

Effect of simultaneous substitution of magnesium and niobium on dielectric properties and phase transition temperature of bismuth sodium barium titanate ceramics

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(Bi_{1/2}Na_{1/2})_{0.94}Ba_{0.06}Ti_{1-x}(Mg_{1/3}Nb_{2/3})_xO₃ ceramic samples with x = 0.0, 0.01, 0.05, 0.15, 0.20 were synthesized by solid state method. Microstructure, dielectric properties, impedance and conductivity of the ceramics were studied. Phase formation was confirmed by X-ray diffraction. Co-doping of the ceramics with Mg and Nb at x = 0.01 raised the dielectric constant from 6510 to 8225 at the frequency of 1 KHz. Further increase in (Mg_{1/3}Nb_{2/3})⁴⁺ concentration up to 0.15 increased the transition temperature from 275 °C to 339 °C and lowered the dielectric constant. The ac impedance measurements showed a linear response with frequency at lower temperature indicating insulating behavior and a single semicircular arc with spike at higher temperature.

Keywords: (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃; dielectric properties; ferroelectric properties; sintering and microstructure

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1. Introduction

Perovskite type oxides like Pb(Mg_{1/3}Nb_{2/3})O₃, Pb(Zn_{1/3}Nb_{2/3})O₃ and Pb(Zr,Ti)O₃ have been shown to be extremely useful for a variety of applications in ferroelectric and piezoelectric devices [1]. Most of these materials are lead based with more than one cation occupying the octahedral lattice sites. The presence of heterovalent ions with different ionic radii, valence states and varying polarizabilities in the octahedral site were found to be effective in enhancing the dielectric, electrical and electromechanical properties. However, the toxicity of lead and volatilization of toxic PbO during processing of these materials have resulted in an increasing demand for alternate environmental friendly materials.

Bismuth sodium titanate (BNT), a perovskite material with Curie temperature $T_C = 320$ °C, remanent polarization $P_r = 38$ μC/cm² and coercive field $E_C = 73$ kV/cm reported by Smolenskii *et al.*, has been projected as a potential candidate in place of lead based piezoelectric ceramics [2]. Nevertheless, the electrical properties of the BNT ceramics are not

as good compared to lead-based piezoelectric ceramics. Takenaka reported that BNT-based solid solutions with a rhombohedral-tetragonal morphotropic phase boundary (MPB) composition showed better piezoelectric and pyroelectric properties when compared with unmodified BNT ceramics [3]. It has been reported by Li *et al.* and others that the composition close to the MPB has relatively good piezoelectric and dielectric properties after the addition of 6 % of BaTiO₃ [4–8]. Lead-free bismuth sodium titanate-sodium niobate (BNT-NN), [Na_{0.5(1-x)}Bi_{0.5(1-x)}](Ti_(1-x)Nb_x)O₃ ceramics was prepared by using conventional ceramic technique by Li *et al.*, [9]. They concluded that d_{33} increased from 64 to 88 pC/N for 2 mol% of NaNbO₃ and then decreased gradually. However, the dielectric constant increased gradually with the increase in NaNbO₃ content. This was attributed to the co-effect of the soft additive Nb⁵⁺ ion doping at B-site and hard additive Na⁺ ion doping at A-site. Another report states that Bismuth Sodium Titanate (BNT) mixed with KNbO₃ (KNN) systems are orthorhombic up to 2 % BNT, tetragonal up to 9 % BNT and cubic thereafter. At the 2 % BNT MPB, a d_{33} of 195 pC/N and a Curie temperature of 395 °C were reported [10]. BNT exhibited relaxor behaviour with

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a less temperature stable dielectric constant [11]. Therefore, several more studies have been made to enhance its ferroelectric properties by forming solid solutions with $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ [12], $\text{Ba}(\text{Ti,Zr})\text{O}_3$ [13], $\text{Bi}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ [14], BiFeO_3 [15] as well as with cations of rare earth and transition metal ions like Ce^{4+} [16], Mn^{4+} [17], La^{3+} [18], Fe^{3+} [19] and Nb^{5+} [20]. Among the various systems that have been reported, bismuth sodium barium titanate $(\text{Bi}_{0.5}\text{Na}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ (BNBT) solid solution that exhibited a morphotropic phase boundary (MPB) near $x = 0.06$ showed relatively enhanced piezoelectric properties. Hence, the present work is undertaken to investigate the effect of simultaneous substitution of Mg and Nb at B site of BNBT, on the dielectric properties, microstructure and phase transition temperatures.

