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Sharp low frequency dissipative effects in tetragonal $BaTiO_3$ ceramics

Liang Dong,[1] Donald S. Stone,[1] and Roderic S. Lakes[2,a)]
[1]*Materials Science Program, University of Wisconsin, Madison, Wisconsin 53706-1687, USA*
[2]*Department of Engineering Physics, Engineering Mechanics Program, Materials Science Program, University of Wisconsin, Madison, Wisconsin 53706-1687, USA*

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Mechanical anomalies (damping peaks sharper than Debye peaks, in contrast to a broad relaxation peak) were observed in tetragonal barium titanate ceramic via broadband viscoelastic spectroscopy at low frequencies (<10 Hz) at ambient temperature after aging at 90 °C for 15 h. The sharp peaks disappear after aging above the Curie point (150 °C for 10 h). Mechanical anomalies are tentatively attributed to negative stiffness heterogeneity, the mechanism of which is proposed based upon the theory of symmetry-conforming short-range order property of point defects. © *2010 American Institute of Physics*. [doi:10.1063/1.3283920]

I. INTRODUCTION

Negative elastic modulus is anticipated in the context of Landau theory of phase transformation. As the temperature T is lowered from a value above the transformation temperature, an energy function of strain and temperature with a single minimum gradually flattens, then develops two or more minima or potential wells. The curvature of this energy function represents an elastic modulus, so flattening of the curve corresponds to a softening of the modulus near a critical temperature T_c. This has been observed experimentally. Below T_c, the reversed curvature at small strain represents a negative modulus. Negative moduli have been used in the design of composites with extremely high values of physical properties. Indeed, the existence of negative bulk modulus was recently inferred from the behavior of tetragonal barium titanate ceramics[1] in a particulate composite of polycrystalline $BaTiO_3$ in Sn. That study reveals an extremely large Young's modulus (even larger than that of diamond) within a narrow range of temperature, where it entails a negative bulk modulus of the ceramic inclusions.[2] A more recent study[3] of well aged barium titanate ceramics below the Curie point discloses mechanical anomalies and negative Poisson's ratio in the tetragonal phase. Specifically, the bulk modulus exhibits a marked softening and Poisson's ratio becomes negative over a narrow temperature range. However, both studies characterized the mechanical properties in the temperature domain. The present study explores the mechanical anomaly in well aged tetragonal barium titanate ceramic in the frequency domain.

II. EXPERIMENT

Broadband viscoelastic spectroscopy[4] has been used to study the mechanical damping and moduli of a barium titanate ceramic (Alfa Aesar, 99.9%) over five decades of frequency at ambient temperature, 25 °C, and at 35 °C with different thermal histories in both bending and torsion. Deformation of the specimen was induced by electromagnetic torque upon a high intensity magnet on the specimen end and was measured by a laser method. Data were captured by a lock-in amplifier and were confirmed by a digital oscilloscope. Neither torque induction nor deformation measurement contributes any resonances or notable phase shifts below the MHz regime. The specimen is supported by a massive steel rod 25 mm in diameter. The resulting large mismatch in mechanical impedance minimizes the effect of instrumental resonance. The specimen was measured as $0.8 \times 1\ \text{mm}^2$ by 9 mm after mechanical cutting and polishing. Gold was sputtered on all the surfaces[5] to provide near short circuit electrical boundary conditions. Aging was done in air at (1) 90 °C for 15 h and at (2) 150 °C for 10 h. The specimen was then cooled freely down to testing temperature, at which the temperature was held for 30 min prior to testing. Excitation strain applied in these tests is 6×10^{-6}. Each test takes approximately 3 h. In the 90 °C aged case, further bending and torsion tests were performed after holding the temperature at the testing temperature for (1) 3 h and (2) 24 h. Optical microscopy observation reveals most of the grains have a size about 25 μm. The smallest domains resolved in the optical microscope are about 1 μm in width.

III. RESULTS AND DISCUSSION

A. Experimental results

Figures 1 and 2 show the subsequent mechanical behaviors at different time intervals at 25 °C (Fig. 1) and at 35 °C (Fig. 2) after aging at either 90 or 150 °C. The left column of Figs. 1 and 2 shows damping (tan δ) and Young's modulus ($|E^*|$) in bending. The right column of Figs. 1 and 2 shows damping (tan δ) and shear modulus ($|G^*|$) in torsion. Coupling of bending modes in the torsion results has been masked off. Peaks in damping (tan δ) sharper than a Debye peak were observed at low frequencies (<10 Hz) after 90 °C aging, but the peaks gradually decreased in magnitude with time at the testing temperature. These mechanical anomalies are more prominent in bending than in torsion. No anomaly was observed in the specimen after 150 °C aging. The fundamental structural resonant frequency is 1270 Hz in bending and 13260 Hz in torsion (tan δ at fundamental structural resonant frequency is 0.022 in bending and 0.0085 in

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[a)]Electronic mail: lakes@cae.wisc.edu.

