Multiple Soft-Mode Vibrations of Lead Zirconate


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Polarized Raman, IR, and time-domain THz spectroscopy of orthorhombic lead zirconate single crystals have yielded a comprehensive picture of temperature-dependent quasiharmonic frequencies of its low-frequency phonon modes. It is argued that these modes primarily involve vibrations of Pb ions and librations of oxygen octahedra. Their relation to phonon modes of the parent cubic phase is proposed. Counts of the observed IR and Raman active modes belonging to distinct irreducible representations agree quite well with group-theory predictions. Analysis of the results yields insight into the phase transition mechanism, involving a soft ferroelectric branch coupled by a trilinear term to another two oxygen octahedra tilt modes.

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Reexamination of the antiferroelectricity in PbZrO$_3$ [1–4] resulted in the renouncement of the original simple two-sublattice Kittel model [5], at least in the case of this canonical antiferroelectric (AFE) oxide. Most recent studies suggest that the AFE state in lead zirconate is induced by a single lattice mode—the ferroelectric (FE) soft mode—through its flexoelastic [6–10] interaction with antiphase lead displacements [4]. The oxygen octahedra tilt displacements are triggered [11] by a biquadratic interaction to the antiphase lead displacements [4]. This novel approach to the antiferroelectricity in PbZrO$_3$ raises many questions not only with respect to this single compound and its widespread derivatives [12–16], but also with respect to interfacial engineering [17,18], design strategy of new antiferroelectrics, and their new application perspectives as well [1,2,19].

Here we describe a detailed polarized IR and Raman spectroscopic study of single domain specimens of AFE PbZrO$_3$. The obtained results demonstrate the existence of multiple soft modes of different symmetry. From their analysis an alternative model has emerged, in which (i) the whole phonon branch related to lead vibrations is intrinsically soft, and (ii) the AFE state is directly stabilized by a trilinear coupling term, that drives the AFE lead displacements and the oxygen octahedra tilts simultaneously.

The paraelectric (PE) phase of PbZrO$_3$ is a simple cubic perovskite with a 5-atom unit cell ($Pnar{3}m$, $Z = 1$). Below the AFE phase transition ($T_c \sim 500$ K), it goes over to an orthorhombic $Pbam$ ($Z = 8$) structure [20,21]. The space-group symmetry change can be well understood [2] as a result of the condensation of 2 order parameters [2,4,17,21–23]: a polarization wave of a propagation vector \( \mathbf{Q}_S = (0.25, 0.25, 0)_{pc} \) and a \( \mathbf{Q}_R = (0.5, 0.5, 0.5)_{pc} \) oxygen octahedra tilt mode (here \( pc \) stands for pseudocubic lattice, see Figs. 1 and 2). Superpositions of \( \mathbf{Q}_S \), \( \mathbf{Q}_R \) include also \( \Gamma, X, M \), and \( \mathbf{Q}_S = (0.25, 0.25, 0.5)_{pc} \) cubic-phase Brillouin zone points. All of these points become Brillouin zone centers in the $Pbam$ phase [see Fig. 2(a)] and the corresponding lattice modes give rise to $16A_u + 16B_{1g} + 14B_{2g} + 14B_{3g} + 12A_u + 11B_{1u} + 17B_{2u} + 17B_{3u}$ optic modes of the $Pbam$ structure. In the AFE phase, the optical spectroscopy thus effectively allows probing phonon modes from the \( \Sigma \) and \( S \) lines.

Density functional theory calculations demonstrated that the cubic structure of PbZrO$_3$ is instable at low temperatures with respect to the Pb ion off centering as well as concerted oxygen octahedra tilts [3,23,25–27,31]. The corresponding finite-temperature phonon frequencies can be estimated from the inelastic neutron and x-ray scattering studies PbTiO$_3$-PbZrO$_3$ solid solutions (PZT) in their common cubic phase. For example, the frequencies of the $M_{x^2}M_{y^2}, X_{x^2}, X_{x^1}$, and $R_{15}$ Pb-dominated modes can be extrapolated from the measurements of the PbTiO$_3$ [28–30] and the PZT single crystals [32]. The acoustic mode dispersion can be estimated from PbZrO$_3$ measurements of Refs. [4,33,34], and the zone-center mode frequency can be estimated from the dielectric measurements [4,35,36]. The lowest frequency phonon dispersion curves of the cubic PbZrO$_3$ obtained in this way (near the phase transition point) are traced in Fig. 2(b).

