Research Article

Electrical transport in low-lead $(1-x)BaTiO_3 - xPbMg_{1/3}Nb_{2/3}O_3$ ceramics

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Abstract: Low-lead (1-x)BaTiO₃-*x*PbMg_{1/3}Nb_{2/3}O₃ ceramics (x=0, 0.025, 0.05, 0.075, 0.1, and 0.15) were prepared by the conventional oxide mixed sintering process, and their optical band gap, Seebeck coefficient, ac (σ_{ac}) and dc (σ_{dc}) conductivities as a function of temperature were investigated for the first time. It was found that all samples have p-type conductivity. The low-frequency (20 Hz–2 MHz) ac conductivity obeys a power law $\sigma_{ac} \sim \omega^s$, which is characteristic for disordered materials. The frequency exponent *s* is a decreasing function of temperature and tends to zero at high temperature. σ_{ac} is proportional to $\omega^{0.07} - \omega^{0.31}$ in the low-frequency region and to $\omega^{0.51} - \omega^{0.98}$ in the high-temperature region. The temperature dependence of the dc conductivity showed a change in slope around the temperature at which the phase transition appeared. Both ac and dc conductivities showed a thermally activated character and possessed linear parts with different activation energies and some irregular changes. It was found that the hopping charge carriers dominate at low temperature and small polarons and oxygen vacancies dominate at higher temperature. (1-x)BaTiO₃-*x*PbMg_{1/3}Nb_{2/3}O₃ ceramics are expected to be promising new candidate for low-lead electronic materials.

Keywords: BT-PMN ceramics; electric properties; Seebeck coefficient

1 Introduction

Barium titanate (BaTiO₃, BT) has been extensively studied and widely applied because of its proven superior electrical and optical properties. From low temperature to high temperature, it undergoes three successive phase transformations: from rhombohedral (R3m) to orthorhombic (Amm2) phase at about -90 °C, then to tetragonal (P4mm) phase at about 5 °C and finally to cubic (Pm3m) phase at about 120 °C [1]. The cubic phase is paraelectric while the other phases are ferroelectric. BT was believed to be a typical displacive-type ferroelectric material, although some experimental results suggest the possibility of formation of pretransitional polar regions in the cubic phase (i.e., an order–disorder mechanism was also postulated) [2,3]. However, the nature and role of the displacive and

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order-disorder components during the phase transition are still controversial and remain far from being completely understood.

Lead magnesium-niobate PbMg_{1/3}Nb_{2/3}O₃ (PMN) is a classical relaxor [4] and possesses cubic (Pm3m)symmetry in the entire temperature range [5]. However, some experimental results pointed to the presence of chemically ordered nanoregions with local Fm3m symmetry. Apart from these Fm3m-type regions, another kind of local symmetry appears in this material, namely, on cooling, the nucleation of polar regions [6]. These polar regions are the consequence of correlated off-center displacements of ions. Shifts of Pb show a spherically symmetric distribution with a mean diameter of 0.33-0.4 Å, while B-site cations are shifted along the [111] direction by about 0.18 Å [7]. At high temperature, ion displacements are independent of each other. When temperature decreases, at the so-called Burns temperature $T_{\rm d} \approx 350$ °C, the correlation between ion shifts leads to the appearance of polar regions with rhombohedral (R3m) symmetry. The presence of chemically ordered and polar regions shows that the cubic (Pm3m) symmetry should be only considered as an average one. Therefore, PMN belongs to the class of disordered and inhomogeneous materials. Long-range polar order is not achieved in PMN without applying an electric field.

Structural disorder is essential for the appearance of relaxor behavior and plays a primary role in specific properties of relaxors. Therefore, it is interesting to check how modifications of PMN change the properties of BT. Pure PMN is very difficult to obtain by a solid-state reaction because of the unwanted pyrochlore-type phase. However, mixing PMN with BT is expected to produce a pure perovskite structure without the presence of undesirable pyrochlore phase.

Owing to the considerations mentioned above, we have undertaken the synthesis of (1-x)BT-xPMN solid solutions (x=0, 0.025, 0.05, 0.075, 0.1, and 0.15) and studied their optical and electrical properties.