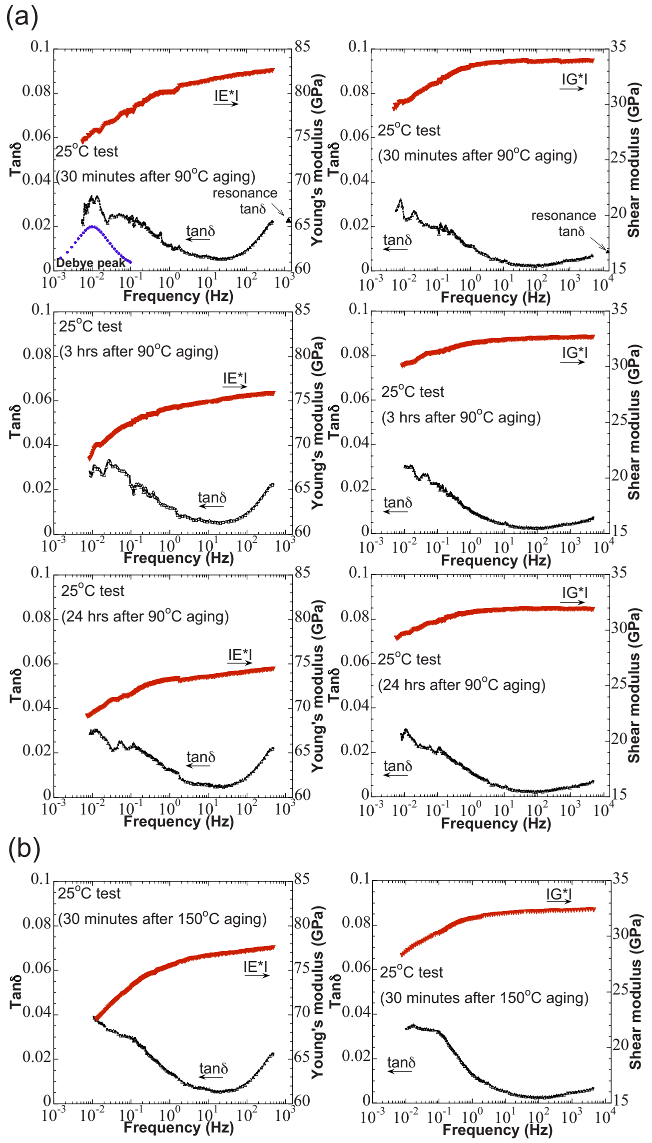

FIG. 1. (Color online) Subsequent mechanical responses in bending (damping tan δ; Young's modulus $|E^{*}|$) (left column) and in torsion (damping tan δ; shear modulus $|G^{*}|$) (right column) at 25 °C after (a) 90 °C aging and after (b) 150 °C aging.

torsion). Damping curves are smooth without any undulations above 10 Hz to the fundamental structural resonant frequency in either bending or torsion.

The observed frequency response is sharper than a Debye peak [shown in the top left frame of Fig. 1(a)]. Relaxation processes cannot account for such sharpness because the sharpest relaxation process, that of a single relaxation time, gives rise to a Debye peak, about one decade (a factor of 10) wide in the frequency domain. Inertial effects can give rise to sharp peaks as in resonance. Resonant behavior of grains and other heterogeneity in a material is not surprising but the peaks observed here are at frequencies too low by orders of magnitude for such resonance. The peak frequencies observed here are too low to have an instrumental origin; moreover, no such peaks were observed in a specimen of aluminum oxide ceramic of structural stiffness similar to that of the test specimen.

