

## **Softening of bulk modulus and negative Poisson ratio in barium titanate ceramic near the Curie point**

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Substantial softening in the bulk modulus (a factor of five) and a negative Poisson ratio (-0.25) have been observed via broadband viscoelastic spectroscopy in the vicinity of the Curie point of a barium titanate ceramic. These effects were observed under electrical short-circuit conditions at low deformation frequencies. Softening was less in an electric open circuit or at higher frequencies. Softening of individual elastic modulus tensor elements is known to occur near phase transformations, but softening of the bulk modulus has not previously been well reported.

### **1. Introduction**

The Poisson ratio can range from -1 to 0.5 for thermodynamically stable isotropic materials, but most solids have a positive Poisson ratio (0.25-0.33). Negative Poisson ratios are known for (anisotropic) single crystals and also occur in designed foams, via unfolding of the cells [1]. Negative values have also been observed experimentally in polymer gels [2, 3] near the volume phase transition. Negative Poisson ratios in 2-D systems containing rotating rigid discs in contact have been studied by computer simulations [4] and understood via a model [5] which has recently been generalized [6]. The negative Poisson ratio in a system composed of identical hexamers in contact arises from the interaction between the hexamer shaped discs.

If the Poisson ratio is less than -1, the bulk modulus becomes negative provided the shear modulus is positive. This is unstable in an object with free surfaces but can be stabilized by constraint [7]. Negative moduli are allowed in elasticity theory (under constraint) and are anticipated in the Landau theory for phase transformations. Specifically, negative stiffness is theoretically predicted in some ferroelastic materials, for example barium titanate, during phase transformations. Landau theory predicts a negative stiffness during ferroelastic phase transformation as the second derivative of Landau energy with respect to strain becomes negative at temperature  $T$  slightly below or above  $T_c$ . The negative stiffness in ferroelastic materials cannot be directly observed in bulk samples free of constraints, since bands and domains will form before the instability occurs [7].

Negative stiffness is of interest in the context of its role in composites. Classical bounds [8] on the properties of a composite predict they cannot exceed those of the constituents. If the stiffness of a constituent is negative, there is initial stored energy which violates the assumption of the bounds that each constituent begins at a minimum of stored energy. Bounds can be violated by embedding negative-stiffness elements into a positive-stiffness matrix. Composite stiffness and damping [9, 10] can tend to infinity if the concentration and stiffness of the constituents are well designed. Negative stiffness [7] can be achieved in systems such as pre-strained objects, in which stored energy is involved [11].

Recent study [12] on a particulate composite of polycrystalline BaTiO<sub>3</sub> in Sn reveals an extremely large Young's modulus (even larger than that of diamond) within a narrow range of temperature

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entailing negative bulk modulus (inverse compressibility) of the ceramic inclusions. Before the bulk modulus becomes negative, it should soften to zero, and the Poisson ratio should go to -1. Mechanical studies on barium titanate ceramics have been performed by some researchers [13-18]. Taken together, these tests have covered a wide range of frequency, and some apparent softening in Young's modulus has been observed during the transformation near the Curie point (tetragonal-cubic), while the softening in shear modulus has been relatively slight. Softening in Young's modulus observed thus far has been modest. More recently, polycrystalline barium titanate [18] was observed to have a slightly negative Poisson ratio (-0.002) near the Curie point under electrically free boundary conditions.

The purpose of the present study is to experimentally observe and understand the conditions under which softening occurs in the bulk modulus of barium titanate ceramic. Both electrical boundary conditions and variation with frequency are explored.

## 2. Experiment

In the present study, broadband viscoelastic spectroscopy has been used to study the mechanical moduli of two barium titanate ceramic specimens over a range of temperature from 25°C to 130°C at frequencies as low as 0.1 Hz. These two specimens were cut adjacent to each other from a piece of barium titanate (Alfa Aesar, 99.9% metals basis). One measured 0.8 mm x 1 mm by 9.56 mm and the other 0.78 mm x 1 mm by 8.68 mm after cutting (with a diamond saw) and polishing. On one specimen (0.8 mm x 1 mm by 9.56 mm) gold was sputtered onto all its surfaces. The electrical resistivity (per length) was measured 0.09  $\Omega$  /mm. The other specimen was not coated.

