Size reduction-induced properties modifications of antiferromagnetic dielectric nanocrystalline Ba$_2$NiMO$_6$ (M = W, Te) double perovskites

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Abstract

The main objective of this work was to synthesize phase pure double perovskites Ba$_2$NiTeO$_6$ (BNTO) and Ba$_2$NiWO$_6$ (BNWO) in nanocrystalline form and to reveal the impact of nanocrystallinity on their magnetic and dielectric properties. The studied double perovskites were synthesized in nanocrystalline form by employing a citrate sol-gel route. A detailed investigation of their structure and properties using X-ray powder diffraction, scanning electron microscopy, Raman spectroscopy technique, energy-dispersive X-ray spectroscopy, SQUID magnetometry and electrical measurements is carefully described. Rietveld refinement of X-ray powder diffraction patterns revealed phase purity of both compounds: BNTO is trigonal ($R$-3m) while BNWO is cubic ($Fm$-3m). Raman spectroscopy studies reveal optical phonons that correspond to vibrations of Te$^{6+}$/W$^{6+}$O$_6$ octahedra, while scanning electron microscopy images show irregular plate-like nanocrystals. Magnetic property measurements speak in favor of antiferromagnetic order but, in both compounds, size reduction affected their properties. BNTO has Néel temperature ($T_N$) of 10.3 K which is higher than previously reported for its bulk form. Magnetic ground state of BNWO can be explained as canted antiferromagnetism with $T_N$ = 48.2 K. Room temperature measurements of dielectric constants at various frequencies suggest that these materials are high-$\kappa$ dielectrics with low dielectric loss. The Nyquist plot reveals depressed a semicircle arc typical for non-Debye type of relaxation phenomena for BNWO ceramic, whereas for BNTO ceramic an almost straight line of $Z''$ versus $Z'$ has been observed, indicating its high insulating behavior. To conclude, size-dependent properties of studied double perovskites are discussed, introducing a possibility for implementation in electronic devices.

Key words: antiferromagnetic; double perovskites; high-$\kappa$ dielectrics nanomaterials; size-dependent.
INTRODUCTION

Applied nanomaterials have become the focus of research due to the plethora of good properties yielding to their potential application. So far, metal and semiconducting nanoparticles have shown size- and shape-dependent electronic, magnetic and optical properties [1–3]. This behavior has marked nanomaterials to be superior than their bulk forms in terms of producing smaller devices with enhanced functionality. So, instead of altering chemical composition, it has become more important to produce nanomaterials with different architectures [3]. Therefore, many efforts have been put into development of rational size- and shape-controlling synthesis procedures, namely solution chemistry routes [4].

Green chemistry approaches have limited the usage of chemicals to be nontoxic and environmentally friendly. Large-scale industrial production demands for them also to be inexpensive, hence in choosing the right synthesis route, one should take into account all these things if possible. Simplicity of the synthesis route is also important. The citrate method was developed by Turkevich et al. [5], and nowadays, citric acid has been used with or without different additives in sol–gel synthesis of perovskite nanomaterials [6–13]. The greatest advantages of aqueous citrate sol–gel route are nontoxicity, eco-friendliness, low cost and simplicity.

Double perovskites have been widely investigated due to the possibility of magnetoelectric coupling within the single-phase material which is suitable for implementation in electronic devices and large variety of other applications, such as optoelectronics and photocatalysis [6, 14–16]. Ba$_2$NiWO$_6$ (BNWO) was firstly prepared by Fressia et al. [17]. Its crystal structure has later been studied by Brixner [18], Nomura [19], Cox [20], Filip’ev [21] and more recently by Sahnoun [22] and Alsbah [23, 24] along with its magnetic properties. Cox et al. [20] reported it to be antiferromagnetic with no further details, while Alsbah [24] reported it to be a semiconductor with indirect optical band gap value of 3.32 eV. Ba$_2$NiTeO$_6$ (BNTO) was first prepared by Turkevich et al. [5], and nowadays, citric acid has been used with or without different additives in sol–gel synthesis of perovskite nanomaterials [6–13]. The greatest advantages of aqueous citrate sol–gel route are nontoxicity, eco-friendliness, low cost and simplicity.