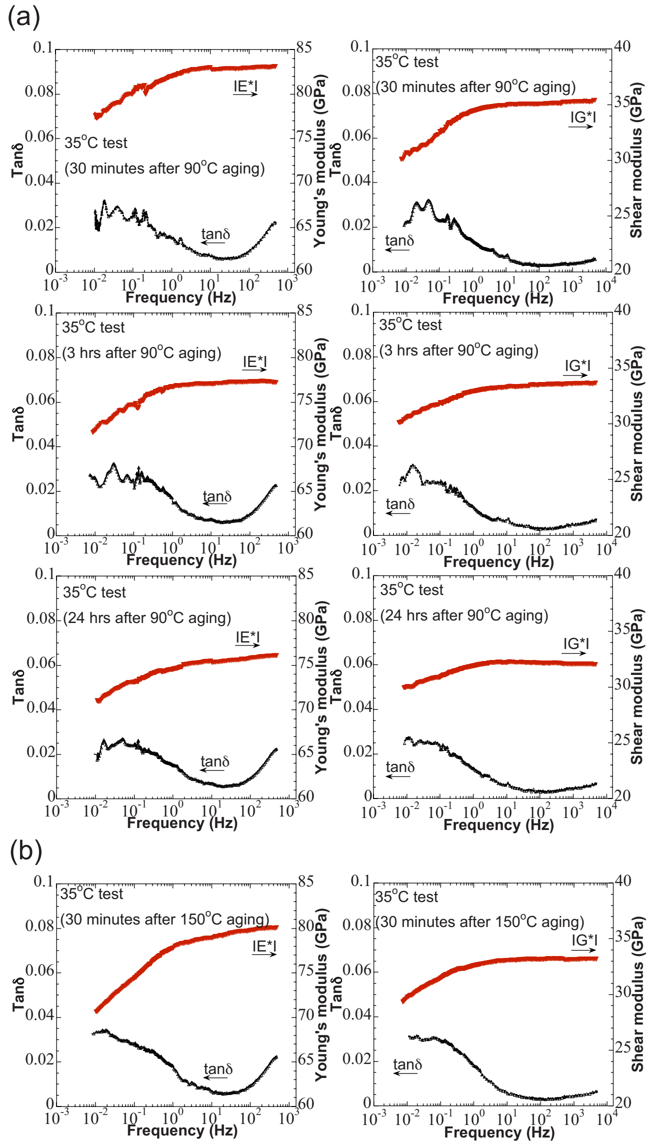

FIG. 2. (Color online) Subsequent mechanical responses in bending (damping tan δ; Young's modulus $|E^{*}|$) (left column) and in torsion (damping tan δ; shear modulus $|G^{*}|$) (right column) at 35 °C after (a) 90 °C aging and after (b) 150 °C aging.

B. Sharp frequency response: Cause

Sharp frequency response is possible if heterogeneity in the material is metastable and has a negative stiffness. For example, low frequency dynamics, as well as stability, of discrete viscoelastic "spring" systems with negative stiffness components have been theoretically analyzed by Lakes *et al.*,[6] and extreme high damping can be obtained at low frequencies in such a system in the stable regime, and singular resonance-like responses in damping in the metastable regime. In real materials, heterogeneity of negative stiffness can give rise to multiple tan δ peaks at discrete frequencies. In the following, a physical model is presented for negative stiffness in ferroelectric ceramic; also a composite analysis, which shows how heterogeneity of negative stiffness can give rise to sharp response at low frequencies.

C. Oxygen vacancies and negative stiffness

Oxygen vacancies (OVs) play an important role in the behavior of barium titanate. They can give rise to new relax-

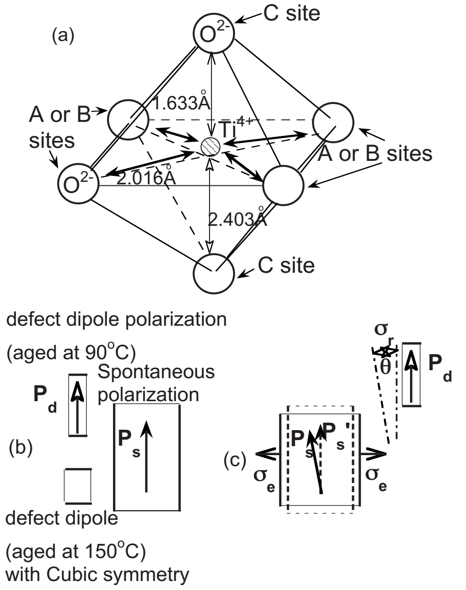

FIG. 3. (a) Oxygen octahedron in a tetragonal barium titanate unit cell. O^{2-} has two kinds of nonequivalent sites of *A* or *B* and *C*. In the cubic phase (above the Curie point), the distances between Ti^{4+} and *A* or *B* and *C* sites are the same. In the tetragonal phase (below the Curie point), the distances between Ti^{4+} and *A* or *B* and *C* sites are as shown in Ref. 7. (b) Presents an 180° domain. After aging at 90 °C, $\mathbf{P_d}$ is generated, $\mathbf{P_s}$ and $\mathbf{P_d}$ are aligned in the same direction, $\theta=0°$. After aging at 150 °C, $\mathbf{P_d}$ is not generated because the material is above the Curie point. Defects then possess cubic symmetry and there is no interaction between $\mathbf{P_s}$ and $\mathbf{P_d}$. (c) When transverse tensional stress σ_e is applied on this 180° domain, $\mathbf{P_s}$ will align θ with respect to $\mathbf{P_d}$ due to breaking of crystal symmetry giving rise to a restoring stress σ_r between $\mathbf{P_s}$ and $\mathbf{P_d}$.

