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Correlated rattling-ion origins of dielectric properties in reentrant dipole glasses BaTiO$_3$-BiScO$_3$

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The local structure of the pseudo-cubic solid solution 0.6BaTiO$_3$-0.4BiScO$_3$, which exhibits reentrant dipole-glass behavior, has been determined using the Reverse Monte Carlo method to simultaneously fit (1) neutron and X-ray total scattering data (including the corresponding real-space pair-distribution functions), (2) Bi and Sc extended X-ray absorption fine structure, and (3) patterns of diffuse scattering in electron diffraction. These structural refinements revealed the multi-site probability density distributions for both Bi (14-sites) and Ti (8 sites), whereas Ba and Sc featured normal unimodal distributions. Bi atoms are displaced along both the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions, while Ti atoms are shifted along $\langle 111 \rangle$. Correlated dynamic hopping of Bi and Ti over their corresponding split sites combined with chemical disorder is proposed as the origin of the strong frequency dispersion observed in dielectric measurements. The existence of split sites also explains the reentrant dipole-glass behavior reported for this system. © 2015 AIP Publishing LLC.

Dielectric relaxation in solids has been intensively investigated for decades. These phenomena, manifested as frequency dispersion in the temperature dependence of the dielectric permittivity, typically occur in materials exhibiting chemical and/or displacive disorder combined with frustration of local electrical dipoles that freeze below a certain temperature. Dipole glasses and relaxor ferroelectrics are two widely researched classes of materials displaying such relaxation effects. Recently, a family of lead-free dielectrics that combines dipole-glass and relaxor features, dubbed “weakly coupled relaxors,” has been reported in solid solutions between BaTiO$_3$ and BiMO$_3$ (M=Sc, Mg$_{1/2}$Ti$_{1/2}$, Zn$_{1/2}$Ti$_{1/2}$). The dielectric properties of BaTiO$_3$-BiMO$_3$ solid solutions differ from those exhibited by relaxor ferroelectrics and relaxor-type ferroelectrics. These new materials crystallize with perovskite-like structures, and exhibit properties that are both fundamentally interesting and practically promising for high-energy, high-temperature capacitors sought for SiC power electronics.

Additions of BiMO$_3$ to BaTiO$_3$ suppress the typical ferroelectric phase transitions. For fractions of BiMO$_3$ greater than $\approx 0.1$, a pseudocubic structure is formed which exhibits a relatively flat dependence of dielectric constant on temperature, with strong frequency dispersion. Analyses of these dielectric data using common relaxation models returned large activation energies up to 0.3 eV. The relaxation mechanism in these systems has been traced to dynamic hopping of the A cations among the symmetry-equivalent strongly off-centered positions; this off-centering is stabilized by shortening of some of the A-O bonds, which is necessary to relieve the otherwise large tensile bond strain around the relatively small A-site species. Below, we propose that the dielectric relaxation observed in BaTiO$_3$-BiScO$_3$ solid solutions is caused by a mechanism similar to that for the disordered pyrochlores.

Our interpretation of the dielectric properties in the BaTiO$_3$-BiScO$_3$ solid solutions relies on the local structures found in these materials: large, partially correlated off-centerings of both Bi and Ti, driven by their bonding requirements, lead to multi-site probability density distributions (PDD) of both species; furthermore, the displacements of the neighboring Bi and Ti atoms are correlated. We use these results to propose a qualitative model that attributes the dielectric properties in the BaTiO$_3$-BiMO$_3$ systems to the presence of two distinctly coordinated ions undergoing correlated rattling (hopping) motions.

This study focuses on a single composition Ba$_{0.6}$Bi$_{0.4}$Ti$_{0.6}$Sc$_{0.4}$O$_3$ (BBTSO) dielectric properties of which have been well documented in the literature. The X-ray and neutron powder diffraction patterns of these samples featured surprisingly narrow (for a multicomponent solid solution) and symmetric Bragg reflections indexable according to a cubic $Pm\bar{3}m$ perovskite structure (Fig. S1). Rietveld

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refinements of this cubic model using the neutron diffraction data (Fig. S2) produced, however, a relatively poor fit with the residual inflated by the modulated background and broad bases of the peaks.\textsuperscript{14} The large refined values of the atomic displacement parameters ($\approx 0.04 \text{Å}^2$) for the Ba/Bi sites point to off-center displacements of Bi.

