Microstructure dynamics in orthorhombic perovskites

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Anelastic loss mechanisms associated with phase transitions in BaCeO3 have been investigated at relatively high frequency ~1 MHz and low stress by resonant ultrasound spectroscopy (RUS), and at relatively low frequency ~1 Hz and high stress by dynamic mechanical analysis (DMA). Changes in the elastic moduli and dissipation behavior clearly indicate phase transitions due to octahedral tilting: Pnma ↔ Imma ↔ R3c ↔ Pm3m structures at 551 K, 670 K, and 1168 K, and strain analysis shows that they are tricritical, first-order, and second-order phase transitions, respectively. Structures with intermediate tilt states (R3c and Imma structures) show substantial anelastic softening and dissipation associated with the mobility of twin walls under applied stress. The Pnma structure shows elastic stiffening which may be due to the simultaneous operation of two discrete order parameters with different symmetries. In contrast with studies of other perovskites, BaCeO3 shows strong dissipation at both DMA and RUS frequencies in the stability field of the Pnma structure. This is evidence that ferroelastic twin walls might become mobile in Pnma perovskites and suggests that shearing of the octahedra may be a significant factor.

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I. INTRODUCTION

The properties and dynamics of twin walls in perovskites have been the focus of intense interest because of their unique and quite specific character as defects in otherwise homogeneous materials and because of their central role in ferroelectric, ferromagnetic, and ferroelastic switching. For example, twin walls in tungsten oxide can be induced to become superconducting while the matrix material is not, and twin walls in CaTiO3 might be ferrielectric in a matrix which contains no electric dipoles. For the particular case of ferroelastic twin walls, the local structural changes are dominated by large strain gradients. In a perfect crystal their mobility might be expected to be unconstrained but in real crystals they experience viscous drag due to strong interaction with strain fields around defects. At low temperatures the pinning effect of defects can become sufficiently strong so that the walls become immobile. Dynamics and structure are thus closely related and can give rise to substantial variations in elastic and anelastic behaviors under the influence of an externally applied stress. Against this broader background it has been found that mechanical spectroscopy is an ideal tool for investigating twin wall properties in materials as disparate as piezoelectrics (e.g., lead-zirconate-titanate) and analog phases for silicate perovskites CaSiO3 and Mg,FeSiO3 in the deep earth [e.g., LaAlO3 and (Ca, Sr)TiO3].

The work presented here arose from a particular conundrum in relation to the anelastic properties of perovskites with the Pnma structure, as opposed to R3c or I4/mcm structures. All three are improper ferroelasticities containing transformation twins but the twin walls appear to be mobile only in the rhombohedral and tetragonal phases of LaAlO3, (Ca, Sr)TiO3, and Sr(Zr, Ti)O3. In Ca1-xSr_xTiO3 with x = 0.4, 0.45, and 0.5, and in SrZrO3, transitions to the Pnma structure are marked by a steep decrease in anelastic softening and dissipation as if twin wall motion is abruptly curtailed. Two different explanations have been offered. Daradkhiev et al.14 suggested that the sign of the volume strain accompanying the transition from the parent cubic phase is important in influencing the twin wall thicknesses and hence in the extent to which they interact with defects. Alternatively, the small total spontaneous strain of Pnma phases is important such that even if the walls are mobile, the strain released is small. A more general explanation could be that the properties of twin walls in materials which have undergone structural phase transitions involving two order parameters with quite different symmetries are fundamentally different from the properties of twin walls depending on relaxations of only a single order parameter. In the case of octahedral tilting transitions, the Pnma structure has nonzero order parameters belonging to irreps M3 and R4, while the order parameter for R3c and I4/mcm belongs to R4 alone. In order to distinguish between these different possibilities the mechanical behavior of other perovskites have been investigated and, quite unexpectedly, it was found that the Pnma phase of BaCeO3 shows strong anelastic dissipation down to ~200 K. This has all the characteristics of being related to twin wall motion and provides evidence that twin walls associated with multiple order parameters in Pnma perovskites might become mobile under mechanical stress.

Phase transitions in BaCeO3 at ambient pressure and changing temperature follow the sequence Pnma ↔ Imma ↔ R3c ↔ Pm3m and have previously been studied by Raman spectroscopy, neutron diffraction, x-ray diffraction (XRD), and thermal analysis. Transition temperatures from the literature are summarized in Table I. In this study, anelastic loss mechanisms associated with the transitions were investigated at relatively high frequency ~1 MHz and low stress by resonant ultrasound spectroscopy (RUS) and at relatively low frequency ~1 Hz and high stress by dynamic mechanical analysis (DMA). The specific objectives were,
first, to compare the \( Pnma \leftrightarrow Imma \leftrightarrow R3\bar{c} \leftrightarrow Pm\bar{3}m \) sequence of \( BaCeO_3 \) with the comparable but subtly different \( Pnma \leftrightarrow Imma \rightarrow I4/mcm \rightarrow Pm\bar{3}m \) sequence of \( SrZrO_3 \), second, to examine the anelastic behavior of the \( Imma \) structure which appears as an intermediate phase in some perovskites but not in others; third, to characterize the anelastic loss behavior of the \( Pnma \) structure and, finally, to correlate the overall elastic behavior with details of the spontaneous strain evolution extracted from high-resolution lattice-parameter data.