Deformation of each specimen was induced by an electromagnetic torque applied on a permanent magnet attached to its free end, and measured by laser light reflected from a mirror mounted on the magnet to a wide-angle two-axis photodiode position sensor (Pacific Silicon Sensor Inc. DL100-7PCBA, Westlake, CA). Data (magnitude and phase of the angular displacement with respect to the torque) were captured by a lock-in amplifier (Stanford Research System SR850) and were observed on a digital oscilloscope. Frequencies used were well below the lowest natural frequency of the specimen (bending: 1200 Hz; torsion: 13000 Hz). Calibration experiments were done using the well-characterized type 6061 Al alloy ( $E_{298K} = 68.9$  GPa,  $G_{298K} = 26$  GPa at 1 Hz). Temperature was monitored by a miniature K-type thermocouple (OMEGA L-0044K), the tip of which was placed 0.5 mm away from the specimen surface near the base. Temperature was either raised or decreased at a rate of 0.008°C/s in uniformly flowing air. The thermal gradient could be controlled within 0.2°C along the length of the specimen. The strain applied was on the order of  $10^{-6}$ .

Reflection optical microscopy observations (Nikon Eclipse 80i light microscope with Nikon DXM1200F digital camera, Japan) were performed on a sample mechanically ground with SiC abrasive papers from 200 grit down to 1200 grit and finally polished with Al<sub>2</sub>O<sub>3</sub> powders (0.3  $\mu$ m) on a nap cloth. The etchant was 100 ml of 10% HCl with several droplets of 48% HF [19], and the specimen was etched for 80 s.

## 3. Results

Optical microscopy observation reveals that most of the grains have a size about 25  $\mu$ m. Domains exhibit a hierarchical structure with the smallest domains resolved in the optical microscope being about 1  $\mu$ m in width (Figure 1). Though there is not a pronounced difference in terms of the grain size and shape between present specimens and those used in Ref. 18, the density of the barium titanate ceramic from Alfa Aesar ( $5.85 \times 10^3$  kg/m<sup>3</sup>) is closer to the theoretical value ( $6.02 \times 10^3$  kg/m<sup>3</sup>); therefore fewer pores exist in the present specimens than those in Ref. 18. Pores can be regarded as one type of defects because they are different from the bulk in terms of elastic and thermal properties.

Figure 2 presents the mechanical softening associated with the cubic-to-tetragonal transformation in the vicinity of the Curie point of the coated specimen under nearly isothermal conditions (0.008

°C/s). A sampling of the data points is plotted to clarify the graph. Polycrystalline barium titanate is isotropic in nature due to the random orientations of the grains. Therefore, the bulk modulus  $|K^*|$  and the Poisson ratio  $\nu$  were calculated from the observed Young's modulus  $|E^*|$  and shear modulus  $|G^*|$  by referring to Equations 1 and 2, which are applicable to isotropic materials:

$$\nu = E/2G - 1 \quad (1)$$

$$K = E/3(1 - 2\nu) \quad (2)$$

The Young's modulus fell considerably through the transition in contrast to the shear modulus which did not vary much. A significant softening occurred in bulk modulus by a factor of five and a transient negative Poisson ratio during the transformation was inferred. The Poisson ratio remains negative within a range of 0.5°C, and reaches a minimum of about -0.25 at about 126.2°C. This temperature region agrees well with theory which predicts that the elastic anomalies will appear within a temperature range of the order of 0.1°C [20].

