Ca-Doping of BiFeO₃: The Role of Strain in Determining Coupling between Ferroelectric Displacements, Magnetic Moments, Octahedral Tilting, and Oxygen-Vacancy Ordering

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ABSTRACT: Elastic and anelastic properties of a member of the BiFeO₃−CaFeO₂.5 perovskite solid solution (BCFO), which is known to have multiple instabilities, have been investigated by resonant ultrasound spectroscopy. This phase, with 64% Bi and 36% Ca on the A site, is antiferromagnetic (Tₘ ~650 K) and has an ordered arrangement of oxygen vacancies with tetragonal lattice geometry. The inverse mechanical quality factor, Qᵢ⁻¹, has a maximum near 100 K, correlating closely with a peak in dielectric loss, reported previously, consistent with a loss mechanism that involves the movement of oxygen vacancies accompanied by local lattice distortion. At higher temperature, there is a further acoustic loss peak that is correlated with complex impedance anomalies. There is no clear relationship to the magnetic transition, and the observations are interpreted as relating to ionic conductivity. A small stiffening, scaling with the square of the magnetic order parameter below Tₘ, indicates that the main coupling with strain is biquadratic, confirming that conventional coupling of magnetic order with symmetry-breaking shear strains is weak in BCFO. Data from the literature for BCFO indicates that local strain fields are likely to be responsible for suppressing the spin cycloid present in BiFeO₃.

KEYWORDS: strain, elasticity, resonant ultrasound spectroscopy, incommensurate, relaxation, multiferroic

INTRODUCTION

BiFeO₃ (BFO) has been the focus of intense interest for its particular multiferroic (ferroelectric, ferroelastic, and antiferromagnetic) properties. Aside from the difficulties in making pure, stoichiometric samples, however, a key issue has been that the cycloidal arrangement of individual moments in the antiferromagnetic structure precludes the development of a remnant magnetic moment under ambient conditions. An additional goal, therefore, has been to identify dopants that might assist with the issues of stability and synthesis, lead to a canting geometry that gives ferromagnetism, provide a means of controlling the nature and strength of magnetoelastic coupling, and generate mechanisms for engineering transformation-related microstructures. Doping with Ca (BCFO) has proved to be promising in this context, primarily because the cycloidal magnetic structure is replaced by a canted antiferromagnetic structure that is indeed weakly ferromagnetic. High levels of doping go beyond simply modifying the properties of the end member phase, however, and lead to additional properties relating particularly to the presence of oxygen vacancies. In the present study, the primary objective was to investigate the role of strain in determining coupling phenomena through observations of elastic and anelastic relaxations related to magnetic ordering, oxygen-vacancy dynamics, and ionic conductivity when the doping is at a relatively high level (36% Bi replaced by Ca). These provide particular insights into the influence of both local and macroscopic strain and provide an informative contrast to behavior at low dopant levels.

Desirable (or undesirable) changes in multiferroic properties are directly related to changes in structure. Influences of chemistry on the latter are most simply reflected in the topology of a subsolidus phase diagram. Charge compensation for the substitution of Ca for Bi in BCFO could occur by the introduction of vacancies on oxygen sites or by oxidation of FeIII to FeIV, giving theoretical solid solutions between BiFeO₃ and CaFeIIIO₂.5 or CaFeIVO₃, respectively. CaFeO₃ can be produced under special conditions of high oxygen pressure and has the Pnma structure (R- and M-point octahedral tilting; unit cell 2a₁/2 × 2a₁ × 2a₂, where a₁ is the edge dimension of the primitive parent structure) at room temperature. It has interesting properties in its own right, including a charge disproportionation transition (Pnma → P2₁/n, 2FeVIB → FeIII + FeIV) below ~290 K and magnetic ordering to an incommensurate antiferromagnetic structure below a Néel temperature, Tₘ, of 115 or 127 K. When they have been characterized by Mössbauer spectroscopy, XANES, or X-ray photoelectron spectroscopy, however, BCFO samples prepared with a wide range of Ca contents in air at 1 atm pressure have been found to contain only FeIII. The clear implication is that the substitution mechanism for the BCFO phases described here
and in the literature involves charge compensation by oxygen vacancies. In this case, the relevant end member phase is CaFeO$_{2.5}$, which has the brownmillerite structure and is orthorhombic (Pnma, 2a$_p^{1/2}$ × 2a$_p^{1/2}$ × 2a$_p^{1/2}$) with an ordered arrangement of oxygen vacancies such that there are planes of FeO$_4$ tetrahedra and FeO$_6$ octahedra perpendicular to the crystallographic b axis (e.g., see Figure 1 of Ross et al. or Figure 1a of Krüger et al.). Octahedra within the FeO$_6$ layers are tilted, and the additional doubling of the unit cell, with respect to the conventional Pnma perovskite structure, is due to the vacancy ordering. CaFeO$_{2.5}$ becomes antiferromagnetic with respect to the conventional FeO$_4$ tetrahedra and FeO$_6$ octahedra perpendicular to the arrangement of oxygen vacancies such that there are planes of ferroelectric plus R-point tilting of FeO$_6$ octahedra) to undergo a first-order transition to the orthorhombic (2a$_p^{1/2}$ × 2a$_p^{1/2}$ × 2a$_p^{1/2}$) and Pbam (2a$_p^{1/2}$ × 2(2a$_p^{1/2}$ × 2a$_p$) and triclinic (a$_p$ × a$_p$ × a$_p$) symmetry have also been reported. Schiener et al. reported two phases at $x = 0.1$, one of which was metrical rhombohedral and the second metrically cubic, but also found evidence for other structure types with different superlattice repeats by electron diffraction. Extrapolation of a linear fit to reported transition temperatures in the low Ca-doping range is directly into this two-phase region, and it seems likely that the additional phases are related to the onset of oxygen-vacancy ordering and that the variability reflects at least a degree of nonequilibrium from different sample preparation conditions and cooling rates. Phase boundaries for the appearance of ordered phases have not yet been established, but heating of a sample with $x = 0.2$ to temperatures above 350 °C after previously being quenched from much higher temperatures caused separation into two structures with different compositions. This single result is used in Figure 1 as a first guess for where the equilibrium cation/oxygen/vacancy ordering field might be approximately located.

