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Effect of Nb doping on the relaxor behaviour of $(Pb_{0.75}Ba_{0.25})(Zr_{0.70}Ti_{0.30})O_3$ ceramics

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Abstract

Strong influence of niobium admixture added to the lead–barium–zirconate–titanate ceramics of a chosen composition Ba/Zr/Ti 25/70/30 on grain structure, dielectric, and pyroelectric properties was confirmed. The Nb-modified ceramics exhibit classical relaxor ferroelectric behaviour similar to other complex lead perovskites such as lead–lanthanum–zirconate–titanate-type ceramics. Additional anomalies in $\varepsilon'(T)$ curves in low frequency range were observed in the paraelectric phase for undoped ceramics. These anomalies and some disturbances in regularities typical for the relaxor ferroelectric behaviour in the vicinity of diffuse ferroelectric–paraelectric phase transition in undoped PBZT ceramics are eliminated by the Nb admixture. An attempt at a quantitative explanation is presented in the paper.

Keywords: Dielectric properties; Ferroelectric properties; Perovskites; (Pb,Ba)(Zr,Ti)O_3

1. Introduction

The (Pb,Ba)(Zr,Ti)O_3, (PBZT) ceramics exhibit, similarly haw take place in some of lanthanum doping PZT ceramics, the properties characteristic for relaxor ferroelectrics.[1] The properties concern PBZT ceramics with Zr/Ti ratios and also barium content located there nearly boundary between ferroelectric (rhombohedral and tetragonal) and paraelectric (cubic) phases. The PBZT 25/70/30 ceramics belong to the mentioned above system, which was also confirmed in our previous papers.[2,3] On the other hand, it is commonly known, that modification of PZT ceramics by substitution of a small amount of isovalent or heterovalent elements for the Pb or Zr/Ti sublattices caused significant improvement of their properties. Especially profitable dopants are lanthanum and niobium. Abundant literature on the subject indicates that these dopants influence on the temperatures of the structural phase transition between the phases of various types of the electric order (FE, AFE and PE) and also dielectric, pyroelectric, piezoelectric, electro-optic and other parameters. This, in particular, concerns the Nb doped Zr-rich Pb(Zr,Ti)O_3 ceramics and also $PbZrO_3$.[4–7] It was shown that the Nb_2O_5 dopant concentration smaller than about 1 mol% is the most favourable, from the properties and application point of view, whereas its higher content leads to deterioration of these properties. Based on the presented results we make investigations concerning influence of niobium dopants on properties of PBZT 25/70/30 ceramics. We have focused on analysing of the ceramics microstructure and relaxor properties. Changes of pyroelectric and thermally stimulated depolarisation currents were also investigated and discussed.

2. Sample preparation

The PBZT ceramics of the composition Ba/Zr/Ti 25/70/30 pure and doped by 1–4 at.% Nb, were prepared by using the conventional mixed-oxide processing technique. The proper amounts of reagents: PbO, $BaCO_3$, TiO_2, ZrO_2 and Nb_2O_5 were weighed and mixed. The content of Nb_2O_5 was varied

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from 0 to 2 mol% (i.e., the concentration of Nb in ceramic samples was running from $x = 0$ to $x = 4$ at.%). It was assumed that the substitution of Nb^{5+} ions for Zr^{4+}/Ti^{4+} ions is the most likely phenomena.[8] Thermal synthesis of mixed and pressed oxides was carried out at 925 °C for 2 h then the crushed, milled and sieved materials were pressed again into cylindrical pellets and sintered at 1250 °C for 4 h. The latter procedure was repeated before the final sintering, carried out at 1300 °C for 7 h and 1360 °C for 10 h, respectively, for undoped and Nb-doped ceramics. The final sintering was carried out as follows: the material was placed in a double crucible with some amount of PbO and ZrO_2, in order to maintain the established composition, and especially to avoid the loss of PbO caused by its sublimation. The weight losses are smaller than 1%. The Archimedes displacement method with distilled water was employed to evaluate sample density. Sample bulk density for undoped ceramics was 6.8 g/cm^3, which was equal to 88% theoretical density. The density increased linearly with the growth content of niobium increased and for ceramics PBZT 25/70/30 with 4 at.% Nb density was equal to 7.9 g/cm^3.