Figure 2 displays a negative Poisson ratio within a narrow range of temperature near the Curie point. The Poisson ratio refers to the negative ratio of the transverse strain to the longitudinal strain during stretching. The negative Poisson ratio observed during the ferroelastic transformation does not violate the stability condition; however, this is an interesting phenomenon rarely reported in stiff isotropic polycrystalline material.

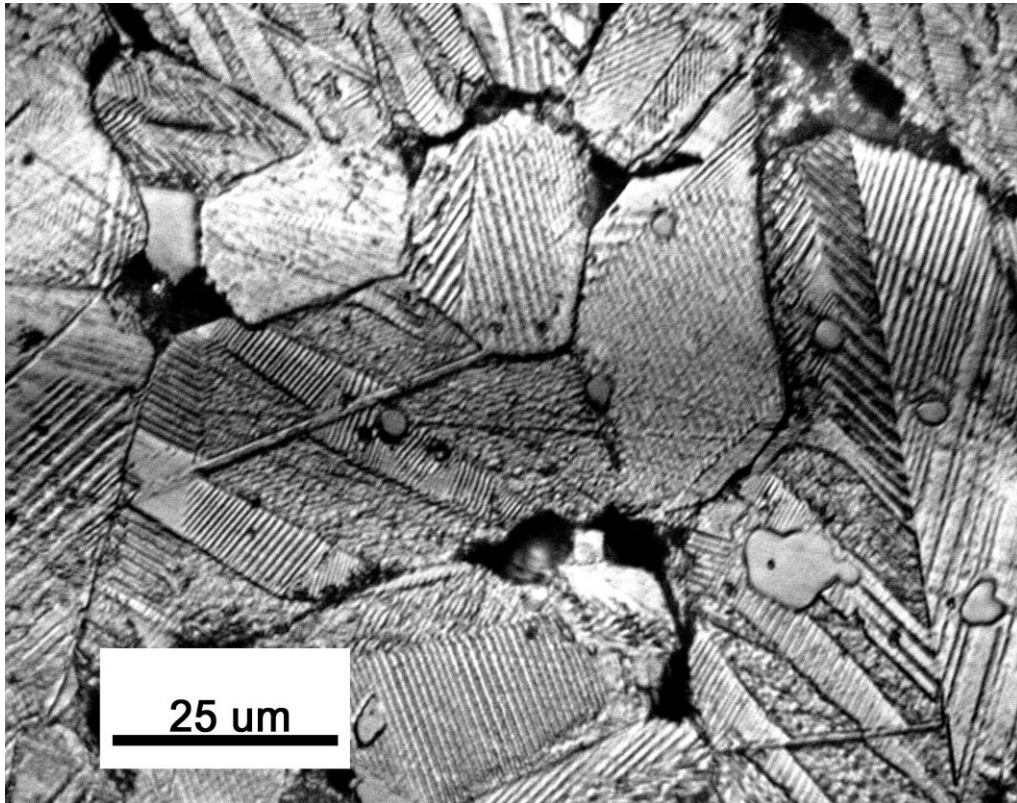


Figure 1. Microstructure of barium titanate ceramic from Alfa Aesar (99.9% metal basis) as revealed by reflection optical microscopy in polarized light.

