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Impedance spectroscopy of bismuth sodium titanate: Barium titanate ceramics with manganese doping

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Abstract

In this work we use Impedance Spectroscopy (IS) to study lead-free ceramics of perovskite structure \((\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3)_{0.925}(\text{BaTiO}_3)_{0.075}\) with Mn doping of 0, 0.2, 1.0, and 2.0 at.%. We compare our IS results with permittivity results, using dielectric to resistivity transformation equations which allow us to display results either as permittivity or as resistivity. We observe ionic conductivity dominating at lower temperatures, giving way to electronic conductivity at higher temperatures. The permittivity shows deviations from Curie-Weiss behavior characteristic of relaxor ferroelectrics. The 0.2% Mn samples show the highest ionic resistivity, which will reduce heating for high voltage piezoelectric applications. They also have the highest Curie-Weiss temperature and Burns temperature.

1 | INTRODUCTION

Ceramics based on grains of piezoelectric perovskite crystals have good piezoelectric response in the vicinity of the morphotropic phase boundary (MPB), but many of them contain lead which is toxic. Bismuth sodium titanate \((\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\) (BNT) based materials attract attention because of their large piezoelectric responses, which are comparable to those of lead-containing \(\text{Pb}(\text{Zr,Ti})\text{O}_3\) (PZT) solid solutions.\(^1\) Most studies of BNT-based compounds include BNT-BaTiO\(_3\),\(^2\)\(^-\)\(^5\) BNT-(\(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3\),\(^6\) BNT-KNbO\(_3\),\(^7\) BNT-BiFeO\(_3\),\(^8\) BNT-SrTiO\(_3\),\(^9\) BNT-(\(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3\)-SrTiO\(_3\),\(^10\) BNT-BaTiO\(_3\)-(K\(\_0.5\)Na\(_{0.5}\))NbO\(_3\),\(^11\) Zr-doped BNT-BaTiO\(_3\),\(^12\) and Mn-doped BNT-BaTiO\(_3\).\(^13\)\(^,\)\(^14\) Among the BNT-based materials, bismuth sodium titanate-barium titanate \((1-y)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-y\text{BaTiO}_3\) solid solutions near the morphotropic phase boundary (MPB) \((y = 0.06\)\(-0.08)\) between rhombohedral and tetragonal structures are of particular interest due to enhanced piezoelectric responses,\(^15\)\(^-\)\(^17\) accompanied by polar nanoregions (PNRs) and large electric \((E)\)-field-induced piezoelectricity.\(^17\)\(^-\)\(^19\) However, as mentioned in a recent review, the lower depolarization temperature \(T_d\) for compositions near the MPB causes concern regarding thermal stability under long-time operation.\(^20\)

We made two previous studies\(^14\)\(^,\)\(^21\) of \((\text{Bi}_{1/2}\text{Na}_{1/2})_{0.925}\text{Ba}_{0.075}(\text{Ti}_{1-x}\text{Mn}_x)\text{O}_3\) for \(x = 0, 0.2, 1.0,\) and 2.0 mol% (BNT7.5BT:x%Mn) ceramics, which are exactly the same four compositions examined in the present work. We found that manganese doping suppressed dielectric permittivity and increased relaxor behavior.\(^21\) Coercive field \((E_c)\) increases while remanent polarization \((P_r)\) decreases as Mn content increases. Most importantly, the depolarization temperature \((T_d)\) was enhanced remarkably to \(~152\)°C for the 0.2% Mn composition, compared to 93°C for no Mn. This enhanced \(T_d\) was attributed to two-phase coexistence and structural thermal stability induced by Mn ions. High-resolution synchrotron XRD and transmission electron microscopy (TEM) revealed two-phase coexistence of rhombohedral and tetragonal structures for \(x = 0\) and 0.2% Mn and an orthorhombic phase in 1 and 2% Mn-doped BNT7.5BT at room temperature.\(^14\) Scanning electron microscopy (SEM) showed grain sizes increasing from 2.1 \(\mu\)m for 0% Mn to 5.2 \(\mu\)m for 2.0% Mn.\(^14\) In situ temperature-dependent Raman spectra of 0% Mn BNT7.5BT revealed a structural transition from two-phase coexistence to
tetragonal phase near 190°C with a phonon softening anomaly.\textsuperscript{14} Also, 0.2%-2% Mn-doped BNT7.5BT showed phonon softening near 290°C upon heating.\textsuperscript{14} We concluded that Mn doping can enhance structural thermal stability in BN7.5BT ceramics as temperature increases.

