Studies on compensating valency substituted $BaTi_{(1-x)}Mn_{x/2}Nb_{x/2}O_3$ ceramics

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Abstract. The paper reports investigations of relative permittivity, e_r, electrical conductivity, s, saturation polarization, P_s, infrared absorption and structural properties of compensating valency substituted $BaTiO_3$. The compositions investigated are $BaTi_{(1-x)}Mn_{x/2}Nb_{x/2}O_3$ for $x = 0.00; 0.025; 0.05; 0.1; 0.2; 0.4$. The compositions for $x < 0.1$ are observed to be ferroelectric and the transition temperature and value of e_r are observed to decrease as concentration of substitution is increased. The dielectric investigations are carried out on two sets of samples (i) as sintered and (ii) annealed. Annealing is observed to improve quality factor 'Q' of the materials with a consequent reduction in the e_r. The observations on e_r and saturation polarization suggest that additional material engineering efforts are required to improve the material properties.

Keywords. Valence compensating ceramic; barium titanate; dielectric constant; electron-transport properties; saturation polarization.

1. Introduction

It has been observed that the relaxors in the ceramic form could be stabilized in the perovskite crystal structure only if they are combined with a certain amount of displacer ferroelectrics like $PbTiO_3$, $BaTiO_3$ (Agrawal 1997). The relaxors are known for their high dielectric constant and piezoelectric coupling coefficient; but the relaxors are found to possess very low Q as a consequence of occurrence of infra-grain space charge layers.

Further the $BaTiO_3$ having its high e_r, low coercive field and moderately high curie temperature is an important dielectric material for piezoelectric and pyroelectric application. Nevertheless the literature survey indicates that $BaTiO_3$ is less intensively investigated for the effect of compensating off valency substitution as compared to PT and PZT materials. One of the possible reasons could be the observation that the compensating off valency substitution depresses the curie point drastically (Nakamura and Nomura 1966). For example, the substitution of 2 Ti by a Fe or a Ta depresses the curie point below 0°C for 10 atom% level of substitution. Taking into consideration the points above, it appears that, the $BaTiO_3$ may exhibit interesting changes in properties for very low levels of off valency substitution, and therefore we have investigated the system as given here: $BaTi_{(1-x)}Mn_{x/2}Nb_{x/2}O_3$ for $x = 0.00; 0.025; 0.05; 0.1; 0.2; 0.4$. (It was expected that the interesting behavioural changes may occur for $x < 0.1$).

2. Experimental

The systems under investigation were synthesized via standard ceramic route. The respective oxides of purity 99.9% were mixed, ground, pelletized and subjected to presintering for 24 h at 1180°C. The effect of sintering schedule on the properties of pure and donor doped $BaTiO_3$ is well reported (Heydrich 1976; Bi-Shiou et al 1987). Also Mn prefers to be in state + 3 for 530°C $< T <$ 940°C (Dean 1987). Applying a qualitative logic the sintering schedule was selected so as to stabilize Mn in state + 3. Further, 1280°C was selected as final sintering temperature. The final sintering was carried out for 6 h. At high temperature the system under investigation was expected to lose traces of oxygen (Shail Upadya et al 1996). Reoxidation may take place if the samples are annealed at temperature below 1200°C for a long time. Additionally annealing may reduce thermal stresses also and may lead to an improvement in quality factor of the material (Scenger et al 1979; Setter et al 1980). To investigate this effect qualitatively we have prepared two sets of samples.

2.1 Sintered

In this case after sintering at 1280°C the samples were allowed to cool in the tubular furnace with its natural cooling rate of 10°C/min up to temperature below 900°C.

2.2 Annealed

The sintered compounds were reheated and maintained at 1150°C for 6 h and cooled below 900°C at the rate of

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The samples were subjected to investigations using Philips PW 1710 X-ray diffractometer. The infrared absorption properties were measured using Perkin-Elmer IR spectrometer. To measure the dielectric dispersion a HP-4284 A impedance bridge was used. The saturation polarization, P_s was measured using a circuit similar to the one reported earlier (Sinha 1965). The observations were taken up at an interval of $2°C$, though the figures of ε_r, P_s s indicate only a few representative points amongst these.