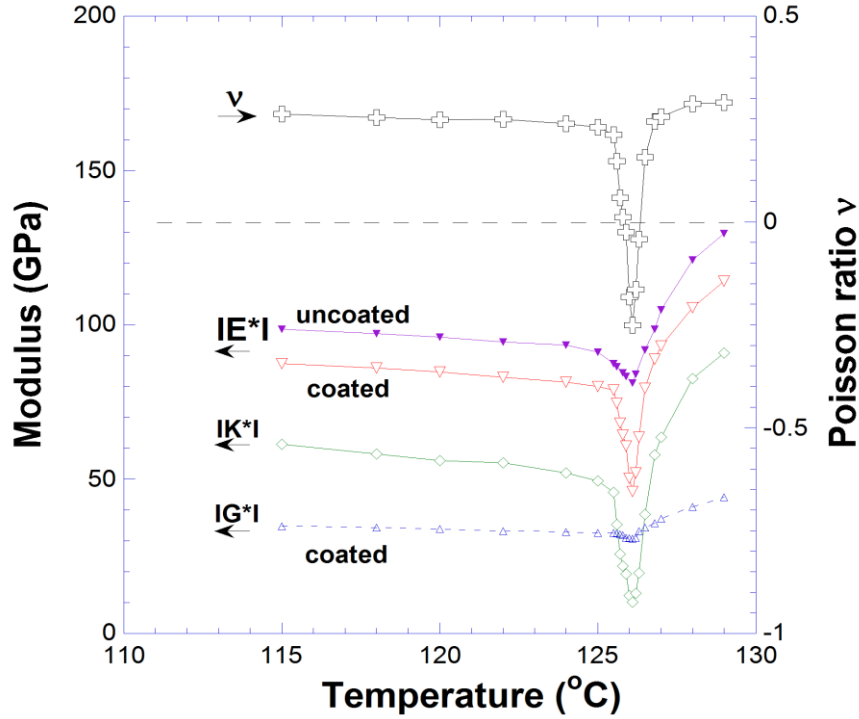


Figure 2. Mechanical softening during phase transformation near the Curie point of coated barium titanate ceramic at 0.1 Hz. The plot includes the observed Young's modulus  $|E^*|$  and shear modulus  $|G^*|$  of the coated ceramic, and Young's modulus of the uncoated ceramic. Also shown are the inferred bulk modulus  $|K^*|$  and the Poisson ratio  $\nu$ .

#### 4. Discussion

A reduction by a factor of five in the bulk modulus occurs during the transition but it does not go to zero. Gradients in temperature, in composition, and in stress upon the crystals in the ceramic could broaden the transition and mitigate the softening effect. However, we argue that temperature gradients do not contribute in the present experiment as detailed below.

Thermal gradients should be controlled during dynamic measurements because they can broaden the apparent transformation. Thermal gradients arise from thermoelastic effects and temperature variations in the apparatus ( $\sim 0.2^\circ\text{C}$  in our case). The thermal gradient across the cantilever arising from thermoelastic effects can be minimized to a negligible level by applying a small strain. During dynamic test, the front and back parts of the cantilever will expand and contract. Temperature changes due to thermoelastic coupling are given by the following formula, for rapid adiabatic deformation [21]:

$$\Delta T = -\alpha E \varepsilon T / C_V \quad (3)$$

in which  $E$  is Young's modulus ( $E = 100$  GPa),  $C_V$  is the heat capacity per unit volume ( $2.53 \times 10^3$  J/K  $\text{m}^3$ ) [22],  $\alpha$  is the linear coefficient of thermal expansion ( $10^{-4}$   $^\circ\text{C}^{-1}$  in the vicinity of the Curie point [7]). A strain of  $10^{-6}$  will cause a thermal gradient of  $0.002^\circ\text{C}$  which is minimal.

A thermal gradient along the cross-section of the cantilever can arise from a delay in thermal diffusion, following Equation (4) [23]:

$$\tau = (1/4) \rho C_p d^2 / k \quad (4)$$

in which  $\tau$ ,  $d$ ,  $k$ ,  $C_p$  and  $\rho$  represent the thermal diffusivity time constant, the depth of penetration of heat in time  $\tau$ , the thermal conductivity, the heat capacity and the mass density, respectively. Given a thermal conductivity of 4.7 W/(m K) [24], a heat capacity of approximately 600 J/(K kg) [25] when the “tetragonal to cubic” transformation takes place, and a mass density of  $5.85 \times 10^3 \text{ kg/m}^3$ , the thermal diffusion was estimated to be about  $5.5 \text{ mm}^2 \text{ s}^{-1}$ . For a cross-section of  $0.8 \text{ mm}^2$ , heat transfer could thus be completed within 0.15 s. As the thermal heating or cooling rate is reduced to  $0.008 \text{ }^\circ\text{C/s}$ , the thermal gradient in the cross-section can be neglected. Moreover, based on this time constant, deformation at the lowest frequency used, 0.1 Hz, is isothermal, not adiabatic, so thermoelastic temperature gradients at low frequency are minimal.