This paper continues in Section 2 with experimental procedure including sample characterization. The presentation and discussion of experimental results in Section 3 begins in Section 3.1 with using ac impedance spectroscopy results to determine ac permittivity behavior. To make this determination we use the conversion relations between impedance and permittivity derived and presented in the Appendix A. These permittivity results in Section 3.1, show intertwined dielectric and conductivity behavior, including effects of phase-shifted conductivity.\textsuperscript{22} The dielectric behavior is typical of relaxor ferroelectrics,\textsuperscript{2} obeying a power law relation above the dielectric peak and then the Curie-Weiss law above the Burns temperature. The ac conductivity behavior is presented in Section 3.2, as Cole-Cole arcs of imaginary vs real resistivity. The plot for each temperature is adjusted from Zhu\textsuperscript{23} can be attributed to these compositions being near the morphotropic phase boundary, where small intended or unintended composition and processing differences can have large effects. In particular, it seems from our XRD results compared with those of Ref. [14], that our samples are closer to the parent cubic perovskite structure than those of Ref. [14], for which indications of rhombohedral, tetragonal, and orthorhombic phases were reported.

Disks were prepared for impedance spectroscopy (IS) by coating both faces with Ted Pella Inc. No. 16032 colloidal silver paste. The disks were not polarized. Fine 30-gauge silver wires were attached by dabs of silver paste to each face, and to the terminals inside a small 10-cm diameter homemade water-cooled oven which can attain 1000°C. These terminals were connected to a Solartron SI 1260 Impedance Gain-Phase Analyzer. Temperature was maintained and monitored with a Eurotherm 2404 controller. Runs were made from 100°C to 500°C or 600°C in 50°C steps using a 3°C/minute ramp rate, and a hold time of 5 minutes before measurements at each temperature. The frequencies used in earlier runs were 1 Hz to 1 MHz in 61 logarithmically spaced steps, and changed to start at 0.1 Hz and use 71 steps in later runs. For the earlier runs we thought that 1 Hz would be sufficient as a lowest frequency, but after analyzing these data we decided that 0.1 Hz for the later runs would be worth the considerable extra experimental time. Four runs through the frequency range were made at each temperature to verify that impedance did not change with time.

2 | EXPERIMENTAL PROCEDURE

The (Bi\textsubscript{1/2}Na\textsubscript{1/2}Ti\textsubscript{3}O\textsubscript{3})\textsubscript{0.92}Ba\textsubscript{0.075}(Ti\textsubscript{1-x}Mn\textsubscript{x})O\textsubscript{3} ceramic disks of about 1 mm thickness and 8.3 mm diameter were fabricated without and with B-site Mn doping, designated BNT7.5BT and BNT7.5BT:x%Mn\textsuperscript{y}, respectively. As indicated in this formula, it is expected that all Mn ions go into perovskite “B” sites, otherwise occupied by Ti ions, because of ionic size and valence considerations. These ceramics were prepared using the solid-state reaction. The starting materials were high purity (>99%) powders of Bi\textsubscript{2}O\textsubscript{3}, Na\textsubscript{2}CO\textsubscript{3}, BaCO\textsubscript{3}, TiO\textsubscript{2}, and MnO\textsubscript{2}. Stoichiometric amounts of powders were ball-milled for more than 24 hours in ethanol. The mixture was calcined at 900°C for 2 hour and a Retsch PM100 planetary ball mill was used to reduce particle size. The calcined powders were then pressed into disks that were sintered for 2 hours at 1170°C.

Three disks each were prepared with x = 0, 0.2, 1.0, and 2.0 at.% Mn doping. These are exactly the same x values as prepared in different ceramic batches in two of our previous works.\textsuperscript{14,21} The compositions are also close to those reported by Zhu et al.\textsuperscript{23} who used 8.0% instead of 7.5% Ba and atomic% Mn x values of 0, 0.45, 0.9, 1.5, 2.25, and 3.0. (They reported wt% MnO values of 0, 0.15, 0.3, 0.5, 0.75, and 1.0, and the conversion factor for wt% to at.% is almost exactly 1 to 3.). Their average density was 5.62 g/cm\textsuperscript{3}. Our densities found by the Archimedes method for samples with 0, 0.2, 1.0, and 2.0% Mn are 5.12, 4.98, 5.67, and 5.74 g/cm\textsuperscript{3}, respectively. The average density reported in Ref. [14] using the Archimedes method for x = 0, 0.2, 1.0, and 2.0% Mn was 5.79 g/cm\textsuperscript{3}. The theoretical full density based on unit cell dimensions from XRD and on the unit cell molecular weight is 5.78 g/cm\textsuperscript{3}.