II. STRAIN ANALYSIS OF SUCCESSIVE PHASE TRANSITIONS

Lattice parameters obtained by Knight\textsuperscript{19} from high-resolution powder neutron diffraction have been used to follow the evolution of individual order parameters, in terms of symmetry-adapted spontaneous strains, through the sequence of phase transitions in \( BaCeO_3 \). The original data are reproduced in Figs. 1(a) and 1(b) for the reduced pseudocubic unit cell, with the orthorhombic values in the \( Pnma \) setting used by Knight.\textsuperscript{25} Values of the cubic reference parameter \( a_0 \) were obtained by fitting a straight line to data at temperatures between 1198 and 1273 K in the stability field of the \( Pm\bar{3}m \) structure, giving \( a_0=4.3384+0.000046T \) with \( T \) in kelvins [Fig. 1(a)]. The volume strain and tetragonal shear strain are defined as

\[
e_a = e_1 + e_2 + e_3, \\
e_{\text{tx}} = \frac{1}{\sqrt{3}}(2e_1 - e_2 - e_3),
\]

and the remaining nonzero shear strain is \( e_4 \). The orientations of unit-cell axes with respect to the reference system for the strain tensor are the same as given by Carpenter \textit{et al.}\textsuperscript{25–27} Expressions for the individual strains in terms of the unit-cell dimensions of \( Pnma \), \( Imma \), and \( R3\bar{c} \) structures are listed in Table II. Variations in the spontaneous strains calculated on this basis are shown in Fig. 1(c). Note that shear strains are insensitive to the choice of \( a_0 \) but uncertainties in \( a_0 \) result in significant uncertainties in the absolute values of \( e_a \).

Octahedral tilting transitions in perovskites can be described by order parameters which are associated with \( M \) and \( R \) points of the Brillouin zone of the cubic parent structure and have symmetry properties of irreps \( M_2^+ \) and \( R_4^+ \), respectively.\textsuperscript{25,28,29} The two order parameters each contain three components. A complete Landau expansion, to sixth order in the order parameters and including coupling with the strains, has been given by Carpenter.\textsuperscript{29} M-point order-parameter components are \( q_1, q_2, \) and \( q_3 \). R-point components are \( q_4, q_5, \) and \( q_6 \): the \( R3\bar{c} \) structure has \( q_4=q_5=q_6 \neq 0 \) and \( q_1=q_2=q_3=0 \), the \( Imma \) structure has \( q_1=q_4 \neq 0 \) and \( q_4=q_5=q_6=0 \), and the \( Pnma \) structure has \( q_3=q_6=0 \), \( q_2 \neq 0 \), and \( q_1=q_2=q_3=0 \). Relationships between these order-parameter components and the spontaneous strains\textsuperscript{25,25,26,30}

![FIG. 1. (a) and (b)](attachment:image.png) Lattice parameter data (Ref. 19) given in terms of the pseudocubic unit cell. The straight line in (a) represents the reference lattice parameter, \( a_0 \), obtained by fitting to data in the temperature interval 1198–1273 K. (c) Symmetry-adapted strains, with respect to the parent \( Pm\bar{3}m \) structure, derived from the lattice parameters in (a) and (b). A straight line fit to data for \( e_4 \) of the \( R3\bar{c} \) structure in the temperature interval 693–1083 K extrapolates to zero at \( T_c = 1170 \pm 2 \) K. Broken lines are fits to \( e_4 \) and \( e_{\text{tx}} \) of the \( Imma \) structure constrained to have \( T_c = 1170 \) K. (d) Variations in linear strains of the \( Pnma \) structure defined with respect to the \( Imma \) structure as reference state. In this case \( e_{\text{tx}}^4 \) and \( e_4^5 \) vary approximately linearly with temperature, implying close to tricritical character for the \( Imma \leftrightarrow Pnma \) transition, with \( T_c = 530 \) K. 

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**TABLE I. Transition temperatures for \( BaCeO_3 \) from previous studies.**

<table>
<thead>
<tr>
<th>Method</th>
<th>( T_1 ) (K)</th>
<th>( T_2 ) (K)</th>
<th>( T_3 ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman spectroscopy (Ref. 18)</td>
<td>1073</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutron diffraction (Ref. 19)</td>
<td>563</td>
<td>673</td>
<td>1173</td>
</tr>
<tr>
<td>Neutron diffraction (Ref. 20)</td>
<td>573</td>
<td>673</td>
<td>1200</td>
</tr>
<tr>
<td>Raman spectroscopy (Ref. 20)</td>
<td>533</td>
<td>700</td>
<td>1153</td>
</tr>
<tr>
<td>Thermal analysis (Ref. 21)</td>
<td>530 \pm 10</td>
<td>665 \pm 10</td>
<td>1170 \pm 20</td>
</tr>
<tr>
<td>Thermal analysis (Ref. 22)</td>
<td>540</td>
<td>600</td>
<td>1180</td>
</tr>
<tr>
<td>Thermal analysis (Ref. 23)</td>
<td>533</td>
<td>658</td>
<td>1168</td>
</tr>
<tr>
<td>X-ray diffraction (Ref. 23)</td>
<td>553</td>
<td>673</td>
<td>1173</td>
</tr>
<tr>
<td>RUS\textsuperscript{a}</td>
<td>551</td>
<td>670</td>
<td>1168</td>
</tr>
<tr>
<td>DMA\textsuperscript{a}</td>
<td>551</td>
<td>670</td>
<td></td>
</tr>
<tr>
<td>Strain analysis\textsuperscript{a}</td>
<td>530</td>
<td>673</td>
<td>1170 \pm 2</td>
</tr>
</tbody>
</table>

\textsuperscript{a}This study.
TABLE II. Relationships between spontaneous strains and order-parameter components of \( R\bar{3}c, \) Imma, and \( Pnma \) structures, with respect to the cubic \( Pm\bar{3}m \) parent structure derived from Eq. (1) of Ref. 29 (see also Refs. 27 and 36). Orientation relationships between crystallographic axes and the reference axes are illustrated in Refs. 25 and 26.