3. Results and discussion

3.1 *XRD*

The XRD was carried out using the JCPD standard data on $BaTiO_3$ and simultaneously using the graphical technique (Hull and Davey 1921; Cullity 1978). The XRD shows a tetragonal structure and observed a, c, c/a are shown in table 1. C/a is observed to be $1·01$ for all the samples. The values of a and c are also constant within the error limits of statistical averaging. The values are observed to be equal to the a, c, c/a for pure $BaTiO_3$ prepared in the same sintering schedule. Thus the structure parameters are independent of x as expected on the basis of relative ionic sizes of Nb ($0·70$ AU), Mn ($0·74$ AU) and Ti ($0·68$ AU).

3.2 *Infrared absorption*

In case of $BaTiO_3$, the absorption at infrared frequencies has been extensively used to probe the interatomic forces and the investigations are more useful to probe the interaction between the Ti and O ions in the octahedral geometry, the TiO_6 octahedron (Mara 1954; Last 1956).

In the system under investigation, the Ti site in ABO_3 crystal structure is being modified. Further, it is also well accepted that the displacement of the Ti ions from its centre caused ferroelectricity in these materials. Therefore investigations of the infrared absorption is expected to reveal a valuable information about the modification

caused in the interatomic forces between Ti and O_6 ions to the substitution.

Figure 1 shows the IR absorption spectra for $x = 0·05$ and the overall nature of the absorption spectra for all the levels of substitution studied is similar to spectrum for $x = 0·05$. Two absorption bands are observed in the frequency range 200–1000 cm^{-1}. The absorption band at higher frequency is labelled as n_1 while the one at lower frequency is labelled as n_2. The band n_1 is more asymmetric as compared to the one at n_2 and the present observations are in confirmation with the observations reported by Last (1956). The values of n_1, n_2, k_s and k_b for varying concentrations are shown in table 2, where k_s and k_b are the force constants for stretching and bending modes of vibrations respectively. The values of n_1 and n_2 for $x = 0$ are also equal to the reported values (Mara 1954; Last 1956). It has been observed that as the value of x increases the absorption band at n_1 becomes more asymmetric and broadened. For $x = 0·2$ and $x = 0·4$ the shoulders are observed in the n_1 band which are characteristic of further lowered symmetry (Last 1956).

The absorption bands at n_1 and n_2 could be associated to the stretching and bending modes of vibrations of TiO_6 octahedron (Last 1956) and the corresponding force con-
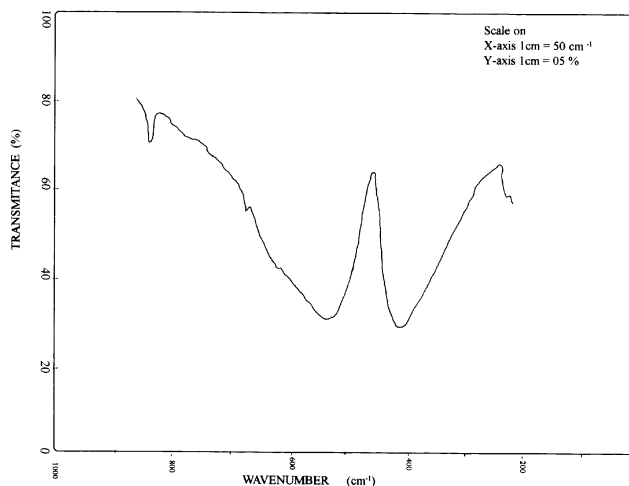

Figure 1. The infrared absorption spectra of $BaTi_{0·95}Nb_{0·025}Mn_{0·025}O_3$.

Table 1. Values of a, c and c/a for $BaTi_{(1-x)}Mn_{x/2}Nb_{x/2}O_3$.

X	a	c	c/a
0·000	3·989	4·029	1·01
0·025	3·991	4·041	1·01
0·050	3·994	4·034	1·01
0·100	3·992	4·032	1·01
0·200	3·994	4·034	1·01
0·400	3·983	4·024	1·01

Table 2. Values of n_1, n_2, K_s K_b for $BaTi_{(1-x)}Mn_{x/2}Nb_{x/2}O_3$.

X	n_1	n_2	K_s	K_b
0·000	540	400	$0·920 \times 10^5$	$0·680 \times 10^5$ as reported
0·000	545	400	$0·798 \times 10^5$	$0·638 \times 10^5$ as reported
0·050	535	395	$0·880 \times 10^5$	$0·740 \times 10^5$
0·200	550	375	$1·040 \times 10^5$	$0·550 \times 10^5$
0·400	560	360	$1·040 \times 10^5$	$0·490 \times 10^5$

stant could be calculated using standard procedure of solving the secular equations.

$$\begin{vmatrix} (m_0 + m_1)2k_s - l & m_0(4k_b) \\ -m_0(2k_s) & (m_0 + m_1)4k_b - l \end{vmatrix} = 0,$$

where m_0 and m_1 are the reciprocal masses of Ti and O ions, respectively.