Herein, we present a simple, effective, low-cost synthesis method for the fabrication of nanocrystalline phase pure BNTO and BNWO double perovskites with detailed structural characterization and the study of size reduction effect on their magnetic and dielectric properties. These materials could have a promising application as antiferromagnetic high-κ dielectrics in electronic devices.

EXPERIMENTAL PROCEDURES

Materials

All chemicals were commercially available and used as purchased. Citric acid monohydrate pro analysis (T.T.T., Croatia) was used to prepare starting reaction solution. Precursor solution of metal cations was prepared by dissolving ammonium tungsten oxide hydrate or ammonium tellurate 99.5% (Alfa Aesar, Germany), Barium(II) nitrate > 99% and Nickel(II) nitrate hexahydrate ≥ 98.5% (Sigma Aldrich, Germany). Concentrated ammonia solution pro analysis (Gram-Mol, Croatia) was used for pH value adjustments.

Synthesis

Synthesis procedure used in this research was previously reported by our group [9, 10]. Stoichiometric amounts of Ba$^{2+}$, Ni$^{2+}$ and Te$^{6+}$/W$^{6+}$ salts were dissolved in 10% solution of citric acid (10 g of citric acid in 100 ml of MiliQ water) and pH value was adjusted to 5 in order to deprotonate citric acid. As-prepared solution was evaporated and constantly stirred at 95°C on a magnetic hotplate stirrer until black mixture was formed which was later dried for 24 h at 120°C in a drying oven. Grinded mixture was further calcined in two steps: 8 h at 600°C and 12 h at 950°C for BNTO and 1000°C for BNWO. The heating rate was kept at 2°C/min for both calcination steps.

All characterization techniques including measurements of magnetic properties were conducted on as-prepared materials in powder form. However, for measurements of dielectric properties, it was necessary to convert prepared powders into pellets because powder could not be placed between electrodes. The sintering of the green pellets of dimension (thickness: 1.5 mm and diameter: 10 mm) for dielectric measurements was conducted at 1250°C using tube furnace. The heating rate was 5°C/min and soaking time 4 h. Pellets were then rubbed with sand-paper to obtain a smooth parallel side and later a silver paste was painted on both the sides which act as an electrode layer during the electrical measurements. Archimedes method was used to measure the density of prepared pellets. It was confirmed that densities are above 91% theoretical density if sintering temperatures are ≥1250°C.

Characterization techniques

Crystal structure, microstructure, chemical composition and morphology determination.

X-ray powder diffraction (XRPD) analysis was performed on a Panalytical X’Pert PRO diffractometer (θ/2θ geometry) with monochromatized CuK$_\alpha$ radiation source (40 kV, 40 mA) at 292 (2) K. Data were collected with the step size of 0.02° in a 2θ range of 10–90°. Computer software FULLPROF [38] was used for the Rietveld refinement of collected XRPD data. In order to perform
size-microstrain analysis, the XRD profile has been modeled by employing modified Thompson–Cox–Hastings pseudo-Voigt function. The main premise was that the line broadening of the deconvoluted profile originated from the individual contributions of the line broadening caused by lattice microstrain and small crystallite sizes. Hence, half-width parameter $X$ ($V = W = 0$) was fixed at the values determined by using LaB$_6$ as a crystalline standard. The quality of the Rietveld refinement was conveyed with discrepancy factor ($R_{wp}$) and the goodness-of-fit ($\chi^2$). Computer software VESTA 3 [39] was used to visualize the crystal structure.

