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Supplementary Information

Lattice dynamics across the ferroelastic phase transition in Ba_2ZnTeO_6: A Raman and first-principles study

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This supplementary information contains details of mode symmetry assignments and eigenvectors of the phonon modes, high-temperature Raman data, thermal response of lattice constants, linewidth of soft mode and central peak, as well as specific heat data and Wyckoff-site splitting scheme.

S1. Temperature dependence of the Raman spectrum (80 – 400 K)

(a) Mode symmetry assignments

Figure S1 depicts the evolution of the phonon bands as temperature progresses from 80 to 400 K. As it is evident from Fig. S1(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, thus lifting its in-plane E_g symmetry (double-degeneracy) to A_g and B_g 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[1, 2]. 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. Our DFT-based calculations further suggest that the soft phonon (Z1 mode) involving the displacement of Ba and Zn atoms along with TeO_6 octahedral rotation 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 T_c, as shown in Fig. S1(b). The modes Z2 and Z4 shift rapidly with temperatures below ~ 150 K as compared to their shifts at higher temperatures (see Fig. S1(b) and Fig. 4 in the 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.*[3], 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 A_g symmetries. The mode Z3 splits into two components at lower temperatures and, hence, at room temperature, it can be assigned to E_g symmetry. Similarly, we observe the splitting of the Z5, Z6, Z7, and Z8 phonon bands into two modes for each of them upon cooling below the transition temperature (~ 150 K). Therefore, all these modes (Z5 to Z8) at room temperature can be assigned to E_g symmetries. According to Moreira *et al.*[3], 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})

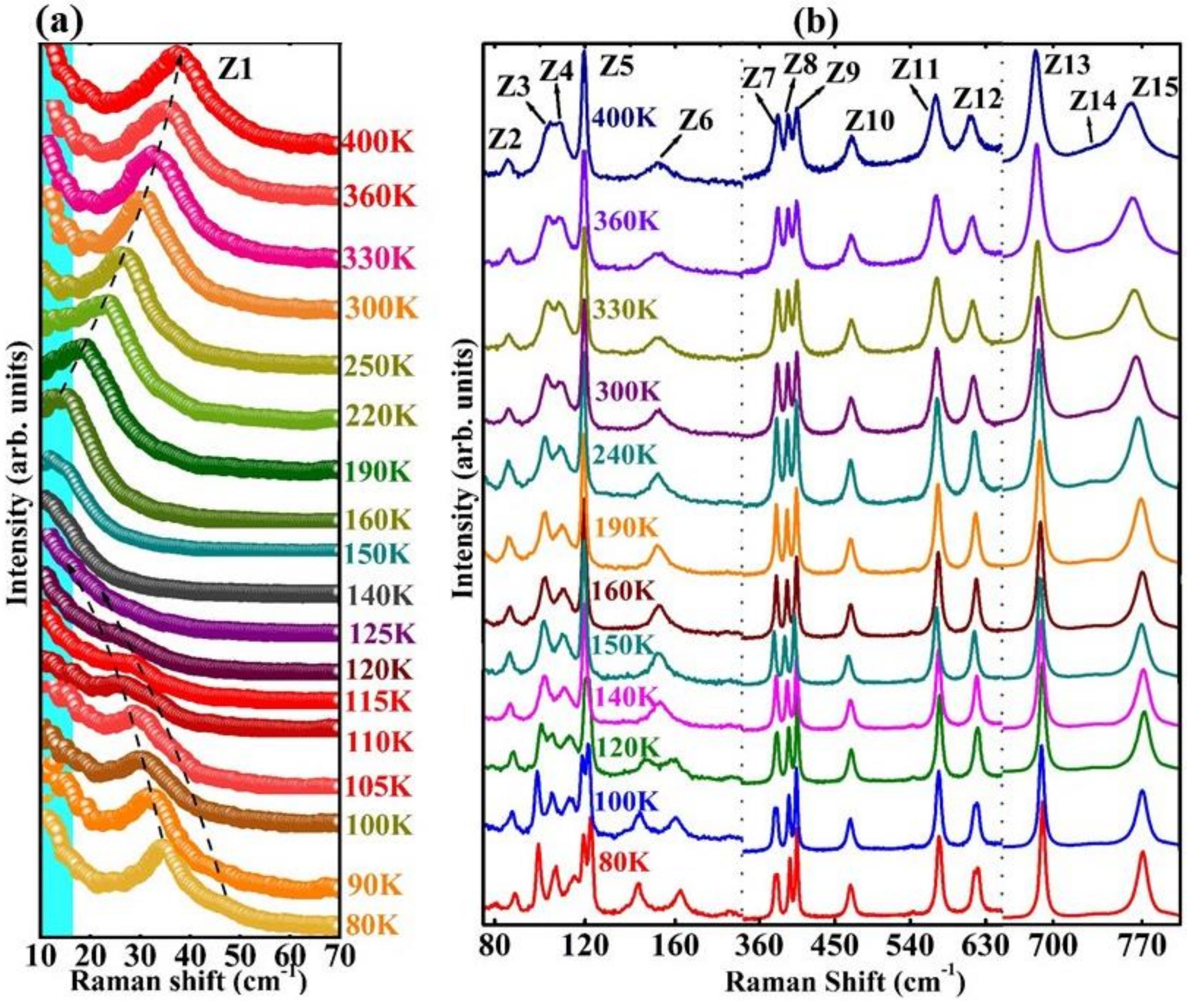
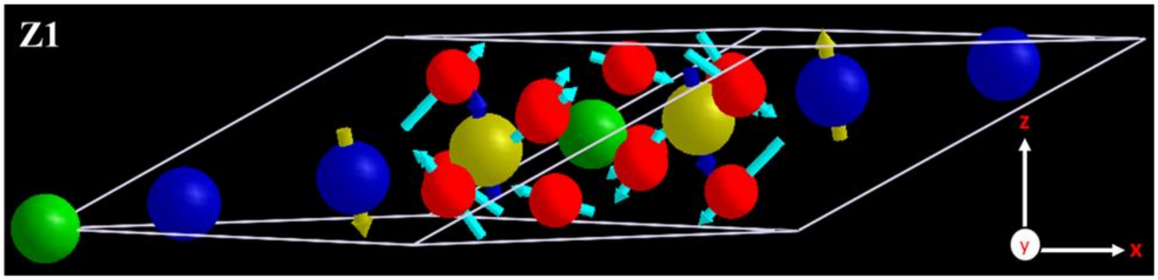