In the limit of vanishing structural distortion (small order parameters), \( \Gamma \)-point modes of the $Pbam$ orthorhombic...
The method of Ref. [37], with either out-of-plane or in-plane c axis [37]. Raman data were collected using a Renishaw microscope spectrometer operated with a 514 nm laser and a low-frequency edge filter, like, e.g., in Refs. [38,39]. IR reflectivity and time-domain THz transmission data were collected using a Fourier-transform Bruker spectrometer and a laboratory built system based on a Ti-sapphire laser, respectively, and then fitted simultaneously to obtain consistent complex dielectric and conductivity spectra in the 10–800 cm⁻¹ range (the same setup and experimental procedure as, e.g., in Refs. [40,41]).

The typical low-frequency, low-temperature Raman spectra are shown in Figs. 3(a) and 3(b). As indicated in the figure, the light was polarized along the PbZrO₃ crystallographic axes so that the assignment of the observed modes to the relevant irreducible representations was rather straightforward. Similarly, the real part of the conductivity spectra allows probing the B₁₄(ζ), B₂₃(μ), and B₃₄(λ) modes independently [see Fig. 3(c)]. Therefore, present data offered a more complete picture than the earlier studies [42–44]. Overall, the numbers of the modes observed in the 0–100 cm⁻¹ frequency range match well the list given in Table I.

Phonon frequencies up to about 150 cm⁻¹ (from fits using damped harmonic oscillator response functions) as a function of temperature are shown in Fig. 4. The lowest frequency B₂₃(μ), B₃₄(λ), and B₄₅(γ) modes can be assigned to the Σ₃, Σ₁, Σ₄, and Σ₄ acoustic modes folded from (Q₁). All other modes of Fig. 4 reveal a considerable frequency increase upon cooling (both the modes in the 0–100 cm⁻¹ range as well as those in the 100–150 cm⁻¹ frequency range). How can this be understood?

The temperature dependence of the fully symmetric mode (A₃g), corresponding to the order parameter, follows naturally from the simplest Landau-type theory. The temperature dependence of the B₁₄(ζ), B₂₃(μ), and B₃₄(λ) components of the Last-type Γ₁₅ mode could be, in principle, explained, e.g., by a positive biquadratic coupling to the primary order parameter [4]. However, the simplest assumption explaining the strikingly similar temperature dependence of so many other phonon frequencies below 100 cm⁻¹ is that PbZrO₃ has a soft branch, rather than a

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FIG. 1 (color online). Crystal structure of PbZrO₃ in its (a) high-temperature cubic phase and (b) its low-temperature orthorhombic phase. The orthorhombic PbZrO₃ elementary unit cell is projected along its z||c axis, the a = (1, -1, 0) pc/√2 and b = (1, 1, 0) pc√2 lattice vectors defining the x and y axes are indicated in the figure. Note that the x components of the AFE displacements of the Pb ions 1 and 2 are opposite to those of 3 and 4. This displacement pattern forms a Σ₁ symmetry mode associated with Q₁ = b′ propagating vector.

structure transform also as Γ, X, R, M, QΣ, or QΣ-point modes of the parent cubic phase. Correlation between irreducible representations of the actual and parent symmetry group for the Pb ion vibration modes is shown in Table I. The items listed in Table I match well the cubic-phase modes shown in Fig. 2(b). Therefore, about 24 optic Pb ion modes are expected in the AFE phase within the 0–100 cm⁻¹ frequency range.

To identify these modes experimentally, we have investigated flux-grown single crystal platelets detwinned using the method of Ref. [37], with either out-of-plane or in-plane c axis [37]. Raman data were collected using a Renishaw microscope spectrometer operated with a 514 nm laser and a low-frequency edge filter, like, e.g., in Refs. [38,39]. IR reflectivity and time-domain THz transmission data were collected using a Fourier-transform Bruker spectrometer and a laboratory built system based on a Ti-sapphire laser, respectively, and then fitted simultaneously to obtain consistent complex dielectric and conductivity spectra in the 10–800 cm⁻¹ range (the same setup and experimental procedure as, e.g., in Refs. [40,41]).