ation phenomena and to stored energy associated with negative stiffness. The oxygen octahedron in a tetragonal $BaTiO_3$ unit cell is illustrated in Fig. 3(a). Spontaneous electric polarization $\mathbf{P_s}$ exists below the Curie point as the crystals then possess tetragonal symmetry. Impurities, such as Al^{3+}, will preferably locate at Ti^{4+} site, and form defect dipoles with OVs.[8] According to the mechanism of symmetry-conforming property of point defects (SCP-PD),[9] OV can occupy either of *A* (or *B*) or *C* sites of the oxygen octahedron with identical conditional probabilities above the Curie point since *A* (or *B*) and *C* sites have the same distances from the center. Below the Curie point, OV tends to migrate to and accumulate at *C* sites, which are closer to the center of octahedron, from *A* (or *B*) sites during aging. Defect dipole polarization $\mathbf{P_d}$ will generate a restoring stress on $\mathbf{P_s}$, forcing $\mathbf{P_s}$ and $\mathbf{P_d}$ to align along the same direction after enough time of aging. This alignment tends to minimize the total free energy of the system. Aging at 90 °C for 15 h allows $\mathbf{P_d}$ to align in the same direction as $\mathbf{P_s}$. In contrast, the material at 150 °C is above the Curie point and the crystals possess cubic symmetry. Aging at 150 °C allows the symmetry of defects to follow the cubic symmetry. Defects will retain this symmetry for a period of time after cooling through the Curie point. Therefore, the interaction between $\mathbf{P_s}$ and $\mathbf{P_d}$ will be introduced in the 90 °C aged case but not in the 150 °C aged case.

A possible mechanism for negative stiffness that can be entailed in the tetragonal phase of barium titanate based upon SCP-PD is presented as follows. Figure 3(b) presents an 180° domain, $\mathbf{P_s}$ and $\mathbf{P_d}$ are labeled. θ (the angle between $\mathbf{P_s}$ and $\mathbf{P_d}$) will be generated because of crystal symmetry breaking (change in distances between Ti^{4+} site and *A*/*B* and *C* sites), which occurs instantaneously when tensional stress (equivalent to compressive stress parallel to $\mathbf{P_s}$) is applied. Due to the time delay between $\mathbf{P_s}$ and $\mathbf{P_d}$, a restoring stress σ_r will be introduced. If σ_e (local stress due to applied stress) is suitable in magnitude, and can achieve a critical state of $\sigma_e=\sigma_r$ at a critical angle θ_c, then as θ increases a bit further due to the delay of nucleation and growth[10] of domain walls (DWs), σ_r will be larger than σ_e, and θ will tend to snap-back due to the nonlinear interaction between dipoles. At this point, the domain or the grain in which the domain resides will exhibit a negative stiffness behavior as it shrinks under tensional stress. 90° domains cannot switch in polycrystalline ceramics[11] so cannot cause negative stiffness. 180° domains have limited switching property, rather than 90° domains which can cause large recoverable strain. Negative stiffness is associated with the short-range interaction between σ_r (determined by the magnitudes of $\mathbf{P_s}$ and $\mathbf{P_d}$ and the split angle between $\mathbf{P_s}$ and $\mathbf{P_d}$) and σ_e. The mechanical and electrical conditions within such localized regions are very complex in polycrystalline materials, and are highly coupled with domain textures, dislocation (located near the DWs) substructure, and thermal conditions. Although there is no bulk volume change in shear, tension component can occur in localized areas due to heterogeneous deformation in polycrystalline ferroelectric ceramic; anomalies observed in shear at low frequencies are thus further evidence of localized negative stiffness elements.

Negative stiffness is always associated with prestored energy.[12] Aging at higher temperature(s) provides residual stress along the grain and domain boundaries after cooling down to ambient temperature due to heterogeneous thermal expansions of crystals. The residual stress is an additional mechanical constraint, which will be relaxed with time; hence the mechanical anomalies will reduce in magnitude with time, too. It is equally sensible to regard high temperature aging to provide another source of stored energy (in addition to the interaction between $\mathbf{P_s}$ and $\mathbf{P_d}$) in that constrained crystals will introduce internal stored energy, and this stored energy will gradually release with relaxation of mechanical boundary constraint (i.e., residual stress).