2. Experimental methods

The starting materials were AR grade Bi_2O_3 , BaCO_3 , TiO_2 , Na_2CO_3 , MgO and Nb_2O_5 . All compositions were prepared by conventional solid-state reaction. Stoichiometric amounts of precursor powders corresponding to the compositions $\text{BNBT}(\text{MN})_x$, where $x = 0.0, 0.01, 0.05, 0.15, 0.20$ were mixed in ethanol media and well ground in an agate mortar. The mixed powders were calcined at 900°C for 3 h. The calcined powders were further ground and formed into pellets with PVA as binder. The pellets were sintered on a platinum foil covered with crucible at 1150°C for 2 h. Phase formation was followed using X-ray diffractometer (PANalytical-X' Pert PRO, Japan) with $\text{CuK}\alpha$ radiation. For dielectric measurements, silver paste with glass frit as binder to form a conductive film after heating was coated on the polished surface of the pellets and fired at 600°C for 30 min. Phase sensitive multimeter (N4L PSM 1700) was used to measure the complex impedance, capacitance, quality factor, resistance, dielectric loss, phase angle and inductance in series and parallel as a function of temperature in the frequencies ranging from 100 Hz to 1 MHz at 3°C per minute heating and cooling rates from room temperature to 400°C . Microstructure of sintered samples was studied by SEM (JEOL-JSM-6610LV, Tokyo, Japan). Phase transition tempera-

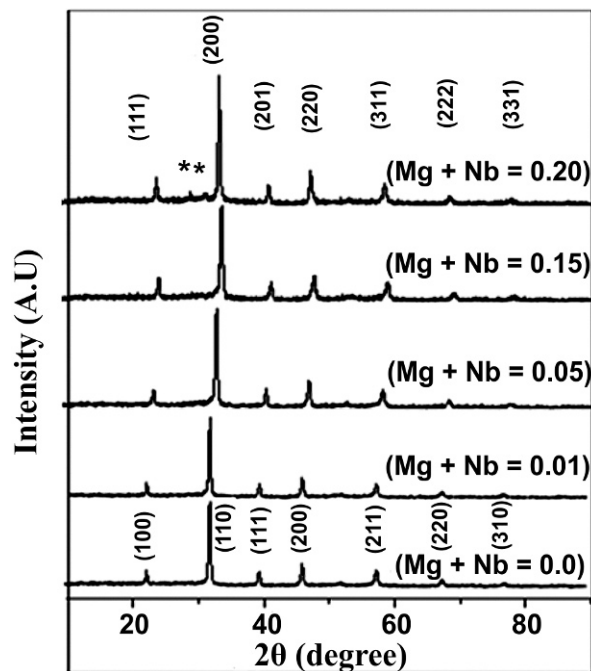


Fig. 1. X-ray diffraction patterns of $\text{BNBT}(\text{MN})_x$ for $x = 0.0, 0.01, 0.05, 0.15$ and 0.20 . The powders were heat treated at 900°C for 3 h.

tures for calcined powder samples were obtained while heating at the rate of 3°C per minute up to 600°C using DSC 823e (METTLER TOLEDO, Japan).

Compositions with $x = 0.0, 0.01, 0.05, 0.15$ and 0.20 in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{Ti}_{1-x}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$ are denoted in subsequent discussion as BNBT, $\text{BNBT}(\text{MN})1$, $\text{BNBT}(\text{MN})5$, $\text{BNBT}(\text{MN})15$ and $\text{BNBT}(\text{MN})20$.

3. Results and discussion

XRD patterns of pure BNBT and $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{Ti}_{1-x}(\text{MN})_x\text{O}_3$ samples with $x = 0.01, 0.05, 0.15, 0.20$, where MN refers to $(\text{Mg}_{1/3}\text{Nb}_{2/3})$, are shown in Fig. 1. From the figure, it can be seen that the XRD patterns of $x = 0.0$ samples are in good agreement with that of rhombohedral $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (JCPDS file No. 36-0340) and XRD patterns for $0 < x \leq 0.15$ samples are in good agreement with XRD pattern of monoclinic BNT (JCPDS file No. 46-0001) indicating the formation of phase pure samples.

Table 1. Lattice parameters and densities of $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{Ti}_{1-x}(\text{Mg}_{\frac{1}{3}}\text{Nb}_{\frac{2}{3}})_x\text{O}_3$ samples, where x refers to a dopant concentration of 0.01, 0.05, 0.15 and 0.20, respectively.

Composition	Lattice parameters in Å			Density	
	a	b	c	Experimental	% Theoretical
BNBT(MN)1	4.1595	2.7607	5.8818	5.684 g/cm ³	99.5 %
BNBT(MN)5	4.1692	2.7560	5.8759	5.587 g/cm ³	98.7 %
BNBT(MN)15	4.140	2.7006	5.7719	5.57 g/cm ³	96.1 %
BNBT(MN)20	4.1352	2.7506	5.6352	5.52 g/cm ³	92.2 %

BNBT(MN)x sample with $x = 0.20$ shows two extra peaks of very small intensity at $2\theta \sim 28^\circ$ and 30° . The extra peaks observed could not currently be assigned to any phase. The lattice parameters of BNBT(MN)x materials with $x = 0.01, 0.05, 0.15$ and 0.20 have been calculated by using a standard computer program “POWD”, and tabulated in Table 1 with corresponding relative densities of 99.5 %, 98.7 %, 96.1 % and 92.2 % respectively. The apparent crystallites size and lattice strain of BNBT(MN)x samples with $x = 0.0, 0.01, 0.05, 0.15$ and 0.20 were estimated by analyzing the X-ray diffraction peak broadening. The corresponding values of crystallite sizes and lattice strains were obtained as 44.2 nm, 28.96 nm, 26.7 nm, 27.6 nm and 1.6×10^{-3} , 2.3×10^{-3} , 2.2×10^{-3} , 1.5×10^{-3} respectively.