3 | RESULTS AND DISCUSSION

3.1 | Permittivity calculated from transformed resistivity

Using the data for 1 Hz, 1 kHz, and 1 MHz for the most recent runs, for which our maximum temperature was...
600°C instead of 500°C, we use Equations A9 and A10 in the Appendix A to plot \( \varepsilon' \) and \( \tan \delta \) vs \( T \). These plots appear in Figure 1 for Mn concentrations of 0, 0.2%, 1.0%, and 2.0%, respectively. The higher temperature points for the 1 MHz runs were fit to the Curie-Weiss law as shown by dashed lines. Four of the points for 1 Hz are off scale because of high conductivity (for \( \tan \delta \)) and the phase-shifted component of this high conductivity (for \( \varepsilon' \)). Specifically, the calculated point for \( \varepsilon' \) for 0% Mn for 1 Hz is not shown because it is off scale (above 9000). Also, the calculated points for \( \tan \delta \) for 1 Hz are not shown for 0%, 1.0%, and 2.0% Mn because they are off scale (above 0.45). The vertical scale is not extended higher because such extension would not provide additional useful permittivity information. It would only provide indirectly some conductivity information, paralleling the conductivity information provided elsewhere in this paper. Specifically, the reason for not extending the vertical scale higher is best understood by looking at the Figure for 0.2% Mn which does show the 1 Hz points for both \( \varepsilon' \) and \( \tan \delta \). Both of these red curves are increasing with temperature almost exponentially at their highest temperatures, where their temperature dependences are governed almost entirely by phase shifted conductivity and by conductivity, respectively, as discussed elsewhere. Extending the vertical scale upward on all four Figure sections would only provide more of such exponential upturns.

The results for the four Mn concentrations show general agreement for both the relaxor ferroelectric permittivity including dielectric loss, and for the conductivity including phase-shifted conductivity. In discussing permittivity and conductivity phenomena, we define permittivity as any response that does not involve carriers moving from one unit cell to another, and conductivity as the response of ions or electrons that do drift from cell to cell under an electric field. One might think that conductivity behavior should appear only in \( \tan \delta \), but because of phase-shifted conductivity it appears also in \( \varepsilon' \). Every point, whether for \( \varepsilon' \) or for \( \tan \delta \), that would appear above the top of the plot, disappears because of the conductivity which increases exponentially with temperature. The upturn in \( \tan \delta \) at high temperature for

![FIGURE 1](color figure can be viewed at wileyonlinelibrary.com)
the 0.2% Mn sample at 1 kHz is also due to conductivity; otherwise it would follow the 1 MHz curve. Our samples show the typical relaxor ferroelectric behavior of a rounded peak rather than the sharp \( \varepsilon' \) peak characteristic of ordinary ferroelectrics. The peaks appear at temperatures \( T_m \) of 206°C to 230°C, and vary somewhat in height. The dielectric (not conductive) anomalies in tan\( \delta \) associated with these \( \varepsilon' \) peaks show up as small rounded peaks in tan\( \delta \) on the low-temperature side.

We compare results in Table 1 for four Mn concentrations in Figure 1 with those shown in Figure 1 of Ref. [21], for samples with the same Mn concentrations prepared in the same laboratory of co-author C.-S. Tu but from different batches. These comparisons are made at 1 MHz, because at lower frequencies some \( \varepsilon' \) peaks are shifted upward or even off scale by the phase-shifted conductivity effect. The results for both sample sets are qualitatively similar. Specifically, the peak permittivities for both sample sets lie between 4090 and 7500, and the temperatures \( T_m \) at these peaks lie between 206°C and 250°C. This strong overlap gives confidence that the temperature, permittivity, and resistivity calibrations in both laboratories are consistent.

To compare \( \varepsilon' \) permittivity for different samples, it is useful to have expressions with parameters which can be fit to the data. Below the temperature \( T_m \) for peak permittivity \( \varepsilon_m \), the fit may be difficult because there may be phase transitions in this region, as seen in figure 9 of Ref. [21], so we attempt to fit the data only above \( T_m \). Above \( T_m \), relaxor ferroelectric behavior caused by dipole clustering can be fit by a power relation up to the Burns temperature \( T_B \). Above \( T_B \), dipole clustering ceases and the sample obeys the Curie-Weiss law as for an ordinary ferroelectric. The \( T_B \) values range from 343°C to 443°C as shown in Table 1.

As usual, the fit to the Curie-Weiss law

\[
\varepsilon'(T,f) = C/(T - T_0) ; 1/\varepsilon' = (T - T_0)/C
\]

is performed by plotting \( 1/\varepsilon' \) vs \( T \). The higher-temperature points fit a straight line well. The temperature at which the extrapolated line hits the 1/\( \varepsilon' \) = 0 axis is the Curie-Weiss temperature \( T_0 \). The inverse of the slope of the line is the Curie-Weiss constant \( C \). Because \( \varepsilon' \) can exhibit an upturn at high temperatures and low frequencies due to phase-shifted conductivity,\(^\text{22}\) we evaluate \( T_0 \) and \( C \) at our highest \( f \) value, 1 MHz. Table 1 presents values for \( T_0 \) and \( C \), including values from Ref. [2].