In addition to these types of thermal gradient that can be controlled by the experimenter, the heterogeneity in transition temperature among different grains (or domains) can broaden the transformation and reduce the softening. Compositional and size difference will broaden and weaken the softening during the transition as different elements will transform at different times. For example, crystal deformation is partially restrained by adjacent crystals (grains) in the polycrystalline ceramic. The strain change of bulk material at the Curie point is about  $2 \times 10^{-4}$ . Suppose the anisotropic strain of the individual crystals is of similar magnitude, then, with a modulus of about 100 GPa, the stress is 20 MPa. Given the published shift of  $T_c$  of  $0.04^\circ\text{C}$  per MPa, this gives a shift of  $0.8^\circ\text{C}$  which is substantial enough to account for much or all of the broadening. If some grains in the polycrystal soften at a particular temperature, the polycrystal will behave as a sponge, softer than the bulk ceramic but the modulus will not go to zero.

Curve fitting has been performed on the data on the right side of the Curie point ( $T > T_c$ ) for the bulk modulus vs. temperature curve of the coated ceramic, as shown in Figure 3 (a). Extrapolation of the fitting curve does approach zero at a temperature between  $126.1^\circ\text{C}$  and  $126.2^\circ\text{C}$ . From the present result, we may say that if the bulk modulus (and the Young’s modulus) can go to zero during the transformation, such a softening will be limited within a temperature range of  $0.1^\circ\text{C}$ . Such a softening to zero may be associated with the discontinuous nature of the weakly first-order transformation. Softening in the shear elastic tensor element  $C_{66}$  to zero has been observed in single-crystal  $\text{KH}_2\text{PO}_4$  [26] during its phase transformation when the thermal gradient is controlled within  $0.001^\circ\text{C}$  and the thermal rate is  $0.002^\circ\text{C/h}$  (zero field is maintained). Although such an observation suggests that improved control of thermal gradient would disclose more pronounced softening of the bulk modulus in the present material, the intercrystalline heterogeneity discussed above can also account for the broadening observed.

Ishidate *et al.* [27] have presented the elastic Curie-Weiss behaviour of the elastic constants of barium titanate in the context of a pressure-induced transformation. In view of the fact that temperature and pressure are equivalent thermodynamic variables, the elastic constants have analogous elastic Curie-Weiss behaviour as for a temperature-induced transformation. Therefore, the elastic anomaly part (subtracting the real value of the bulk modulus from the linear part given by the broken line in Figure 3(a)) of the bulk modulus is expected to be proportional to the inverse of  $T-T_0$  [27], i.e.,  $\Delta K \sim 1/(T-T_0)$ , except near  $T_c$ . This behaviour is shown in Figure 3(b) with  $T_0$  equal to approximately  $126.2^\circ\text{C}$ . In the immediate vicinity of  $T_c$ , as the bulk modulus approaches zero,  $\Delta K$  deviates from a linear response to the form  $\Delta K \sim 1/(T-T_0)^2$ , similar to the behaviour of the susceptibility [28].

A sufficiently low excitation frequency is also crucial for observing the softening during transformation. Only if the characteristic time (relaxation time) of the transformation, which decreases with decreasing strain [29], is sufficiently short compared to the period of excitation stress [30] is a very large softening expected to be observed. The relaxation time of the transformation near the Curie point is of the order of  $10^{-11} - 10^{-10}$  s; therefore, this effect can only become prominent at high frequencies in ultrasonic tests, for which the acoustic frequency is in the range  $10^5 - 10^9$  Hz [20]. The frequency dependence of the modulus softening for both coated and uncoated specimens from 0.1 Hz up to 10 Hz is given in Figure 4 (only a sampling of the data points is given to clarify the graph). The strain applied is of the order of  $10^{-6}$ . Though the excitation frequencies are much lower than the

acoustic frequency, the effect of frequency on the modulus softening is still noticeable in the vicinity of the phase transformation. The reason is that there are other sources of frequency dependence as discussed below.