3.1. Thermal analysis

Differential scanning calorimeter measurements carried out on calcined powder samples showed a significant influence of magnesium and niobium co-doping on the two anomalous transition temperatures of bismuth sodium barium titanate as depicted in Fig. 2. The phase transformation temperatures determined for the base material BNBT ($T_d = 88^\circ\text{C}$ and $T_C = 275^\circ\text{C}$) are relatively close to the results reported by Xu *et al.* [21]. Each DSC curve of BNBT(MN)x for $x = 0.0, 0.01, 0.05$ and 0.15 samples shows two small endothermic peaks assigned as antiferroelectric to ferroelectric (AFE-FE) at 88.25°C , 88.22°C , 88.85°C and ferroelectric to paraelectric (FE-PE) at 304°C , 333°C , 339°C phase transition temperatures, respectively. The figures show that the substitution of Mg^{2+} and Nb^{5+} in place of Ti^{4+} in the host compound increases the

transition temperature (T_C) from 275°C to 304°C , 333°C and 339°C for $x = 0.0, 0.1, 0.05$ and 0.15 , respectively. This increase in the T_C may be explained in terms of variations in ionic sizes. The ionic radius of Mg^{2+} (0.72 Å) and Nb^{5+} (0.64 Å) are larger than that of Ti^{4+} (0.62 Å), that may have caused a lattice distortion or expansion, and resulted in an increase of dielectric constant and transformation temperature (T_C), which is consistent with the X-ray studies.

3.2. Dielectric studies

Temperature dependence of dielectric constant ϵ' and dielectric loss at 1 KHz, 10 KHz and 50 KHz for the samples BNBT(MN)x with $x = 0.0, 0.01$ and 0.05 , sintered at 1150°C for 2 h are shown in Fig. 3.

In the measured frequency range of 1, 10 and 50 KHz all samples exhibited the highest dielectric constant at 1 KHz. BNBT(MN)1 showed higher ϵ_{max} values of 8225, 6270 and 5592 compared to the 6510, 5429 and 4340 values for pure BNBT at 1, 10 and 50 KHz, respectively. The variation in $\tan \delta$ was also less for BNBT(MN)1 compared to BNBT up to 300°C . When the concentration of $(\text{Mg}_{\frac{1}{3}}\text{Nb}_{\frac{2}{3}})^{4+}$ increased above 0.05, the values of ϵ' decreased below that of pure BNBT. The maximum values of dielectric constant and dielectric loss tangent were shifted to higher temperature both with increasing frequency and concentration of $(\text{Mg}_{\frac{1}{3}}\text{Nb}_{\frac{2}{3}})^{4+}$. The increase in dielectric loss tangent at expense of dielectric constant at temperatures above 300°C might be due to the migration of high number of charge carriers, like sodium metal ions because of their small ionic size. The BNBT(MN)x samples showed relaxor behavior in terms of variation of