2 Experimental procedure

BaTiO₃ ceramics were prepared by the conventional method. The starting materials (TiO₂ (99.95%) and BaCO₃ (99.95%) both from "Ciech") were weighed according to the chemical formula, homogenized and milled in an agate ball mill in ethanol for 24 h, and then

dried and calcined at 1300 $^{\circ}$ C for 2 h. After calcination, the powders were ground in ethanol, cold pressed (100 MPa), and sintered for 1 h using conventional ceramic technology at a temperature of 1460 $^{\circ}$ C.

The BT-PMN specimens were prepared by a solid-state reaction method. First, magnesium oxide MgO (Fluka, 99.5%) and niobium pentoxide Nb₂O₅ (Aldrich, 99.5%) with 5 mol% excess MgO [8,9] were ball milled in ethanol using zirconia balls for 12 h and calcined at 1000 °C for 3 h in an alumina crucible to form magnesium niobate MgNb₂O₆ (columbite). 5 mol% excess MgO was added to avoid the undesired pyrochlore phase. In the second step, the appropriate amounts of barium titanate BaTiO₃ (Inframat Advanced Materials, obtained from BaCO₃ (99.95%) and TiO₂ (99.95%)) powders and lead oxide PbO (Chempur, 99%) were weighed and mixed with magnesium niobate MgNb₂O₆ by ball milling in ethanol using zirconia balls for 24 h. 3 mol% excess of PbO was added to compensate the lead oxide volatility [8]. The obtained powders were uniaxially pressed into disk samples with a diameter of 10 mm and a thickness of 1 mm. Polyvinyl alcohol was used as binder. The samples were sintered in sealed alumina crucibles at 1250 °C for 2.5 h with a heating rate of 2.5 °C/min, and then the furnace was cooled. PbO volatilization during sintering was minimized by surrounding each pellet with "atmosphere powders" of chemical composition 80 vol% (1-x)BaTiO₃-xPb(Mg_{1/3}Nb_{2/3})O₃ and 20 vol% PbO.

The microstructure analysis was undertaken by a scanning electron microscope (SEM; Model Hitachi S4700 with field emission) and the Noran Vantage EDS system.

The densities were measured by the Archimedes method. Phase formation was analyzed by X-ray diffraction (XRD). Structural studies of the materials were carried out using a Panalytical Empyrean diffractometer in the range of 10° – 110° with Cu Ka radiation.

The optical band gap of the investigated materials was determined from diffuse reflectance spectra. A UV–VIS–NIR spectrophotometer (PerkinElmer Lambda 950S) with a 150 mm integrating sphere (Labsphere SRS-99-020) was used for diffuse reflectance measurements over 250–1000 nm range.

Frequency dependence (20 Hz–2 MHz) of the ac conductivity (σ_{ac}) was measured in a temperature range

from room temperature to 400 °C for silver electrode samples using a GW 821 LCR meter. The data were collected regularly with a step of 0.1 °C upon heating and cooling, with a temperature change rate of 100 °C/h, using an automatic temperature controller. The dc current–voltage characteristics of the samples were prepared. Based on them, we applied voltage within the range of applicability of Ohm's law. The dc conductivity (σ_{dc}) was measured using a Keithley 6517A electrometer.

In order to determine the value of the Seebeck

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Fig. 1 SEM micrographs of fracture surface of (1-x)BT-xPMN ceramics: (a) x = 0, (b) x = 0.025, (c) x = 0.05, (d) x = 0.075, (e) x = 0.1, and (f) x = 0.15.

coefficient and the conductivity type of the samples, the electromotive force was measured at various temperature gradients for different average temperatures of the samples (for details see Ref. [10]).

3 Results and discussion

SEM micrographs of the investigated ceramics reveal dense microstructures with a clear grain boundary (Fig. 1). The average grain size decreases as a result of PMN doping from about 6 μ m for BaTiO₃ to about 2 μ m for 0.95BT–0.05PMN. With further increase of PMN content, the grain size increases to about 4 μ m. Furthermore, with increasing PMN content, a wide distribution of grain size and some large grains with irregular rectangular shapes are visible. This complex grain structure of BT–PMN ceramics is related to far lower sintering temperature in comparison with pure BT, and variations in valence state, ionic radius, and

electronegativity of Pb, Mg, and Nb ions substituted to BT, which would change the degree of diffusion. EDS analysis confirms the high purity and the expected chemical composition of the samples.