At intermediate compositions ($0.2 < x < 0.5$), the BCFO solid solution has a field of stability for a structure with cation and oxygen/vacancy ordering. Currently, there is some inconsistency relating to details of the structure of bulk samples, however. On the basis of powder diffraction data, Chen et al. reported metrical cubic lattice geometry across the entire composition range, but metrically tetragonal dimensions were found at Ca-rich compositions by Schiener et al. Lepoittevin et al. obtained an orthorhombic fit for a sample with $x = 0.5$. Electron diffraction reveals a superlattice repeat that is incommensurate ($2a_p × 2a_p × n a_p$, $n ≈ 5.5$ at $x = 0.2$ to $n ≈ 4$ at $x = 0.5$) in the samples of Schiener et al. and commensurate ($n = 8$, fringe spacing 4) in the sample of Lepoittevin et al. Chen et al. reported commensurate superlattice repeats of $X5$ and $X8$ in samples with $x = 0.33$ and 0.2, respectively, but found substantial local variability and did not characterize the full lattice geometry. Models of the structure have blocks of perovskite containing FeO$_6$ octahedra alternating with layers containing Fe in square pyramidal (FeO$_4$) and tetrahedral (FeO$_4$) coordination because of ordering of the oxygen vacancies. There is, as yet, no information available in relation to whether octahedra in the perovskite layers are tilted. Lepoittevin et al. attempted a structure refinement under the orthorhombic space group Bnmm, but this was only one of a number of possibilities.

Individual samples with compositions in the intermediate range contain abundant twinning on an electron optical scale. With respect to a parent cubic structure, it is inevitable that the boundaries between at least some of these would be twin walls with ferroelastic character. A two-phase field of the intermediate ordered structure plus CaFeO$_{2.5}$ extends from $x ≈ 0.5$. There are no experimental results available that might indicate ordering transition temperatures for any compositions of the intermediate phase, but these could be above the synthesis temperatures, which are usually ~900–950 °C. If this is correct, then the observed transformation-related microstructures must develop during growth and annealing of the polycrystalline samples.

Definitive determination of ferroelectricity is restricted to the rhombohedral structure. Chen et al. claim to have obtained a ferroelectric hysteresis loop from a sample with $x = 0.3$,
however. They did not report the structure type of their sample, but their conclusions suggest that it is possible that the intermediate structure could become ferroelectric. Attempts by Schiemer et al.\textsuperscript{34} to obtain saturated ferroelectric loops for a wider range of compositions were not successful, likely because of high intrinsic conductivity. Conventional analysis of the real and imaginary components of the dielectric response at frequencies between ~1 Hz and 10 MHz reveals loss behavior that can be characterized in terms of Arrhenius behavior. Reported values of the activation energy, $E_a$, are 0.3 eV for $x = 0.5$,\textsuperscript{36,37} 0.22 eV for $x = 0.36$,\textsuperscript{38} 0.42–0.27 for $x = 0.33–0.6$,\textsuperscript{39} and ~0.65 eV for $x = 0.2$.\textsuperscript{34} These values are generally discussed in the context of a mechanism involving mobile oxygen vacancies, which has been confirmed by a study of the influence of oxygen fugacity.\textsuperscript{35}