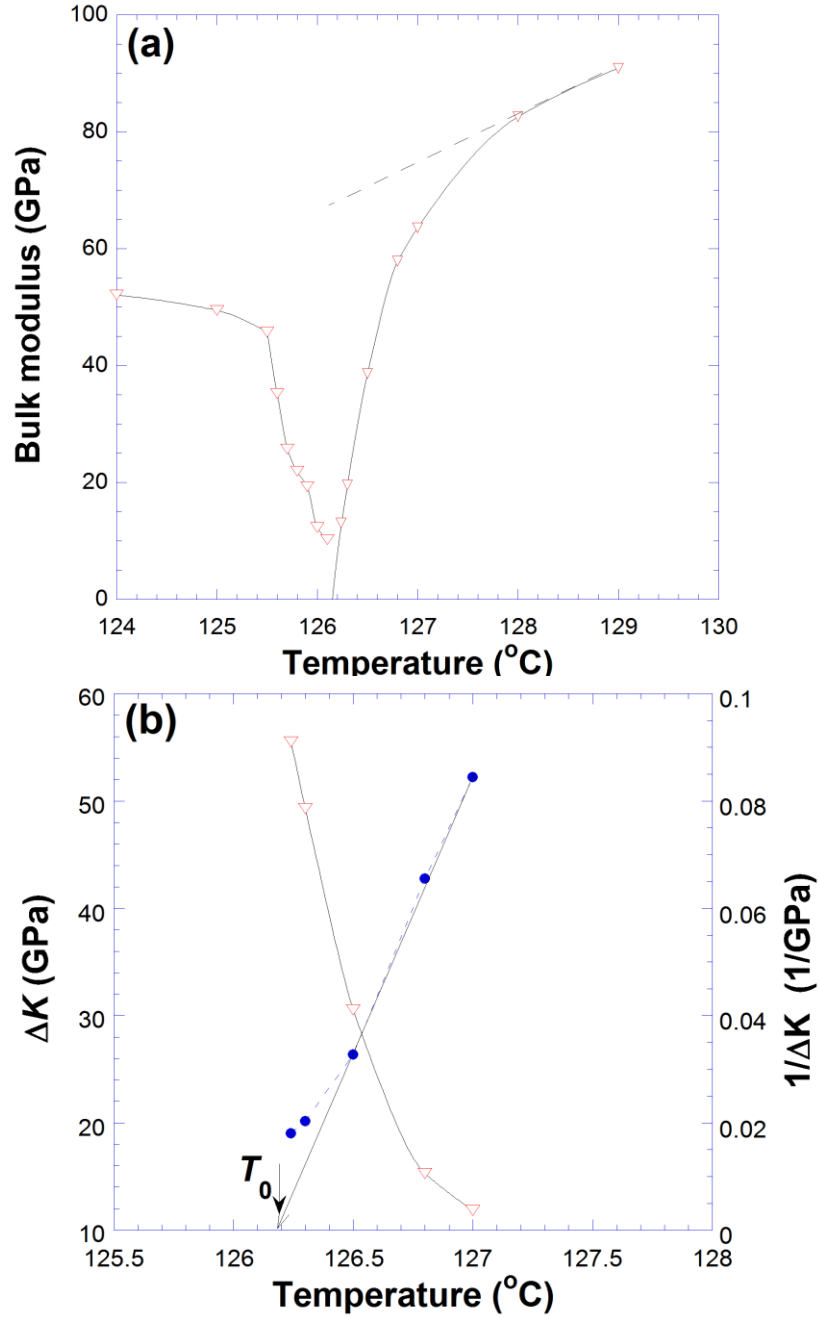


Figure 3. (a) Curve fitting for the bulk modulus of the coated ceramic in the vicinity of the transformation. Solid lines are guides to the eye. Extrapolation suggests the bulk modulus will approach zero between 126.1°C and 126.2°C. (b)  $\Delta K$  (inverted triangles) and  $1/\Delta K$  (solid circles) vs. temperature near the Curie point.  $\Delta K$  is obtained by subtracting the real value of  $K$  from the linear part shown with the broken line in Figure 3(a).  $\Delta K$  follows an elastic Curie-Weiss law except near  $T_c$ , with  $T_0 = 126.2^\circ\text{C}$ .

Electrical boundary conditions influence the softening, in particular the coated specimen under short-circuited condition exhibited more softening than the uncoated specimen. Effects of electrical boundary conditions are well known in single-crystal ferroelectrics. If the crystal is insulated (so that the electric field is free to vary), polarization caused by stress