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Dielectric relaxation near 25 K in multiferroic BiFeO₃ ceramics

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Our investigations using low-temperature Raman spectroscopy, dielectric, and magnetodielectric studies of as-prepared and vacuum-annealed BiFeO₃ ceramics revealed two dielectric anomalies near 25 and 281 K. Systematic studies were carried out to probe the anomaly near 25 K which exhibits clear frequency dependence and falls close to a previously observed magnetic transition. The low-temperature dielectric relaxation behavior yielded characteristic energy scales of ~ 30 and ~ 34 meV for the as-prepared and vacuum-annealed BiFeO₃ samples, respectively. Raman spectra showed hardening of the $E(TO6)$ and $E(TO9)$ modes near 25 K, and the Raman shift in phonon frequencies is found to be broader in the vacuum-annealed BiFeO₃ than in the as-prepared BiFeO₃. We observed a linear magnetodielectric coupling in both samples at 25 K. These experimental results suggest that coupling among spin, lattice, and dielectric properties persist to low temperatures in BiFeO₃. © 2011 American Institute of Physics. [doi:10.1063/1.3662182]

I. INTRODUCTION

Magnetoelectric multiferroics¹ are technologically and scientifically relevant because of their potential applications in data storage, spin valves, spintronics, and microelectronic devices applications.^{2–4} BiFeO₃ is a single-phase multiferroic that is particularly interesting because both magnetic order and ferroelectric order develop above room temperature. BiFeO₃ exhibits ferroelectricity with a Curie temperature^{5,6} of $T_C \approx 1083$ – 1103 K, and antiferromagnetism below $T_N \approx 625$ – 643 K.^{5–7} At the same time, BiFeO₃ is a model magnetoelectric perovskite because it presents a number of properties making the system more tractable including a simple chemical formula, exchange interactions only in the Fe³⁺ sublattice, and stereo-chemically active 6s² lone pair of Bi³⁺ as a main origin of ferroelectricity.⁸

There have been a restricted number of investigations probing phonon properties in BiFeO₃, despite the fact that these studies can provide useful insight into microscopic properties such as softening of dynamic ferroelectric modes, structure-property relations, different behavior of local symmetry from the global symmetry in a nanoscale range, and the spin-phonon coupling.^{9,10} Additionally, there are considerable discrepancies among the Raman scattering results reported on BiFeO₃ single crystals and epitaxially grown thin films, providing strong motivation for further studies.^{11–14} Recently, Kumar *et al.*¹⁵ and Redfern *et al.*¹⁶ have reported Raman spectral studies of BiFeO₃ thin film and single crystal, respectively, and have proposed new magnetic transitions developing below room temperature. These experiments suggest that the magnetic structure of BiFeO₃ may show a number of changes at low temperatures, with evidence for spin glass and spin reorientation transitions observed at a range of temperatures, including 50, 140, 200, and 230 K.^{15,16} Recently, Kamba *et al.* have studied frequency-dependent dielectric properties of BiFeO₃ ceramics over a temperature range from 10–300 K.¹⁷ They observed an anomaly near 250 K in BiFeO₃ ceramics, which was explained by a

Maxwell-Wagner type contribution to the permittivity as consequence of a relaxation arising at the interfaces between grains and grain boundaries.^{17,18}

II. EXPERIMENTAL DETAILS

Very recently, we reported on the low-temperature magnetocaloric effect in polycrystalline BiFeO₃ sample that exhibited a few magnetic transitions near 38, 150, 178, 215, and 250 K, suggesting a persistent spin-lattice coupling,¹⁹ and we also investigated the electronic structure of BiFeO₃ ceramic to understand the conductivity mechanisms and intrinsic leakage currents for the optimization of magnetoelectric coupling in this multiferroic system.²⁰ In order to more fully investigate the low-temperature behavior of BiFeO₃ and specifically to explore the possibility of cross-coupling among different properties at the proposed transition, we have measured the magnetic, dielectric, and Raman response of BiFeO₃ below room temperature. Furthermore, in order to attempt to redress some of the experimental differences among different measurements, we have studied both as-prepared (air-annealed) and vacuum-annealed samples to determine how oxygen non-stoichiometry may affect the physical properties of BiFeO₃. In order to study oxygen deficient BiFeO₃ ceramics, we annealed the sample at 525 °C for 2 h in vacuum at 3×10^{-5} Pa to introduce oxygen vacancies.