Unpolarized Raman spectroscopy was used to complement the powder X-ray diffraction results. It was recorded on powders placed on microscope slides at room temperature on Renishaw inVia Raman microscope system with a backscattering geometry, HeNe laser (633 nm, 2 mW) in the range of 50–1100 cm$^{-1}$.

Scanning electron microscope (M/S FEI Nova NanoSEM 450) was used for examination of morphology of powdered samples. Energy-dispersive X-ray spectroscopy detector coupled with scanning electron microscope was used for calculation of chemical composition.

**Magnetic properties measurements.**

Temperature-dependent susceptibility and isothermal magnetization have been investigated with a Quantum Design MPMS-XL-5 magnetometer on a powder sample. All presented data have been corrected for a temperature-independent sample holder contribution and a diamagnetic contribution estimated from Pascal’s constants [40].

**Dielectric measurements.**

The electrical properties like dielectric and impedance were done using a computer-operated LCR meter (Hikoi IM3570) in the frequency sweep of 0.1 kHz to 1 MHz and at room temperature.

**RESULTS AND DISCUSSIONS**

**XRD analysis**

Room temperature powder X-ray diffraction patterns confirm a perovskite phase formation for all synthesized compounds (Fig. 1a and b), and their phase purity since all observed Bragg reflections were matched with the calculated reflections based on the assumed structural models. Rietveld refinement analysis reveals that the BNTO crystallizes in centrosymmetric rhombohedra I space group $R$-3$m$ with $a = 5.7976(2)$, $c = 28.604(1)$ Å ($\gamma = 120^\circ$) for the unit cell in the trigonal setting, while BNWO crystallizes in cubic centrosymmetric space group $Fm$-3$m$ with lattice parameter $a = 8.0679(2)$ Å. The outcome of the Rietveld refinement is displayed in Fig. 1 whilst the results of the refinement are summarized in Table 1 and Supplementary Tables S1 and S2 in Supplementary data. Selected interatomic distances for both compounds are summarized in Table 2. Trigonal BNTO consists of face-sharing trimers, Ni$_2$TeO$_{12}$, which are alternatively interconnected via TeO$_6$ octahedra forming a typical 12-layer perovskite motif as displayed in Fig. 2 (left). Cubic BNWO is rock-salt ordered consisting of regular BaO$_{12}$ cuboctahedra and corner-sharing regular NiO$_6$ and WO$_6$ octahedra. Due to the similar size, ions located on the B sites of double perovskite structure were allowed to occupy the antistructures each other [41]. For BNTO compound, occupancies of Te and Ni were refined by imposing linear constraints of the site occupancies: $g$(Te$_{ni}$) = 1 – $g$(Ni), $g$(Te) = 1 – $g$(Te$_{ni}$), $g$(Ni$_{te}$) = 1 – $g$(Te), where $g$(B) refers to the site occupancy of B ion at the corresponding site while Te$_{ni}$ and Ni$_{te}$ denote antisite ions at the 6c and 3a/3b, respectively. The outcome of such constraint refinement revealed $g$(Te$_{ni}$) = 0.1191% or 11.92(5)% Ni/Te ions occupy antistructures each other. For BNWO compound there is only one site for W ions 4a and Ni ions 4b, and the constraint refinements yielded 5.2(2)% W$_{4a}$ (Ni$_{4b}$) antisite disorder. The refinement of oxygen site occupancy factors did not reveal any deviation from full occupancy within the standard deviation.

The line-broadening analysis performed within the Rietveld refinement reveals that BNWO shows higher crystallinity (average crystallite size equals to 88 nm) compared to BNTO (58 nm). In both cases, the Rietveld refinement has shown that the level of microstrain is negligible, i.e. parameter U was fixed to its instrumental value. The average crystallite size for BNTO is a bit larger compared to the value reported by Djerdj et al. [8], where a similar synthesis approach was used. Rietveld refinement yields satisfactory values of fitting quality parameter, $R_{wp}$ implying the right phase was chosen with appropriate lattice parameter values. Goodness of fitting (GoF) parameters are low within the standard deviation.