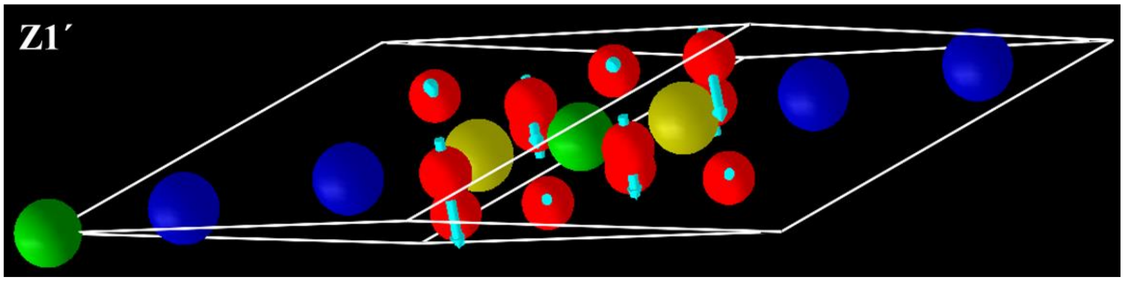
Figure S1: (a) *Evolution of soft phonon (Z1) as a function of temperature where dotted arrows represent a guide to the eye and the shaded region in blue indicates signatures of the central peak.* **(b)** *Raman spectra of Ba_2ZnTeO_6 at temperatures up to 400 K. Dotted lines separate different regions of frequency which are scaled accordingly for showing the low-intensity peaks and phonon splitting at low temperatures.*