III. RESULTS AND DISCUSSION

In order to investigate the effects of oxygen non-stoichiometry on the electronic structure and Fe valence in the as-prepared BiFeO₃ (BFOAP) and vacuum-annealed BiFeO₃ (BFOVA) ceramics, x-ray photoelectron spectroscopy (XPS) was employed. These XPS measurements confirmed the presence of only the Fe³⁺ valence state in both the as-prepared and vacuum-annealed samples as shown in Fig. 1(a). We do not find evidence for any Fe²⁺ impurities in vacuum-annealed sample. To confirm that vacuum-annealing

did introduce oxygen vacancies, XPS spectra of the O1s peaks of both samples were recorded, as shown in Fig. 1(b). There is a small shift in binding energy and broadening of O1s peak of BFOVA (530.7 eV) compared to that of BFOAP (530.2 eV), which establishes the creation of oxygen vacancy defects in vacuum-annealed BiFeO₃ ceramic sample.

The temperature and frequency-dependent dielectric response of the BFOAP and BFOVA ceramic samples were investigated from 10 to 350 K using a precision LCR meter (Agilent 4284 A) in a frequency range from 10 kHz to 1 MHz. The temperature-dependent dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) measured at 30 kHz are shown for both samples in Fig. 2(a). We observe two anomalies, at 25 and 281 K, in the dielectric response of both BFOAP and BFOVA samples. We believe that the higher temperature feature at 281 K may correspond to an antiferromagnetic to spin glass transition, which has been observed in previous magnetization and magneto-caloric effect studies.¹⁹ This anomaly is considerably broader in the vacuum-annealed sample as compared to that of as-prepared sample. We attribute the broadening of the high temperature dielectric loss peak in the BFOVA sample to the additional disorder pro-

duced by oxygen non-stoichiometry. Although an increase in electrical conductivity in the vacuum-annealed sample could also result in broader dielectric features, the magnitude of the loss tangent is similar for the two samples. This suggests that the leakage current should be similar for the two samples, consistent with our observation that the valence state of Fe is not changed in the vacuum-annealed sample.

The low-temperature dielectric anomaly near 25 K may be due to a magnetic transition, but glassy and with magneto-electric coupling, which has been observed in BiFeO₃ ceramics and single crystals.¹⁶ Our measurement of ac magnetic susceptibility do not show any clear features associated with this 25 K anomaly, in either BFOAP or BFOVA (S1),³⁵ although these low-temperature magnetic spin glass transitions do not seem to be observed in all sample.^{21,22} Given this lack of any significant magnetic signature, we suggest this low-temperature feature may result primarily from some structural distortion, leading to a significant dielectric response. We measured the frequency-dependant dielectric constant and dielectric loss of the BFOAP and BFOVA ceramics at low temperatures in the vicinity of this anomaly, with the dielectric constant plotted in Figs. 2(b) and 2(c). The peak temperature (T_p) shifts from 23.7 to 31.9 K for BFOAP and from 24.4 to 33.9 K for BFOVA as the frequency is varied from 10 kHz to 1 MHz.

In analyzing the dielectric relaxation, as shown in Fig. 2(d), we found that the data fit well to an Arrhenius expression, $f = f_0 \exp(-E/k_B T)$, where f_0 is the relaxation frequency, E is the activation energy, and k_B is the Boltzmann constant. The extracted activation energies and relaxation frequencies of this dielectric relaxation process are found to be 29.6 meV and 1.24×10^{11} Hz for BFOAP and 34.3 meV and 2.20×10^{10} Hz for BFOVA, respectively. This activation energy scale corresponds to approximately 340 and 400 K for BFOAP and BFOVA, respectively. Although these activation energies are comparable to the 470 K activation barrier found in the case of the conventional relaxor ferroelectric PbMg_{1/3}Nb_{2/3}O₃,²³ this system exhibits Vogel-Fulcher relaxation while our results clearly suggest that the low-temperature dielectric relaxation in BiFeO₃ appears to be related to relaxor ferroelectrics with weakly interacting ferroelectric domains. It is known that weakly interacting clusters lead to Arrhenius rather than Vogel-Fulcher relaxation, implying superparaelectric, rather than glassy, behavior.²³