The scanning electron microscope JSM-5410 with an energy dispersive X-ray spectrometer (EDS) was used for investigating structure and composition of the obtained ceramics. The grain size measurements were performed on structure surface of the ceramics. The imagines of microstructure of PBZT 25/70/30 ceramics with Nb content 1 and 4 at.% are shown in Fig. 1, as an example. The average grain size of undoped ceramics was larger than 15 μm. In the case of ceramics doped by Nb could not precisely determine the average grain size, because when the content Nb was equal to 1 at.% in ceramics appeared two kinds of grains, significantly differ with size. Their quantity was larger in the case of a higher concentration of Nb. The similar behaviour was observed in the case of $PbZrO_3$ and PZT 92/8 ceramics.[8] The authors of the mentioned paper, used the TEM microscope and EDX analysis, affirmed differences in composition of smaller and larger grains. As the authors claimed these differences could consequently appear, in large concentration of the niobium, new chemical compound, for example, $PbNb_2O_6$. It is very probably, that the similar behaviour appears in the case of ceramics discussed in this paper.

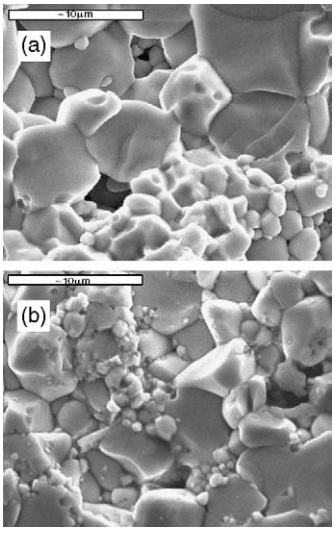

Fig. 1. Scanning electron microscope images of the fracture surface of PBZT 25/70/30 ceramics with Nb contents 1 at.% (a) and 4 at.% (b).

The samples of appropriate size were prepared for dielectric and pyroelectric measurements. The cut and polished samples were coated with silver electrodes, by using silver paste, without thermal treatment.

3. Dielectric measurements

Samples 0.6 mm thick were used for measurements of dielectric constant as a function of temperature. Measurements were performed in a field of several frequencies in the range 0.1–20 kHz by using a computerised automatic system, based on a Tesla BM-595 LRC meter. They were performed in successive heating-cooling cycles with a constant rate of 2 K min^{-1}. The samples were deaged by thermal treatment at 450 °C prior to measurements. Part of the frozen defects, formed during the sintering process, recombined and the tensions caused by mechanical treatment relaxed. The characteristics $\varepsilon'(T)$ for a number of frequencies of the measuring field are shown as an example in Fig. 2. The two groups of $\varepsilon'(T)$ curves presented for the undoped and Nb (4 at.%) doped ceramics, show o strongly diffused character of FE-PE phase transition. The temperatures T_m, corresponding to the broadened maximum in the $\varepsilon'(T)$ curves and ε'_{max} are

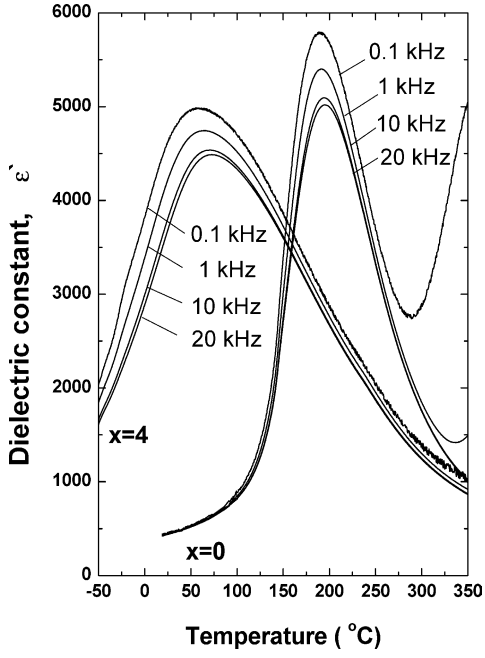

Fig. 2. Dielectric constant as a function of temperature measured on heating at various frequencies of measuring field, for undoped ($x = 0$) and Nb-modified ($x = 4$) ceramics.