It is observed that n_2 and k_b decreases as the level of substitution is increased while n_1 and k_s increases with the increasing level of substitution. The force constant, k_s, in this case is related to change in the bond length of O$_I$–Ti–O$_I$ ions along the polar axis. Therefore increasing values of n_1 correlate to increasing asymmetry in the O$_{II}$–Ti–O$_{II}$ bond. As c is observed independent of concentration, this increased asymmetry may lead to an increase in the asymmetry of O$_I$–Ti–O$_I$ ions.

From the basic theory of infrared oscillations (Hertz-berg 1945), the force constant k_b is inversely proportional to the displacement of Ti (or NbMn pair) from its centre

in TiO$_6$ octahedron. Now as increasing k_s leads to increasing asymmetry same phenomenon should lead to increasing displacement and decreasing k_b and n_2.

3.3 *Dielectric constant*

Figures 2 and 3 show the relative permittivity e_r as a function of temperature for the sintered (*S*) and annealed (*A*) samples. The general observations are as follows.

(I) The system for $x < 0.1$ is ferroelectric at room temperature. Therefore the behaviour of dielectric constant for $x = 0.2$ and $x = 0.4$ are not shown in the figure.

(II) The value of e_r for S-type sample is more than that for A-type sample and $Q(A) > Q(S)$.

(III) The peak is observed in the e_r vs T behaviour and it is a diffused one.

(IV) T_c appears decreasing as the substitution x is increased. The e_{rmax} initially increases and then decreases with x leading to non-ferroelectric compositions (table 3).
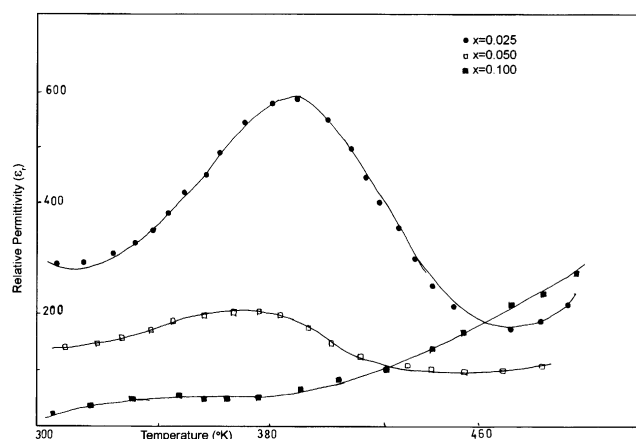
(V) The relative permittivity vs temperature behaviour for $x = 0$ is observed on the similar lines as reported earlier (Flores-Ramirez *et al* 1989) and the T_c is observed at 120°C. It is important to note that the behaviour of e_r vs temperature is sensitive to the sintering temperature. As the sintering temperature used is 1280°C the e_r vs T behaviour is expected to show a broad rather than a sharp peak.

The observations $e_r(S) > e_r(A)$ and $Q(A) > Q(S)$ show that the total impedance of the material is increased as the samples are annealed (about 2 times for $x = 0.025$ and 0.05). Further, corollaries of this observation are as follows.