The frequency dependence of the relaxation temperature can be parameterized using the dimensionless parameter $\phi = \Delta \log T_p / T_p \Delta \log \omega$, where T_p is peak temperature and ω is frequency, yielding $\phi = 0.15$ for BFOAP and $\phi = 0.16$ for BFOVA, respectively. These relatively large values of ϕ indicate a strong dependence of relaxation temperature on frequency and are characteristic of superparaelectric rather than glassy relaxation,²³ confirming that the relaxing clusters are non- or weakly-interacting. Low-temperature pyrocurrent measurement on the as-prepared BiFeO₃ sample (S2)³⁵ finds no evidence for any anomaly at 25 K, indicating that there is a negligible change in polarization associated with this relaxation. The size of BiFeO₃ superparaelectric clusters having a

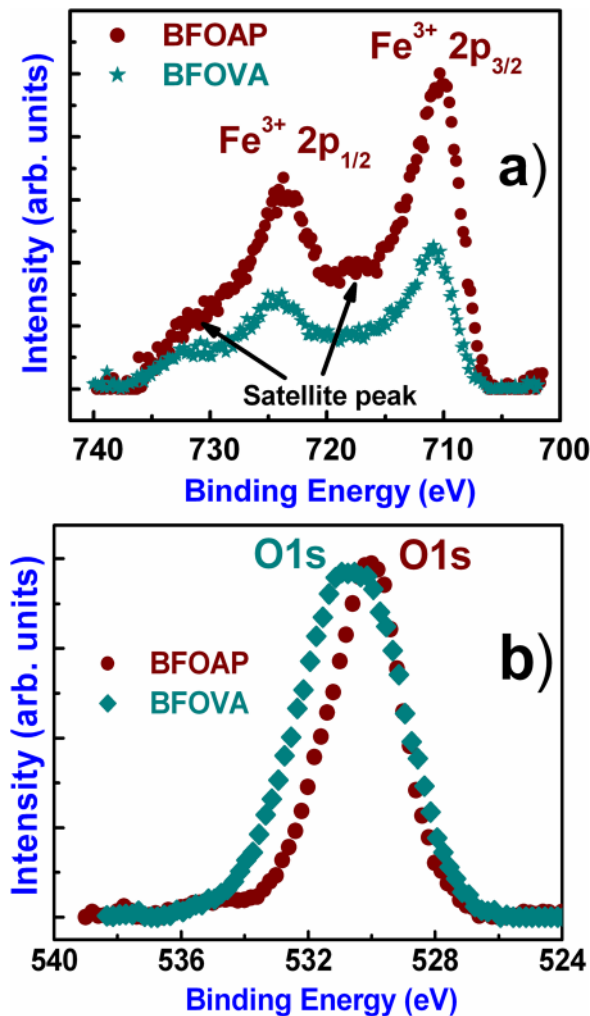


FIG. 1. (Color online) (a) XPS spectra of the Fe element, and (b) XPS spectra of the O1s of as-prepared and vacuum-annealed BiFeO₃ ceramics (BFOAP and BFOVA).