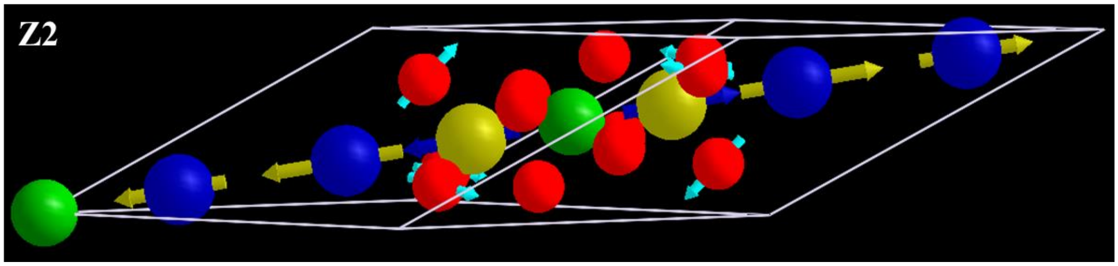
above ~ 150 K, as shown in Fig. S1(b). Therefore, we assign Z6 to E_g symmetry contrary to the earlier assignment of A_{1g} symmetry[3]. As shown in Fig. 3 in the main text, the mode Z6′ is clearly visible in the low-temperature monoclinic phase possessing a normal shift in frequency with temperature. 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[3], it can be assigned to B_g symmetry. Moreira *et al.*[3] 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[3]. 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 with the earlier report[3].

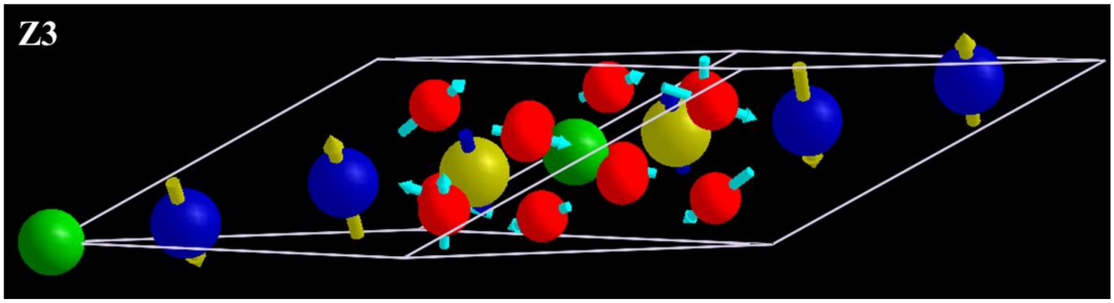
(b) Phonon eigenvectors

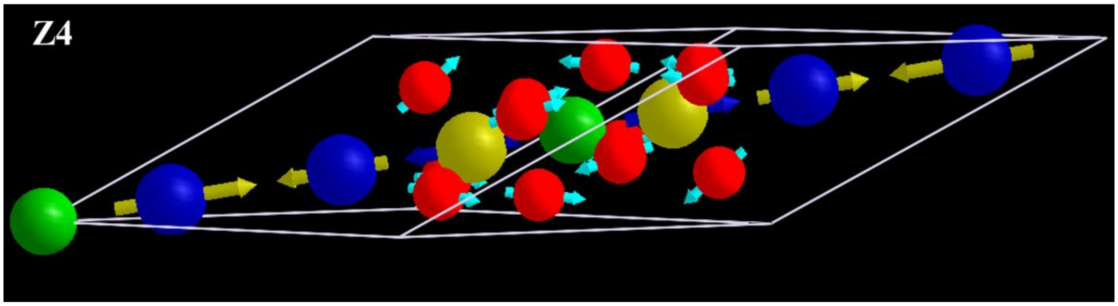
The eigenvectors corresponding to the Raman active phonon vibrations in the trigonal phase of Ba_2ZnTeO_6 are shown in Fig. S2 below. Based on our DFT calculations, we find negative phonon modes Z1 and Z1′ at -62 cm^{-1} (E_g) and -24 cm^{-1} (A_{2g}) (Raman inactive in trigonal phase), respectively. It can be observed that the E_g mode arises due to TeO_6 rotation along with translation of Ba and Zn atoms whereas the A_{2g} mode originates from the rotation of both ZnO_6 and TeO_6 octahedra. As we move towards the positive frequencies (Z2 – Z6′), the translational motion of all atoms is seen accompanied by TeO_6 and ZnO_6 octahedral rotations as described in Table I of the main text. Further on moving towards the higher frequency modes (Z7 – Z15), we observe scissoring motion, and symmetric and asymmetric stretching of the O atoms. However, the phonon modes Z9 and Z15 could not be assigned theoretically in contrast to experiments in the trigonal phase.