will generate surface charges which in turn give rise to a depolarizing field significantly reducing the polarization. So the elastic compliance is not expected to behave as anomalously as in the case of a short circuit. For a polycrystalline material, the effect of an electric short circuit on modulus softening will not be expected to be as pronounced compared with a single crystal. A small specimen size, however, may enhance the effect. The specimens in the present study were about 100 grains wide in cross-section. A stronger effect for small specimens may not, therefore, be due to grain size but to the influence of heterogeneity of residual stress or composition.

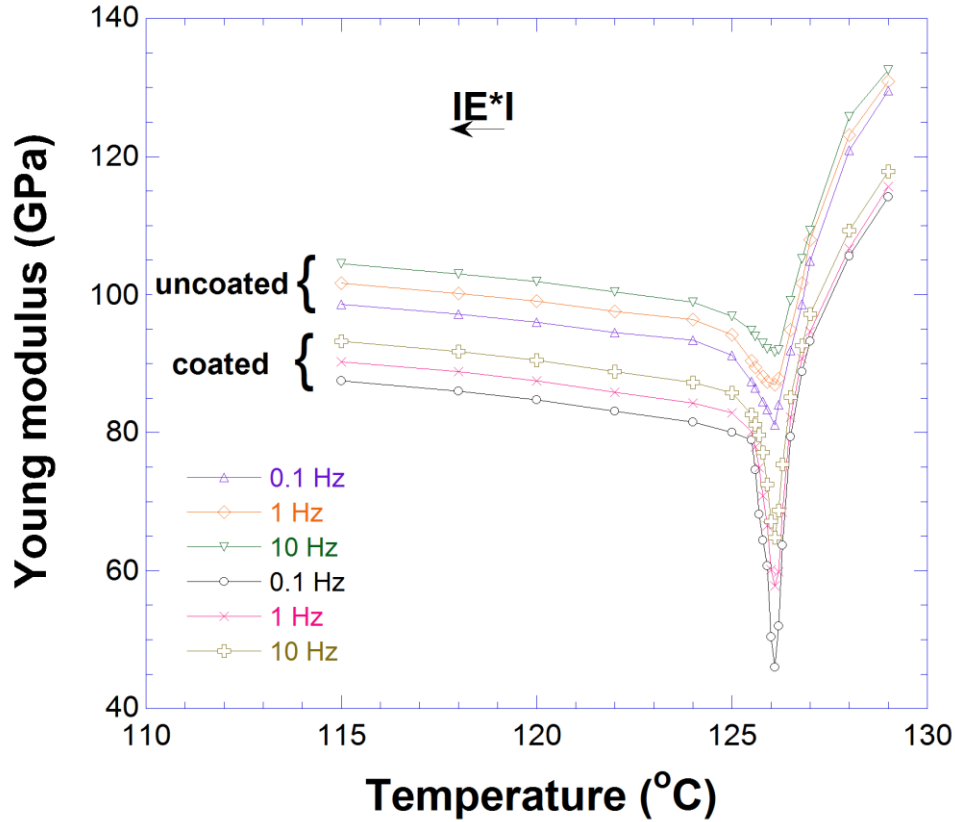


Figure 4. Frequency dependence of Young's modulus from 0.1 Hz to 10 Hz for both coated and uncoated specimens in the vicinity of the Curie point. A slow rate of temperature change ( $0.008^{\circ}\text{C/s}$ ) is maintained. The strain applied is of the order of  $10^{-6}$ .