Turning to the power-law region for which dipole clustering is prevalent, we are still at temperatures above the usual piezoelectric application range. For this region, the power-law-fit parameters \( \gamma \) and \( \Delta \). The power relation, which is applicable between \( T_m \) and \( T_B \), is written as

\[
1/\varepsilon' = (1/\varepsilon'_m) \left( 1 + \frac{1}{2} [(T - T_m)/\Delta]^{\gamma} \right) \tag{2}
\]

This relation was apparently first proposed by Martirena and Burfoot.\(^\text{24}\) They stated that the value 2 for the power \( \gamma \) corresponds to behavior for a “diffuse ferroelectric transition” which now is called relaxor ferroelectric behavior, whereas the value 1 corresponds to Curie-Weiss behavior. An expression similar to Equation 2 appears in Ref. [21], except that only \((T - T_m)\) is taken to the power \( \gamma \), while \( 1/\Delta' \) is replaced by \( 1/\Delta^2 \). In that Ref. [21] expression, \( \Delta \) which they call the broadening constant has dimensions of temperature only if \( \gamma = 2 \).

The method\(^\text{21}\) for determining the power \( \gamma \) starts by rewriting Equation 2 in terms of natural logarithms using the following steps, in which only \( \varepsilon' \) is a function of \( T \):

\[
\varepsilon'_m/\varepsilon' = 1 + (\varepsilon'_m - \varepsilon')/\varepsilon' = 1 + \frac{1}{2} [(T - T_m)/\Delta]^{\gamma} \tag{3}
\]

Subtracting 1 from each side and taking the \( \ln \), we obtain

\[
\ln[(\varepsilon'_m - \varepsilon')/\varepsilon'] = \gamma \ln(T - T_m) - \ln 2 - \gamma \ln \Delta \tag{4}
\]

Next, we plot \( \ln[(\varepsilon'_m - \varepsilon')/\varepsilon'] \) vs \( \ln(T - T_m) \) over the range \( T_m < T < T_B \), using equal horizontal and vertical scales, as shown in Figure 2. We fit the data points for each temperature to a straight line whose slope is \( \gamma \). The

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Curie-Weiss and power law fit parameters and peak permittivities for various Mn concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>( T_B ) °C</td>
</tr>
<tr>
<td>0.02</td>
<td>417</td>
</tr>
<tr>
<td>0.2</td>
<td>417</td>
</tr>
<tr>
<td>1.0</td>
<td>420</td>
</tr>
<tr>
<td>2.0</td>
<td>429</td>
</tr>
<tr>
<td>2.0</td>
<td>413</td>
</tr>
</tbody>
</table>
broadening constant $\Delta$ is found by rearranging Equation 4 as

$$\Delta = (T_B - T_m) / [2(\varepsilon_m - \varepsilon_B) / \varepsilon_B]^{1/\gamma},$$

where $\varepsilon_B$ is the permittivity found from the Curie-Weiss fit line at $T_B$. This formula for $\Delta$ allows no magnitude discontinuity between the power law and Curie-Weiss fit lines at $T_B$. There will, however, be a slope discontinuity. Such a discontinuity can be expected because Equation 2 is merely an empirical fit not derived from basic physics. Its value is in providing the constants $\gamma$ and $\Delta$ describing the relaxor behavior. Table 1 presents values from our work and Ref. [21] for $\gamma$ and $\Delta$. The agreement between the Ref. [21] results and ours for $\gamma$ and $\Delta$ is quite satisfying. Their exponent $\gamma$ increases with Mn content monotonically toward 2, agreeing with our values almost exactly except for the 1% Mn sample, where we found $\gamma = 2.12$. Note that $\gamma > 2$ is theoretically possible; it just means that the permittivity at higher temperatures drops off faster than predicted by the power law with $\gamma = 2$. The width parameter $\Delta$ values from both labs agree well, showing an upward trend with increasing Mn content. These upward trends for both $\gamma$ and $\Delta$ indicate increasing relaxor behavior.