Now the materials being investigated are displacer substituted relaxors and the annealing is expected to homogenize the material and reduce thermal stress. The relaxors are believed to possess microchemical inhomogeneity and corresponding space charge regions are
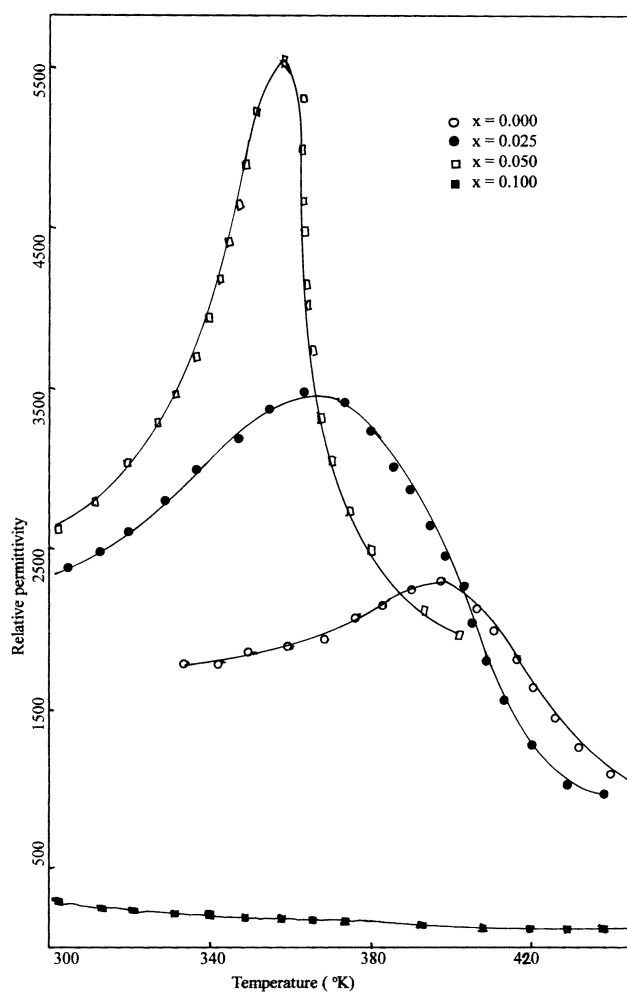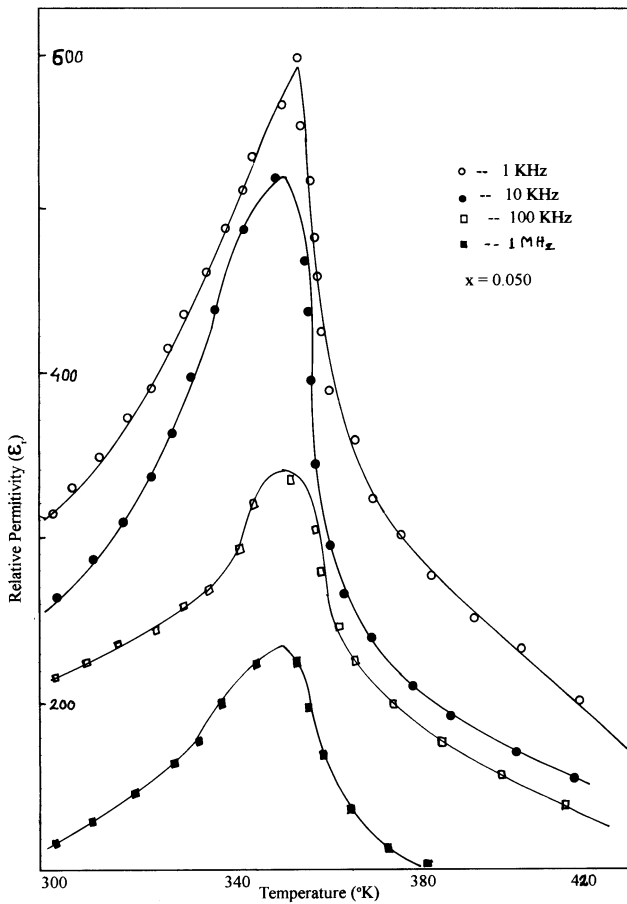

Figure 2. Variation of relative permittivity e_r with temperature for BaTi$_{(1-x)}$Nb$_{x/2}$Mn$_{x/2}$O$_3$ (sintered).
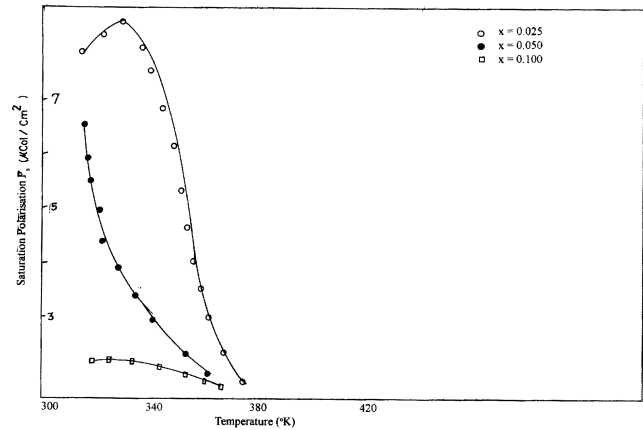

Figure 3. Variation of relative permittivity with temperature for BaTi$_{(1-x)}$Nb$_{x/2}$Mn$_{x/2}$O$_3$ (annealed).