**Raman spectroscopy**

Raman spectroscopy has been carried out in order to investigate possible occurrences in disordered and nanocrystalline materials, such as phonon confinement effects. Also, bond length...
stretching was inspected. Recorded Raman spectra are shown in Fig. 3 for both BNTO and BNWO. Positions and assignment of observed Raman bands are summarized in Supplementary Table S3. According to Kroumova et al. [42], cubic BNWO has $A_{1g} + E_g + 2T_{2g}$, 4 first-order Raman active modes and trigonal BNTO has $7A_{1g} + 9E_g$ which is 16 first-order Raman active modes.

Figure 3a shows Raman spectrum of cubic BNWO where lattice translational mode is observed at 134 cm$^{-1}$, while oxygen bending mode can be seen at 432 cm$^{-1}$. Although according to Ayala et al. [43], $v_3$ octahedral stretching mode is absent in most cubic perovskites, it is observed here for BNWO at 552 cm$^{-1}$. The other octahedral stretching mode, $v_1$ is assigned to the highest wavenumber appearing in Raman spectrum, 807 cm$^{-1}$. Asymmetric broadening of Raman shifts in both compounds occur due to phonon confinement effect in nanocrystalline compounds [44–46]. Raman spectrum depicted in Fig. 3b shows six modes in total for trigonal BNTO. Lattice translational ($t$) and librational ($l$) modes [47] are depicted by two peaks: at 108 and 120 cm$^{-1}$ and at 220 and 250 cm$^{-1}$, respectively. Oxygen bending in TeO$_6$ octahedra ($v_5$ mode) can be seen in the range of 350–450 cm$^{-1}$. Modes $v_1$ (>700 cm$^{-1}$), $v_2$ (470–650 cm$^{-1}$) and $v_3$ (580–715 cm$^{-1}$) are assigned to octahedral BO$_6$ stretching according to Silva et al. [47]. For the case of studied BNTO compound, $v_1$ and $v_3$ vibrations are detected at 745 and 683 cm$^{-1}$, respectively. The differences in the line broadening of the Raman bands are similar to Sr$_3$Co$_2$WO$_9$ [10] and Sr$_3$Fe$_2$WO$_9$ [9], where it was explained by the structural disorder which is also present in this case in the form of antisite disorder (Ni/Te and Ni/W). A similar Raman spectrum of BNTO has already been reported by Djerdj et al. [8]. A larger difference in $v_1$ mode position is perceived between Te$^{6-}$- and W$^{6-}$-based compound which amounts to ~62 cm$^{-1}$. This is comparable to the previously reported observations for similar compounds [47]. Silva et al. [47] gave an explanation that the rise in wavenumber value in W-containing double perovskites compared to Te-containing correlates is a result of the increase of the bonding energy of W–O bond in WO$_6$ octahedron. The reason behind this is in $d$-orbital occupation of Te$^{6+}$ ($d^{10}$) and W$^{6+}$ ($d^2$). Fully occupied $d$ orbital avoids the formation of $\pi$-type Te–O bondings while empty $d$ orbital allows the overlap of the $t_{2g}$ orbitals [48]. Overlapping of $t_{2g}$ orbitals is responsible for the increase of bonding energy of W–O bond in WO$_6$ octahedron [47]. Even though the shortest bond in BNWO is apical Ni–O bond [1.956(11) Å], the formation of $\pi$-type W–O bondings took place. As a result, the increase of W–O bonding energy occurred. Consequently, Raman modes of W$^{6-}$O$_6$ prevailed causing the absence of Ni$^{2+}$O$_6$ vibrations.