Crystal-chemical considerations suggest that local deviations from cubic symmetry in this system are inevitable because of the dissimilar ionic radii and charges of the constituent metal species. The presence of relatively large Ba ($R_{\text{Ba}} = 1.61 \text{ Å}$)$^{15}$ on the 12-fold coordinated A-sites and Sc ($R_{\text{Sc}} = 0.745 \text{ Å}$) on the 6-fold coordinated B-sites creates strongly oversized A-site cages for the Bi ions ($R_{\text{Bi}} \approx 1.31 \text{ Å}$) leading to abnormally stretched Bi-O bonds in an ideal cubic arrangement. Thus, Bi atoms are expected to be strongly off-centered to form short Bi-O bonds, thereby relieving the tensile bond strain. Octahedral tilting, which is a common distortion mechanism for reducing the A-O bond strain in perovskites, is precluded by a significant concentration of large Ba atoms.

A real-space atomic pair-distribution function (PDF)$^{16}$ obtained from the neutron total scattering confirms deviations from the average cubic model at least on the unit-cell scale (Fig. 1(a), Fig. S3). The presence of short Ti-O bonds (a negative\textsuperscript{17} peak at \( \approx 1.87 \text{ Å} \)) indicates that Ti atoms ($R_{\text{Ti}} = 0.605 \text{ Å}$) are off-centered within the oxygen octahedra; a peak corresponding to the longer Ti-O distances overlaps completely with the Sc-O peak (a positive peak at \( \approx 2.12 \text{ Å} \)). Direct interpretation of the local displacements/distortions for the A-cations is precluded by the close overlap of peaks corresponding to the A-O, O-O, and Sc-O distances. Fitting the neutron PDF over variable distance ranges (up to 80 Å) using crystallographic models\textsuperscript{18} (constrained according to cubic and tetragonal symmetries) provided no indication of a well-defined lattice distortion. Likewise, analysis of the difference between the experimental and calculated (cubic model) PDFs as a function of interatomic separation revealed no trends identifiable with distorted nano-regions that would average to a cubic structure at longer distances.

Another manifestation of the local atomic displacements is observed in electron diffraction patterns which exhibit pronounced structured diffuse scattering (Fig. 1(b)). Most of this scattering can be attributed to traces of the diffuse (111) sheets that pass through the Bragg reflections; the sheets are extinct through the origin and reflections with \( h + k + l = 2n + 1 \).

Similar diffuse scattering observed in several Pb- and Bi-based complex perovskites, including Pb(Zr,Ti)O$_3$\textsuperscript{19} Na$_x$Bi$_y$TiO$_3$\textsuperscript{20} and BaTiO$_3$-Bi$_5$Mg$_3$TiO$_9$\textsuperscript{21} has been ascribed to (111) displacements of the Pb/Bi and Ti cations correlated along the (111) directions. The distribution of the diffuse intensity appears to be inhomogeneous with visible condensation at certain locations, which may indicate the presence of not only longitudinal but also the transverse correlations.

We determined the ambient-temperature local structure of BBTSO using a Reverse Monte Carlo (RMC) algorithm, implemented in a modified version of the RMC Profile software,\textsuperscript{21–23} to refine instantaneous atomic positions against the multiple sets of experimental data. A random distribution of metal cations over the A (Ba/Bi) and B (Ti/Sc) sites was assumed.\textsuperscript{24} The following experimental datasets (a total of 17) were fitted simultaneously: (1) neutron total-scattering signal, S(Q); (2) neutron PDF, G(r); (3) X-ray S(Q); (4) X-ray G(r)\textsuperscript{14}; (5) neutron Bragg-peak intensities; (6) Bi L$_3$ edge extended X-ray absorption fine structure (EXAFS); (7) Sc K-edge EXAFS; (8) magnitude of the local Ti off-centering as determined from the intensity of the pre-edge peak in the Ti K-edge X-ray absorption spectra (XAS).\textsuperscript{25} (9) patterns of diffuse scattering in electron diffraction patterns representing \{221\}, \{331\}, and \{112\} sections of reciprocal space (a total of 9 patterns—3 permutations of equivalent hkl indices per section). The weights assigned to the individual datasets were adjusted continuously during the fit according to an algorithm which ensured that all the residuals eventually decreased to small preset values. The details of this algorithm will be reported separately.