Table 3. Values of e_{rmax}, e_{RT}, T_c, Q_{RT} and t for $BaTi_{(1-x)}Mn_{x/2}Nb_{x/2}O_3$.

X	As sintered					Annealed				
	T_c	$e_{rmax\,(-/+5)}$	$e_{rRT\,(-/+5)}$	Q_{RT}	t	T_c	e_{rmax}	e_{rRT}	Q_{RT}	t
0·000	395	2400	1700	1·22	–	390	280	190	13·9	–
0·025	372	3600	1800	1·57	0·85	388	600	285	13·18	0·97
0·050	365	5700	2000	1·19	0·75	378	210	130	2·32	0·91
0·100	303	280	280	2·08	0·61	~303	56	025	3·80	–

Figure 4. Variation of relative permittivity with temperature for different frequencies of $BaTi_{(1-x)}Nb_{x/2}Mn_{x/2}O_3$ for annealed.

Figure 5. Variation of saturation polarization P_s with temperature for $BaTi_{(1-x)}Nb_{x/2}Mn_{x/2}O_3$ (annealed).

$$e_r^{-1} = e_{rmax}^{-1} + A(T-T_c)^t,$$

where $t = 1$ for displacer material and $t = 2$ for the relaxor (Pandey *et al* 1997).

It has been observed that the $Pb_xCa_{(1-x)}Ni_{y/2}W_{y/2}Ti_{(1-y)}O_3$ systems possess t between 1 and 2 (Prasad *et al* 1996). $1 < t < 2$ is associated to partially relaxors nature of the material. The values of e_{rmax}, e_r (A), e_r (S), $Q(A)$, $Q(S)$ t for varying values of x are given in table 3. It is observed that $t < 1$. For NbMn systems the phase transition is a diffused one and has been associated with the chemical inhomogeneity within the grain. If the phase transition is a diffused one t may appear even less than 1 also and may not clearly indicate whether material is displacer or relaxor. To determine whether the material has at least partial relaxor behaviour, we have measured the e_r as a function of both temperature and frequency. Figure 4 shows e_r as function of both temperature and frequency for $x = 0.05$. From figure 4 it is apparent that the T_c increases slightly as frequency is increased. This observation has confirmed the relaxor contribution to the material. Another important feature of the measurement is that the $BaTiO_3$ at 1 KHz show that the e_r increases with temperature in the paraelectric region. This behaviour is ascribed to the polycrystallinity of the material (Flores-Ramirez *et al* 1989).
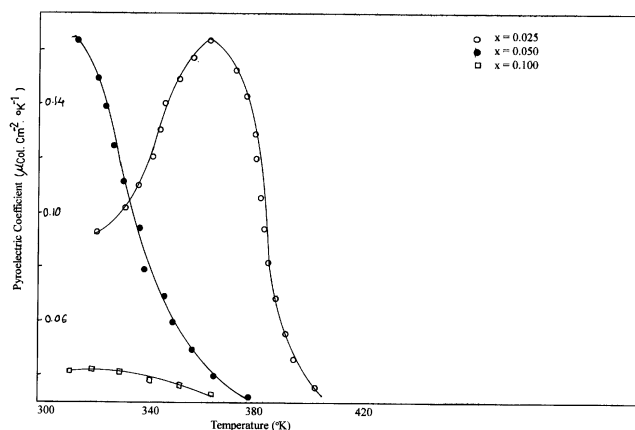
responsible for the high value of their dielectric constant (Agrawal 1997). The material under investigation could be a partially relaxor material. It is reported for the relaxors that the annealing of the material leads to an ordered state, where the dielectric constant is reduced and Q increased (Scenger *et al* 1979; Setter and Cross 1980). Therefore the present observations of reduced e_r and increased Q for annealed samples indicate that the materials under investigation are at least partially relaxors. The behaviour of e_r in the paraelectric region has been fitted to an equation

Figure 6. Variation of pyroelectric coefficient with temperature for BaTi$_{(1-x)}$Nb$_{x/2}$Mn$_{x/2}$O$_3$ (annealed).