**Strain Analysis and Order Parameter Coupling.** The critical property in the context of elastic and anelastic behavior is strain. Figure 2 shows shear strains, as defined with respect to a parent cubic reference state, at room temperature for each of the structure types at different compositions across the BCFO solid solution. These were obtained from lattice parameters in the usual way for spontaneous strains associated with phase transitions.\textsuperscript{36} In principle, the symmetry of BFO is reduced to monoclinic if the magnetic cycloid ordering scheme has only one out of the three possible symmetry-related directions of the rhombohedral structure\textsuperscript{3} or it is replaced by a weakly ferromagnetic scheme in which the sublattice magnetizations are oriented in the (111) plane.\textsuperscript{37} A very small monoclinic distortion has been reported for some samples by Sosnowska et al.\textsuperscript{38} whereas Wang et al.\textsuperscript{39} favored triclinic lattice geometry. The dominant nonzero shear strain at low Ca contents is $\varepsilon_{P}$ which is given by $\varepsilon_{4} = \cos \alpha$, where $\alpha$ is the rhombohedral lattice angle. In a tetragonal structure, the shear strain is $\varepsilon_{ao} = 1/(3(2\varepsilon_{4} - \varepsilon_{1} - \varepsilon_{2}))^{1/2}$, where $\varepsilon_{1} = \varepsilon_{P} = (a_{P} - a_{0})/a_{0}$ and $\varepsilon_{4} = \varepsilon_{4}$ (the absence of $a_{P}$ for the parent cubic structure, $a_{0}$ is estimated as $a_{0} = (a_{P}^{2}/3)^{1/3}$). Nonzero shear strains of the $Pnma$ structure are $\varepsilon_{4}$ and $\varepsilon_{ao}$ for which expressions in terms of the lattice parameters are given by McKnight et al.\textsuperscript{40} A clear pattern shown by Figure 2 is that the shear strains at room temperature reduce slightly with increasing Ca content across the $R3c$ field and are close to zero at Ca-rich compositions in the intermediate phase (or strictly zero if the lattice geometry is cubic) but increase toward $x = 0.5$. There is a very obvious first-order discontinuity in $\varepsilon_{4}$ near $x = 0.1$. Coupling of shear strains with the order parameter for cation/oxygen/vacancy ordering clearly varies with composition, but the shear strains of CaFeO$_{2.5}$ do not match up with this pattern in that they are large and have opposite sign. There are no data for the lattice parameter of a high-temperature parent cubic structure at any compositions, so it is not possible to determine the extent of coupling with volume strain.

Changes in magnetic structure accompany variations in structure type across the solid solution. Remarkably, however, the Néel temperature barely changes (Figure 1), and the evolution of the antiferromagnetic order parameter also follows a very similar temperature dependence at compositions between $x = 0$ and 0.6.\textsuperscript{7} There are slight variations in magnetic structure, but the basic ordering scheme is believed to be G-type antiferromagnetic at all compositions.\textsuperscript{7} Pure BFO is antiferromagnetic with a cycloid structure.\textsuperscript{3,41,42} Ca-doped rhombohedral samples are weakly ferromagnetic, which is attributed to canting allowed by symmetry if the cycloid is suppressed.\textsuperscript{4,5,7,10,37,43} The intermediate phases ($x \geq 0.2–0.5$, tetragonal or orthorhombic) are antiferromagnetic.\textsuperscript{7,18,34,44–46} With respect to strain coupling, a small change occurs in the trend of the rhombohedral lattice angle of BFO between ~650 and ~800 K in BFO\textsuperscript{47} and is also just about visible in the data shown in Figure 8 of Sardar et al.\textsuperscript{19} for samples with $x = 0.03$ and 0.05. Even if this is due to coupling with the antiferromagnetic order parameter, the total shear strain is clearly very small. However, there is a distinct break in slope of the $a$ (pseudocubic) lattice parameter and unit cell volume at ~650 K in both sets of data, implying a negative volume strain that amounts to $\sim 0.001$ at 300 K. The most recent lattice parameter determination\textsuperscript{48} is also consistent with these small strain variations. In other words, there is weak coupling of the magnetic order parameter(s) to volume strain. No equivalent data are yet available for more Ca-rich compositions, but the expectation is that coupling with shear strains will also be weak/negligible and only weak with the volume strain. These views, which are based on empirical data, are also entirely consistent with the conclusions of Ederer and Spaldin,\textsuperscript{49} which are based on first principles density functional calculations, that ferroelectric polarization in BFO is insensitive to strain and the presence of oxygen vacancies. They found also that magnetoization is unaffected by strain but the introduction of vacancies can alter it slightly.

The phase diagram and strain data in Figures 1 and 2 provide constraints on the overall coupling behavior of ferroic and multiferroic phases in the BCFO solid solution. First, magnetic ordering occurs below an almost constant Néel temperature and follows the same temperature dependence, irrespective of crystallographic structure, cation/oxygen/vacancy ordering, ferroelectric order, or ferroelastic (shear) strain. From this, it can be concluded that the antiferromagnetic order parameter does not couple, or couples only very weakly, with order parameters relating to the other processes. Independent confirmation of weak and unfavorable coupling between ferroelectric and magnetic order parameters has also been provided by observations of Fe and Bi displacements as a function of temperature in BFO.\textsuperscript{48} Furthermore, the only detectable coupling of the magnetic order parameter with strain is restricted to volume strains. There must be subtle structural/chemical influences which favor cycloidal, weakly ferromagnetic, or purely antiferromagnetic ordering schemes, but this can be only a very minor variation. Second, ferroelectric...
ordering appears to be restricted to the rhombohedral structure. In BFO with low Ca-doping, there must be a balance between competing R- and M-point octahedral tilting, which would favor Pnma, and ferroelectric displacements coupling with R-point tilting, which favors R3c. This balance favors Pnma with the addition of Ca. At high enough vacancy concentrations, the tilting and ferroelectric order parameters become overwhelmed by the cation/oxygen/vacancy ordering. In particular, movement of oxygen vacancies add to the expected in both dielectric and acoustic loss as well as for switching in the intermediate structure of BCFO. This has implications for the domain walls might have locally different magnetic states.