XRD patterns of (1-x)BT-xPMN ceramics show the formation of a single-phase perovskite structure (Fig. 2). This indicates that PMN diffuses into BT lattice structure to form solid solutions. The temperature range of the cubic phase existence



Fig. 2 XRD patterns of (1-x)BT-xPMN ceramics: (a) x = 0, (b) x = 0.025, (c) x = 0.05, (d) x = 0.075, (e) x = 0.1, and (f) x = 0.15. Note that Fig. 2(a) presents XRD pattern in the wide angle range of 20°–80°. For clarity of the presentation, Figs. 2(b)–2(f) show the respective XRD patterns in a narrower angle range.

increases with increasing PMN content (Fig. 2). The maximum temperature of the electric permittivity (T_m) , which approximately corresponds to the phase transition, is about 125, 115, 89, 72, 33, and -40 °C for BT, 0.975BT-0.025PMN, 0.95BT-0.05PMN, 0.0925BT-0.075PMN, 0.9BT-0.1PMN, and 0.085BT-0.15PMN, respectively (Fig. 3). It is clear from Fig. 3 that $\varepsilon(T)$ peaks broaden and a decrease of the respective temperature of the phase transition is observed with increasing PMN content, in accordance with the XRD results. In addition, a shift of T_m with increasing frequency typical for relaxors, is observed (inset in Fig. 3).

Progressive addition of PMN to BT results in an increase in lattice volume. This is in accordance with the fact that, although the ionic radius of Pb^{2+} (1.49 Å) is smaller than that of Ba^{2+} (1.61 Å), the (Mg,Nb)⁴⁺ ion (0.975 Å) is much larger than the Ti⁴⁺ ion (0.605 Å).

In a series of absorption studies of pure BaTiO₃, it has been determined that the absorption edge of the tetragonal phase has a Urbach tail due to phonon assisted transitions [2,11]. Most theoretical calculations of the energy band structure of BaTiO₃ deal with the highly symmetric cubic phase, while the tetragonal phase, stable at room temperature, is less-well investigated. These studies are made difficult by small atomic displacements and energy differences during the phase transition. The effect of tetragonality on band structure has been found to be very small [12,13]. In view of uncertainties in the electron valence band



Fig. 3 Temperature evolution of the electric permittivity ε of (1-x)BT-xPMN ceramics on cooling. Inset is the temperature/frequency dependence of ε of 0.9BT-0.1PMN ceramic showing relaxor behavior.

structure and low-energy exponential tailing off interband absorption edge, it is difficult to definitively assign a type to the fundamental interband transition [14]. Many interband transitions can be associated with the optical spectra. For example, Frova and Boddy [15] and Michel-Calelendini and Mesnard [13] suggested that the fundamental absorption edge can be a combination of direct and indirect transitions (3.2 eV). Sanna et al. [16] presented the results of first-principles calculations of the electronic structure of cubic and tetragonal BaTiO₃ in the framework of the DFT-OGA. They reported that BaTiO₃ has an indirect band gap $(R \rightarrow \Gamma \text{ transition in the cubic and } A \rightarrow \Gamma \text{ in the tetragonal}$ phase, where Γ , R, A are the high-symmetry points in the Brillouin zone). However, as they pointed out, the uppermost valence band is relatively flat, so that BaTiO₃ can be approximatively regarded as a direct material at Γ in both cases.

When the material scatters and absorbs light, and is opaque, the band gap can be estimated from the diffuse reflectance measurement. For such materials (e.g., powdered samples), the Kubelka–Munk (K–M) equation can be expressed as follows [17,18]:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \equiv F(R) \tag{1}$$

where K is the K–M absorption coefficient which is proportional to the linear absorption coefficient α and scattering coefficient S which is constant with the wavelength, and F(R) is the so-called Kubelka–Munk function.