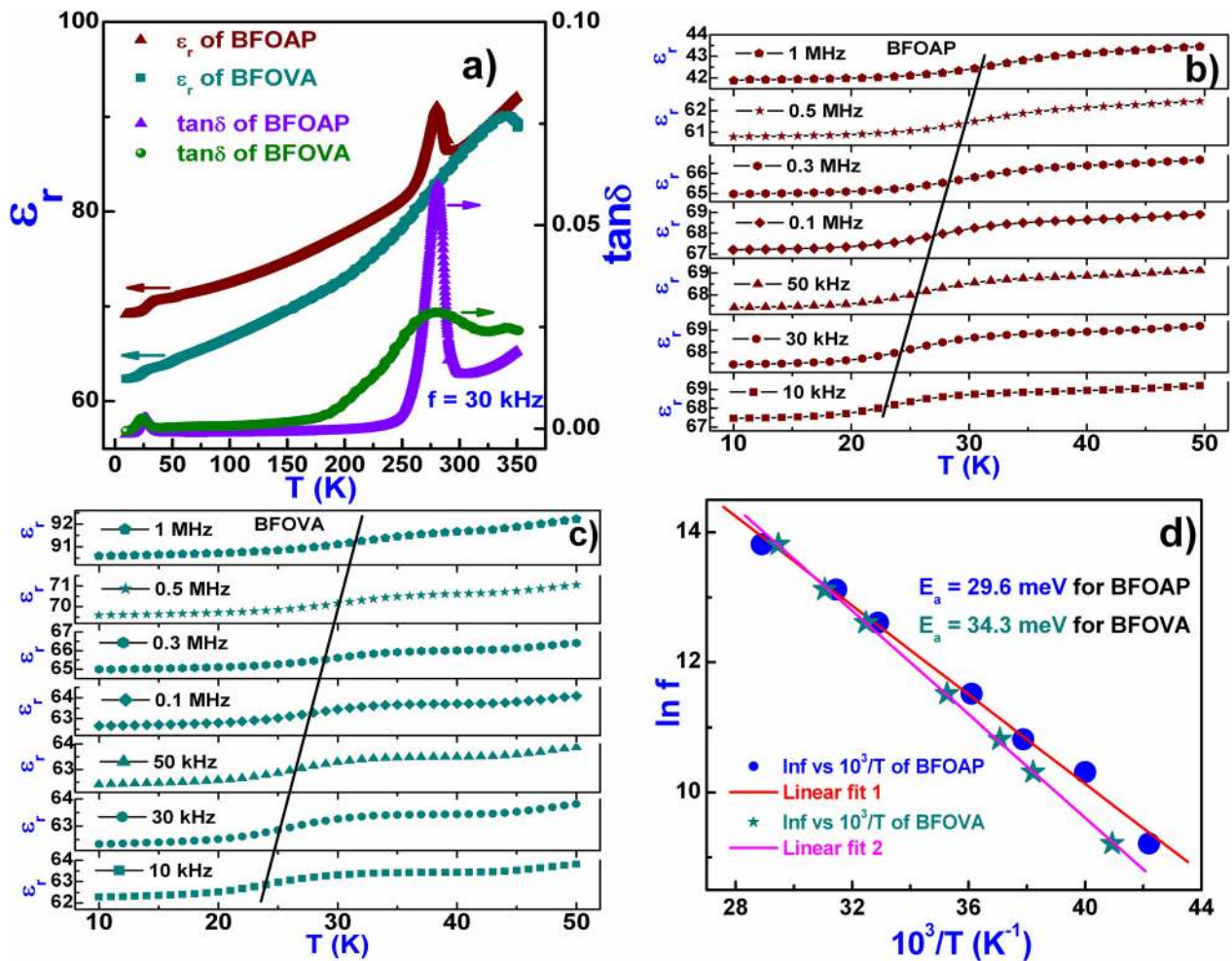


FIG. 2. (Color online) (a) Temperature-dependent dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) of BFOAP and BFOVA samples measured at 30 kHz; (b) frequency-dependent dielectric constant of BFOAP near 25 K; (c) frequency-dependent dielectric constant of BFOVA near 25 K; and (d) $\ln f$ vs $10^3/T$ plots of BFOAP and BFOVA samples.

freezing temperature of 25 K has been estimated to be only a few nanometers,²⁴ so these putative clusters could perhaps be associated with grain boundaries. Although these dielectric measurements suggest the presence of superparaelectric clusters that freeze out at low temperatures, the number of dipoles involved in this relaxation must be relatively small. As-prepared BiFeO₃ sample shows both spontaneous polarization with a well-defined hysteresis loop (S3),³⁵ and micron-sized ferroelectric domains (S4)³⁵ at room temperature, which means that the majority of the dipoles contribute to the ferroelectrically ordered state rather than superparaelectric clusters.

Although we did not observe any ac magnetic response associated with this low-temperature dielectric relaxation, we probed possible spin-charge coupling at this anomaly using magnetodielectric measurements. We plot the magnetic field dependence of the relative change in dielectric constant for BFOAP and BFOVA at 25 K in Fig. 3(a), using a measuring frequency of 30 kHz. Both samples show practically identical behavior, with a negative magnetodielectric shift of approximately 0.03% in a magnetic field of 50 kOe. Although the oxygen non-stoichiometry in BFOVA sample

produces some minor changes in relaxation parameters, there is apparently no change in the magnetodielectric coupling. Most significantly, Fig. 3(a) shows a linear magnetodielectric shift in both BFOAP and BFOVA samples. This can be seen more clearly in Fig. 3(b), where we plot the magnetodielectric shift in BFOAP against the sample magnetization measured at 25 K.¹⁹ Beyond some small rounding off near $H = 0$, the relative change in dielectric constant is linear with magnetization.