**Morphology and chemical composition**

To investigate morphology of synthesized compounds and to confirm targeted chemical composition, scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectrosopy (EDS) was performed on powder samples. EDS spectra of both BNTO and BNWO are shown in Supplementary Figs S1 and S2 and quantitative composition is given in Supplementary Table S3.
Table S4. From the obtained data, empirical formulas that correspond to targeted compounds are calculated. SEM images of both compounds are shown in Fig. 4.

Figure 4 shows that both compounds are indeed nanocrystalline. The shape of crystal grains for BNTO is irregular hexagonal-like, while for BNWO is rather irregular plate-like and heterogeneous in size, similar as it was reported earlier for Ba$_3$Fe$_2$WO$_9$ [9] synthesized using the same synthesis procedure. The average grain size was calculated for the powder samples by the line intercept method. The obtained values are 73 and 101 nm for BNTO and BNWO, respectively. These values are larger than the average crystallite size values determined from the line broadening of powder XRD patterns. This is, however, expected because grains imaged by SEM may consist of several crystallites. Also, the line intercept method is not fully precise. The average grain sizes were also determined by the line intercept method for pelletized samples and they amount to 125 and 142 nm for BNTO and BNWO, respectively. These values are larger in comparison to the corresponding values obtained from the materials in powder form, which is the result of the sintering process.

Magnetic properties

As shown in Fig. 5, temperature-dependent susceptibility measurements were carried out while a magnetic field of 1000 Oe was applied. A maximum of susceptibility at $T_N = 10.3$ K is a clear evidence of a phase transition from paramagnetic to antiferromagnetic state. The measured $T_N$ is slightly higher than the reported 8.6 K [8, 26]. The difference can be attributed to the nanosized material with the average crystallite size of 58 nm used in our research. It has been shown that the increase in $T_N$ value is caused by the decrease of the crystallite size [30–36].

A zero-field-cooled (ZFC) and field-cooled (FC) susceptibility was measured in BNTO with no observed differences between the two cooling regimes. In a high-temperature region ($T > 200$ K) a Curie-Weiss law $\chi = C/(T-\theta)$ was used in order to describe the measured susceptibility. A full line in $\chi^{-1}$ versus $T$ plot (inset in Fig. 5) shows the best correspondence between the measured data. We obtained the Curie constant $C = 1.44$ emu K/mol and Curie-Weiss temperature $\theta = -155$ K. The effective magnetic moment $\mu = \sqrt{8}\mu_B = 3.4\mu_B$ is in a good agreement with the theoretical value for Ni(II) ions with a total electronic spin $S = 1$ and nonzero orbital contribution $L$ [49], while the negative Curie-Weiss temperature confirms the presence of antiferromagnetic interaction between the magnetic ions.

The high-temperature susceptibility (above $\sim 150$ K, Fig. 5) and inverse susceptibility of BNWO are similar to those of BNTO. Using data for $T > 200$ K in a Curie-Weiss fit, we obtained the Curie constant $C = 1.36$ emu K/mol (effective magnetic moment $3.3\mu_B$) and Curie-Weiss temperature $\theta = -110$ K for BNWO. These conclusions, obtained from the high-temperature susceptibility data, coincide with the previously published
They reported type II antiferromagnetism in BNWO with a TN of 48 K using a neutron diffraction study. Below 50 K we have found a large splitting between the ZFC and FC susceptibility (Fig. 5). However, the FC susceptibility sharply increases below the $T_c = 45.5$ K, which is an indication of ferromagnetic behavior below this critical temperature rather than antiferromagnetic as previously reported.

In order to obtain a deeper insight into the magnetic ground state of BNWO, additional temperature-dependent susceptibility measurements in different magnetic fields and isothermal magnetizations at several temperatures below and above the $T_c$ were carried out. The outcomes are displayed in Fig. 6.