The band gap E_g of the material is often determinated from the well-known Tauc formula. When Eq. (1) is fulfilled, the absorption of the material is proportional to F(R) and the Tauc general formula can be expressed by the following equation [19,20]:

$$(F(R)h\nu)^n = A(h\nu - E_g)$$
(2)

where *A* is a constant, *n* is a coefficient: n = 2 for a direct allowed transition and n = 1/2 for an indirect allowed transition, and $(F(R)h\nu)^n$ is called the modified Kubelka–Munk function.

The band gap E_g can be estimated by the plot of $(F(R)h\nu)^n$ (for n=2 and 1/2) versus $h\nu$ and extrapolating the linear portion of the plot to $F(R)h\nu = 0$ (Tauc plot). The *n* value for the specific transition is determined from the best linear fit of the plot.

In our work, the band gap energy for the different samples was calculated using the equation:

$$E_{\rm g} = -\frac{m}{b} \tag{3} .$$

where *m* and *b* are obtained by the linear fit (y = mx + b) of the flat section of the plot of $(F(R)hv)^n$ (for n = 2 or 1/2) versus photon energy hv.

We determined the Tauc plots for both direct and indirect gaps. Figure 4 shows the plots of the modified Kubelka–Munk function $(F(R)h\nu)^2$ versus the photon energy $h\nu$ for all samples (Nos. 1–6) and graphical linear fits to the plots. The linear fits to the plots of $(F(R)h\nu)^{1/2}$ (not presented here) were not as good.

The obtained values of $E_{\rm g}$ for all investigated samples are shown in Table 1 and Fig. 5. The band gap of pure BaTiO₃ is equal to 3.04 eV. When PMN is added to BT, the value of the gap $E_{\rm g}$ increases up to the maximal value of 3.30 eV for 10% of PMN. For 15% PMN content, $E_{\rm g}$ decreases slightly. This tendency is in agreement with the results of optical band gap investigations obtained for PMN single crystals ($E_{\rm g}$ = 3.41 eV) [21].

 $\ln \sigma$ plot as a function of 1000/T for various frequencies including σ_{dc} is shown in Fig. 6. The conductivity data for all samples demonstrate



Fig. 4 Plots of modified Kubelka–Munk function $(F(R)hv)^2$ versus photon energy hv for all samples.

Table 1 Gap energy E_g versus the composition of the samples. The values of E_g were estimated from the plots of the modified Kubelka–Munk function

No.	1– <i>x</i> of BaTiO ₃	$x \text{ of PbMg}_{1/3}\text{Nb}_{2/33}\text{O}_3$	$E_{\rm g}$ (eV)
1	1.000	0	3.04
2	0.975	0.025	3.15
3	0.950	0.050	3.26
4	0.925	0.075	3.28
5	0.900	0.100	3.30
6	0.850	0.150	3.29



Fig. 5 Band gap $E_{\rm g}$ estimated from the plots of the modified Kubelka–Munk function versus composition of the samples. The solid curve has been drawn to guide the eyes.

semiconducting behavior over the measured temperature range, with an anomaly at the phase transition. The dc conductivity is less than the ac conductivity and some difference in its temperature dependence is also visible. This is a usual behavior as the dc conductivity is determined by migration of the charge carriers between the electrodes, while the ac conductivity relates to the easiest local motion of the charges. σ_{dc} increases with increasing temperature and the linear relation between $\ln \sigma_{dc}$ and 1000/T indicates the validity of the relation [22]:

$$\sigma_{\rm dc} = \sigma_0 \exp\left(-\frac{E_{\rm c}}{kT}\right) \tag{4}$$

where σ_0 is a constant, E_c is the activation energy, k is the Boltzmann's constant, and T is the temperature. The rise of conductivity with increasing temperature is due to thermally generated carriers, and hence semiconductor conductivity becomes apparent.