Generically, magnetodielectric effect arises from terms proportional to P^2M^2 in a Ginzburg-Landau free energy, which are always allowed by symmetry. This coupling leads to a quadratic dependence of the dielectric constant on magnetization (or magnetic field), which is observed in a wide range of insulating magnetic systems such as SeCuO₃/TeCuO₃, EuTiO₃, BiMnO₃, among others.^{25–28} Quadratic magnetodielectric coupling is also observed in magnetoelectric multiferroics, including BiMnO₃²⁷ and Ga and In substituted YMnO₃,^{29,30} which exhibit shifts in the dielectric constants proportional to the square of the magnetization in the magnetically ordered phase. The linear magnetodielectric coupling in BiFeO₃ shown in Fig. 3

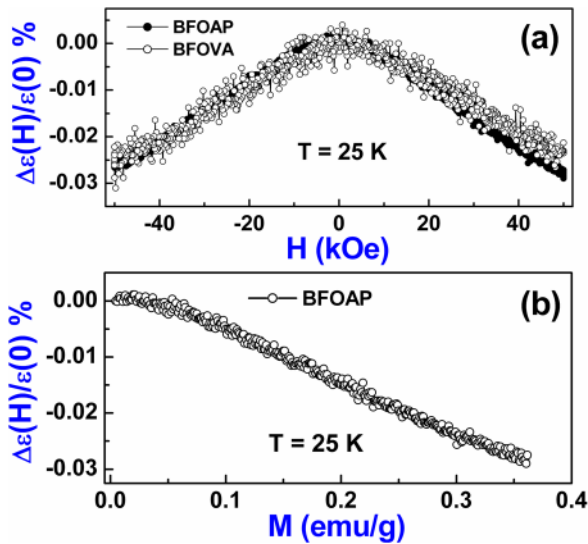


FIG. 3. (Color online) (a) Relative change in dielectric constant of BFOAP (closed circles) and BFOVA (open circles) with applied magnetic field at $T = 25$ K; (b) relative change in the dielectric constant of BFOAP plotted against sample magnetization at 25 K.

suggests some additional atypical spin-charge coupling is present in the system. This magnetization-linear dielectric shift could be produced by an additional term proportional to P^2M in the free energy, but could also be produced by a linear magnetoelectric coupling producing a shift in the bi-quadratic P^2M^2 free energy term. A similar model has been proposed for magnetodielectric coupling in magnetically-induced multiferroics.³¹ While linear magnetoelectric effects in BiFeO_3 with the spin-cycloid phase suppressed have been discussed theoretically³² and observed experimentally under high magnetic fields,³³ the origins of this linear magnetodielectric response at low temperatures remains unclear.

In order to more fully investigate the relaxation at 25 K, we conducted temperature-dependent Raman spectroscopy studies on both the BFOAP and BFOVA ceramic samples. For these measurements, well-sintered pellets of as-prepared BiFeO_3 and vacuum-annealed BiFeO_3 were polished then cleaned thoroughly with acetone. The samples were mounted on an optical microscopy cryostat (Janis ST-500) to control the temperature from 10 to 100 K. The Raman spectra were recorded in a back scattering geometry using a Horiba-Jobin-Yvon HR8000 (France) spectrometer (using 514.5 nm Ar-ion laser line) the equipped with a liquid nitrogen (LN_2) cooled back thinned charge couple device detector.

Figures 4(a) and 4(b) show the Raman spectra for BFOAP and BFOVA samples recorded at temperatures ranging from 10 to 100 K. Group theory predicts that BiFeO_3 , a highly rhombohedrally distorted perovskite structure with $R3c$ space group, should have 13 ($4A_1 + 9E$) Raman active modes.^{12–14} The Raman spectra [Figs. 4(a) and 4(b)] show peaks at 134, 143.5, 175.5, 223.5, 264.5, 279.5, 295.0, 349.3, 373.0, 472.5, 523.0, and 552.0 cm^{-1} . The three peaks at 264.5, 349.3, and 523.0 cm^{-1} and a peak at 134.0 cm^{-1} can be assigned to $A_1(LO)$ modes and $A_1(TO)$ modes, respec-

tively.¹⁴ The eight remaining peaks at 143.5, 175.5, 223.5, 279.5, 295.0, 349.3, 373.0, 472.5, and 552.0 cm^{-1} are assigned to the $E(TO)$ modes.¹⁴ The first A_1 and E modes have been only observed below 90 cm^{-1} ,¹⁴ contrary to the experimental observation of two Raman modes¹² which are not seen in this study due to spectrometer constraints. The spectra plotted in Figs. 4a and 4b show a large number of modes for both samples, many of which evolve with temperature. However, there are particularly striking changes in the $E(TO6)$ and $E(TO9)$ modes at 295 and 552 cm^{-1} in both samples as temperature is varied. These anomalies in the Raman spectra confirm that dielectric anomaly near 25 K is produced by intrinsic effects, rather than due to electrode effects.