The mechanical softening during a first-order phase transformation has three contributions, and can be expressed theoretically in terms of changes in Young's modulus  $E$  as [31]:

$$\Delta E = \Delta E_{\text{transient}} + \Delta E_{\text{PT}} + \Delta E_{\text{intrinsic}} \quad (5)$$

in which the three terms on the right side of the equation refer to (1) the contribution from transient experimental conditions (thermal rate and frequency), (2) the contribution from the phase transformation itself, and (3) the contribution from the transformation twin walls, respectively. Similarly, damping in a first-order transformation can be decomposed into three terms [31]. These various contributions have been verified by experiment in other systems. The first contribution has been

mentioned above. For an isothermal experiment, the thermal rate applied should be sufficiently slow to allow enough time for heat to flow in the specimen, equalizing the temperature. A fast thermal rate can lead to a sigmoid-shaped anomaly in the modulus versus temperature curve near the transformation [32] owing to the effect of constrained negative stiffness elements; no effects of this type are observed here because the thermal rate is so slow. Moreover, for full transformation to occur, the inverse of the excitation frequency should be longer than the transformation relaxation time. The main origin of elastic softening during a ferroelastic phase transformation comes from the coupling between spontaneous strain and the order parameter (contribution from the second term), which relates to a certain tilt angle of the oxygen octahedron [33]. At a particular macroscopic strain (spontaneous strain) level, the restoring force opposing the tilting of the octahedron becomes too small to recover the tilt, and the system becomes soft. The movement of twin walls can introduce additional elastic softening in that twin band deformation will be accounted for in the macroscopic strain.

A negative Poisson ratio and reduced bulk modulus are linked (via Eq. (1), (2)) only in isotropic materials such as polycrystalline aggregates. Softening in one or some of the elastic modulus tensor elements, typically the shear moduli, of single crystals is known to occur during phase transformations, but not in the bulk modulus of polycrystalline aggregates. Single crystals may exhibit a negative Poisson ratio [34] for a restricted range of angle of deformation, but there is typically nothing unusual about the bulk modulus. Cooperative rotation of groups of atoms is one mechanism that can lead to a negative Poisson ratio [35]. Softening of the bulk modulus near volume-change phase transformations may be more general in nature. Such softening has been observed in gels [2, 3].

Softening of moduli is predicted to increase with a decrease in frequency in both first-order and second-order transformations [36]; this analysis is one-dimensional and makes no distinction between shear and bulk effects. For transformations in which diffusion occurs the compressibility is predicted [37] to diverge (bulk modulus softens to zero), and the time constant in relaxation to become progressively longer as the critical temperature is approached. Such stress-induced diffusion was demonstrated experimentally as softening of Young's modulus and slowing of the relaxation upon approach to a critical temperature in niobium with dissolved hydrogen [38]. Barium titanate exhibits both displacive and (diffusional) order-disorder aspects in its transformation [39]. Softening of the bulk modulus can result from a variety of physical mechanisms in phase transformations which admit a change in volume, including those in polymer gels [2]; the effect may be universal in that sense.

## 5. Conclusions

The work described in this paper provides evidence for a significant softening of the bulk modulus and a negative Poisson ratio in barium titanate ceramic during the ferroelastic transformation near the Curie point. Softening was less in electric open-circuit conditions or at high deformation frequencies.

## Acknowledgment

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