The splitting between ZFC and FC susceptibility measured in 100 Oe is even larger than the one measured in 1000 Oe. From the data shown in Fig. 6a, we can conclude that with increasing the magnetic field in which the susceptibility was measured, the splitting between ZFC and FC susceptibility decreases. The splitting almost vanishes in magnetic field of 30 kOe where ZFC and FC curves practically coincide. The inset in Fig. 6a shows susceptibility around the transition temperature measured in 100 Oe (the smallest used magnetic field) and 50 kOe (the largest used magnetic field). While the abrupt increase of the susceptibility at $T_c = 45.5$ K when measured in 100 Oe clearly suggests the paramagnetic to ferromagnetic transition, the measured maximum of the susceptibility in 50 kOe at $T_N = 48.2$ K and no abrupt increase of the susceptibility immediately below this temperature confirm the previously reported antiferromagnetic ground state.

The magnetization curves shown in Fig. 6b are in agreement with already-described dual nature of the system. In a full scale, between $-50$ kOe and $50$ kOe, the magnetization curves at all investigated temperatures between $50$ K and $2$ K are linear up to the maximal magnetic field. The magnetization of $\sim 0.07 \mu_B$ per Ni$^{2+}$ ion measured in a maximal magnetic field of $50$ kOe ion is almost constant below $50$ K. This value is considerably smaller than the theoretical saturation value for Ni(II) ions ($J = S = 1$) of $gJ\mu_B = 2 \mu_B$. So this ‘full range’ picture suggests the antiferromagnetic ground state.

However, when the magnetization is observed in a small enough magnetic field (inset in Fig. 6b), clear hysteresis loops are seen for the measurements at $40$ K and below. The remanent magnetization at $2$ K is $2.4 \times 10^{-3} \mu_B$/Ni and almost linearly decreases down to zero at $45$ K. We tentatively attribute this weak ferromagnetic signal to a non-completely colinear antiferromagnetic arrangement of nickel magnetic moments. Thus the magnetic ground state of BNWO nanocrystalline system may be classified as a canted antiferromagnetism.

Dielectric and impedance properties

Figures 7a and b show the dielectric constant and loss factor versus frequency plot, respectively, for BNTO and Figs 7c and d for BNWO ceramics at room temperature. For both BNTO and BNWO ceramics, the dielectric constant value is higher in the low-frequency area which is considered to be $<10$ kHz. The high-frequency area is $>10$ kHz. The dielectric constant value in the low-frequency region has several polarization contributions whereas the effect of polarization fades at a higher frequency region, while in the high-frequency region its value becomes almost constant [51]. As the frequency increases, the switching polarity period is reduced as the electric field keeps on deviating very quickly and the space charge polarization also fades in this region. Therefore, the charge carriers fail to act in response to the fast-varying electric field. The reduction of the dielectric constant along with the frequency is associated with the hopping mechanism. The $W^{n+}$ has an effective positive charge in BNWO which leads to conduction of electrons leading to higher dielectric constant of 290 than BNTO which is 96 at 0.1 kHz. The frequency dependence of the loss factor follows the dielectric constant behavior for both the BNTO and BNWO samples. It is
noteworthy that loss factor for BNTO compound is significantly lower compared to BNWO: 0.21 for BNTO compared to 1.6 for BNWO at 0.1 kHz. The loss factor increases in the low-frequency region whereas in the high-frequency region it reduces. The reason behind this can be the rise in leakage current from various ionic charge balance or dislocation [52]. Also, average crystallite size and average grain size are larger in BNWO than in BNTO. This might cause the difference in values of dielectric constant aside from chemical composition. Various authors have shown that dielectric constant increases with the increase of grain size [53–55].