## EXPERIMENTAL SECTION

### Synthesis

The sample investigated was of nominal composition Bi0.64Ca0.36FeO2.82 (BCFO 36) and was from the same batch used in Schiemer et al.18 This sample was prepared by a rapid two-stage reaction method using high-purity Bi2O3, CaCO3, and Fe2O3 powders. The starting powders were first homogenized for ~20 min in an agate mortar before calcination at 850 °C for 20 min. The sample was then reground for a further 20 min, pressed into a pellet at 480 MPa in a 13 mm diameter cylindrical uniaxial steel die, and sintered at 990 °C for 20 min. This sample showed no secondary phases from XRD or SEM examination, although some local inhomogeneity (on the order of 1% composition) was detected in back-scattering mode and via EDX in the SEM, as described in Schiemer et al.18 The resultant pellet was cut into a rectangular parallelepiped for RUS measurement using an anular diamond saw. The measured dimensions, 4.229 × 2.703 × 1.812 mm3, and mass 0.1349 g, give an estimated density of 6.513 g cm−3.

### RUS

The RUS method has been described in detail elsewhere.66 In Cambridge, spectra are routinely collected using in-house built room-temperature, low-temperature, and high-temperature RUS heads. Room-temperature spectra were collected with the sample held directly between the piezoelectric (PZT) transducers across pairs of corners, pairs of edges, and pairs of faces. Values of the shear (G) and bulk (K) moduli were then determined by fitting to the frequencies of resonance peaks with the software described by Migliori and Sarrac.66 Low-temperature RUS data were collected using dynamic resonance system (DRS) "modulus II" electronics and an Orange helium-flow cryostat, as described by McKnight et al.55 The sample was held across a pair of faces directly between the transducers. The automated sequence involved collection of spectra at 30 K intervals during heating from ~280 to ~10 K, with a period of 20 min allowed for thermal equilibration before data collection. This was followed by heating between ~10 and ~305 K, with data collection at 5 K intervals and the same thermal equilibration period at each temperature. Each spectrum contained 65 000 data points in the frequency range 50–1200 kHz. Measured temperatures are believed to be accurate to within ±1 K, and temperature stability during data collection is better than ±0.1 K.

High-temperature spectra were collected with the sample balanced across a pair of corners between the tips of two alumina rods protruding into a horizontal tube furnace. In this system, the transducers are on the ends of the rods, outside the furnace, as described by McKnight et al.,58 and spectra are collected using Stanford electronics.59 Temperature is monitored by a thermocouple sited within a few millimeters of the sample and checked from time to time against the α–β transition temperature of quartz, giving an experimental uncertainty of ±1 K. Spectra were collected in heating and cooling sequences between 295 and ~810 K, with ~20 K steps during heating and ~10 K steps during cooling. A period of 20 min was again allowed for thermal equilibration at each temperature. Individual spectra contained 65 000 data points in the frequency range 100–1200 kHz.

Raw spectra were transferred to the software package Igor (WaveMetrics) for analysis. Selected peaks were fit with an asymmetric Lorentzian function to determine their peak frequencies, f0, and widths at half-maximum height, Δf. Each resonance mode depends on some combination of elastic constants that scales with f02. Because individual resonances are dominated by shearing, with generally small contributions from breathing modes, they provide information mainly relating to the shear modulus when the sample is polycrystalline. Acoustic loss is measured in terms of the mechanical quality factor, Q, which is usually determined as Q−1 = Δf/f0.

### Electrical Spectroscopy

Dielectric properties have already been collected on a different sample from the same material as was used for RUS measurements in the present study. These were collected using a high-precision LCR meter (Agilent 4284A), as described more fully in Schiemer et al.18 Impedance measurements were collected on a high-temperature measurement system (Xian Jiaotong University, China) via a precision LCR meter (Agilent, E4980A).

### Magnetism

Remnant magnetization measurements were made on the same sample as used for the RUS measurements in a MPMS XL SQUID magnetometer. The magnetic moment was collected in zero applied field during a heating sequence from 5 K to room temperature.

## RESULTS

### Room Temperature

Table 1 gives values of the bulk and shear moduli obtained from fitting to the frequencies of 39 peaks measured at room temperature. The rms error for the fit was 0.25%. Also given are values corrected for porosity using the expressions of Ledbetter et al.60 Literature data for these types of materials are sparse, but single-crystal values for BiFeO3 (BFO) have been calculated from first principles61 and partially validated experimentally.62 Voigt–Reuss–Hill averages of Table 1. Values of the Bulk and Shear Moduli Determined in the Present Study in Comparison with Data from the Literature, Including Voigt–Reuss–Hill Averages of Single-Crystal Data Given by Ruello et al.62 for BiFeO3

| sample         | K (GPa)  | G (GPa)  |
|----------------|----------|----------|
| BCFO 36        | 95.7 ± 0.7 | 52.7 ± 0.1 |
| BCFO 36, corrected for 5.5% porosity | 109.0 | 58.6 |
| BFO, Voigt–Reuss–Hill average | 112.0 | 40.8 |
| BFO, Zhu et al.63 | 97.3 | |
| Bi0.9Nd0.1Fe2O3, Schiemer et al.64 | 105.0 | 45.1 |
| Bi0.9Sm0.1Fe2O3, Schiemer et al.64 | 115.4 | 48.5 |

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of the preferred set given by Ruello et al.\textsuperscript{62} are listed in Table 1. There is also a single measurement of K as 97.3 GPa for BFO from equation-of-state measurements.\textsuperscript{63} Bulk and shear moduli of polycrystalline samples of Bi\textsubscript{0.5}La\textsubscript{0.5}FeO\textsubscript{3} (Ln = Nd, Sm) were previously measured by RUS,\textsuperscript{64} and values corrected for porosity confirm that K for all of these materials is in the range ∼100–115 GPa, whereas the shear modulus of BCFO 36 is distinctly higher than for BFO or BFO with a small amount of the second component in solid solution.