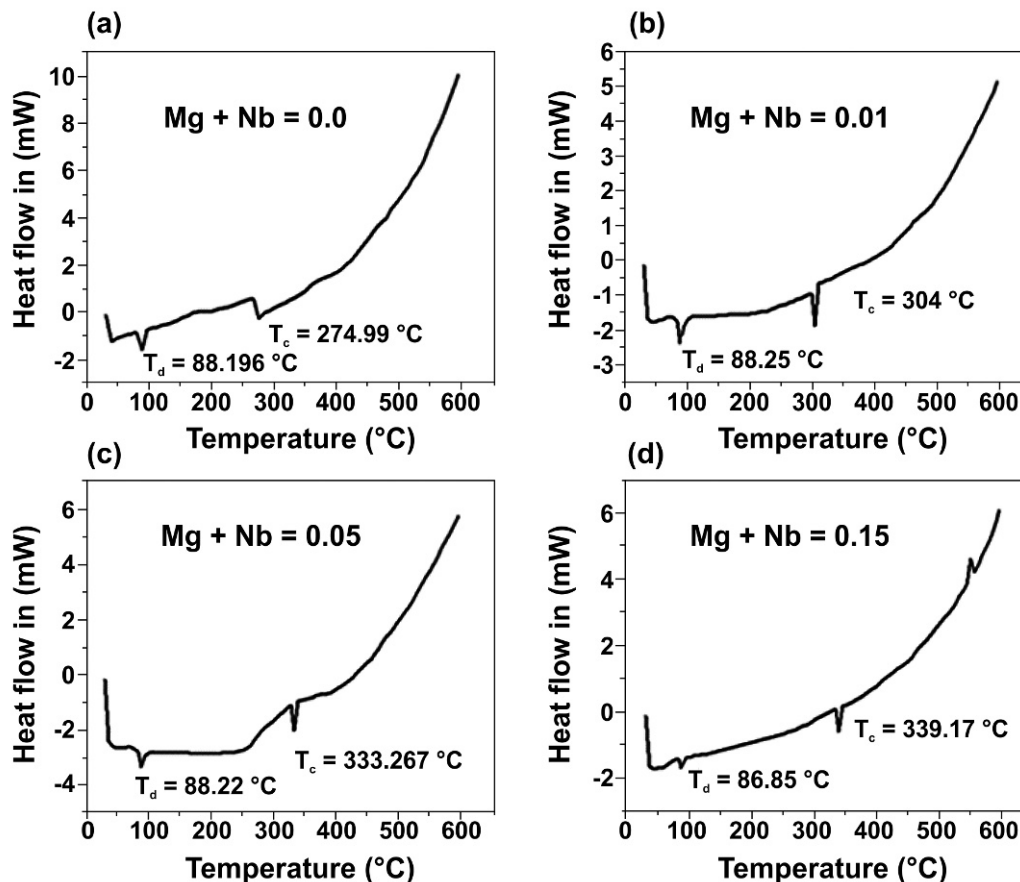


Fig. 2. DSC curves of powder ceramic samples of BNBT(MN) x with $x = 0.0, 0.01, 0.05$ and 0.15 from room temperature to $600\text{ }^{\circ}\text{C}$ at the heating rate of $3\text{ }^{\circ}\text{C}$ per minute.

ϵ' with frequency as shown in Fig. 3. This may be due to the heterogeneity caused by Na^+ , Ba^{2+} , Bi^{3+} and Ti^{4+} , Mg^{2+} Nb^{5+} cations in the A and B lattice sites respectively.

3.3. Microstructure

Fig. 4 shows the SEM micrographs of fractured surfaces of sintered pellets of pure and, magnesium and niobium co-doped BNBT. All samples have shown dense microstructure for the compositions BNBT(MN) x , where $x = 0.0, 0.01, 0.05$ and 0.15 with average grain sizes in the range of $1\text{ }\mu\text{m}$. However, from the grain size variations seen in SEM micrographs, it may be noticed that there is a slight increase in grain size for niobium and magnesium content of 0.15 . This may be due to the increase in magnesium ion concentration at the grain boundary of BNBT crystal.

3.4. Impedance spectroscopy

The variation of real and imaginary part of impedance as a function of applied field frequency (Nyquist plot) for BNBT(MN) x with $x = 0.01, 0.05$ and 0.15 are compared in Fig. 5. The real impedance of each sample is high at low frequencies and decreases rapidly with the applied frequency and temperature. Space charge was mentioned as one of the reasons for the high real impedance at low frequencies for ferroelectric ceramic materials. A large volume percentage of polycrystalline materials consist of grain and grain boundaries. These boundaries contain defects that cause a positive or negative space charge distribution at the interfaces. The space charges can be moved by the application of an external electric field and when they are trapped by the defects, lots of dipole moments are