The experimental and calculated signals for a subset of the fitted room-temperature data are illustrated in Fig. 2. The partial PDFs obtained from the RMC refinements confirm the strong off-centering of Bi which is accompanied by the formation of short ($\approx 2.2 \text{ Å}$) Bi-O bonds having a narrow distribution. This short Bi-O bond length appears to be common

![FIG. 1. (a) A low-r portion of the neutron PDF with the first few peaks labelled. (b) A representative (221) selected area electron diffraction pattern revealing the streaks of diffuse scattering.](image-url)
for the Bi-based perovskites that have been analyzed so far, as well as for the Bi-based displacively disordered pyrochlores. Likewise, the Ti-O partial PDF reflects a significant off-centering of Ti relative to oxygen (0.27 Å), which is larger than that in BaTiO$_3$ (0.22 Å). This enhanced Ti off-centering contrasts with the smaller average volume of the [TiO$_6$] octahedra in the solid solutions relative to BaTiO$_3$ and is evidently promoted by the large Bi displacements. The distributions of the Sc-O and Ba-O distances are unimodal.

The probability density distributions for the A and B cations at room temperature are summarized in Figs. 3 and 4. Clearly, Bi exhibits a 14-site distribution caused by its strong off-centering along both the (111) (8 sites) and (100) (6 sites) directions. The separation between the closest (111)- and (100)-displaced sites is ≈0.50 Å, whereas the separation between the distinct (111)-displaced sites is ≈0.8 Å. In contrast to Bi, Ba atoms feature a normal single-site distribution having a width similar to those for the individual Bi sites (Fig. 3(d)). The PDD of Ti acquires a well-defined cubic shape which is consistent with an 8-site distribution resembling that encountered in BaTiO$_3$. In this distribution, the individual sites are displaced from the ideal central position along (111) directions. The separation of the split Ti sites (≈0.16 Å) is similar to the displacements associated with “normal” thermal motion (≈0.15 Å) and, therefore, the 8 sites closely overlap. This separation corresponds to the Ti off-center displacements of ≈0.08 Å, which are similar to those previously measured for BaTiO$_3$ (≈0.1 Å).3,5 These measured Ti displacements are significantly smaller than those predicted from first principles in Ba(Zr,Ti)O$_3$.33 Scandium, like Ba, exhibits a unimodal PDF with a width similar to that observed for the individual Ti sites. Thus, both Bi and Ti acquire complex split-site PDDs, whereas Ba and Sc behave ordinarily. The oxygen atoms also display strongly anisotropic PDDs with preferential displacements along the (110) directions. These distributions can be attributed to strong oxygen displacements toward the nearest Bi ions; that is, both Bi and oxygen atoms shift toward each other to form the short Bi-O bonds.

As expected from the presence of the structured diffuse scattering, the cation displacements are correlated at least along the (111) directions. The correlation parameters (defined as in Ref. 22) decrease to zero over a distance of $\xi \approx 1.4$ nm. The correlations decay rapidly beyond the unit-cell scale presumably because of the chemical disorder with mixtures of smaller polarizable (Bi, Ti) and larger “blocking” (Ba, Sc) ions present on both A and B sites. This short correlation length is consistent with the widths of the diffuse streaks in the electron diffraction patterns. The correlation parameter (≈0.25) for the nearest A-B pairs, with all the chemically distinct pairs included in the calculations, is relatively small. However, correlations between the displacements of the Bi atoms residing in one of the B sites displaced along (111) directions with those of the nearest Ti atoms are significantly larger, yielding a correlation parameter of ≈0.5. These correlations minimize deviations of the bond valence sum$^{35}$ for the oxygen atoms from its ideal value (2 valence units). We also searched for the presence of negative (“antiferroelectric”) correlations among the directions of the cation displacements using the correlation function described in Refs. 33, 36; however, no significant correlations of this type could be observed.