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| Table I. Correlation between D₂₃r irreducible representations of PbZn Pb-ion zone-center vibrations (top row of the table) and their counterparts in the parent cubic phase. Σ₁ and Σ₃ stands for modes associated with Q₁ and Q₅ wave vectors, respectively. Other labels are as those of Ref. [31]. |
|---|---|---|---|---|---|---|---|---|
| A₃g | B₁₄(ζ) | B₂₃(μ) | B₃₄(λ) | A₄ | B₁₄(ζ) | B₂₃(μ) | B₃₄(λ) |
| Γ   | Γ₁₅   | Γ₁₅   | Γ₁₅   | X₂   | X₅   | X₅   |
| X   |       |       |       |     |       |       |
| M   | M₃'   | M₃'   |       |     |       |       |
| R   | R₁₅   | R₁₅   |       |     |       |       |
| Σ   | Σ₃    | Σ₄    | Σ₄    |     | Σ₃    | Σ₁    |
| S   | S₃    | S₃    | S₄    |     | S₃    | S₁    |

FIG. 2. Brillouin zone points involved in the phase transition and low-frequency phonon branches of cubic PbZrO₃. Panel (a) indicates Γ, X, R, M, QΣ, and Q₅ Brillouin zone points of cubic PbZrO₃; panel (b) shows corresponding phonon frequencies estimated from the available PbTiO₃ and PbTiO₃-PbZrO₃ spectroscopic data. Indices of the symmetry labels denoting phonon branches are those of Ref. [24].
Actually, present results even suggest that both modes have the same column in Table I are coupled in the AFE phase. Due to the mode mixing, in particular, modes listed within the AFE phase spectra \[48\]. Since the bare mode is close to the IR plasma frequency of the Last soft mode \[\text{Last} \equiv \Omega_R \text{Last} = 618 \text{ cm}^{-1}\]. It provides an estimate of the squared oscillator frequency of the bare Last mode. Values of \(\epsilon(0)\) are taken from the joint THz-IR fit (point symbols). Independently measured 900 kHz data (available only along the c axis) are shown by the continuous line. The yellow-shaded region indicates soft oxygen octahedra libration modes.

FIG. 3 (color online). Typical low-frequency phonon spectra of PbZrO\(_3\). Panels (a) and (b) shows polarized Raman spectra at 80 K. The scattering geometry is indicated using standard Porto notation. Panel (c) shows the real part of the low-frequency conductivity spectra, as obtained from a combined fit to the spectra of IR reflectivity and time-domain THz spectroscopy, showing peaks at the transverse optic mode frequencies of the \(B_{1u}(z), B_{2u}(y),\) and \(B_{3u}(x)\) modes. The \(x, y,\) and \(z\) labels correspond to the crystallographic axes of the orthorhombic \(Pbam\) structure.

Are the observed temperature variations of phonon frequencies large or small? Within the Landau theory of the second-order structural phase transition, the squared soft-phonon frequency shows a linear temperature dependence (Cochran law). A stronger, nonlinear temperature dependence is expected below a first-order phase transition point, but the relation of the inverse static permittivity to the soft-mode frequency via the Lyddane-Sachs-Teller relation should be still valid. To estimate the expected soft-mode frequency, we have thus multiplied the inverse of the static permittivity by the square of the mode plasma frequency of the Last mode \(\Omega_{\text{Last}} = 618 \text{ cm}^{-1}\). It provides an estimate of the squared oscillator frequency of the bare Last mode. Values of \(\epsilon(0)\) are taken from the joint THz-IR fit (point symbols). Independently measured 900 kHz data (available only along the c axis) are shown by the continuous line. The yellow-shaded region indicates soft oxygen octahedra libration modes.

FIG. 4 (color online). Temperature dependence of squared frequencies of Raman active (a)–(d) and IR active (e)–(g) modes of AFE PbZrO\(_3\). Panel (h) shows inverse static permittivity multiplied by the square of the plasma frequency of the Last mode \(\Omega_{\text{Last}} = 618 \text{ cm}^{-1}\). It provides an estimate of the squared oscillator frequency of the bare Last mode. Values of \(\epsilon(0)\) are taken from the joint THz-IR fit (point symbols). Independently measured 900 kHz data (available only along the c axis) are shown by the continuous line. The yellow-shaded region indicates soft oxygen octahedra libration modes.