3.2 | Impedance spectroscopy

Using ac impedance spectroscopy (IS), we obtained impedance plots of $\rho''$ vs $\rho'$ for four Mn concentrations from 100°C to 600°C. A plot of $-\rho''$ vs $\rho'$ for a 1% Mn sample at 250°C appears in Figure 3. It is untypical in that it shows two arcs more prominently than any of the other plots. In Figure 4 we present four plots, one for each Mn concentration, with the data “collapsed” or “scaled” to factor out the large thermally activated temperature dependence of the impedance. We used a similar presentation method previously for Bi$_{1-x}$Nd$_x$FeO$_3$ multiferroic ceramics. To collapse the data for a given sample for different temperatures, instead of plotting $-\rho''$ vs $\rho'$, we plot $-\rho''e^x$ vs $\rho'e^y$, where

$$e^x = \exp\left[(E_a/k_B)(1/673 - 1/T)\right].$$

Here, $E_a$ is the activation energy in joules, $k_B$ is Boltzmann’s constant, 673 is the Kelvin temperature corresponding to 400°C, and $T$ is the Kelvin temperature for a
given run. For a run at 400°C, the collapse factor $e^x$ is just 1. The activation energy $E_a$ is taken from Table 1 and is determined by a procedure explained below. To avoid cluttering the plots, we only present data at 100°C intervals, and only show data points for frequencies at integral powers of 10.

We first discuss the plot for the 0.2% Mn sample S3, because it is a “textbook example” of how collapsing the data improves its presentation. Only the results for 400°C, 500°C, and 600°C are shown, corresponding to the range of exponential temperature dependence resulting from electronic conductivity. The tendency for points for a given frequency to move leftward on an arc as temperature decreases is illustrated by the two points at the top of the arc, where for 400°C the top of the arc is at 100 Hz, whereas at 500°C the top of the arc is at 10 kHz. These arc plots often appear as slightly distorted and depressed circular arcs, or sometimes as more than one arc. In the plot for 0.2% Mn there is one arc, depressed to the extent that its center is at $(49 \ 500, 0)$ ohm-m instead of $(49 \ 500, 0)$ ohm-m. To fit a depressed semicircle to the arc, one can use the following relation:

$$-\rho'' = [\left(\frac{\rho_{dc}^2}{8\rho_{pk}} - \rho_{pk}/2\right)^2 + \rho_{dc}^2/8\rho_{pk}]^{1/2}$$

$$+ \rho_{pk}/2 - \rho_{dc}^2/8\rho_{pk}.$$  (7)

Here, $\rho_{pk}$ is the peak value of $-\rho''$ for a given $T$. We note the corresponding $\rho_{pk}'$ value and assume a symmetric main arc, so that $\rho_{dc} = 2\rho_{pk}'$.

The 0% Mn arcs are depressed more than the 0.2% Mn arcs. Also, the shape deviates from that for only one depressed arc, and consists of considerably depressed arcs at the left merging with the beginnings of second arcs on the right. The widest temperature range, from 100°C to 600°C, could be used for the 1% Mn sample arcs. At 100°C there is only a single arc. At 200°C there are two arcs of similar size. At 300°C there is one very asymmetric arc, while at higher temperatures there are large arcs at high frequency and small and flat arcs at low frequency. For 2% Mn there are two different activation energies used in the $e^x$ collapse factors. For 200°C and 300°C the lower activation energy corresponding to ionic conductivity is used, and there are large arcs merging into the beginnings of smaller arcs. For 500°C and 600°C the higher activation energy is used.

FIGURE 4 “Collapsed” resistivity plots for samples with 0%, 0.2%, 1.0%, and 2.0% Mn. The collapse factor is $e^x \equiv \exp\left[\left(E_a/k_B\right)(1/673 - 1/T)\right]$ as discussed in the text associated with Equation 6. Because 673 K is the Kelvin temperature associated with the 400°C runs, the 400°C resistivities correspond to the numbers on the horizontal and vertical scales because $e^x = 1$. The $E_a$ activation energies appear in Table 2 and must be multiplied by $1.602 \times 10^{-19}$ J/eV for use in the $e^x$ formula. The symbols are shown only for frequencies at each decade, $10^{-1}$-$10^6$ Hz, giving 8 points for each temperature [Color figure can be viewed at wileyonlinelibrary.com]
energy corresponding to electronic conductivity is used. There is a large arc at 500°C but only the tail end of a large arc at 600°C, both merging into low flat arcs. Appearance of a second arc in ceramics is generally attributed to grain boundary effects. In equivalent circuits, there is a grain boundary resistor in parallel with a grain boundary capacitor. This parallel pair is in series with a bulk resistor, and this three-element circuit is in parallel with a geometric capacitor. In a single crystal, the grain boundary resistor and capacitor would be absent. In a relaxor ferroelectric, the different dielectric responses of local polar regions can be expected to contribute additional arc flattening beyond the effects of grains and grain boundaries.