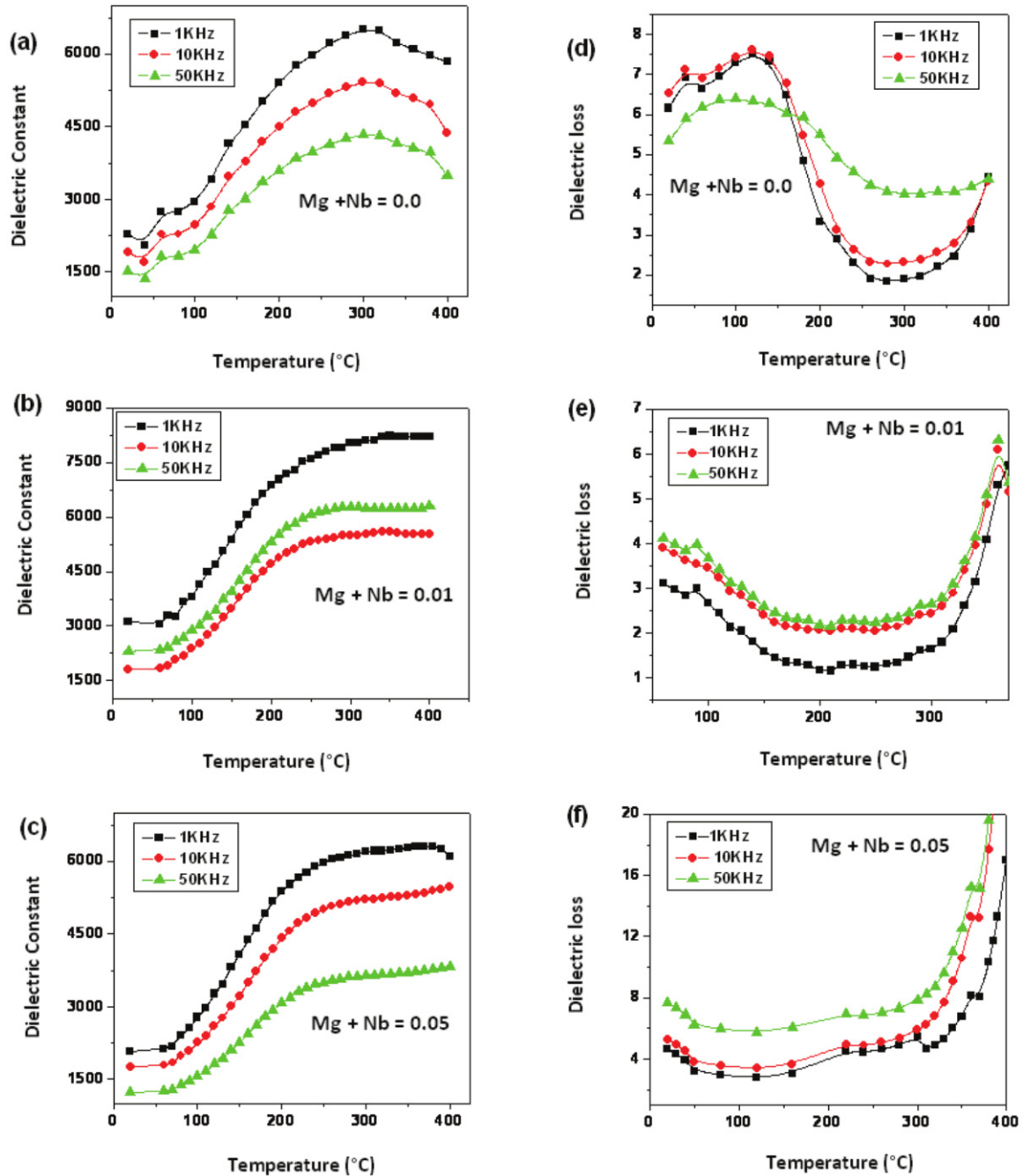


Fig. 3. Variation of dielectric permittivity (a – c) and dielectric loss (d – f) measured as a function of temperature at 1, 10 and 50 KHz for BNBT(MN)_x, where $x = 0.0, 0.01$ and 0.05 for the samples sintered at 1150°C .

formed. However, the increase in the real impedance at lower frequencies for polar materials is attributed to the contribution of multi-component polarization mechanisms (*i.e.* electronic, ionic, orientation and space charge). At higher frequency the dipoles

cannot rotate rapidly, so that their oscillations lag behind those of the field. When the frequency is further raised, the dipoles are completely unable to follow the field and the space charge polarization ceases, so the real impedance (Z') decreases and