D. Sharp response: Composite analysis

In this section, resonance of heterogeneity of negative stiffness is analyzed. In Sec. III E, other explanations of anomalous low frequency resonances are reviewed.

Negative stiffness allows heterogeneity in the material to have a much lower natural frequency than it would otherwise. Calculations of the natural frequency were done using the formulation of Dubrovskiy and Morochnik.[13] The effect of the heterogeneity was idealized as radial vibration of a spherical inclusion, and was evaluated assuming the inclusion to have the same density as the matrix and twice the shear modulus. An embedded heterogeneity can have a negative bulk modulus (inverse compressibility) and yet be stable based on the partial constraint of the surrounding material.[14] Poisson's ratio can exhibit values outside the normal range.

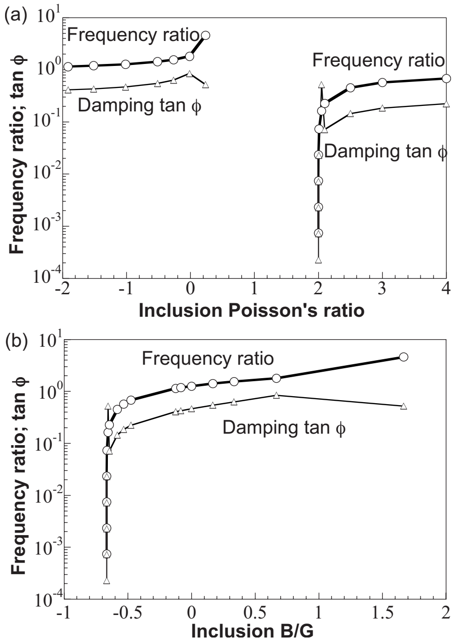

FIG. 4. Normalized natural frequency for radial vibrations (frequency ratio) and damping based on radiation of sound from a vibrating inclusion vs (a) inclusion Poisson's ratio and vs (b) the ratio of inclusion bulk modulus to shear modulus.

The output of the analysis is a normalized natural frequency for radial vibrations expressed as a frequency ratio, and a damping based on radiation of sound from the vibrating inclusion. Results of the analysis are shown in Fig. 4. The stability boundary for the assumed properties corresponds to an inclusion Poisson's ratio of 2 and a bulk modulus -0.66 times the shear modulus. As the stability boundary is approached, the natural frequency tends asymptotically to zero, and the radiative damping becomes small due to the mismatch in impedance. The total damping will contain contributions due to dissipative processes within the ceramic.

This analysis accounts for the sharp peaks observed at low frequency. The gradual disappearance of these peaks is attributed to low temperature annealing of the stored energy, which gives rise to the negative modulus of heterogeneities. Discrete breathers, localized resonant effects in nonlinear systems,[15] were considered as an alternative explanation but no plausible mechanism for lowering of the frequency was evident.

E. Sharp response: Prior concepts and discussion

Sharp response resembling resonance was also observed at audio frequency in crystalline polymers[16] and polycrystalline metals[17] subject to a steady stress giving rise to plastic deformation. The effects, at frequencies well below known structural resonance frequencies, were attributed variously to quantum mechanical phenomena and to parametric resonances.[18] These results were critiqued as instrumental[19] in origin; nevertheless, similar audio frequency response was reported by others using different apparatus.[18] Parametric resonance may be pertinent to stretched wire specimens under static tension but no corresponding effect is envisaged in the present experiments in which there is no external static force.

The present results indicate that metastable heterogeneity of negative stiffness in a material can give rise to frequency domain response sharper than a Debye peak. For barium titanate ceramic, impurities and vacancies cause heterogeneity via electromagnetic interaction with DWs. Negative stiffness elements can induce mechanical resonance dispersions below the fundamental structural resonant frequency based on the composite analysis discussed above. Negative stiffness inclusions have been predicted by molecular modeling to appear naturally on a fine scale[20] in amorphous materials.

IV. CONCLUSION

In conclusion, mechanical anomalies ($\tan\delta$ peaks sharper than a Debye peak, rather than broad relaxation peaks) were observed at low frequencies (<10 Hz) in well aged tetragonal barium titanate ceramic at ambient temperature, 25 °C, and at 35 °C. Metastable, negative stiffness heterogeneities are considered to be responsible, associated with an OV mechanism.

ACKNOWLEDGMENT

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