The relative Raman shifts associated with these modes are plotted as a function of temperature in Figs. 4(c) and 4(d). Both the $E(TO6)$ and $E(TO9)$ modes show very clear hardening near the 25 K anomaly, with the peak frequency increasing by $\sim 3\%$ and $\sim 0.4\%$ for the $E(TO6)$ and $E(TO9)$ phonon, respectively. This hardening at the anomaly is considerably broader in the vacuum-annealed sample than in the as-prepared sample. We attribute this broadening to increased disorder in the oxygen deficient ceramic, which may be expected to lead to broadening of the structural distortions, similar to the dielectric broadening observed in the 25 K dielectric anomaly (Fig. 2). The $E(TO2)$ Raman mode at 144 cm^{-1} has also been found to soften above 25 K and become less intense. This reduction in intensity of the $E(TO2)$ mode allows the appearance of the mode $A_1(TO1)$ at 134 cm^{-1} . The low frequency Raman modes are related to the Bi–O bonds whereas the higher modes are associated with the Fe–O bonds.³⁴ In particular, the 552 cm^{-1} peak which is the $E(TO9)$ mode and also related to ferroelectric domain of BiFeO_3 (Ref. 13) and therefore can be attributed to the Fe–O bonds. First, the oxygen atoms are involved in an antiferromagnetic order due to the superexchange interaction. Thus, the evolution of the 295 and 552 cm^{-1} peaks with temperature may be explained by its coupling with the magnetic sublattice. This seems to be closely related to the strong hybridization between Bi ($6s^26p^3$) and O ($2s^22p^4$) that causes a significant structural distortion. It is also seen an anomaly in data related to magneto-caloric effect in BiFeO_3 ceramics at 38 K.²⁰ This possible local structural distortion mediated dielectric and magnetic properties may be due to strong coupling between magnetic and electric order parameters near 25 K.

IV. SUMMARY

We have investigated the low-temperature Raman response, and temperature-dependent and magnetic field dependent dielectric properties of as-prepared and vacuum-annealed BiFeO_3 ceramics. A dielectric anomaly near 25 K for both as-prepared BiFeO_3 (BFOAP) and vacuum-annealed BiFeO_3 (BFOVA) has been found to increase in temperature monotonically with an increase in frequency, consistent with relaxor ferroelectric behavior but with a strong frequency dependence suggesting non-interacting clusters. The estimated barrier energies for relaxation, being 340 and 400 K for