### 3.3 DC resistivity

The values chosen for dc resistivity \( \rho_{dc} \) are based on where each main high-frequency \(-\rho'' vs \rho'\) arc, such as those shown in Figures 3 and 4, extrapolates to the horizontal \( \rho' \) axis. If the arc has the shape of a flattened circular arc (circular but less than 180° of arc), then we use the procedure associated with Equation 7 to find our assumed \( \rho_{dc} \). If the shape of the arc is clearly not circular, but instead shows a point of inflection in going to a second arc, we extrapolate the curvature of the initial arc until it meets the \( \rho' \) axis.

A graph showing \( \rho_{dc} \) points plotted as \( \log(\rho_{dc}) \) vs \( 10^3/T \) appears in Figure 5. The points for a given sample are generally fit by a straight line. For the 2% Mn sample S3, the fit is to two straight lines, corresponding to what we believe is an ionic conduction mechanism at lower temperatures and an electronic conduction mechanism at higher temperatures. To complement the Figure 5 graph, Table 2 presents resistivities and their activation energies and their error bars. One might think that because for thermally activated conductivity with a single activation energy the resistivity obeys

\[
\rho = \rho_0 \exp(E_a/kT),
\]

one need only find and present error bars for \( \rho_0 \) and \( E_a \). One would do this by taking the log,

\[
\log \rho = \log \rho_0 + \left( E_a/kT \right) = \log(e) \log \rho_0 + 0.4343E_a/kT,
\]

and doing a least-squares fit to a straight line for the log \( \rho \) vs \( 1/T \) points using \( \log \rho \) and \( E_a/k \) as fit parameters. This is an inefficient and misleading procedure for two reasons. First, these two fitting parameters are highly correlated. Second, the error bars on \( \log \rho_0 \) will be much larger than the correct error bars on the data points because of the large extrapolation from the data points to the \( 1/T = 0 \) point corresponding to \( \rho_0 \). Instead, we pick a reference temperature near the middle of the data range, at Kelvin temperature \( T_r \), and use the corresponding log \( \rho_r \) as the fitting parameter, which will have only a weak correlation with the other fitting parameter, \( E_a/k \). Then the fit equation changes from Equation 8 to

\[
\log \rho = \log \rho_r + 0.4343(E_a/k)(1/T - 1/T_r).
\]

Then we find the \( (\log \rho_r, E_a/k) \) pair giving the least rms error \( \sigma \) for the \( n \) data points, using

\[
\sigma = \left[ \sum_{i=1}^{n} (\rho_{i\text{meas}} - \rho_{i\text{calc}})^2/(n-1) \right]^{1/2}.
\]

From Equation 10 this \( \sigma \) will be the rms error for the \( T_r \) temperature point, because the second term on the right vanishes and so it is assumed that the error for \( E_a/k \) does not enter.

To find the error bar for \( E_a/k \), we assume that by adding this error to the best fitting \( E_a/k \) value, but keeping the best fitting value for \( \rho_r \), we get the same increase in \( \sigma \) using Equation 4 as we get using the best fitting value for \( E_a/k \) but increasing the \( \rho_r \) value by the best-fit \( \sigma \) value. Once both of these error bars are found, we can use Equation 10 with \( 1/T \) set to 0 to find \( \rho_0 \). By using the error bars for

