term for a phonon mode $'i' $can be made using the Grüneisen relation

$$\frac{\Delta \omega^i}{\omega^i} = \gamma^i \frac{\Delta V}{V}$$  

[1]
where, $\gamma^l$ is the mode Grüneisen parameter, $\frac{\Delta V}{V}$ represents the relative change in volume which is extracted from XRD data and $\frac{\Delta \omega^l}{\omega^l}$ represents the relative change in frequency when the temperature is varied.

In the pure trigonal phase (above 230 K), the relative change in volume $\left(\frac{\Delta V}{V}\right)$ of the unit cell over temperature is $\sim 0.5\%$ (discussed below). Assuming $\gamma^l \sim 1$ in Eq. 1, the quasi-harmonic contribution $\Delta \omega_{qh}(T)$ is evaluated to be roughly around $0.14\text{ cm}^{-1} \left(\frac{\Delta \omega_{qh}}{\omega} \sim 0.5\%\right)$ for the high temperature branch of the soft mode (Z1). Notably, the quasi-harmonic contribution is negligibly small as compared to the overall shift in the frequency in pure trigonal phase. This implies that the volume-dependent part has negligible contribution to the observed phonon shift. As a result, it can be proposed that the unusually large shift in the phonon frequency originates entirely due to strong phonon-phonon anharmonic interactions. Thus, in the present scenario the anharmonicity can be estimated simply as the relative change in frequency $\frac{\Delta \omega}{\omega} = \frac{\omega(T_{max}) - \omega(T_{low})}{\omega(T_{low})}$, where $T_{max}$ is the maximum temperature recorded (400 K in our case) and the lowest frequency ($\omega(T_{low})$) of the soft mode is taken at 170 K (in the high temperature phase) since the soft mode is not resolvable at $T_c \sim 150$K. An estimation of the anharmonicity $\left(\frac{\Delta \omega}{\omega}\right)$ using the temperature-dependent shift in frequency yields a value of $\sim 120\%$ (between 170 and 400 K) for the Z1 mode which is very large as compared to the typically observed anharmonic shifts of $\sim 1-2\%$. Similarly, the anharmonicity of its low-temperature split components is $\sim 145\%$ for $A_{1g}$ and $\sim 94\%$ for $B_g$ mode below $T_c$ down to 80 K. This suggests that the soft mode (Z1) exhibits a very strong anharmonicity throughout the recorded temperature range. The origin of this strong anharmonicity can be associated to the lattice instability near $T_c$ and large structural anisotropy (large $c/a$-ratio).

**SM3. Variation of lattice parameter with temperature above the transition**

The Rietveld refinement of the x-ray diffraction profile at room temperature confirms a trigonal structure of the unit cell with lattice constant values as $a = 5.8236$ Å and $c = 28.692$ Å as shown in Fig. 1 of the main text. Figure S3 presents the variation of lattice constants as the temperature is increased in the region where the crystal is present in the pure trigonal phase. From the Fig. S3, it is clear that both the lattice constants ($a$ and $c$) increase with increasing temperature indicating a positive thermal expansion of the lattice above $T_c$. It can be observed that the lattice parameters,
and c, exhibit a change of ~ 0.2 % and ~ 0.1 %, respectively, with the variation of temperature that correspond to a change in volume by ~ 0.5 %. This, therefore, would correspond to a negligibly small quasi-harmonic contribution (0.5 %) to the phonon shifts thus justifying our attribution of the unprecedented phonon shift (in Z1 mode) to a very strong phonon anharmonicity as discussed above.

Figure S3: Variation of lattice parameters of Ba2ZnTeO6 as a function of temperature where solid lines represent the linear fits to the experimental data.

SM4. Signatures of the central peak

In addition to the observed strong anharmonicity of the soft mode, the low-frequency region near the Rayleigh scattered profile (central peak) of BZT shows an anomalous rise in intensity around the transition temperature (Tc ~ 150 K). The active lattice dynamical processes at lower frequencies across the Tc, especially in ferroic systems exhibiting soft mode, may lead to an anomalous rise in the intensity of the Rayleigh profile i.e. the spectral region close to the excitation wavelength (near ~ 0 cm⁻¹), a characteristic feature which is known as central peak. A comparative analysis of the frequency (ω) and linewidth (Γ) (shown in the inset of Fig. S4 (a)) of the soft mode suggests that the mode is underdamped (because $\frac{\Gamma}{\omega} < 1$) away from Tc though the damping ($\frac{\Gamma}{\omega}$) of both the $A_g$
and $E_g$ modes increases on approaching the transition temperature. From the Raman spectra recorded at various temperatures near the structural transition, it appears that the intensity of the soft mode is transferred (spectral weight transfer) to the central peak. Thus, the soft mode is completely masked by the central peak and we observe a sharp rise in the intensity (spectral weight) of the central peak which is evident from Fig. S2(a) where the central peak is marked with shaded background in the lowest-frequency region and the Fig. 5(b) in the main text.