**Low Temperatures.** Segments of the low-temperature spectra are shown in Figure 3, stacked in proportion to the

![Figure 3. Segments of RUS spectra from the low temperature instrument.](image)

temperatures at which they were collected. They show a trend of increasing frequency of individual resonances (elastic stiffening) with falling temperature, as might generally be expected, except that there is clearly a subtle change in trend below ∼150 K. This change in trend is confirmed in frequency data from two resonance peaks, as shown in Figure 4. The square of the resonance frequency scales predominantly with the shear modulus, G, and has a steeper slope below ∼130 K than above. Not so evident in the raw spectra, however, is a broad peak in Q\textsuperscript{−1} below ∼200 K and centered near 100 K. The temperature dependence of the shear modulus is expected to have zero slope as T → 0 K, as represented by the Varshni equation for single-crystal elastic constants, c\textsubscript{ij}

\[
c_{ij} = c_{ij}^0 - \frac{S}{(1 + T/T_0)^{1/2} - 1}
\]

(1)

where c\textsubscript{ij}\textsuperscript{0} is the value of the elastic constant at 0 K and S and t are constants.\textsuperscript{65} Fits of the data to the temperature interval ∼145–300 K are shown in Figure 4. The extrapolation to 0 K reveals the nature of the anomaly as being a marked but small (up to ∼2\%) amount of stiffening of the shear modulus below ∼130 K. If they are directly related, then the elastic stiffening below ∼130 K and the peak in Q\textsuperscript{−1} are indicative of some thermally activated strain-relaxation process. In this case, a single Debye peak in Q\textsuperscript{−1} measured as a function of temperature at constant frequency can be described by

\[
Q^{-1}(T) = Q_{m}^{-1}
\left[
\cosh\left(\frac{E_a}{kT}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right)
\right]^{-1}
\]

(2)

where Q\textsubscript{m} is the maximum value of the loss within the peak, E\textsubscript{a} is the activation energy, k is the Boltzmann constant, r\textsubscript{f}(β) is a parameter that reflects the width of a Gaussian spread in the relaxation times, and T\textsubscript{m} is the temperature at which the mechanical losses are maximal.\textsuperscript{66,67} Following Carpenter et al.\textsuperscript{58} and Thomson et al.\textsuperscript{69} eq 2 was initially fit to variations of Q\textsuperscript{−1} that are in excess of a linear baseline (Figure 5) using r\textsubscript{f}(β) = 1 and giving fit parameters T\textsubscript{m} = 108 K, Q\textsubscript{m} = 7.95 × 10\textsuperscript{−4}, and E\textsubscript{a} = 0.022 eV for the 600 kHz Q\textsuperscript{−1} data. A single relaxation process r\textsubscript{f}(β) = 1 with a fixed activation energy would also be expected to give loss peaks at different temperatures, depending on the measuring frequency according to (from eqs 3.5–5 of Norwick and Berry\textsuperscript{70}):

\[
\ln\left(\frac{\omega_2}{\omega_1}\right) = \frac{E_a}{k}\left(\frac{1}{T_{m1}} - \frac{1}{T_{m2}}\right)
\]

(3)

Here, T\textsubscript{m1} and T\textsubscript{m2} are the temperatures of maxima in Q\textsuperscript{−1} as measured at frequencies ω\textsubscript{1} and ω\textsubscript{2} (ω = 2πf).

Dielectric data presented in Figure 11 of Schiemer et al.\textsuperscript{18} (1 kHz to 1 MHz, 100–180 K) show a pronounced, frequency-dependent loss peak, and room-temperature measurements are consistent with a classic Debye pattern. Standard Arrhenius treatment using the frequencies at which the dielectric loss was at a maximum also showed that the data can be well represented by a single-relaxation process following

\[
f = f_0 e^{-E_a/kT_m}
\]

(4)

with E\textsubscript{a} = 0.22 eV and f\textsubscript{0} = 1.89 × 10\textsuperscript{14} Hz. The temperature dependence of the dielectric loss at 300 and 800 kHz is reproduced in Figure 6 to show that it is essentially indistinguishable in form from the acoustic loss measured at almost the same frequencies. Figure 7 is an equivalent plot
comparing dielectric permittivity with elastic compliance \(1/f^2\), and again the two sets of data are closely similar in form.

Values of K and G from fitting with 35–40 resonance peaks (with rms errors of 0.24–0.3%) are shown in Figure 8. The scatter in the data is too great to determine whether the break in slope of G near 130 K occurs also in K, but they are adequate to yield temperature dependences below temperature of \(dK/dT = -12.22\) MPa K\(^{-1}\) and \(dG/dT = -12.248\) MPa K\(^{-1}\).