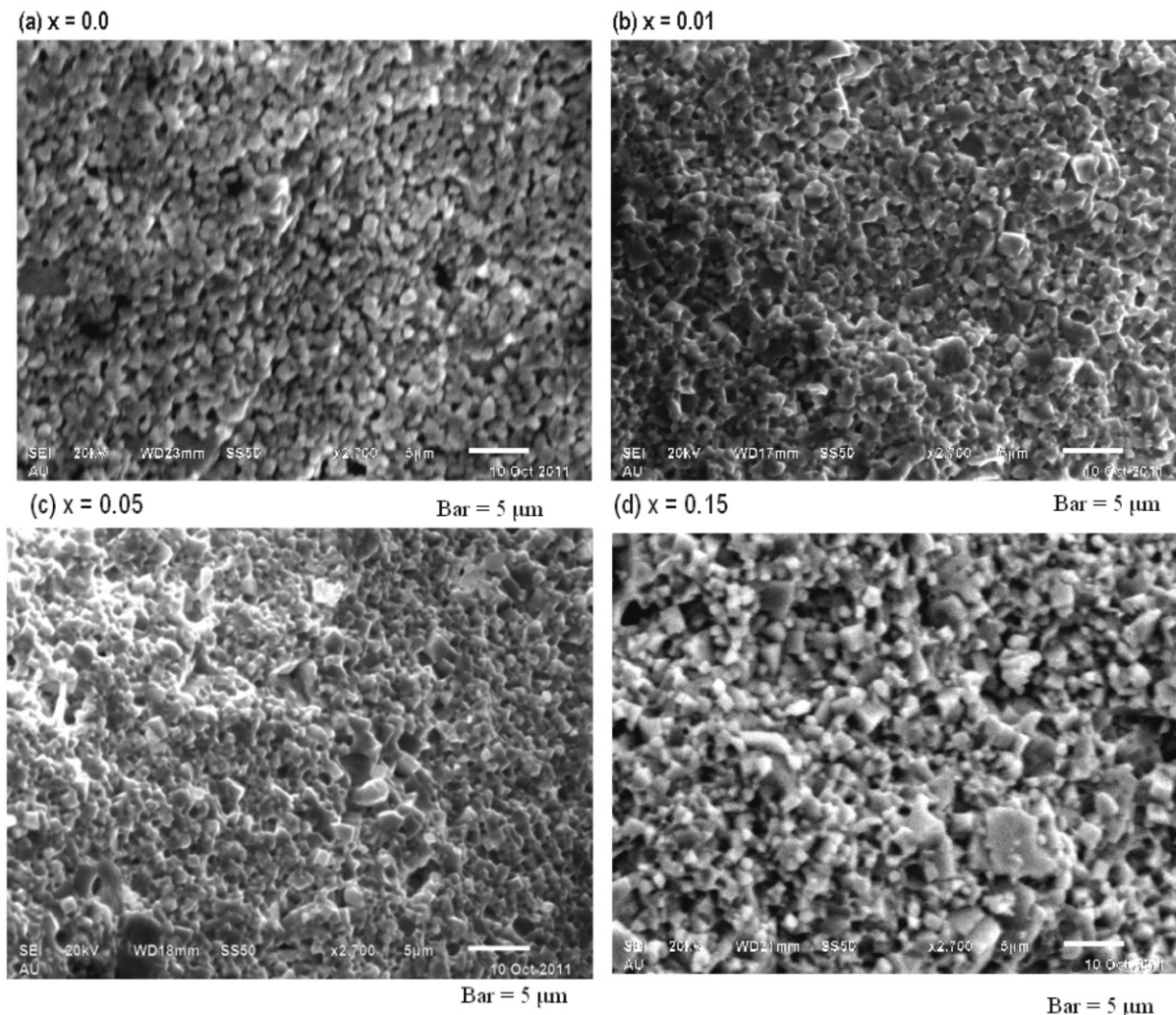


Fig. 4. SEM micrographs of BNBT(MN) x fractured surfaces of sintered pellets (a) $x = 0.0$ (b) $x = 0.01$, (c) $x = 0.05$ and (d) $x = 0.15$.

attains a constant value at high frequencies. This may be one of the reasons for the merging of real impedance curves for all compositions at higher frequencies as illustrated in Fig. 5. The real and imaginary impedance values are decreased with the increase in the concentration of magnesium and niobium at the same frequency and temperature as illustrated in the figures. The magnitude of Z' and Z'' in BNBT(MN)1 is relatively high in all the studied temperature and frequency ranges when compared with the BNBT(MN)5 and BNBT(MN)15. For instance, for BNBT(MN)1 sample, the values of real (Z') and imaginary (Z'') impedance at the temperature of 350 °C and frequency of 100 Hz are

1900 k Ω and 535 k Ω respectively. The corresponding values for the BNBT(MN)5 sample are 111 k Ω and 70.6 k Ω . For the BNBT(MN)15 sample, the values are decreased to 7.2 k Ω and 0.8 k Ω respectively at the same temperature and frequency. Fig. 5(d – f) also shows the peak values of Z'' (Z''_{max}) which decrease with the increase in temperature. The peak frequency ($f_{Z_{max}}$) shifts towards higher frequency side, which indicates the spread of impedance relaxation times observed particularly in the samples BNBT(MN)5 and BNBT(MN)1.

Fig. 6a and b show the Cole-Cole plot of BNBT(MN)15 sample at different temperatures in the frequency range of 100 Hz – 1 MHz, which