![Figure 5](image-url)
TABLE 2  Resistivity properties as functions of temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>T range</th>
<th>Fit range</th>
<th>$T_r$</th>
<th>$E_a$ (eV)</th>
<th>$\rho_0$ (ohm-m)</th>
<th>$\rho_0$ (ohm-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% Mn</td>
<td>100-500</td>
<td>150-500</td>
<td>300</td>
<td>0.77 ± 0.02</td>
<td>2.9 ± 0.2 × 10^3</td>
<td>4.8 ± 1.6 × 10^{-4}</td>
</tr>
<tr>
<td>0% Mn</td>
<td>100-600</td>
<td>150-600</td>
<td>350</td>
<td>0.74 ± 0.01</td>
<td>8.1 ± 0.6 × 10^2</td>
<td>7.8 ± 1.8 × 10^{-4}</td>
</tr>
<tr>
<td>0% Mn, “A”</td>
<td>25-600</td>
<td>400-600</td>
<td>500</td>
<td>1.66 ± 0.30</td>
<td>1.7 ± 0.7 × 10^4</td>
<td>2.3 ± 10^{-7a}</td>
</tr>
<tr>
<td>0.2% Mn S2</td>
<td>100-500</td>
<td>350-500</td>
<td>400</td>
<td>1.62 ± 0.01</td>
<td>6.0 ± 0.1 × 10^4</td>
<td>4.7 ± 0.8 × 10^{-8}</td>
</tr>
<tr>
<td>0.2% Mn S3</td>
<td>100-600</td>
<td>350-600</td>
<td>450</td>
<td>1.71 ± 0.01</td>
<td>1.26 ± 0.03 × 10^4</td>
<td>1.4 ± 0.2 × 10^{-8}</td>
</tr>
<tr>
<td>1% Mn</td>
<td>100-500</td>
<td>100-500</td>
<td>250</td>
<td>0.74 ± 0.07</td>
<td>1.4 ± 0.6 × 10^3</td>
<td>1.3 ± 10^{-4b}</td>
</tr>
<tr>
<td>1% Mn</td>
<td>100-600</td>
<td>100-600</td>
<td>300</td>
<td>0.68 ± 0.03</td>
<td>3.2 ± 0.8 × 10^2</td>
<td>3.2 ± 2.1 × 10^{-4}</td>
</tr>
<tr>
<td>2% Mn S2</td>
<td>100-500</td>
<td>100-400</td>
<td>200</td>
<td>0.63 ± 0.02</td>
<td>1.87 ± 0.16 × 10^3</td>
<td>3.4 ± 2.4 × 10^{-2}</td>
</tr>
<tr>
<td>2% Mn S3</td>
<td>100-600</td>
<td>150-350</td>
<td>250</td>
<td>0.53 ± 0.03</td>
<td>3.1 ± 0.2 × 10^4</td>
<td>2.4 ± 0.1 × 10^{-1}</td>
</tr>
<tr>
<td>2% Mn</td>
<td>100-600</td>
<td>450-600</td>
<td>500</td>
<td>1.46 ± 0.06</td>
<td>1.00 ± 0.05 × 10^2</td>
<td>3.0 × 10^{-6c}</td>
</tr>
</tbody>
</table>

For sample “A” the dielectric data presented in Ref. [2] were converted to resistivity as described in Section 3.3. Fit $T$ range is for log$\rho$ points that fall nearly on a straight line vs $10^{3}/T$. Here, $T_r$ is the reference temperature near the midpoint of the measurement range whose corresponding $\rho_0$ is a fit parameter. Both + and − error bars are shown for $\rho_0$ values if they are significantly different because of the long extrapolation to zero reciprocal temperature of the exponential resistivity function. $E_a$ values below and above 1 eV are assumed to correspond, respectively, to ionic and electronic conductions.

For sample “A” the dielectric data presented in Ref. [2] were converted to resistivity as described in Section 3.3. Fit $T$ range is for log$\rho$ points that fall nearly on a straight line vs $10^{3}/T$. Here, $T_r$ is the reference temperature near the midpoint of the measurement range whose corresponding $\rho_0$ is a fit parameter. Both + and − error bars are shown for $\rho_0$ values if they are significantly different because of the long extrapolation to zero reciprocal temperature of the exponential resistivity function. $E_a$ values below and above 1 eV are assumed to correspond, respectively, to ionic and electronic conductions.

We ran two 1% Mn samples, S1 up to 500°C and S2 to 600°C, and obtained excellent agreement. They had low activation energy characteristic of ionic conductivity. Their resistivity was the lowest of all the samples, low enough that on Figure 5 the data points (as also found for 0% Mn samples S2 and S3) did not reach the region where one would expect curvature to a higher slope indicating crossover to electronic conductivity.

For the first two 2% Mn samples, both run up to 500°C, there was disagreement in that the second sample S2 showed lower resistivity. Both showed low activation energies consistent with ionic conductivity, and a steepening of the slope at high temperature indicating the beginning of a crossover to electronic conductivity. To clarify this situation, we ran a third sample S3, up to 600°C. Up to 500°C the results from samples S2 and S3 agreed well, and by going to 600°C we obtained three data points for sample S3 falling on a steep straight line in Figure 5. This is the only sample for which we obtained two straight-line segments in Figure 5, indicating a low temperature region where ionic conductivity dominates and a high temperature region where electronic conductivity dominates.

4 | SUMMARY

Impedance spectroscopy measurements were made on (Bi$_{1/2}$Na$_{1/2}$)$_{0.925}$Ba$_{0.075}$(Ti$_{1-x}$Mn$_x$)$_3$O$_9$ ceramics ($x = 0\%$, 0.2\%, 1.0\%, and 2.0\%). The results are presented on Cole-Cole plots of arcs of imaginary vs real resistivity. The resistivities are multiplied by $c$ collapse factors which remove the exponential temperature dependence. Extrapolation to zero frequency of the primary (high frequency) arc provides assumed dc resistivities. From logarithmic plots of dc resistivities vs inverse temperature we determine the activation energies for the conductivity. These fall into two groups, above 1 eV attributed to electronic conductivity, and below 1 eV attributed to ionic conductivity.