<table>
<thead>
<tr>
<th>( \bar{R}\bar{3}c )</th>
<th>Imma</th>
<th>( Pnma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( e_{x} = \frac{3\bar{a}q_{1}}{4(C_{1}+2C_{2})} )</td>
<td>( e_{x} = \frac{2\bar{a}q_{1}}{3(C_{1}+2C_{2})} )</td>
<td>( e_{x} = \frac{(\bar{a}q_{1}+2\bar{a}q_{2})}{3(C_{1}+2C_{2})} )</td>
</tr>
<tr>
<td>( e_{ix} = 0 )</td>
<td>( e_{ix} = 0 )</td>
<td>( e_{ix} = 0 )</td>
</tr>
<tr>
<td>( e_{ix} = 0 )</td>
<td>( e_{iy} = \frac{2\bar{a}q_{1}}{3(C_{1}+C_{2})} )</td>
<td>( e_{ix} = \frac{(\bar{a}q_{1}+3\bar{a}q_{2})}{3(C_{1}+C_{2})} )</td>
</tr>
<tr>
<td>( e_{iy} = e_{is} = e_{x} = \frac{\lambda q_{2}}{3C_{4}} )</td>
<td>( e_{iy} = \frac{\lambda q_{2}}{C_{4}} )</td>
<td>( e_{iy} = \frac{\lambda q_{1}+\lambda q_{2}+\lambda q_{4}+\lambda q_{5}}{C_{4}} )</td>
</tr>
<tr>
<td>( e_{iy} = e_{i} = \frac{b - \bar{a}q_{0}}{a} )</td>
<td>( e_{iy} = \frac{b - \bar{a}q_{0}}{a} )</td>
<td>( e_{iy} = \frac{b - \bar{a}q_{0}}{a} )</td>
</tr>
<tr>
<td>( e_{iz} = e_{j} = \frac{\bar{a}q_{0}}{a} )</td>
<td>( e_{iz} = \frac{\bar{a}q_{0}}{a} )</td>
<td>( e_{iz} = \frac{\bar{a}q_{0}}{a} )</td>
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<td>( e_{iz} = e_{j} = \frac{\bar{a}q_{0}}{a} )</td>
<td>( e_{iz} = \frac{\bar{a}q_{0}}{a} )</td>
<td>( e_{iz} = \frac{\bar{a}q_{0}}{a} )</td>
</tr>
</tbody>
</table>

are listed in Table II, with \( C_{4} \) representing elastic constants of the \( Pm\bar{3}m \) reference structure in the usual way. In the \( R\bar{3}c \) structure, \( e_{x} \) is expected to scale with \( q_{2} \) and the data are consistent with \( e_{x} \approx q_{2}^{3} \times T \) [Fig. 1(c)]. The \( Pm\bar{3}m \rightarrow R\bar{3}c \) transition is therefore second order in character and the straight line fit to data for the temperature interval 693–1083 K give \( T_{c} = 1170 \pm 2 \) K. Data for the temperature interval 1093–1148 K fall below the linear trend but at such small values the deviations from cubic geometry are at or below the limits of resolution of the primary diffraction data.

The \( R\bar{3}c \rightarrow Imma \) transition is marked by small discontinuities in \( e_{x} \) and \( e_{y} \) [Fig. 1(c)] and is first order in character.\(^{19,24} \) In principle, there is a metastable \( Pm\bar{3}m \rightarrow Imma \) transition with the same critical temperature as for the \( Pm\bar{3}m \rightarrow R\bar{3}c \) transition. Limited data for \( e_{iy} \) and \( e_{iy} \) of the \( Imma \) phase (both \( \approx q_{2}^{3} \)) can at least be interpreted on this basis [Fig. 1(c)]. As in the case of the \( Pm\bar{3}m \rightarrow I4/mcm \rightarrow Imma \rightarrow Pnma \) sequence in SrZrO\(_{3}\) (Ref. 15) and the \( Pm\bar{3}m \rightarrow I4/mcm \rightarrow Pnma \) sequence in CaTiO\(_{3}\),\(^{25} \) \( e_{x} \) does not scale linearly with the shear strains, suggesting higher order coupling effects or a temperature-dependent order-parameter coupling coefficient for the volume strain.

Lattice parameter data show continuous variations through the \( Imma \rightarrow Pnma \) transition [Fig. 1(a)] and these convert to continuous variations in the magnitudes of both \( e_{y} \) and \( e_{x} \) [Fig. 1(c)], though with nonlinear dependences on temperature. If the reference state for this transition is taken as the \( Imma \) structure, the transition will have a single order parameter, \( Q \), and the linear strains are expected to scale as \( e_{x} \approx e_{x} \approx e_{y} \approx Q^{2} \). Using straight line fits to the data for \( a, b, \) and \( c \) of the \( Imma \) structure to obtain \( a_{0}, b_{0}, \) and \( c_{0}, \) the linear strains \( e_{1} = (a-a_{0})/a_{0}, \) \( e_{2} = (b-b_{0})/b_{0}, \) and \( e_{3} = (c-c_{0})/c_{0} \) (reference axes \( X||a, Y||b, \) and \( Z||c \)) have been determined and these scale with temperature approximately as \( e_{1}^{2} \approx e_{2}^{2} \approx e_{3}^{2} \approx Q^{2} \times T \) [Fig. 1(d)]. The transition is thus close to tricritical, with \( T_{c}=530 \) K.