3.4 *Saturation polarization*

The ceramic samples have inherent porosity and reduced dielectric strength. Therefore we have used maximum electrical field of 3·5–4 kV/cm. The observed loops are typical of polycrystalline material (Bera and Choudhary 1997). The behaviour of P_s vs temperature is shown in figure 5. The saturation polarization, P_s decreases as the level of substitution is increased and the P_s vs T behaviour shows a smear in the phase transition region typical of the DPT (Jun Kawata *et al* 1982). It is interesting to note that the P_s increases slightly near room temperature. This could be due to a smear in P_s due to orthorhombic to tetragonal phase transition, expected near 0°C from the investigation on substituted BaTiO$_3$. The observed saturation polarization shows that as x is increased the material tends to be non-ferroelectric for $x = 0.025$ (~ 7 μCol/cm^2) and is within the range that is reported for pure ceramic BaTiO$_3$. Using the P_s as T behaviour we have calculated the pyroelectric coefficient g as shown in figure 6. The g is also observed to decrease as x is increased.

3.5 *Conductivity*

The measurement of conductivity (figure 7) also shows a behaviour similar to the PTCR effect (Pandey *et al* 1997) near curie point, but the resistivity is observed to be sufficiently high at ~ 10^{-6} ohm m, both above and below the curie point. To explain such a behaviour a refined two level model is essential (Pandey *et al* 1997). Few observations are noteworthy.

(I) The very high values of the resistivity for all the observations suggest that the Mn is stabilized in oxidation state + 3.
(II) The conductivity is observed to decrease with T slowly in the PTCR region and the effect is a diffused one rather than being a sharp transition as in case of
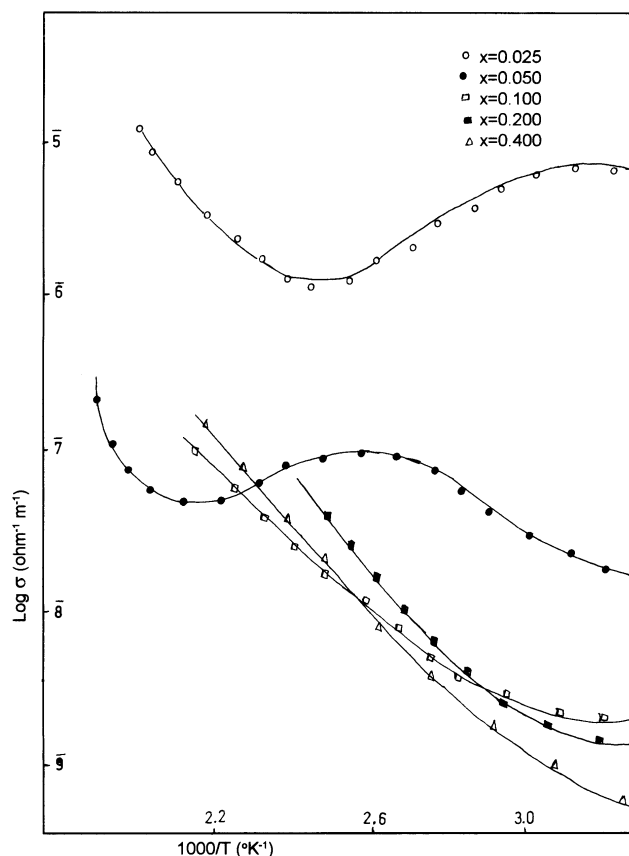
Figure 7. Variation of log s with 1000/T for BaTi$_{(1-x)}$Nb$_{x/2}$Mn$_{x/2}$O$_3$ (annealed).

donor doped BaTiO$_3$. In case of donor doped BaTiO$_3$ Hewang's model predicts a barrier layer at grain boundary, where the barrier potential is proportional to 1/e For the samples under investigation the phase transition is diffused and e decreases in a diffused manner with T in paraelectric region. This may lead to diffused PTCR effect.
(III) e_{max} reduces with x and also the log s decreases with x. This feature could be correlated at least qualitatively on the basis of the Hawang's model.

4. Conclusion

The substitution of Mn$_{1/2}$ Nb$_{1/2}$ for a Ti, in case of BaTiO$_3$ suppresses the transition temperature (T_c). For very low concentration of substitution the e_r is observed to increase owing to the added contribution of the space charge layers due to the microchemical inhomogeneity. The increased level of substitution leads to tetragonal but non-ferroelectric composition. The observations on e_r and saturation polarization suggest that the additional material engineering efforts are required to improve the material properties.

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