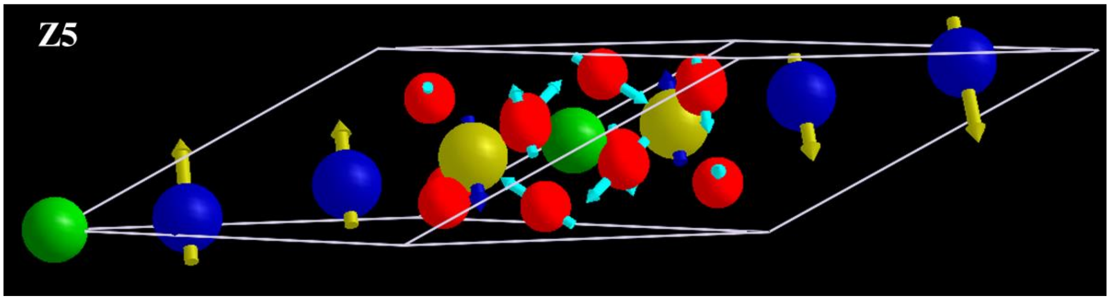


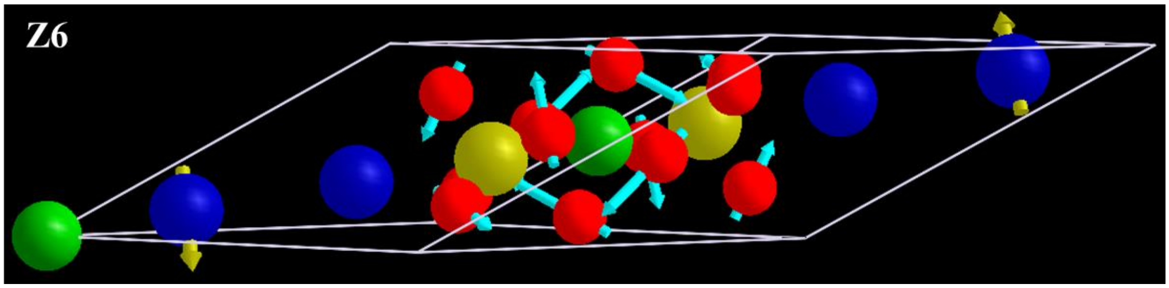

Z1′

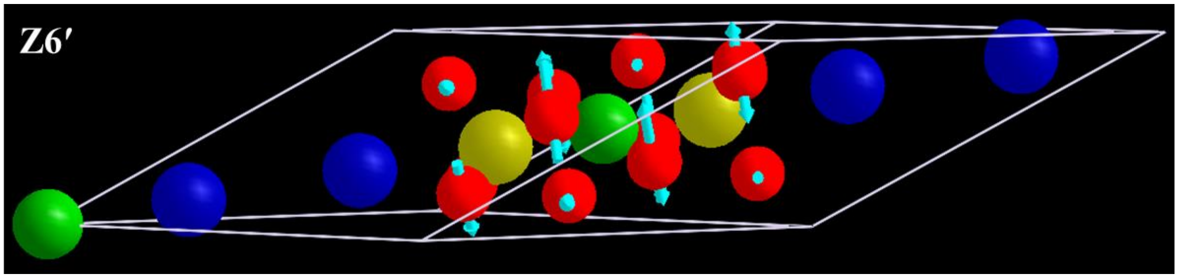

Z2

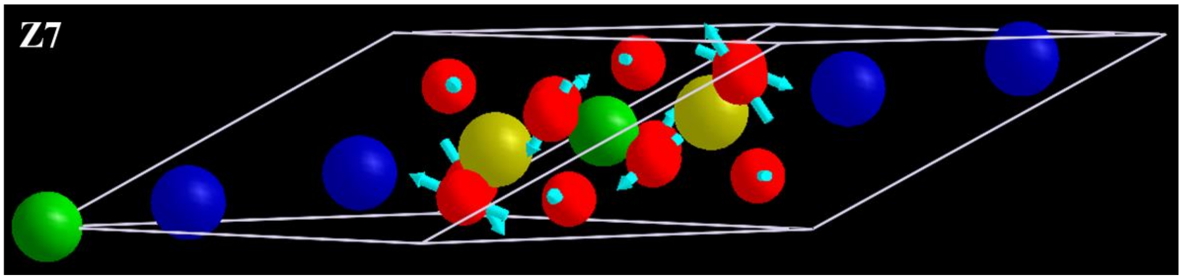

Z3

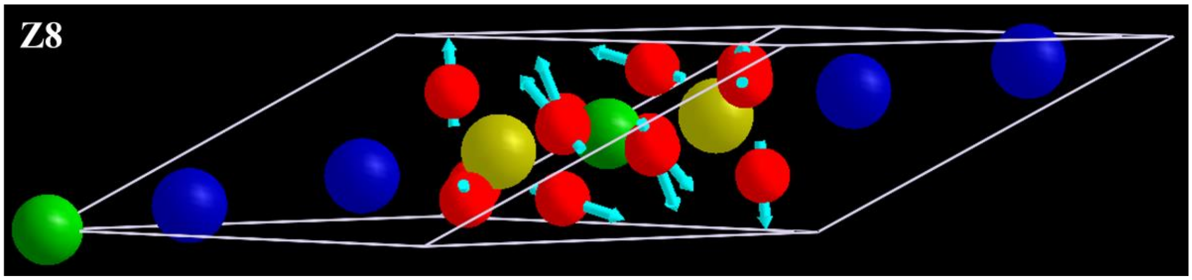

Z4

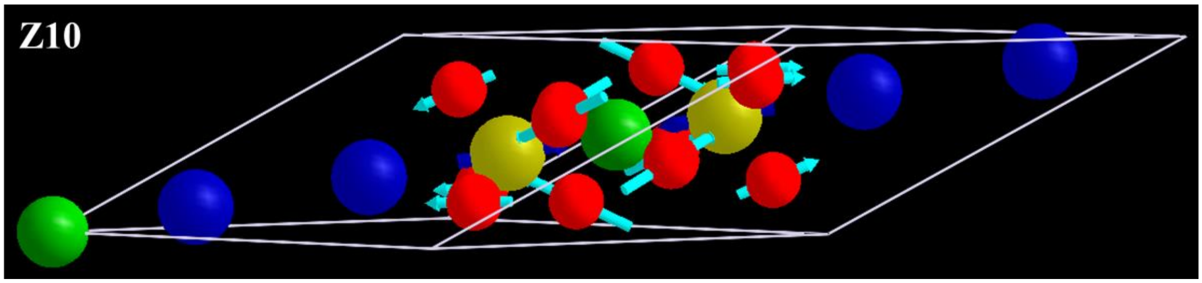

Z5


Z6


Z6′


Z7


Z8


Z10

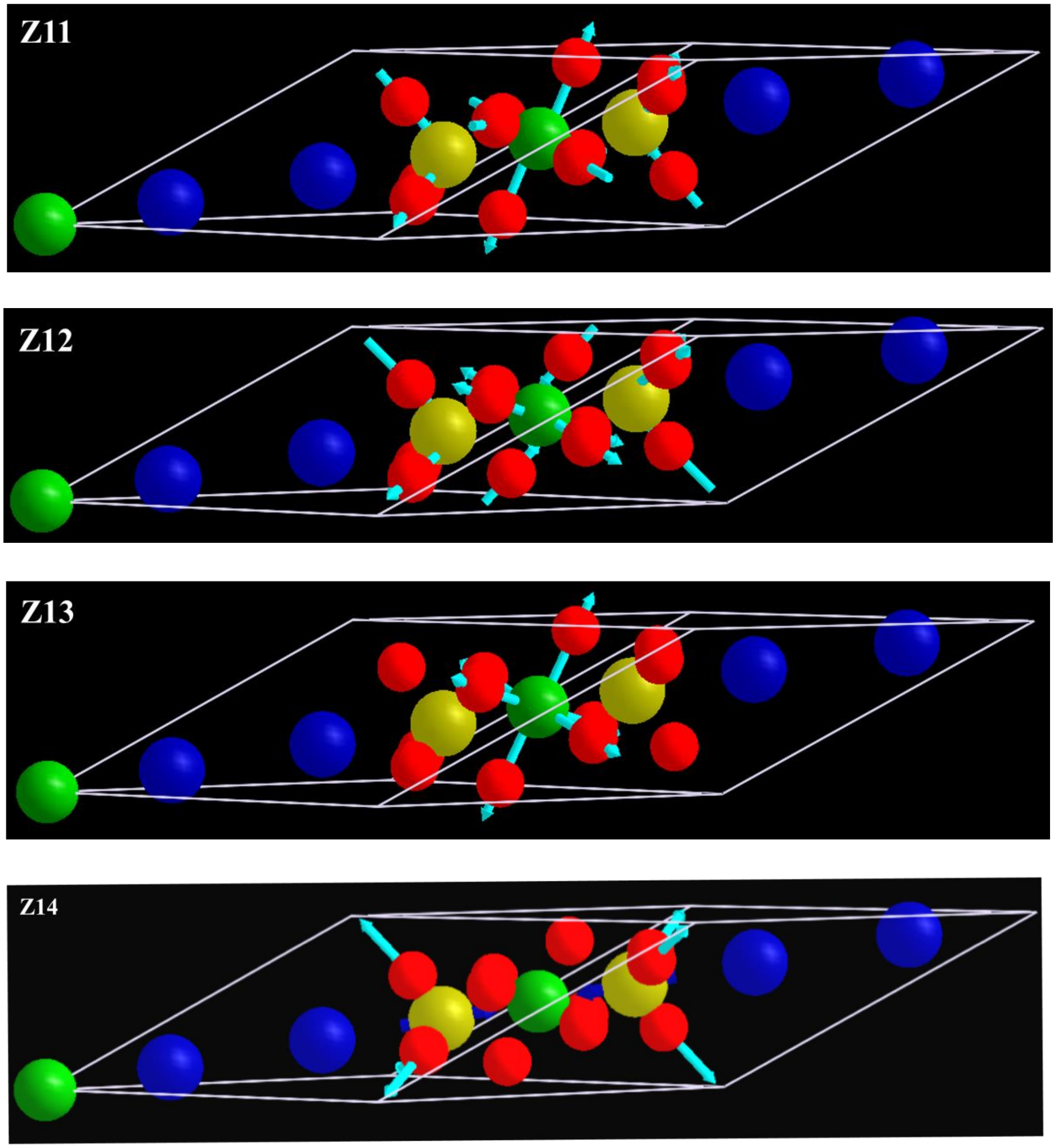


Figure S2: *Eigenvectors for the phonon modes of* Ba_2ZnTeO_6 *in the trigonal phase. The atoms shown with blue, green, yellow, and red colors are Ba, Te, Zn, and O atoms, respectively. Arrows are shown to indicate the direction of vibration of atoms.*

(c) Quasi-harmonic and phonon-phonon anharmonic interactions

As we notice the frequency response of the soft mode Z1 over-temperature, remarkably large shift in frequency was observed than usually expected. An unusually large shift in the