To further understand the electrical properties of synthesized compounds, the complex impedance (Z*) has been studied in order to disclose the resistive or/and capacitive contribution to conductivity of the material after applying AC electric field [56]. The impedance spectroscopy is convenient to investigate the conduction mechanism and electrical properties. Cole–Cole plots (Nyquist plots) are represented by the variation of imaginary part (Z″) against the real part (Z′) of the complex impedance (Z*), as shown in Fig. 8. Nyquist plot (Z′ vs Z″) displayed in Fig. 8 sheds light upon the morphology, for instance, bulk effect and extrinsic effects like grain boundaries formed after the sintering, specimen, electrode interfaces, defects, etc. The relaxation process is resembled by means of a semicircle in the Nyquist plot. If Debye-type conduction occurs then the semicircle center lies on the real Z′ axis while for the non-Debye-type process, the center will lie down under the real Z′ axis making a depression angle. A perfect semicircular arc with a single relaxation mechanism is depicted in homogeneous materials. As a consequence, arcs can be described in relation to the parallel RC circuit which is known as Debye-type behavior. For BNTO compound depicted in Fig. 8b, one can observe nearly straight line of Z″ versus Z′. This indicates a high insulating behavior in BNTO double perovskite. BNWO shows depressed semicircle arc (Fig. 8a) representing the non-Debye type of relaxation mechanism most probably due to inhomogeneity in grain sizes of ceramic samples. This is confirmed by SEM images of pelletized samples in insets of Fig. 4. The fitting of the experimental impedance data with the equivalent electrical circuit was performed by using demo version of ZSWIMP WIN software which is limited to only fitting features but restricts to achieve the values of the resistances and capacitances. For both materials BNTO and BNWO, the Nyquist plot shows that there is a contribution of grain and grain boundary in the materials at room temperature. The experimental impedance data are fitted with the RQC-RC equivalent circuit model depicting the contribution of grain and grain boundary.

**CONCLUSIONS**

In this study two nanocrystalline double perovskites, BNTO and BNWO were successfully synthesized by employing simple, low-cost and nontoxic aqueous citrate sol–gel method. According to the powder XRD measurements and Raman spectroscopy, they are single-phased. Synthesized double perovskites crystallize in centrosymmetric cubic space group Fm-3m (BNWO) and centrosymmetric rhombohedral space group R-3m (BNTO). Both materials are nanocrystalline having an average crystallite size of 58 nm for BNTO and 88 nm for BNWO with negligible microstrain. Partial disorder has been observed for both compounds in terms of Te/WNi antisite disorder which is a bit more pronounced for BNTO [11.92(5) %]. Both compounds are antiferromagnetic with pronounced size-effect modifications. BNTO has a larger value of TN = 10.3 K than previously reported in literature due to crystallite size reduction to 58 nm. For BNWO, Néel temperature has been measured in the field of 50 kOe and it amounts to 48.2 K. However, in the field of 100 Oe there is a clear ferromagnetic transition with TC = 45.5 K. This behavior speaks in favor of canted antiferromagnetism. Measurements of room temperature dielectric constant versus frequency reveal that both double perovskites possess relatively large dielectric constants at low frequencies (BNWO 290, BNTO
96 at 0.1 kHz). The observed reduction of dielectric constants along with the frequency is associated with the hopping mechanism. Impedance spectroscopy results in the form of Nyquist plot revealed depressed semicircle arc suggested the non-Debye type of relaxation phenomena for BNWO ceramic, whereas for BNTO ceramic nearly straight line of $Z''$ versus $Z'$ has been observed indicating its high-insulating behavior.

**SUPPLEMENTARY DATA**

Supplementary data is available at Oxford Open Materials Science online.

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**AUTHORS’ CONTRIBUTIONS**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. I.D. contributed to conceptualization and funding acquisition; J.B. and D.T. optimized the synthesis method and prepared samples for all measurements. J.B. also performed formal analysis and wrote the original draft with the inputs from other co-authors; I.D. did detailed Rietveld refinement of all XRD data in the article; Z.J. measured and characterized all the magnetic properties; M.S. is responsible for the detailed dielectric and impedance studies along with its characterization; I.D. did the review and editing.

**CONFLICT OF INTEREST STATEMENT**

There are no conflicts of interest to declare.

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