After cooling from \(\sim 800\) K to room temperature in the furnace used for high-temperature RUS measurements and then down to 5 K in zero field in the SQUID magnetometer, the BCFO sample had a magnetic moment of \(\sim 2 \times 10^{-6}\) emu. As shown in Figure 9, there were no obvious changes in moment during heating to \(\sim 220\) K, but a smooth and relatively steep anomaly occurred between \(\sim 220\) and 250 K. The form of the anomaly closely resembles that shown by hematite, Fe\(_2\)O\(_3\), which has a first-order transition from antiferromagnetic below the Morin transition at \(\sim 260\) K to weakly ferromagnetic (canted antiferromagnet) above it. The change in moment observed here is \(\sim 1000\) times smaller than obtained for a polycrystalline RUS sample of hematite (+\(\sim 3\)% magnetite) with similar dimensions to the sample used in the present study (see Figure 8 of Oravova et al.\(^7\)). It seems likely, therefore, that the magnetic measurements indicate the presence of some trace amount of hematite as an impurity phase. There is no overt evidence in the data that BCFO 36 itself undergoes significant changes in magnetic structure below room temperature.

### High Temperatures

Figure 10 contains segments of spectra from the high-temperature instrument, stacked in proportion to the temperature at which they were collected. These show a break in trend of the peak frequencies and a marked increase in linewidths below \(\sim 650\)–700 K, as...
quantiﬁed by data for \( f^2 \) and \( Q^{-1} \) from ﬁtting of the two peaks (Figure 11). Also shown is the Néel temperature (\( \sim 645 \) K) for a sample with \( x = 0.4 \), taken from Figure 9 of Chen et al.\(^7\) This nearly coincides with the break in slope of frequency with temperature and falls just below the onset in the steep rise in \( Q^{-1} \).

Complex impedance data have been collected between room temperature and 700 K. They are shown here in Figure 12. Highly capacitive behavior is seen, as expected, at room temperature, with resistivity of \( 10^2 - 10^3 \) \( \Omega \) m and reactance of \( 10^1 - 10^2 \) \( \Omega \) m and a frequency dependent peak in the resistivity near 350 K. The resistivity drops sharply to \( \sim 1 \) \( \Omega \) m by \( \sim 450 \) K, at which point it plateaus and develops a frequency dispersion. This anomaly persists until \( \sim 525 \) K, above which the resistivity continues to drop, with a low value of \( 10^{-1} \) \( \Omega \) m at 700 K. By 400 K, the reactance has increased to \( \sim 10^{-1} \) \( \Omega \) m, and above the anomalous region, from 550 K, the reactance is slightly positive (\( \sim 10^{-2} - 10^{-1} \) \( \Omega \) m), indicating inductive, rather than capacitive, behavior and suggesting that the material has become a conductor. Attempting to examine this in terms of thermally activated Arrhenius behavior yields the information in Figure 13. This shows that two distinct regions of slope exist, typical of the behavior of doped semiconductors, with the region on the right related to the thermal activation of extrinsic dopant charge carriers and the region on the left related to intrinsic conductivity. There is a marked frequency dispersion in the transition region at around 500 K. The line shown on the ﬁgure is that of a linear ﬁt to \( E_a/\kappa T \) with activation energy of 0.22 eV, as previously found by Schiemer et al.\(^{18}\) for this system at low temperature. This gives a reasonable ﬁt for the lower-temperature slope, suggesting that the transition region occurs as all oxygen vacancies become thermally activated.

**DISCUSSION**

Patterns of phase transitions across the phase diagram, the spontaneous strains that accompany changes in structural state, anomalies in the elastic and anelastic properties of BCFO 36, and correlations between elastic behavior and dielectric behavior are all revealing of the nature and strength of coupling between the multiple order parameters that operate in BFO—CFO. These are due to octahedral tilting, \( q \), cation/oxygen/vacancy ordering, \( q_{\text{o/p}} \), ferroelectric polarization, \( p \), and antiferromagnetic ordering, \( m \). The nonzero strains couple with each order parameter as \( \lambda_{eq}^2 \), \( \lambda_{q_{\text{o/p}}}^2 \), \( \lambda_p^2 \), and \( \lambda_m^2 \), whereas coupling between the order parameters themselves, either directly or indirectly through common strains, is biquadratic (i.e., \( \lambda_q^2 q_{\text{o/p}} \), \( \lambda_q^2 p \), \( \lambda_q^2 m \), \( \lambda_{q_{\text{o/p}}}^2 p \), \( \lambda_{q_{\text{o/p}}}^2 m \), and \( \lambda_p^2 m \)). Two separate tilt order parameters, \( q_R \) and \( q_M \), relate to R- and M-point tilting schemes. Possible patterns of structural
evolution in systems with two instabilities and biquadratic coupling between the order parameters have been set out by Salje and Devarajan.47 The most general characteristic behavior when the order parameters are able to relax on a fast time scale is of sequences of stability fields for different structures that may be separated by first- or second-order transitions. In the present system, however, it is unlikely that the degree of cation/oxygen/vacancy order re-equilibrates in response to changes in p, m, or q under laboratory time scales at temperatures less than ~1000 K. In this case, the influence of $\lambda_q q_{\lambda}^2$ is as an effective field that would renormalize the critical temperature of the instability to which it is coupled. In other words, samples with different degrees of cation/oxygen/vacancy order would be expected to have different magnetic, ferroelectric, and tilting transition temperatures.