frequency of the soft 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, ruling out the contributions from spin-phonon and electron-phonon interactions 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.

On examination of tellurium-based systems like Sr_2ZnTeO_6 [4], the Grüneisen parameters (γ) for different modes were found to be typically in the range of ~ 0.9 – 2, suggesting a small contribution to the frequency shift from the quasi-harmonic term. Therefore, we expect the quasi-harmonic contribution in BZT to be comparable to that in Sr_2ZnTeO_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

$$\frac{\Delta\omega^i}{\omega^i} = -\gamma^i \frac{\Delta V}{V} \quad [1]$$

where, γ^i is the mode Grüneisen parameter, $\frac{\Delta V}{V}$ represents the relative change in volume which is extracted from XRD data and $\frac{\Delta\omega^i}{\omega^i}$ 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 ~ 0.5 % (discussed below). Assuming $\gamma^i \sim 1$ in Eq. 1, the quasi-harmonic contribution $\Delta\omega_{qh}(T)$ is evaluated to be roughly around 0.14 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 the pure trigonal phase. This implies that the volume-dependent part has a 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 ~ 120 % (between 170 and 400 K) for the Z1 mode which is very large as compared to the typically observed quasi-harmonic shifts of ~ 1-2 %.

Similarly, the anharmonicity of its low-temperature split components is ~ 145 % for B_g and ~ 94 % for A_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 rendered by TeO_6 octahedral rotations and its coupling to the Z1′ phonon mode as suggested by DFT calculations.