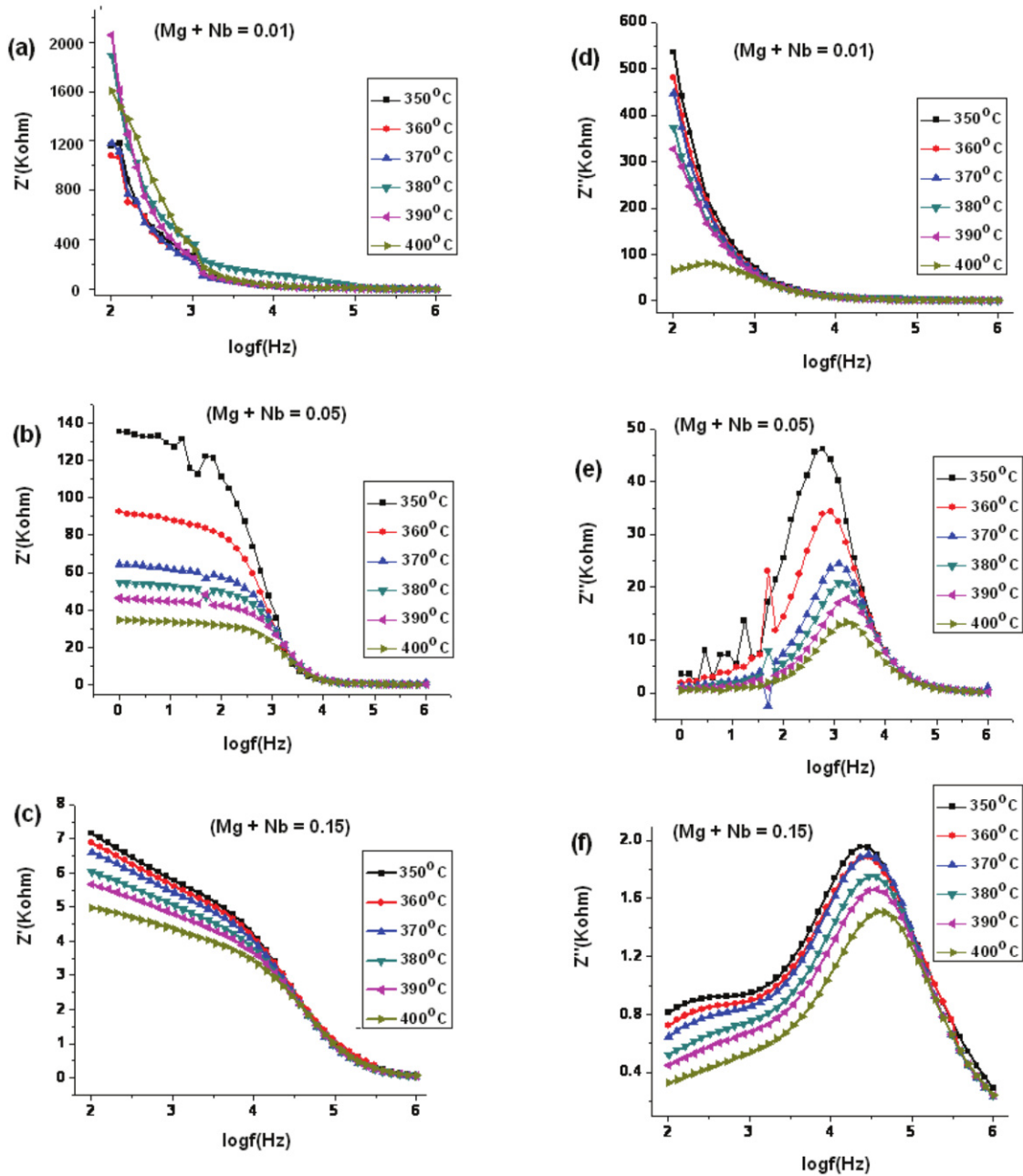


Fig. 5. The dependence of the real and imaginary part of impedance versus frequency for BNBT(MN) x samples with $x = 0.01, 0.05$ and 0.15 at $350, 360, 370, 380, 390$ at different temperatures.

shows a linear response in Z'' at lower temperature, indicating the insulating behavior of the sample. As the temperature increases, the linear response gradually changes to semicircular arc which become smaller and shifts towards lower Z' values, indicating a reduction in grain resistance (R_g). The spikes are observed in the impedance at higher temperatu-

res. In this case, the capacitance value has been obtained from the high frequency semicircle and low frequency spikes that correspond to the bulk and electrode polarization effect, respectively. The centre of the semi-circles lies below the x-axis which indicates non-Debye type relaxation process in the material [22]. The value of grain resistance (R_g) at

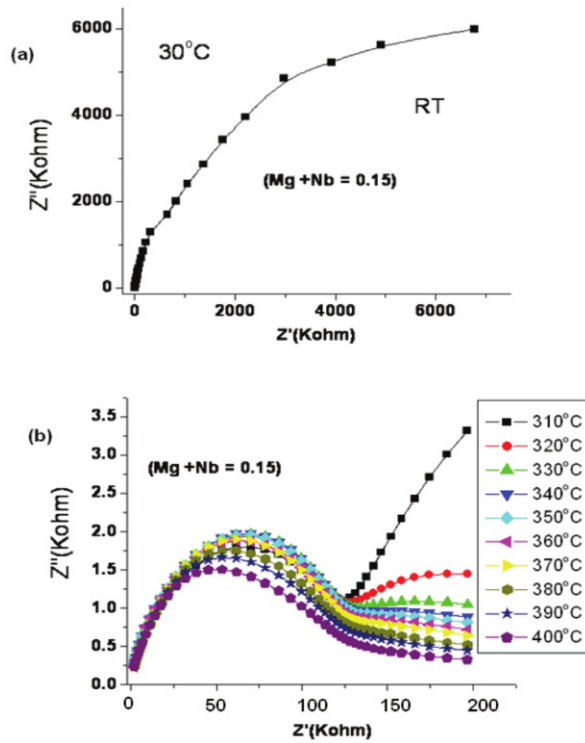


Fig. 6. Impedance plots of BNBT(MN)15 at different temperatures.

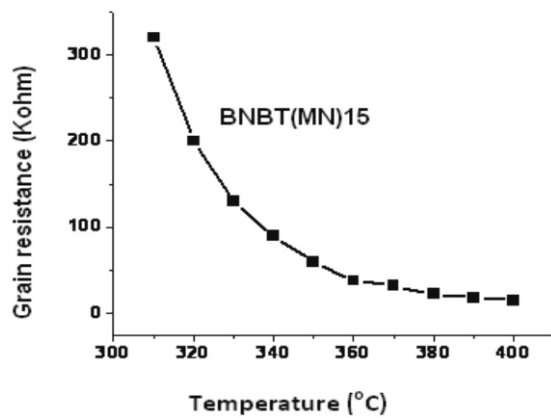


Fig. 7. Temperature dependence of grain resistance of BNBT(MN)15.

different temperatures ($310 - 400^\circ\text{C}$) has been obtained from the intercept of the semicircular arc on the real axis (Z') for BNBT(MN)15 sample, which is depicted in Fig. 7. From this figure it is clear that the (R_g) value of the sample decreases with the rise in temperature, which indicates a negative tempe-