The split-site PDDs for Bi and Ti hint at dynamic site hopping of these species as a possible mechanism of dielectric relaxation in the BaTiO$_3$-BiScO$_3$ solid solutions, in a manner reminiscent of that in disordered pyrochlores.12,13 The hopping processes for each of these rattling ions would have their own potential barriers and relaxation times distributed broadly because of the chemical disorder. The concurrent hopping of
Bi and Ti is expected to yield an even broader overall distribution of relaxation times thereby accounting for the strong frequency dispersion observed experimentally.\textsuperscript{1,7,9}

In the pyrochlore $\text{Bi}_1.2\text{Zn}_{0.92}\text{Nb}_{1.3}\text{O}_{6.92}$, the split Bi/Zn sites are separated by $\approx 0.4\AA$.\textsuperscript{12} and the energy barriers associated with the site hopping by Bi and Zn, disordered on the A-sites, are distributed between 0 eV and 0.2 eV.\textsuperscript{12,13} A simple Arrhenius fit to the dependence of frequency on the temperature of the dielectric-loss maximum yields an activation energy of 0.16 eV, which corresponds to the highest potential barrier.\textsuperscript{12} Recent theoretical calculations\textsuperscript{13} support these values. Another disordered pyrochlore $\text{Ca}_{1.5}\text{Ti}_{1.5}\text{NbO}_7$, featuring a mixture of Ca and Ti on the A-sites, exhibits dielectric relaxation with an even higher activation energy of 0.32 eV.\textsuperscript{11,13} which has been attributed to Ti hopping over the split sites separated by 0.7 Å. In BBTSO, the smallest site separation for the Bi sites ($\approx 0.5\AA$) is consistent with activation energies of 0.2 eV–0.3 eV. In fact, Bi sites displaced along $\langle 100 \rangle$ directions may correspond to local minima of the potential, thus providing pathways for Bi to move between the distinct $\langle 111 \rangle$-displaced sites. Crystal-chemical reasons suggest that the energy barriers for the site hopping should be lowered if neighboring Bi and Ti atoms move concurrently: such correlated displacements are supported by our experimental data; additionally, the oxygen atoms are also chemically affected by the hopping. Similar to the pyrochlores,\textsuperscript{13} the probabilities of hops between the nearest sites are expected to be the largest, especially for Bi. Considering that all the experimental data exhibited relatively small changes on cooling (these results will be reported in the follow up publication), we assume that the site separation is fixed by the local chemistry.

In pyrochlores, long-range ferroelectric order is precluded by frustration associated with the topology of a triangular lattice. In perovskite-like $\text{BaTiO}_3$-$\text{BiScO}_3$ solid solutions, such polar order is hindered by chemical frustration, which is caused by a random distribution of ions having strongly dissimilar sizes and charges. We believe that the correlated displacements/rattling of Bi and Ti are the key for partial unlocking of local polarization. This model does not invoke extended polar nanoregions of the kind encountered in relaxor, the existence or absence of which could not be confirmed from the present analysis. A somewhat similar (from the crystal-chemical point of view) correlated tunneling of the Li ion pairs within the multi-well potential has been previously observed in the Li-doped KBr.\textsuperscript{38,39}

The split sites and the site-hopping relaxation mechanism can also explain the non-monotonic dependence of remnant polarization on temperature with a maximum observed at the dipole-glass transition ($T_{\text{DG}}$).\textsuperscript{7} Our explanation assumes that in the temperature range over which a slim barrier is present, $P_r$. Upon further cooling ($T < T_{\text{DG}}$), the probability of site switching becomes small even under large electric fields and thus the polarization develops mostly via the intra-well ionic displacements. The relaxation times for these perturbations are still sufficiently short, yielding $P_r \approx 0$.

This model proposes that a coupled rattling motion on the A- and B-sites gives rise to the observed dielectric relaxation; while still a conjecture, it provides a crystal-chemical framework for rationalizing and tailoring the properties of $\text{BaTiO}_3$-$\text{BiMo}_3$ dielectrics. For example, substitution of smaller Sr for Ba is predicted to reduce the size of the A-site cages thereby diminishing the Bi off-centering and split-site separation, thus reducing the activation energy, modifying the characteristic relaxation times, etc. Given the potential practical importance of these materials, more detailed experimental and theoretical studies (e.g., broadband dielectric measurements, calculations of energy barriers associated with the site hopping, etc.) of the mechanisms underlying the properties of these materials are warranted.

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14See supplementary material at http://dx.doi.org/10.1063/1.4935417 for details of sample characterization.
17The contributions of Ti-O distances into neutron PDFs are negative because of the negative neutron scattering length of Ti.
24Distributions of the four constituent cation species mimicking local segregation and ordering were tried but yielded worse fits. High-angle annular dark field images recorded in a scanning transmission electron microscope revealed no significant variance in the distribution of Bi and Ba within the limitations of the projected imaging.
27The off-centering of Ti depends on both Ti and O displacements.