In general, $\sigma_{\rm dc}(T)$ curves show linear behavior with different slopes (below $T_{\rm m}$ and above $T_{\rm m}$). We can conclude that the phase transition affects the energies of the trapped carriers, thereby influencing the dc conductivity activation energies, resulting in different slopes of the curve (i.e., above and below the phase transition temperature). The estimated activation energies for the investigated samples for the low and high temperature regions are 0.07–0.51 eV and 0.86–1.41 eV, respectively. These activation energies are markedly lower than the optical energy gap $E_{\rm g}$, and hence the electric conductivity of the investigated samples is due to impurities. The different activation



Fig. 6 Variation of electric conductivity with 1000/T for various frequencies for (1-x)BT-xPMN ceramics: (a) x = 0, (b) x = 0.025, (c) x = 0.05, (d) x = 0.075, (e) x = 0.1, and (f) x = 0.15.

energies in different temperature ranges are due to difference in the conductivity mechanism and also the domain configuration [22]. The lower value of E_c in the ferroelectric phase may be due to the carrier transport mechanism attributed to hopping between localization sites (from Ti⁴⁺ to Ti³⁺ and from (Mg, Nb)⁴⁺ to $(Mg, Nb)^{3+}$)). The intermediate value of the activation energy (0.3-0.51 eV) may be associated with the small polarons created by the electron and/or hole-phonon interaction and is reinforced by lattice deformation in the phase transition region. The higher value of the activation energy (at about 1 eV) is related to the hopping of oxygen vacancies, similarly to other perovskites [23]. With an increase in temperature, the motion of domain walls increases and is pinned due to the deposition of excess oxygen vacancies at higher temperature. This is also responsible for the higher activation energy in this temperature range. The change in the activation energy in the temperature range above $T_{\rm m}$ can be related to changes of concentration of the ionized vacancies. For samples with PMN amount >5 at%, polar regions exist in the cubic phase, and influence the electric conductivity.

The ac conductivity varies with frequency for all investigated compositions (Fig. 7), which may be due to the existence of free as well as bound carriers. In the first case, the conductivity must decrease with increasing frequency [24]. In the second case, the conductivity increases with increasing frequency, which is the case for our samples. This increase of conductivity with increasing frequency may be explained by hopping of charge carriers between the trap levels situated in the energy gap of the materials according to the following power law [25]:

$$\sigma_{\rm ac} = A\omega^s \tag{5}$$

where A is a function of temperature, and s assumes a value of 0 < s < 1 and is a function of both temperature and frequency. The exponent s represents the degree of interaction between the mobile charge carriers with the lattice. A lower value of s indicates an increase of the dc conductivity contribution (i.e., σ_{ac} comes to σ_{dc} when s comes to 0). The electric conductivity σ_{ac} follows Eq. (5) with s = 0.07-0.31 for low frequency (up to about 50 kHz). For higher frequency, s lies between 0.51 and 0.98 (Fig. 7). The value of s = 1 implies Debye behavior (the interaction between the neighboring dipoles is almost negligible). The parameter s is found to decrease with increasing temperature. This variation

of s is due to an increase in randomness in the material and is also predicted by the hopping model [26]. Hence, we conclude that the ac conductivity in our samples is a hopping-type conduction. However, this conclusion is weakened by the inhomogeneity existing in our systems (grains and grain boundaries), as the hopping model is predicted for homogeneous systems.

We have performed an impedance analysis. The real and imaginary parts Z' and Z'' of the impedance are calculated based on the electric permittivity using the equations [27]:

$$\varepsilon^* = \frac{1}{j\omega C_0 Z^*}, \quad Z^* = Z' + jZ'' \tag{6}$$

where ω is the angular frequency and C_0 is the capacitance of free space.

Figure 8 shows the Nyquist diagrams of the compounds (a) for several compositions and (b) at different temperatures. It can be seen from Fig. 8(b) that, at lower temperature, a single semicircular arc occurs. At higher temperature, another arc semicircle appears, thus the spectrum consists of two semicircular arcs with their centers lying below the real axis. In this type the right semicircle of formalism, (in the low-frequency region) represents the grain boundary while the left one (in the high-frequency region) corresponds to the bulk of the grains. These semicircles indicate that both grain and grain boundary resistances have an active role in the electrical properties and conduction mechanism at high temperature.