However, no such case is known. In fact, in a good AFE
material, one should be also able to switch the staggered polarization configuration to the FE one by an electric field. This suggests that AFE materials should have both the zone-center and zone-boundary soft mode. It is most naturally realized when the whole polarization branch is soft [Fig. 5(c)]. This often results in an incommensurate instability [45–47]. A combination of the present experimental results and those of Ref. [4] implies that PbZrO$_3$ does exhibit a flat soft polarization branch, still without any trace of a local minimum near the AFE wave vector [Fig. 5(d)]. Therefore, an additional ingredient responsible for the antiferroelectricity is needed beyond the quasiharmonic approximation, i.e., a nonlinear coupling term. The existence of the second family of soft modes (range 100–150 cm$^{-1}$) suggests that this term involves the oxygen octahedra tilts.

To illustrate this idea, we consider a 1D chain of alternating lead and oxygen ions in the direction of the AFE wave vector, e.g., all ions located on the line connecting (1) and (3) Pb ions shown in Fig. 1. A simple soft branch potential related to $x$ displacement of $n$th lead ion $p_n$ reads

$$\sum \left[ \frac{\alpha}{2} p_n^2 + \frac{\beta}{4} p_n^4 + \frac{J}{2} (p_{n+1} - p_n)^2 \right],$$

(1)

with $\alpha, \beta, J > 0$. Note that the usual Landau term $\alpha/2 \sum p_n^2$ for the soft macroscopic polarization is replaced with an effective-Hamiltonian-like [23,25] $\alpha/2 \sum p_n^2$ expression describing the soft microscopic polarization. Therefore, this term directly controls the stability of both AFE and FE modes. The second ingredient is a potential associated with $x$ and $y$ displacements of the $n$th oxygen ion $x_n, y_n$ and a coupling term to adjacent Pb ions that favors their AFE arrangement, such as

$$\sum \left[ \frac{A}{2} (x_n^2 + y_n^2) + \frac{B}{4} (x_n^4 + y_n^4) + \frac{K}{2} (p_{n+1} - p_n) x_n y_n \right].$$

(2)

with $A, B > 0$. The phase diagram of this model is sketched in Fig. 5(e). The direct paraelectric ($p_n = 0$) to AFE [$p_n = p(-1)^n$] phase transition occurs if $|K| > K_0 \approx 0.9425$. For a smaller magnitude of $K$, the AFE transition is preceded by the FE one ($p_n = p$), as in the Zr-rich side of the temperature-concentration-phase diagram of the PZT system. Similar phase diagrams can be expected to hold for a more realistic, 3D lattice model with all the trilinear coupling terms allowed by symmetry, such as that involving the product of the $\Sigma_3$ polarization wave with $R_{25}$ and $S_3$ octahedra rotation modes [49]. In this sense the AFE phase transition of PbZrO$_3$ is analogous to the avalanche [50–52] and “hybrid-improper-like” [53] transitions.

In summary, this polarized Raman, IR, and THz spectroscopic study of AFE PbZrO$_3$ single crystals has established that there are several low frequency modes with anomalously temperature dependent phonon frequencies distributed among seven active irreducible representations. We conclude that the modes around 130 cm$^{-1}$ are associated with oxygen octahedra tilt vibrations, while those below about 100 cm$^{-1}$ are due to the Pb ion fluctuations. Softening of the latter can be understood as a consequence of a soft and flat phonon branch, without having to recall specific biquadratic couplings for each such mode separately. It is emphasized that, in general, flat soft polarization branches ensure a simultaneous instability with respect to both the homogeneous and the staggered polarization, that seems to be the essential prerequisite of an AFE material [54,55]. Switching is actually easier when the AFE instability is weaker than the FE one. However, this situation requires an additional element stabilizing the staggered polarization, such as the above proposed trilinear term for PbZrO$_3$. We hope that this piece of understanding can help to discover new useful antiferroelectrics as well as to model the finite-temperature properties of the current PbZrO$_3$-based materials.

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