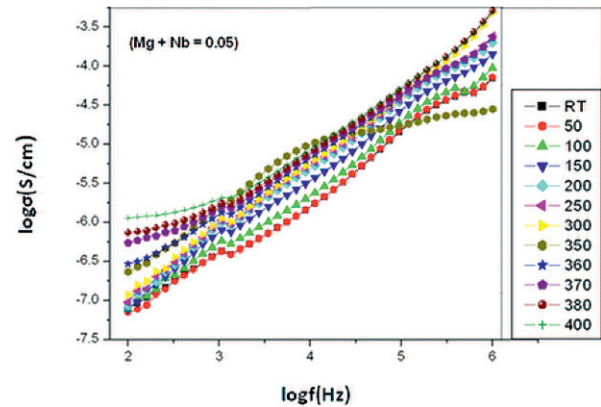


Fig. 8. Frequency dependence of ac conductivity of BNBT(MN)5 at various temperatures.

perature coefficient behavior of resistivity like that of semiconductors [23, 24].

3.5. Conductivity studies

Fig. 8 shows the dependences of electrical conductivity of BNBT(MN)5 on frequency at various temperatures. The patterns of the conductivity spectra of BNBT(MN) x with $x = 0.01, 0.05$ and 0.15 , at the same measuring temperature and in the studied frequency range have been similar.

The conductivity curves in Fig. 8 for BNBT(MN)5 ceramics, which have been displayed as an example, increased with increasing frequency and merged at high temperature [25, 26]. The trend representing conductivity in the BNBT(MN) x ceramic materials follows the universal power law, $\sigma(\omega) = \sigma_o + A\omega^n$, where σ_o is the dc conductivity, A is the pre-exponential factor and n is the fractional exponent between 0 and 1 [27]. The value of n (*i.e.* the slope of σ_{ac} versus frequency plot), was found to be in the range of $(0.6 - 0.8)$ and it slightly varied with temperature (Table 2), indicating that the correlated barrier hopping model (CBH) could be considered more appropriate for explaining the ac conduction in the ceramic samples in the present study.

From Fig. 8, it can also be seen that the ac conductivity also slightly increases with an increase in temperature. In the absence of an applied field, ions make random jumps over a barrier separating two sites. But in the presence of an applied field, ions

Table 2. Parameters determined for BNBT(MN)5 sample by the relation: $\sigma(\omega) = \sigma_o + A\omega^n$.

Tem(°C)	n(T))	logA(T)	Tem(°C)	n(T))	logA(T)
30	0.76106	-8.71683	300	0.85868	-8.63908
50	0.77783	-8.78908	350	0.53232	-7.41782
100	0.77194	-8.6504	360	0.74459	-8.13446
150	0.80356	-8.63238	370	0.6902	-7.84791
200	0.82594	-8.61433	380	0.72194	-7.8866
250	0.83009	-8.59006	400	0.67543	-7.64519

migrate preferentially in the direction of the field, which effectively lowers the energy barriers in the forward direction. Usually, when the temperature increases, the number of ions taking part in conduction mechanism increases and causes an increase in conductivity. But for the ceramic samples in the present study the ac conductivity slightly changed with temperature, indicating that the number of charge carriers did not increase considerably with the increase in temperature. The relatively low n and high $\log A$ values near T_{max} , observed in the Table 2, might be one of the most probable reason for the high dielectric constant found in BNBT(MN)x ceramic materials. The values of activation energy calculated in high temperature regions (300 – 400 °C) at three different frequencies (0.92 eV at 100 Hz, 0.86 eV at 1 KHz and 1.02 eV at 1 MHz) support the presence of oxygen vacancies in the sintered ceramic samples.

4. Conclusions

Lead-free ferroelectric ceramics BNBT(MN)x with $x = 0.0, 0.01, 0.05, 0.15, 0.20$ have been prepared by conventional solid-state method. X-ray diffraction studies of magnesium and niobium co-doping in the B site of BNBT indicated the formation of phase pure materials with monoclinic structure in the studied range of dopant concentration $0.0 < x \leq 0.15$. Scanning Electron Micrographs (SEM) observation revealed dense microstructure with average grain size of 1 μm for $(\text{Mg}_{\frac{1}{3}}\text{Nb}_{\frac{2}{3}})^{4+}$ substituted BNBT samples under study. Co-doping with 0.01 raised the dielectric constant from 6510 to 8225 at the frequency of 1 KHz and the increase in $(\text{Mg}_{\frac{1}{3}}\text{Nb}_{\frac{1}{3}})^{4+}$ concentration up to 0.15 increased the

transition temperature from 275 °C to 339 °C. The studies revealed that the maxima of the curves of ϵ' versus temperature for the studied materials were affected by the concentration of $(\text{Mg}_{\frac{1}{3}}\text{Nb}_{\frac{2}{3}})^{4+}$ and frequency. Impedance measurements of the pure and modified BNBT indicated negative temperature coefficients for the samples under investigation, which is typical of semiconductor materials. The ac electrical conductivity (σ_{ac}) study of BNBT(MN)x samples showed frequency dependence. The value of n or the slope of σ_{ac} versus frequency plot was found to be in the range of 0.6 – 0.8 and slightly varied with temperature. The correlated barrier hopping model (CBH) seems to be appropriate for explaining the ac conduction in the ceramic samples considered in the present study.

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