Figure 9 shows the variations with frequency of the (a) real and (b) imaginary parts of the impedance at different temperatures for a representative sample. The value of Z' (Fig. 9(a)) changes with frequency. Furthermore, Z' has high values at low frequency and decreases to low values (almost constant) at high frequency. This indicates relaxation-type behavior in the examined sample. Similar behavior occurs for the imaginary part of impedance (Fig. 9(b)). Z'' values decrease sharply at low temperature. This behavior indicates that the relaxation spices are immobile. It can also be noticed from this figure that there are one well-defined peak and a small hump, particularly visible for the high temperature region (inset of Fig. 9(b)). Each corresponds to a relaxation process.

The relaxation time has been estimated using the frequency according to the relation $\tau = 1 / f_{\text{max}}$, where f_{max} is the frequency corresponding to Z''_{max} . The activation energy characteristic for the relaxation



Fig. 7 Ac conductivity as a function of frequency at different temperatures for (1-x)BT-xPMN ceramics: (a) x = 0, (b) x = 0.025, (c) x = 0.05, (d) x = 0.075, (e) x = 0.1, and (f) x = 0.15.



Fig. 8 Complex impedance Z'' versus Z' plots: (a) at temperature 330 °C for selected compositions; (b) for 0.9BT–0.1PMN ceramic at different temperatures.



Fig. 9 Frequency plots of (a) Z' and (b) Z'' at different temperatures for 0.9BT-0.1PMN. Inset shows the frequency dependence of Z'' at high temperature.

process can then be obtained assuming that the relaxation time τ of each peak follows an Arrhenius relation given by the equation:

$$\tau = \tau_0 \exp\left(-\frac{E_c}{KT}\right) \tag{7}$$

where τ_0 is the characteristic relaxation time corresponding to infinite temperature and a characteristic of the material, k is the Boltzmann constant, T is the absolute temperature, and E_c is the activation energy calculated from the slope of $\ln \tau$ versus 1000/T (Table 2).

As can be seen from Table 2, the activation energies obtained by impedance spectroscopy are similar to those evaluated by electric conductivity analyses.

Figure 10 shows the Seebeck coefficient α as a function of temperature for the samples under investigation. All samples exhibit p-type behavior, indicating that majority of charge carriers have hole-like characteristics. As can be seen from Fig. 10,

Table 2 Activation energy of grains (E_{cg}) and grain boundaries (E_{cgb}) for (1-x)BT-xPMN

Sample	$E_{\rm cg}({\rm eV})$	$E_{\rm cgb} ({\rm eV})$
0.975BT-0.025PMN	0.10	0.75
0.950BT-0.050PMN	0.86	0.51
0.925BT-0.075PMN	0.71	0.87
0.900BT-0.100PMN	1.40	0.56
0.850BT-0.150PMN	0.27	0.64



Fig. 10 Seebeck coefficient as a function of temperature for (1-x)BT-xPMN ceramics. Inset shows the Seebeck coefficient and electric conductivity obtained at 170 °C vs. PMN content. The solid lines are only an eye-guide.

the Seebeck coefficient changes irregularly under the influence of the PMN dopant to BT and has a lower value than for pure BT. The Seebeck coefficients show two different trends: nearly invariant between 150 and 165 $^{\circ}$ C and then increasing up to 210 $^{\circ}$ C. This increase is almost linear, which is a typical behavior of heavily doped semiconductors or degenerate semiconductors.

The concentration of charge carriers *n* is given by the formula [28]:

$$n = \frac{N}{\exp\left(\frac{\alpha e}{k}\right)} \tag{8}$$

where N is the effective density of states (N= 1.555×10²⁸, 1.554×10²⁸, 1.553×10²⁸, 1.5525×10²⁸, 1.552×10²⁸, 1.552×10²⁸, and 1.551×10²⁸ m⁻³ for x=0, 0.025, 0.05, 0.075, 0.1, and 0.15, respectively), α is the Seebeck coefficient, *e* is the charge of the carriers, and *k* is the Boltzmann constant.