Intensity data for \( M- \) and \( R- \) point superlattice reflections are reproduced from Ref. 24 in Fig. 2(a). They show a continuous decrease to zero at \( \approx 540 \) K and \( \approx 1170 \) K, respectively, with a small discontinuity at \( \approx 673 \) K. Intensities of the \( R- \) point reflections, \( I_{R}, \) are expected to be proportional to \( Q^{3}, \) where \( Q \) is the scalar order parameter and \( |Q|=\sqrt{3}q_{4}^{2} \) for the \( R\bar{3}c \) structure, or \( |Q|=\sqrt{2}q_{4}^{2} \) for the \( Imma \) structure. For the \( R\bar{3}c \) structure, \( e_{x} \approx |Q| \) is observed [Fig. 2(b)], though a straight line through the data does not pass through the origin (probably as a consequence of Debye-
Waller contributions or because the background intensity was not accounted for quite correctly). The $e_4$ data have been plotted in Fig. 2(b) as $3e_4$ and $2e_4$, respectively, for the $R \bar{3}c$ and Imma structures (since $e_4 = -\lambda_4 q_z^2 / C_{44}$ in each case) to test whether the discontinuity is due entirely to the discontinuity in $Q$ or whether there is also a change in the strength of the coupling coefficient, $\lambda_4$. The fact that the Imma values plot slightly below the $R \bar{3}c$ values implies that $\lambda_4$ reduces slightly in the Imma structure. On the other hand, data for $e_4$ follow the same trend for both structures, implying that $\lambda_2$ remains the same. Thus the $R \bar{3}c \leftrightarrow$ Imma transition is marked by a small reduction in both the R-point order parameter and in the strength of coupling with $e_4$.

The tetragonal shear strain $e_{tx}$ decreases at the Imma $\leftrightarrow$ Pnma transition due to the influence of M-point tilting (Table II). On the other hand, $e_4$ couples with the M-point order parameter only as $(\lambda_6 + \lambda_7)q_z^2$ and this coupling influences the strain evolution as (from Refs. 15 and 29)

$$e_4 = -\frac{\lambda_6 q_z^2}{C_{44} + 2(\lambda_6 + \lambda_7)q_z^2}. \quad (3)$$

It is generally assumed that $C_{44}$ is much greater than $(\lambda_6 + \lambda_7)q_z^2$ so that the additional term in the denominator can be dropped. In this case, $e_4$ should continue to increase with $I_R$ in the stability field of the Pnma structure but it actually decreases [Figs. 1(c) and 2(b)]. This can be explained by the operation of an additional, secondary, order parameter of the Pnma structure. From a symmetry analysis of cooperative Jahn-Teller transitions in perovskites two types of ordering of distorted octahedra were identified by Carpenter and Howard.\textsuperscript{27} These are associated with irreps $\Gamma_3^1$ and $M_2^7$ of the parent cubic space group and correspond to ordering of the unique axis of uniaxially distorted octahedra parallel to the crystallographic $b$ axis or ordered in a staggered arrangement within planes parallel to $(010)$. The $\Gamma_3^1$ order parameter couples biquadratically with $e_{tx}$ and therefore would be expected to contribute to $e_4$ only in the same manner as $q_z$ in Eq. (3). On the other hand, the $M_2^7$ order parameter (components $q_{1JT} = q_{2JT} = 0$ and $q_{3JT} \neq 0$ under Pnma symmetry) has a coupling term of the form $\lambda_{eM2+M3}e_{tx}q_z^2q_{2JT}$ so that the variation in $e_4$ becomes (from Ref. 27)

$$e_4 = -\frac{\lambda_{eM2+M3}q_z^2}{C_{44}}. \quad (4)$$

If $q_{2JT}$ varies approximately linearly with $q_z$, the observed pattern of nonlinear variation in $e_4$ for a tricritical transition would result. In other words, the strain evolution can be understood in terms of the normal effects of octahedral tilting together with a significant contribution from deformation of individual octahedra which mimics the larger distortions that occur at cooperative Jahn-Teller transitions in perovskites with the Pnma structure, as described by Carpenter and Howard.\textsuperscript{27,31}

In summary, the magnitudes of the strains are generally typical of those accompanying octahedral tilting transitions in perovskites. Formal strain analysis confirms second-order character for the $Pm\bar{3}m \leftrightarrow R\bar{3}c$ transition, first-order character for the $R\bar{3}c \leftrightarrow$ Imma transition, and approximately tricritical character for the Imma $\leftrightarrow$ Pnma transition. The $R\bar{3}c \leftrightarrow$ Imma transition is accompanied by a small reduction in the amount of R-point tilting and a small reduction in the strength of coupling with the shear strain $e_4$. The data do not provide evidence of whether the strength of coupling between R-point order-parameter components and $e_{tx}$ (coupling coefficient $\lambda_4$) differs between the $R\bar{3}c$, Imma, and Pnma structures. The Imma $\leftrightarrow$ Pnma transition gives rise to a reduction in the magnitude of both $e_{tx}$ and $e_4$, indicating that strain-mediated coupling between the M-point and R-point tilts is unfavorable. Evidence of the nonlinear dependence of the volume strain $e_4$ and the contribution of an $M_2^7$ component to $e_4$ implies that the overall transition mechanism involves some degree of deformation of the CeO$_6$ octahedra.