S2. Variation of lattice parameter with temperature above the transition

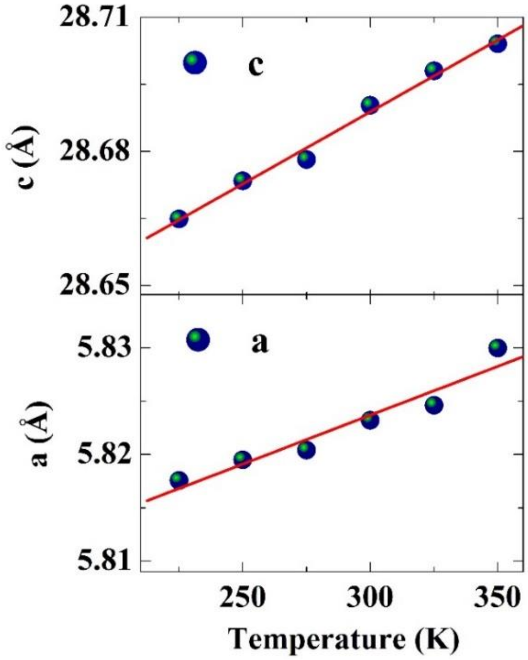


Figure S3: *Variation of lattice parameters of Ba_2ZnTeO_6 as a function of temperature where solid lines represent the linear fits to the experimental data.*

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 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, a and c, exhibit a change of ~ 0.2 % and ~ 0.1 %, respectively, with the varying temperature that corresponds 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.

S3. 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 ($T_c \sim 150$ K). The active lattice dynamical processes at lower frequencies across the T_c, 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[5]. A comparative analysis of the frequency (ω) and linewidth (Γ) (shown in the inset of Fig. 5(a) in main text) of the soft mode suggests that the mode is underdamped (because $\frac{\Gamma}{\omega} < 1$) away from T_c though the damping $\left(\frac{\Gamma}{\omega}\right)$ 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. S1(a) where the central peak is marked with shaded background in the lowest-frequency region.

Upon careful examination, we observe that the relaxation time (linewidth) of the central peak increases (decreases) near T_c as shown in Fig. 5(d) in main text. A simultaneous increase in the intensity of the central peak near T_c (see Fig. S1(a)) indicates the involvement of relaxation mechanisms[6-9]. The relaxation time (τ) is derived from the relation $\tau = \frac{1}{\pi c \Gamma}$ where 'c' is the speed of the light and Γ represents the linewidth of the central peak[10]. It is 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 (~ 8 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.

S4. Specific heat measurement

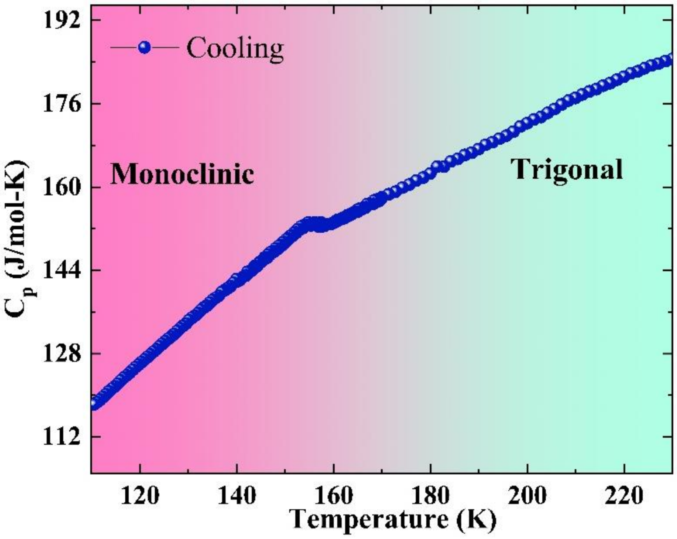


Figure S4: *Specific heat as a function of temperature showing a broad anomaly at ~ 150 K.*

In order to avoid any ambiguity regarding the smeared feature observed in the specific heat data, the measurement was carried out in the range of 110 – 230 K (as shown in Fig. S4) in the cooling cycle with a step size of ~ 0.25 K in between 140 and 170 K wherein a sharp transition has been observed in the Raman measurement through the splitting of some of the phonon bands. Notably, other phonon modes exhibit hysteretic thermal response, suggesting the presence of coexisting phases. We observed that the smeared transition (in specific heat) 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 presence of an anticipated sharp feature in the specific heat in this temperature range.

S5. Group-subgroup symmetry transformation and Wyckoff-site splitting scheme

BZT undergoes a structural transition from the high-symmetry trigonal to the low-temperature monoclinic phase. The high-temperature trigonal phase comprises of a total of 12 symmetry elements (E, 2C_3, 3C_2, i, 2S_6, 3σ_d) that define the point group '-3m' while the low-temperature monoclinic phase contains only 4 symmetry components (E, C_2, i, σ_h). 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 SI. 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[11]. 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 Raman data 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 SI. *Wyckoff-site splitting scheme for a phase transformation from the trigonal to the monoclinic system.*

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

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