The mobility of charge carriers μ is given by the formula [29]:

$$\mu = \frac{\sigma}{en} \tag{9}$$

Based on formulas (8) and (9), we calculate the concentration n and mobility μ of charge carriers for investigated ceramics (Figs. 11(a) and 11(b)). Weak temperature dependence of concentration of charge carriers also indicates degenerate semiconductor

behavior for all samples (Fig. 11(a)). The low value of the mobility of charge carriers (far lower than $1 \text{ cm}^2/(\text{V}\cdot\text{s})$) can also suggest that the hopping mechanism has a large impact on the electrical conductivity [29] in all samples (Fig. 11(b)). As shown in the inset of Fig. 11(b), the mobility varies approximately as $T^{-3/2}$ in the high temperature range, which indicates that acoustic phonon scattering is the dominant carrier scattering mechanism, and approximately as $T^{-1/2}$ in low temperature range, which reveals the effect of increased grain boundary scattering.

In BT, a small deficiency of ions in the A- or B-site and oxygen vacancies can exist. Cation and oxide vacancies should be produced as [30,31]:

$$BaO \rightarrow Ba_{Ba}^{\times} + O_{O}^{\times} + V_{Ti}^{\prime\prime\prime} + 2V_{O}^{\bullet\bullet}$$
(10)

$$\mathrm{TiO}_{2} \rightarrow \mathrm{V}_{\mathrm{Ba}}'' + \mathrm{Ti}_{\mathrm{Ti}}^{\times} + 2\mathrm{O}_{\mathrm{O}}^{\times} + \mathrm{V}_{\mathrm{O}}^{\bullet\bullet}$$
(11)

Cationic vacancies (likely in the titanate site) can arise for example during the technological process or during annealing of the sample. The effective negative charge of cation vacancies ($V_{Ti}^{""} \cong V_{Ti}^{4-}$) can be compensated by a transition of four neighboring oxygen ions to a lower oxidation state. The effective charge of these anions is positive. The electron holes and centers connected with cation vacancies in this manner created are acceptors—the material is a p-type semiconductor.



Fig. 11 (a) Concentration of charge carriers as a function of temperature and (b) mobility of charge carriers as a function of temperature for (1-x)BT-xPMN ceramics. Inset shows the same as a function of 1000/T, presenting grain boundary and acoustic phonon scattering as the dominant carrier scattering mechanism in the low temperature and high temperature ranges, respectively.

Low valence acceptor impurities in TiO2 and excess Mg substituting for Nb may contribute to p-type behavior. Adding PMN with p-type conductivity to BT can support the p-type conductivity. However, it is also possible to compensate the p-type conductivity by this doping. For example, a niobate ion put in the place of titanate ion (titanate vacancy) can be an effective donor center. Initially, this leads to an increase of conductivity (inset in Fig. 10) due to a decrease of the positive Seebeck coefficient (inset in Fig. 10) owing to the compensation of already existing holes by electrons, originating from the donor dopant. A large degree of compensation of the p-type conductivity occurs at about 10 at% of PMN dopant to BT which acts as donor (inset in Fig. 10). This proves that there probably exists a relatively low concentration of Ba and Pb-vacancies acting as acceptors. When the PMN content exceeds 7.5 at%, the electric conductivity decreases. Considering the attraction caused by Columb force, the dopant ions and oxygen vacancies form associate defect pairs (for example, $Mg''_{Ti} - V_0^{\bullet \bullet}$). These defects are immobile so that the conductivity decreases for higher concentration of PMN. The existence of polar regions in the cubic phase and the more complex grain structure (Fig. 1) of these specimens can be responsible for the observed changes of σ and α .

4 Conclusions

Good quality ceramics of (1-x)BT-xPMN (x=0, 0.025,0.05, 0.075, 0.1, and 0.15) were obtained via a two-step solid-state reaction process. X-ray and microstructure studies revealed that Pb and (Mg/Nb) diffuse into BaTiO₃ lattices to form solid solution with a single perovskite structure. The first results of optical band gap, Seebeck coefficient, and ac and dc conductivity studies for these ceramics were presented. The optical band gap was found to increase with increasing PMN content from 3.04 eV for BT to 3.30 eV for 10 at% of PMN dopant. The temperature variation of dc conductivity followed the Arrhenius law and had two different values of the activation energy for different temperature ranges. This might be due to different conduction mechanisms and the influence of domains in the ferroelectric phase. It was found that the electrical conductivity occurs due to hopping charge carriers in the low temperature range and small polaron and oxygen vacancies at higher temperature. The

presented ceramics are expected to be useful as new low-lead electronic materials.

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