As well as having opposite sign, the pattern of variation in $e_4$ in the Pnma structure of BaCeO$_3$ differs from that shown by CaTiO$_3$ (Ref. 25) and SrZrO$_3$.\textsuperscript{15} Finally, $e_4$ is negative in CaTiO$_3$ (Ref. 25) and BaCeO$_3$ (this analysis) and positive at most temperatures in SrZrO$_3$.\textsuperscript{15}

### III. Elasticity: Experimental Details

BaCeO$_3$ powder, used by Knight\textsuperscript{10,24} for neutron-diffraction experiments, was ground in acetone using an agate ball mill at 600 rpm for 1 h with PULVERISSETTE 7 from FRITSCH. The milled powder, ~5 g, was pressed into a cylindrical pellet of diameter 13 mm and height ~6 mm using a pellet die under ~1800 psi for 5 min with an Omega Bench Press from SHINN FU. The pellet was sintered in air at 1450 °C for 48 h and the detailed procedure is as follows.

1. Heated from 20 to 1400 °C at 10 °C/min.
2. Held at 1400 °C for 2 h.
3. Heated from 1400 to 1450 °C at 5 °C/min.
4. Held at 1450 °C for 48 h.
5. Cooled from 1450 to 20 °C at 3 °C/min.

Rectangular parallelepiped samples were cut from the sintered pellet using an annular diamond saw, lubricated with paraffin. The parallelepiped used for RUS measurements had dimensions $1.66 \times 2.11 \times 2.64$ mm$^3$ and mass 0.053 g. The density determined from these parameters is 5.73 g/cm$^3$, which is ~91% of the theoretical density, 6.29 g/cm$^3$.\textsuperscript{32} For DMA tests, a sample was polished to the dimensions $\sim 0.22 \times 2.00 \times 7.20$ mm$^3$. An offcut of the sample was also crushed and investigated by XRD, using a Bruker D8 diffractometer with Cu $K_{α}$ radiation at 40 kV and 40 mA. The diffraction angle $2θ$ was scanned from 5° to 95°. Steps were in increments of 0.02° and the counts were collected for 3 s at each step. The diffraction pattern was entirely consistent with the known orthorhombic structure of BaCeO$_3$.

RUS data were collected at low temperatures (10–300 K) using dynamic resonance system modulus II electronics, and an orange helium flow cryostat, as described by McKnight et al.\textsuperscript{33} Frequency was scanned from 100 to 1200 kHz. High-temperature data (300–1300 K) for the same frequency range were collected using alumina buffer rods protruding into a horizontal Netzsch furnace and Stanford electronics described by Migliori and Maynard.\textsuperscript{35} The elastic moduli were
FIG. 3. Stacks of RUS scans. (a) Low temperatures: the weak background peaks at very low temperatures are noise from somewhere in the sample holder. (b) High temperatures: the regularly spaced background peaks are due to alumina rods.

determined from fitting 27 resonance peaks with an overall root-mean-square error of $\sim0.3\%$. In addition, internal friction, i.e., inverse of quality factor $Q$ was obtained from asymmetric Lorentz fitting of the resonance peak, $Q^{-1} = \Delta f/f_0$. $\Delta f$ is full width at half maximum of the resonance peak, and $f_0$ is the resonance frequency. Temperature measured by a thermocouple close to the sample was calibrated using Eq. (5), determined from known transition temperatures of single-crystal quartz (846 K), LaAlO$_3$ (817 K), and Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ (1204 K), as described by McKnight et al. (Ref. 15).

$$T_{cal} = 4.3766 + 0.98604 \times T_{read}$$  \hspace{1cm} (5)

DMA tests were performed using a diamond DMA from PerkinElmer within the temperature range 150–800 K. The sample was mounted on knife edges in three-point bending geometry. Static and dynamic forces $F_s + F_d \exp(i\omega t)$ are applied in the frequency range of 0.1–100 Hz using a steel rod. There is a phase lag $\delta$ between the applied force and the sample’s deflection response, which is read out via the displacement of the rod $u_d$. Attenuation $\tan \delta$, storage modulus $E'$ (real component of complex Young’s modulus), and loss modulus $E''$ (imaginary component of complex Young’s modulus) were determined.

![FIG. 4. Temperature dependencies of elastic moduli and inverse quality factor $Q^{-1}$ determined by RUS.](image)

$$\tan \delta = E''/E'$$  \hspace{1cm} (6)

$$E = E' + iE'' = \frac{\beta^2}{4l^3} F_D \exp(i\delta).$$  \hspace{1cm} (7)

$l$ is the spacing between the two bottom knife edges, 5.00 mm; $r$ is the thickness of the sample, $\sim0.22$ mm; and $w$ is the width of the sample, $\sim2.00$ mm. $F_s = 60$ mN, $F_D = 50$ mN, gain 1, amplitude 5 $\mu$m, and maximum deformation 100 $\mu$m were used for all measurements. The sample was heated from room temperature to 800 K and then cooled back to room temperature. Next, the sample was cooled to 150 K and then heated back to room temperature. The heating and cooling rates were all at 3 °C/min.