Upon careful examination, we observe that the relaxation time (linewidth) of the central peak increases (decreases), as shown in Fig. S4(b) in addition to the intensity near $T_c$ (see Fig. S2(a)) indicating involvement of relaxation mechanisms [11-14]. The relaxation time ($\tau$) is derived from the relation $\tau = \frac{1}{\pi c \Gamma}$ where ‘c’ is the speed of the light and $\Gamma$ represent the linewidth of the central peak [15]. To be noted that the behavior of linewidth and relaxation time is derived for a qualitative understanding of the mechanisms involved and not for a quantitative analysis due to an instrumental limitation on the lowest measurable frequency ($\sim 8 \text{ cm}^{-1}$) and associated instrumental broadening of the spectral linewidth. An increase in the relaxation time indicates slowing down of the lattice dynamical processes near the phase transition owing to the dynamical lattice defects, phonon density and entropy fluctuations as well as the motion of the domain walls in the coexisting phases (in the hysteretic region) as also discussed in the main text.
SM5. Specific heat measurement

**Figure S5:** Specific heat as a function of temperature showing a broad anomaly at ~ 150 K.

In order to avoid any ambiguity regarding the smeared (broad) feature observed in the specific heat data, the measurement was carried out in the range of 110 – 230 K (as shown in Fig. S5) in the cooling cycle with a step size of ~ 0.25 K in between 140 and 170 K. Though a sharp transition has been observed in the Raman measurement through splitting of some phonon bands, other phonon modes exhibit hysteretic thermal response thus suggesting the presence of coexisting phases. We observed that the smeared transition is consistent even with smaller step size confirming our conjecture that both the high (trigonal) and low temperature (monoclinic) phases coexist with each other averaging out the anticipated sharp feature in the specific heat in this temperature range.

SM6. Group-subgroup symmetry transformation and Wyckoff-site splitting scheme

BZT undergoes a structural transition from high-symmetry trigonal to low temperature monoclinic phase. The high temperature trigonal phase comprises of a total of 12 symmetry elements (E, 2C3, 3C2, i, 2S6, 3σd) that define the point group ‘-3m’ while the low temperature monoclinic phase contains only 4 symmetry components (E, C2, i, σh). A descent in the symmetry can be clearly marked for the low temperature phase with a decrease in the number of symmetry components. Further, an increase in the number of phonons in the monoclinic phase can be described with the Wyckoff-site splitting scheme for the group-subgroup (-3m → 2/m) chain. In the trigonal (high temperature) phase of BZT, atoms occupy the 3a, 3b, 6c, and 18h crystallographic Wyckoff-sites.
Upon transition to the monoclinic (low temperature) phase, these sites are observed to transform according to the scheme presented in Table SIII. It can be noted that the high-temperature Wyckoff positions 3a and 3b transform into 2a and 2c, respectively, in the low-temperature phase. According to group theoretical analysis, 3a(2a), and 3b(2c)-sites occupied by non-magnetic Te atoms do not give rise to Raman active phonons in either the trigonal or monoclinic phases [4]. In contrast, the Ba(1), Ba(2), and Zn atoms, located at the 6c-site, lead to six Raman active phonons in the high symmetry (trigonal) phase. The 6c position transforms into the 4i-site in the low-symmetry monoclinic phase, giving rise to a total of nine modes. Further, the 18h-site of the high-symmetry trigonal phase, which leads to ten Raman active phonons, is occupied by the oxygen atoms O(1) and O(2). The 18h crystallographic position splits into 4i and 8j sites giving rise to a total of 18 phonons in the low-symmetry monoclinic phase. Thus, the low-temperature monoclinic phase predicts a total of 27 phonons with $A_g$ and $B_g$ symmetries as compared to 16 phonon modes with $A_{1g}$ and $E_g$ symmetries in the high temperature trigonal phase. As can be noted in our Raman data, we have clearly observed 15 modes (and one very weak $A_{1g}$ mode owing to low scattering cross-section) in the high temperature phase while 25 modes in the low temperature phase. The two missing phonon modes in the low temperature phase are likely to be of $A_g$ and $B_g$ symmetries and are not vividly present possibly due to their low scattering cross-section.

**Table SIII.** Wyckoff-site splitting scheme for a phase transformation from trigonal to monoclinic system.

| Wyckoff-site (Trigonal symmetry) | Wyckoff-site (Monoclinic symmetry) |
|----------------------------------|-----------------------------------|
| 3a                              | 2a                                |
| 3b                              | 2c                                |
| 6c                              | 4i                                |
| 18h                             | 4i                                |
|                                 | 8j                                |

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