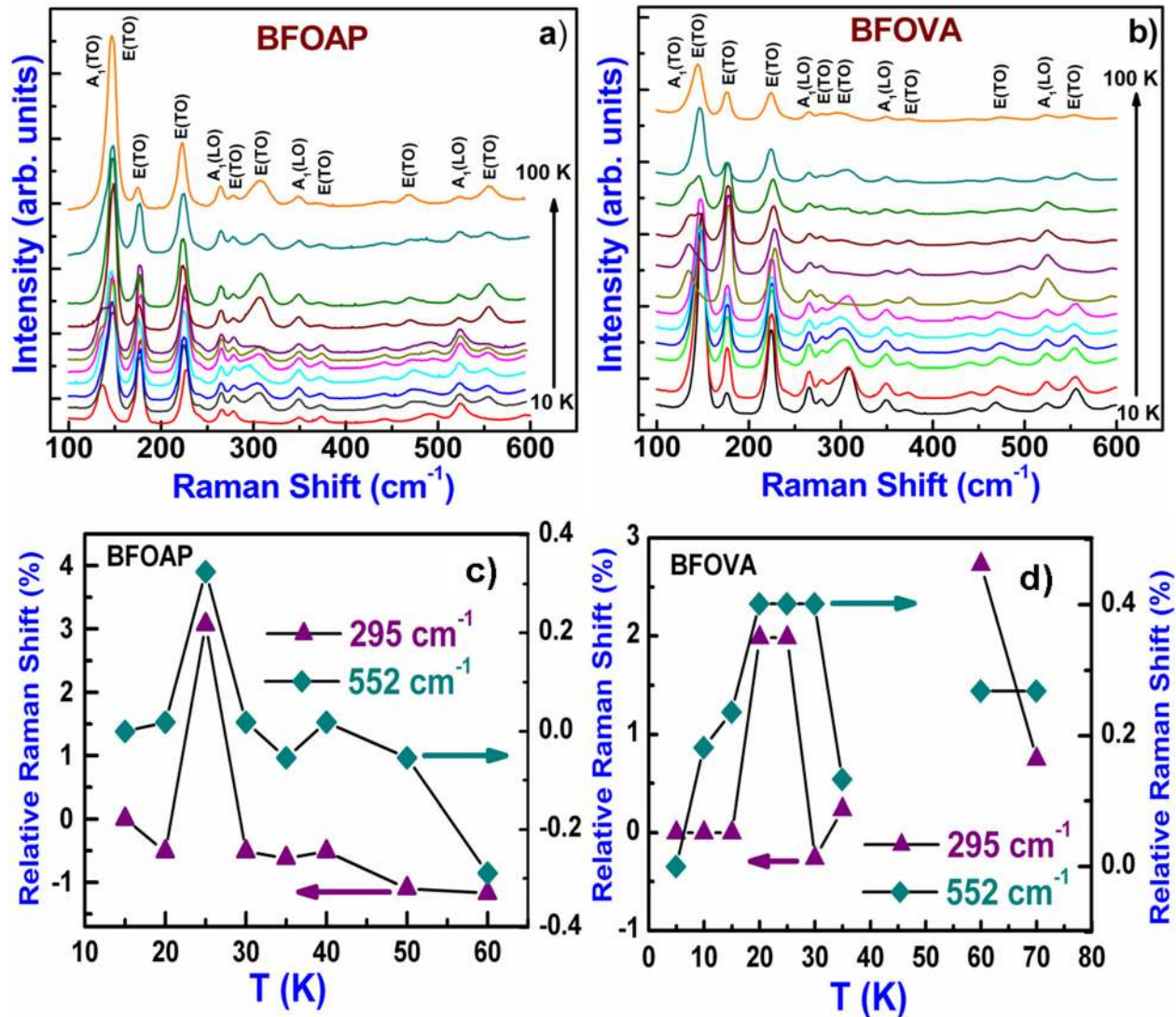


FIG. 4. (Color online) (a) Raman spectra of as-prepared BiFeO_3 ceramics (BFOAP) recorded in the temperature range, 10–100 K; (b) Raman spectra of vacuum-annealed BiFeO_3 (BFOVA) ceramics recorded in the temperature range, 5–100 K; (c) temperature-dependent relative Raman shift of 295 cm^{-1} [$E(\text{TO}6)$] and 552 cm^{-1} [$E(\text{TO}9)$] modes of as-prepared BiFeO_3 (BFOAP) near 25 K; and (d) temperature-dependent relative Raman shift of 295 cm^{-1} [$E(\text{TO}6)$] and 552 cm^{-1} [$E(\text{TO}9)$] modes of vacuum-annealed BiFeO_3 (BFOVA) near 25 K.

BFOAP and BFOVA samples, respectively, are comparable to those found in relaxor ferroelectrics, suggesting similar mechanisms may be responsible for the relaxation in these different systems. There is also a small linear shift in dielectric constant with applied magnetic field at this anomaly, which indicates significant magnetoelectric coupling is present in BiFeO_3 at low temperatures. We also find hardening of the $E(\text{TO}6)$ and $E(\text{TO}9)$ modes near 25 K, and the Raman shift in phonon frequencies is found to be broader in the vacuum-annealed BiFeO_3 sample than in the as-prepared BiFeO_3 . These observations together provide evidence for some structural distortion near $T = 25 \text{ K}$, which affects charge, spin, and structural degrees of freedom. While there are minor quantitative differences between the as-prepared and vacuum-annealed samples, both show qualitatively similar behavior, suggesting that oxygen non-stoichiometry may not have a very significant effect on the low-temperature dielectric and structural response of BiFeO_3 .

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