**IV. ELASTICITY RESULTS**

The elastic moduli determined by RUS at room temperature are as follows. The bulk modulus $K$ of BaCeO$_3$ is 88.9 GPa, the shear modulus $G$ is 42.4 GPa, the longitudinal modulus $L$ is 145.4 GPa, Young’s modulus $E$ is 109.6 GPa, and Poisson’s ratio $\nu$ is 0.294. Stacks of RUS scans at low and high temperatures are shown in Figs. 3(a) and 3(b), respectively. In general, the resonance frequencies decrease with increasing temperature. There are clear anomalies in the general trend at 551 K, 670 K, 1130 K and 1168 K, respectively. These correspond closely to the $Pnma \leftrightarrow Imma \leftrightarrow R3c \leftrightarrow Pm3m$ transitions determined from the strain analysis given above, with the exception of the frequency minimum at $\sim1130$ K, which occurs $\sim40$ K below the $R3c \leftrightarrow Pm3m$ transition point. The transition temperatures are consistent with the reports in literature, which are summarized in Table I. The temperature dependencies of shear modulus $G$, bulk modulus $K$, and Young’s modulus $E$ are illustrated in Fig. 4(a). At temperatures below 298 K and
above 1180 K, the resonance peaks were strong and values of the elastic parameters are from fitting. Between 298 and 1180 K, most of the resonance peaks were too weak to be detected but the variation in shear modulus over the entire temperature range could still be determined from the frequencies of the first resonance peak. This is essentially due to a pure shear mode and its frequency was calibrated using

\[ G_T = \frac{f_1^2 G_{298}}{f_{298}^2}, \]

where \( f_{298} \) and \( G_{298} \) are, respectively, the frequency of the first peak and the fitted value of \( G \) at 298 K. Good agreement is obtained with data obtained from peak fitting at lower temperatures. In general, the elastic moduli decrease with increasing temperature up to the cubic ↔ rhombohedral transition. Stability limits for the different phases from diffraction data have been added to Fig. 4 to show that anomalies correspond to the known transition temperatures. Figure 4(b) shows the temperature dependence of \( Q^{-1} \) determined by RUS at temperatures where individual resonance peaks were well resolved and distinct from regularly spaced background peaks due to the alumina rods. Dissipation in the \( Pnma \) phase increases with increasing temperature and is not measureable above \( \sim 0.011 \) at \( \sim 290 \) K. Dissipation is then relatively low in the \( Pm\bar{3}m \) stability field.

Figure 5(a) shows the temperature dependence of the storage modulus determined by DMA. It is consistent with the result obtained by RUS as shown in Fig. 4(a). Note, of course, that RUS gives the shear modulus while the storage modulus in DMA relates to Young’s modulus. In general, the storage modulus decreases with increasing temperature. The changes in slope indicate phase transitions. Kinks are shown at the transitions \( Pnma ↔ \text{Imma} \) at \( \sim 551 \) K and \( \text{Imma} ↔ R\bar{3}c \) at \( \sim 670 \) K, respectively. With increasing frequency, the storage modulus increases slightly and the transition temperatures remain the same. The temperature dependencies of the dissipation measured at different frequencies are shown in Fig. 5(b). There are a few distinct peaks, labeled \( P_1 \) – \( P_4 \) from high temperature to low temperature. The sharp peak \( P_1 \) at \( \sim 670 \) K clearly relates directly to the first-order \( \text{Imma} ↔ \text{R\bar{3}c} \) transition. It has a sharp maximum, which reduces in magnitude but does not shift in temperature with increasing frequency. Peak \( P_2 \) at \( \sim 551 \) K is small and clearly relates to the \( Pnma ↔ \text{Imma} \) transition. It does not obviously vary with frequency. Peaks \( P_3 \) and \( P_4 \) are broad and occur at \( \sim 460 \) K and \( \sim 200 \) K, respectively, within the stability field of the \( Pnma \) structure. With increasing frequency, both peaks shift to higher temperatures implying that they are related to thermally activated dissipation processes. The activation energy \( E_a \) has been determined from the frequencies and temperatures for peak \( P_4 \) using the temperature of maximum in \( Q^{-1} \),

\[ \ln f = \ln f_0 - \frac{E_a}{RT}, \]

This gives \( E_a = 29.8 \pm 0.4 \) kJ/mol and \( f_0 = 44.4 \) MHz (Fig. 6). Peak \( P_3 \) is not reproducible in heating and cooling (Fig. 7), and therefore has not been fitted in the same way.

V. DISCUSSION

RUS and DMA data show clear patterns of changes in the elastic moduli and dissipation behavior of BaCeO\(_3\) due to octahedral tilting transitions. In particular, close agreement has been found between the temperatures of each anomaly in the elastic properties and the transition temperatures obtained from lattice-parameter variations and other measurements. As found in previous RUS (Refs. 12, 15, and 16) and DMA studies,\(^{8,9,14}\) structures with intermediate tilt states (\( \text{I}_4/mcm, \text{R\bar{3}c}, \) and \( \text{Imma} \)) have significantly smaller values of shear modulus than the cubic \( Pm\bar{3}m \) and the orthorhombic \( Pnma \) structures. In contrast with studies of other perovskites, however, BaCeO\(_3\) shows strong dissipation at both DMA and RUS frequencies in the stability field of the \( Pnma \) structure.
A. Elastic softening