Coupling between p and q stabilizes a ferroelectric structure with only one tilt system, with respect to one with two tilts (i.e., $\lambda_q 0 q_{\lambda}^2$ is probably favorable). The introduction of oxygen vacancies causes the ferroelectric structure to be suppressed, but if there is any cation/oxygen/vacancy ordering involved, then it is presumably restricted to a local length scale because there is no evidence for long-range ordering in the Pnma structure. On the basis of very low shear strains in the intermediate structure, it appears that cation/oxygen/vacancy ordering suppresses tilting (i.e., $\lambda_q q_{\lambda}^2$ terms are unfavorable). This contrasts with CaFeO$_{1.5}$ with its large shear strains and known tilting of octahedra in the perovskite layers. On this basis, incommensurate ordering appears to be incompatible with tilting.

In the absence of tilting, the lowering of symmetry from cubic to tetragonal or orthorhombic at intermediate compositions would likely be due to only ordering of cations and oxygen vacancies. Volume strains tend to be small for both tilting and cation ordering, with the result that the bulk modulus at room temperature is likely to be relatively insensitive to structural state. However, significant softening of the shear elastic constants accompanies tilting transitions. In LaAlO$_3$, for example, the cubic ↔ rhombohedral transition results in a lowering of the shear modulus, G$_\lambda$, by ~25% (Carpenter et al.). BFO has a significant shear strain at room temperature, whereas BCFO 36 is close to being metrically cubic. The shear modulus of BFO at room temperature could be as much as 30% softer than that of BCFO 36 (Table 1), and much of this is likely to be due to the tilting in the former and the lack of tilting in the latter.

All of the evidence from the phase diagram and the elasticity data presented here indicates that the magnetic order parameter is only weakly coupled with the other order parameters, if at all. In particular, $T_N$ values are essentially independent of composition and structure type (Figure 1), and the antiferromagnetic order parameter, m, has almost exactly the same temperature dependence in phases with different compositions across the solid solution. In other words, the coupling coefficients for $\lambda q_{\lambda} m^2$, $\lambda q_{\lambda} m^2$, and $\lambda p m^2$ must be small, and the latter has also been shown to be unfavorable. The most likely explanation for this is, first, that any direct coupling is weak and, second, that m couples only very weakly with strain, e. Weak coupling between e and m means that the possibilities for indirect coupling with any other order parameters via common strains are strictly limited. The lack of coupling of m with shear strains is confirmed by the absence of softening of the shear modulus below $T_N$ in BCFO 36 (this study) and also in Bi$_{0.9}$Nd$_{0.1}$FeO$_3$. Elastic softening below the transition point is typical of systems with linear-quadratic coupling ($\lambda m^2$ here) if the order parameter (m) relaxes in response to an applied stress on the time scale of the measurement. From the discussion of strains above, it appears that there is a small volume strain associated with the magnetic ordering, in which case a small degree of softening of the bulk modulus is expected.

Biquadratic coupling of strains with an order parameter, $\lambda e m^2$ in the present case, is always allowed by symmetry, and even a zero or very small shear strain e would cause a renormalization of the shear elastic constant, C$_{ii}$, according to C$_{ii} = C_{0} + 2\lambda_e m^2$, where C$_{0}$ is the elastic constant of the paramagnetic phase extrapolated into the stability field of the antiferromagnetic phase. This is easily tested since the change in elastic properties becomes an excess, with respect to the para phase, which should scale with the square of the order parameter. The straight line shown in Figure 11 is a linear fit to data above $T_N$, representing the shear modulus of the paramagnetic phase of BCFO 36. Differences between this and the observed values of $\Delta f^2$, $\Delta f^2$, are shown in Figure 14 along with values of m$^2$ extracted from the data for a sample with x = 0.4 from Figure 8 of Chen et al.\textsuperscript{7}

In marked contrast with the independence of $T_N$ and the evolution of m with respect to ferroelectric behavior, octahedral tilting, and cation/oxygen/vacancy ordering, the crossover from a cycloidal antiferromagnetic ordering scheme to a commensurate scheme that is weakly ferromagnetic is highly sensitive to composition. The stability field of the cycloid does not extend very far into the solid solution because the room temperature structures at x = 0.03 display weak ferromagnetism; its boundary does not appear to be coincident with any of the structural transitions. Macroscopic strains do not modify the antiferromagnetic G-type ordering of Fe$^{III}$ moments, but local strain heterogeneity associated with replacing Bi$^{III}$ ions (Shannon ionic radius 1.17 Å in 8-fold coordination) with Ca$^{II}$ (1.12 Å in 8-fold coordination), with the resultant loss of the natural off-centering created by the Bi$^{III}$ lone pair and the creation of oxygen vacancies, could provide the mechanism for disrupting the classic order parameter gradient coupling.
required to stabilize an incommensurate structure. Strain fields around impurity atoms in oxide perovskites can be thought of as spheres of local distortion with radii of ~8–9 Å that effectively start to impinge on each other at a doping level of ~1.5%. The acoustic loss behavior discussed below provides evidence of strain relaxation around individual vacant oxygen sites, and this would presumably modify tilting and shearing of neighboring octahedra across the same length scale. The local state of oxide solid solutions, more generally, is also of overlapping strain fields, which gives rise to a degree of local heterogeneity that can be characterized by measurements of line broadening in infrared spectra. On this basis, the limit of stability of the cycloid ordering scheme would be expected to be at or below ~1% doping.