Various effects can cause variations in results from different samples. These include possible differences in
preparation technique, and differences in electrical history (poling or piezoelectric measurements which require large applies voltage) which can affect phase coexistence and domain texturing,1,16,17 as well as effects of Mn valence.14 Correlations among results include increasing power law exponent $\gamma$ and increasing permittivity peak width parameter $\Delta$ with increasing Mn content, both for our present and previous results.21

We found previously21 that 0.2% Mn doping gives the highest depolarization temperature $T_d$ of 152°C, which is important for piezoelectric applications, compared to only 93°C for 0% Mn. The piezoelectric coefficient $d_{33}$ of 170 pC/N for 0.2% Mn is only slightly lower than the 186 pC/N value for 0% Mn.21 Because this 0.2% Mn doping seems best for applications, we mention here how the 0.2% Mn results of our present study differ from those for the other compositions. The 0.2% Mn samples show considerably lower ionic conductivities, which will reduce heating for high voltage piezoelectric applications. They also have the highest Curie-Weiss temperature and Burns temperature. These results add to the knowledge base concerning lead-free piezoelectric ceramics, and how doping can improve performance and enhance thermal stability to allow operation of piezoelectric devices at higher temperatures and at higher power levels.

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**SUPPORTING INFORMATION**

Additional Supporting Information may be found online in the supporting information tab for this article.

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**APPENDIX A**

**RELATION BETWEEN IMPEDANCE**

**ρ = ρ' + jρ'' AND PERMITTIVITY ε = ε' + jε''**

The apparatus supplies an ac voltage \( V \) to a sample that is a uniform slab of thickness \( d \) and area \( A \), so that the electric field is \( V/d = E = E_0 \exp(j\omega t) \). Then the current density \( J \) can be described in terms of complex conductivity \( \sigma \) as

\[
J = \sigma E = (\sigma' + j\sigma'')E. \tag{A1}
\]

We describe the response in terms of complex resistivity \( \rho = 1/\sigma \), so

\[
\sigma = 1/\rho = 1/(\rho' + j\rho'') = (\rho' - j\rho'')/(\rho'^2 + \rho''^2). \tag{A2}
\]

Then the response in Equation A1 can be written as

\[
J = [(\rho' - j\rho'')/(\rho'^2 + \rho''^2)]E. \tag{A3}
\]

The current density \( J \) can also be described as the time derivative of the electric displacement \( D \), where

\[
D \equiv \varepsilon_0 E + P. \tag{A4}
\]

For a linear dielectric this can be written

\[
D = \varepsilon_0 E = \varepsilon_0 (\varepsilon' + j\varepsilon''). \tag{A5}
\]

To find the corresponding \( J \), we take the time derivative of Equation A5 and obtain

\[
J = j\omega_0 (\varepsilon' + j\varepsilon'')E = \omega_0 (\varepsilon' - \varepsilon'' + j\varepsilon'). \tag{A6}
\]

The \(-\omega_0 \varepsilon''E\) term is the conduction current density. The \(j\omega_0 \varepsilon'E\) term is the capacitive charging current density which leads the field by 90°. Equating the real parts of Equations A3 and A6, we get

\[
\varepsilon' = -\rho'/\omega_0 (\rho'^2 + \rho''^2). \tag{A9}
\]

Then we plug \( \varepsilon' \) from Equation A9 into Equation A8 and solve for tan \( \delta \) by equating the real parts of Equation A3 and A8. From the imaginary terms we get

\[
\varepsilon'' = -\rho''/\omega_0 (\rho'^2 + \rho''^2). \tag{A10}
\]

To obtain the inverse relations, we start by noting that from Equation A10, \( \rho' = -\rho''\tan \delta \). Then we insert this relation for \( \rho' \) into Equation A9 and solve for \( \rho'' \), to obtain

\[
\rho'' = \rho'/\omega_0 \varepsilon' (\tan^2 \delta + 1). \tag{A11}
\]

Finally, we combine Equations A10 and A11 to solve for \( \rho' \), and obtain

\[
\rho' = \tan \delta/\omega_0 \varepsilon' (\tan^2 \delta + 1) \tag{A12}
\]

Using Equations A9-A12, we can transform between the resistivity and permittivity representations, without assumptions about an equivalent circuit. Expressions related to Equations A9-A12 appear elsewhere\textsuperscript{25,27} but without the derivation, and in terms of \( \varepsilon'' \) instead of tan \( \delta \), and complex impedance \( Z \) together with empty-cell capacitance instead of complex resistivity \( \rho \).