The pattern of anomalies in the shear modulus observed at RUS frequencies for the transformation sequence $Pnma \leftrightarrow Imma \leftrightarrow R\bar{3}c \leftrightarrow Pm\bar{3}m$ in BaCeO$_3$ is essentially the same as for the $Pnma \leftrightarrow Imma \leftrightarrow I4/mcm \leftrightarrow Pm\bar{3}m$ sequence in SrZrO$_3$ reported by McKnight et al.\textsuperscript{15} During cooling the first transition from the parent cubic structure is marked by a steep softening. In the case of a second-order transition, the standard Landau solution would be for a reduction in elastic constants which is independent of temperature. Similar patterns have been seen for other compositions across the Sr(Zr,Ti)O$_3$ solid solution.\textsuperscript{16} In the case of the $R\bar{3}c \leftrightarrow Pm\bar{3}m$ transition in LaAlO$_3$, additional softening in the rhombohedral phase through an interval of $\sim 100$ K below $T_c$ due to coupling of acoustic modes with a central peak mode.\textsuperscript{16} The same mechanism is likely to account for the nonlinear softening of BaCeO$_3$ as the transition is approached from below $T_c$ [Fig. 4(a)].

On the basis of a standard Landau model, the first-order transitions $Imma \leftrightarrow R\bar{3}c$ in BaCeO$_3$ and $Imma \leftrightarrow I4/mcm$ in SrZrO$_3$, would be expected to be marked simply by a small discontinuity in elastic constants. Instead, some softening is observed as the transition temperature is approached from both sides and this has been attributed to a degree of local fluctuations between different tilt orientations.\textsuperscript{15} In both materials the $Pnma \leftrightarrow Imma$ transition is close to tricritical in character, with a break in slope of the shear modulus and marked stiffening in the $Pnma$ phase. Similar stiffening is seen as a function of composition in (Ca,Sr)TiO$_3$.\textsuperscript{37} Elastic stiffening, rather than softening at an improper ferroelastic transition implies that the usual mechanism of order-parameter relaxation due to some applied stress does not operate. The pattern of stiffening observed in SrAl$_2$O$_4$ by Carpenter et al.\textsuperscript{38} was also not consistent with this mechanism and the feature in common between these two completely different structures is the existence of two separate order parameters belonging to different irreducible representations. The physical origin of this change in behavior is not understood and it remains to be seen whether it is a universal phenomenon.

The pattern of elastic softening (and acoustic dissipation) observed at DMA frequencies for BaCeO$_3$ is also closely similar to that reported for the sequence $Pnma \leftrightarrow Imma \leftrightarrow I4/mcm \leftrightarrow Pm\bar{3}m$ in Sr,Ba$_{1-x}$SnO$_3$ by Daraktchiev et al.\textsuperscript{14} On the basis of transition temperatures given in Daraktchiev et al.\textsuperscript{39} the composition appears to be $x=0.9$ rather than $x=0.8$ as given (see, also, discussion in Ref. 15).

B. Anelastic dissipation

The Peak P$_1$ in Fig. 5(b) shows that $\tan \delta$ increases with decreasing measurement frequency, $f$. Assuming a relaxation process with relaxation time $\tau$, dissipation is expected to follow $\tan \delta = \frac{\omega \tau}{1 + \omega^2 \tau^2}$, where $\omega = 2\pi f$. To obtain the observed increase in $\tan \delta$ with decreasing frequency one then would have to assume $\omega \tau > 1$ even at 0.1 Hz, leading to $\tau > 1.6$ s. There are at least two possible origins for such a slow dynamics. First, heat diffusion could lead to such a low-frequency dynamics as in KMnF$_3$.\textsuperscript{40} However, a calculation of the corresponding relaxation time (Ref. 41) $\tau_{th} = \frac{\pi D_{th}}{\omega}$, where $t=0.022$ cm is the sample thickness and $D_{th} = 0.004$ cm$^2$/s (Ref. 22), gives $\tau_{th}=0.012$ s which is far too short in comparison with the estimated value of $\tau=1.6$ s. Moreover an evaluation of the Pippard relations using the thermal expansivity $\alpha \approx 10^{-5}$ K$^{-1}$ (Ref. 42) yields a difference of the adiabatic and isothermal elastic constants $C^S - C^T = 0.1$ GPa at $T_2$. Therefore an isothermal adiabatic crossover due to heat diffusion can be ruled out for a possible origin of the P$_1$ peak.

The second possibility for low-frequency dispersion of the P$_1$ peak in BaCeO$_3$ could be phase front motion due to the first-order nature of the phase transition. Internal friction peaks associated with the movement of interfaces between coexisting phases at a first-order transition have been measured in a number of systems including BaTiO$_3$,\textsuperscript{43,44} Fe-Mn alloy,\textsuperscript{45} and CuAlBe alloy.\textsuperscript{46} These internal friction peaks have in common that the peak height increases with decreasing frequency and is independent of the measuring strain amplitude. Zhang et al.\textsuperscript{47} have calculated the dissipation function resulting from the movement of first-order-induced interfaces, yielding
FIG. 8. Double logarithmic plot ln(tan δ) vs ln(f) for maxima in dissipation of peak P1. Two fitting processes were used to determine values of tan δ. The first was for no baseline correction (zero baseline). The second used a baseline tangential to data points at ~600 and ~750 K. The decay is consistent with power law tan δ = Afn, where −0.301 < n < −0.122.

\[ Q^{-1} = A(T) \left( \frac{T}{\omega} \right)^{n_1} + B(T) \omega^{-n_2}, \]  

(10)

where \( T \) is the heating/cooling rate, and \( A(T) \) and \( B(T) \) are temperature-dependent coefficients. Since \( \delta = Q^{-1} \) (Ref. 48) the theoretical analysis of the frequency dependence of the loss angle in the transition regime leads to the power-law dependence of Eq. (10). A double-logarithmic plot of the frequency dependence of the height of the loss peak is consistent with power law tan δ = Afn, where \( n \) is between −0.301 and −0.122 (Fig. 8). The value of the exponent \( n \) is very similar to the value −0.2 in Ref. 46.