Acoustic losses occur in two temperature intervals and coincide at low temperature with dielectric losses measured at similar frequencies and at high temperature with anomalous conductivity behavior. The correlation between the dielectric and (an)elastic properties below room temperature is so close (Figures 6 and 7) that they must be due to essentially the same process driven either by an external electric field or by external stress. The description of the response to these fields in terms of thermally activated processes and the magnitude of the activation energy are consistent with the loss mechanism being related to the movement of oxygen vacancies. If the treatment is correct, it also implies a wide spread of relaxation times that, in turn, implies the oxygen vacancies involved are not in a uniform environment. Variations in environment could be due to local ordering/clustering and proximity to twin walls. As stated in the introduction above, variations in local potential between twin walls and uniform twin domains almost inevitably leads to energetically preferred locations for oxygen vacancies in perovskites. TEM observations confirm the existence of twin walls in the intermediate phase of BCFO, and given that the macroscopic symmetry is lower than cubic, some of these must inevitably be ferroelastic in character. However, walls between domains for which the difference is primarily due to cation or oxygen/vacancy ordering will not be mobile to anything like the extent expected for twin walls between domains where the difference is due to a displacive order parameter. For the moment, it is only possible to propose that there are a range of environments for oxygen vacancies in BCFO 36, that their movement involves a change in local dielectric properties and strain, and that freezing of this movement occurs in the temperature range ~50–200 K at measurable frequencies of a few hundred kilohertz. Maximal losses occur near 100 K at these frequencies. Associated with the loss behavior are small changes in the shear elastic constant and the dielectric permittivity, indicating small differences in these properties between the unrelaxed states (high measuring frequencies) and the relaxed states (low measuring frequencies), according to the Debye relations.

Large acoustic losses and anomalous conductivity have been observed above ~350–400 K (Figures 11 and 13) and, again, the correlation is permissive of a common loss mechanism. The overall pattern is consistent with increasing ionic conductivity with increasing temperature. Movement of oxygen ions and vacancies under the influence of an applied electric field will be coupled to local strain clouds. Conversely, therefore, application of a stress field can cause analogous displacements. There is no evidence from the elasticity measurements of a structural transition at ~430 K, so the onset of ionic conductivity is not obviously related to some specific change in structural state. Q−1 for BCFO 36 is low at high temperatures but increases steeply below ~750 K (Figure 11). This could perhaps include some acoustic loss behavior associated with the antiferromagnetic ordering, but it is still within a temperature interval of anomalous impedance (Figure 13) and could simply be a function of the dynamics of oxygen-vacancy mobility. Dielectric measurements on BFO with lower levels of Ca-doping show increasing loss above only ~500 K and a pattern that could be more directly related to the magnetic ordering.

■ CONCLUSIONS

The pervasive influence of local and macroscopic strain associated with phase transitions in the binary system BiFeO3–CaFeO2.5 has been investigated indirectly by an analysis of the overall phase relationships and directly for a single representative of the intermediate phase by resonant ultrasound spectroscopy. The general conclusions are as follows. (1) Biquadratic coupling is permitted between multiple order parameters of the system. This is sufficiently strong for coupling between ferroelectric polarization, octahedral tilting, and cation/oxygen/vacancy ordering to determine the stability fields of the $R_3c$, $Pmna$, and tetragonal/orthorhombic structures. In particular, coupling between p and q$_p$ appears to be favorable, whereas coupling between q and q$_ad$ is unfavorable. (2) Linear-quadratic coupling of tilt and ferroelectric order parameters is relatively strong in comparison with coupling of strain with cation/oxygen/vacancy ordering. In marked contrast, linear-quadratic coupling of shear strains with the antiferromagnetic order parameter is weak across the entire solid solution. Elastic stiffening below the Neel point of BCFO 36 confirms that biquadratic (λε$^2$m$^2$) terms predominate instead. (3) The crossover from a cycloidal antiferromagnetic ordering scheme to one that is weakly ferromagnetic does not appear to be related to changes in macroscopic strain or to changes in the other macroscopic order parameters. It is proposed, rather, that the key factor would be the development of local strain heterogeneities at low doping levels, which would act to suppress coupling between gradients of the magnetic order parameter. (4) Large dielectric and acoustic loss behavior at low temperatures has highlighted a common loss mechanism involving freezing of oxygen-vacancy motion. The vacancies are mobile via thermal activation, with a wide spectrum of relaxation times under the influence both of electric and stress fields. Similar correlations at high temperatures are attributed to the onset of ionic conductivity and are different in the intermediate phase in comparison with what is seen at low doping.

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Author Contributions
The manuscript was written with contributions from all authors, and J.S. also carried out the experiments and analyzed the data. All authors have given approval to the final version of the manuscript.

Notes
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