The small P2 peak is independent of frequency but, in marked contrast with Ca0.3Sr0.7TiO3 and SrBa1−xSnO3,14 it is followed by a temperature interval of high tan δ rather than a steep reduction in anelastic loss. Peak P4 does not appear to be reproducible between samples whereas peak P2 seems to be a well-defined Debye peak for a thermally activated dissipation process. Overall the evolution of tan δ in the Pnma field of BaCeO3 is similar to that observed in the R3c field of LaAlO3,49 and in the I4/mcm field of Ca0.3Sr0.7TiO3,9 except that the Debye peak is shifted down from ~410 to ~250 K and the activation energy is reduced from ~80–100 to ~30 kJ/mol. Harrison et al.11 were able to determine by direct observation of twin wall motion that the Debye peak in LaAlO3 is due to a freezing process whereby the walls become effectively pinned by defects. The defects are believed to be oxygen vacancies. By analogy it is proposed here that the loss behavior in BaCeO3 is due to mobile transformation twin walls, making this the first perovskite in which the Pnma structure has twin walls which are potentially mobile on a time scale of seconds. If the loss at DMA frequencies and applied stresses is due to twin wall motion, Fig. 6 implies that freezing at 400 kHz would be at 760 K. Substantial dissipation occurs well below this temperature at RUS frequencies, however, suggesting that a slightly different twin wall related loss mechanism operates under conditions of low stress as in the case of LaAlO3.13

C. Strain behavior

Elastic anomalies are characteristically related to strain anomalies so that similarities and differences in the elastic behavior of BaCeO3 relative to other perovskites should also be reflected in the spontaneous strains accompanying each of the phase transitions. In terms of Landau parameters, the principal difference between SrZrO3 and BaCeO3 is the value of one of the two fourth-order coefficients for the R1+ order parameter, as renormalized by coupling with shear strains. Equation (11) includes two such coefficients and leads to the constraint \( b'' > 0 \) for R3c stability and \( b'' < 0 \) for I4/mcm stability,36 where

\[ b'' = b' + \frac{\lambda_3^2}{C_{44}^2} - \frac{12\lambda_2^2}{2(C_{11} - C_{12})^2}. \]  

(11)

The coefficients \( \lambda_3 \) and \( \lambda_4 \) describe the strength of coupling between the order parameter and rhombohedral and tetragonal/orthorhombic strains, respectively. The change in transition sequences can be understood simply in terms of the relative strengths of these two couplings but it is not clear how this difference, by itself, could be responsible for different anelastic properties of the Pnma structure.

Daraktchiev et al.14 drew attention to the sign of the volume strain as a potentially important factor. LaAlO3 and Sr0.3Ba0.7TiO3 both have positive volume strains associated with the cubic to rhombohedral or tetragonal transition while CaTiO3 and Ca0.6Sr0.4TiO3 have negative volume strains. They postulated that this would result in thick twin walls in the former and relatively thin walls in the latter and, hence, in different strengths of interaction with defects. In SrZrO3 the volume strain is negative over a small temperature interval and then positive but shows no dissipation in the Pnma stability field.15 BaCeO3 has a negative volume strain [Fig. 2(c)] and apparently mobile twin walls, so there is no systematic correlation.

Data given in Refs. 15 and 25 and Fig. 2 show that the tetragonal shear strain \( \epsilon_{44} \) has a similar evolution in SrZrO3, CaTiO3, and BaCeO3, making this an unlikely factor in the context of different dynamic behavior for Pnma twin walls. On the other hand, SrZrO3 and CaTiO3 both have positive \( \epsilon_{44} \) strains with anomalous dependence on tilt angles while BaCeO3 has a negative \( \epsilon_{44} \) strain which follows the M3+ and R1+ tilts exactly as would be expected on the basis of the lowest-order coupling terms [Fig. 2(c)]. Equation (4) shows that the second tilt system, M3+, contributes to \( \epsilon_{44} \) only via distortions of the perovskite octahedra. Regular distortions which scale with the M3+ tilt apparently occur in BaCeO3 while some other style of shearing of the octahedra would be required to produce the \( \epsilon_{44} \) shear strain shown by SrZrO3. If there is a significant difference in structural distortions of the bulk material, it follows that there will also be differences in the structure of the twin walls. Either there is then some additional geometrical constraint to twin wall motion arising from an alternative style of octahedral shearing or the twin wall thicknesses change. As discussed in detail by Lee et al.50 and qualitatively by Daraktchiev et al.,14 thick walls are expected to interact less strongly with defects than thin walls and, in the event that the width of the walls becomes greater than the effective dimension of the defect, the interaction will tend to zero. For BaCeO3 there is dissipation in the
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