strongly dependent on Nb content and frequency of the measuring field. It should be noted that undoped PBZT 25/70/30 ceramics show two kinds of dispersion. One of them was connected with diffuse phase transition occurred in the range of T_m temperature. This behaviour is characteristic for ferroelectric relaxor. The second dispersion occurred in temperatures $T > 300\,^{\circ}C$, i.e., in the PE phase. It is more visible for lower frequency and gradually disappears when the frequency is in excess of about 10 kHz. Insert ion of the Nb doped to ceramics caused complete loss of the second kind of dispersion, whereas at the same time the first kind of dispersion increased. Similar results were described in the case of ceramics PBZT 25/70/30 doped by lanthanum ions.[9] The comparison of the $\varepsilon'(T)$ curves, measured at 1 kHz frequency, for all studied ceramics, is shown in Fig. 3. The addition of niobium caused increased maximum value of dielectric constant (ε'_{max}). Additionally, increase of niobium concentration led up to reduction of temperature T_m, which had a linear character from 2 at.% of niobium (see the inserted plot in Fig. 3). Similar character of changes was observed in the case of PZT ceramics.[8]

All the investigated PBZT 25/70/30 ceramics (undoped and Nb-modified) show the behaviour typical for ferroelectric relaxors. Namely all the $\varepsilon'(T)$ curves measured at various frequencies show the reduction of ε'_{max} and shift of the corresponding temperature T_m with the frequency increase. This behaviour is more distinct for Nb-modified ceramics. In this material we made an attempt of describing the degree of frequency dispersion through the value of $\Delta\varepsilon'_{max}$ (was defined here as the difference between the ε'_{max} measured at 0.1 kHz and that measured at 20 kHz) and ΔT_m (defined in the similar manner). The value of $\Delta\varepsilon'_{max}$ and ΔT_m increased with niobium concentration (Fig. 4). The observed frequency dependence of T_m was empirically evaluated by using the Vogel–Fulcher relationship, adopted from the theory of magnetic relaxation in spin glass systems:

$$\omega = \omega_0 \exp\left[\frac{-E_a}{k(T_m - T_f)}\right] \quad (1)$$

where E_a is the activation energy, T_f is the freezing temperature of polarisation fluctuation, and ω_0 is the pre-exponential factor. The values of E_a increased with niobium doped, whereas the temperature T_f was on the decrease (see Fig. 5).

The $\varepsilon'(T)$ curves presented for undoped ceramics show a strongly diffuse character of FE–PE phase transition. Diffusion increases insignificantly for annealing ceramics. The quantitative assessment of the diffusion (γ) in the paraelectric phase was evaluated by using the expression given by Martirena and Burfoot:[10]

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_{max}} = \frac{(T - T_m)^{\gamma}}{2\delta^2} \quad (2)$$

where γ and δ are constants. It is known that the value of γ ($1 \le \gamma \le 2$) is the expression of the degree of dielectric relaxation in the ferroelectric relaxors. The coefficient γ increases really insignificantly with the content of niobium (from 1.94 to 1.97 for undoped and ceramics with 4 at.% Nb, respectively). The Curie–Weiss law ($\gamma = 1$) was observed only at temperatures much higher than T_m (above the temperature T_B). The observed behaviour of $\varepsilon'(T)$ in the range of paraelectric phase can be also described by the Curie–Weiss formula,

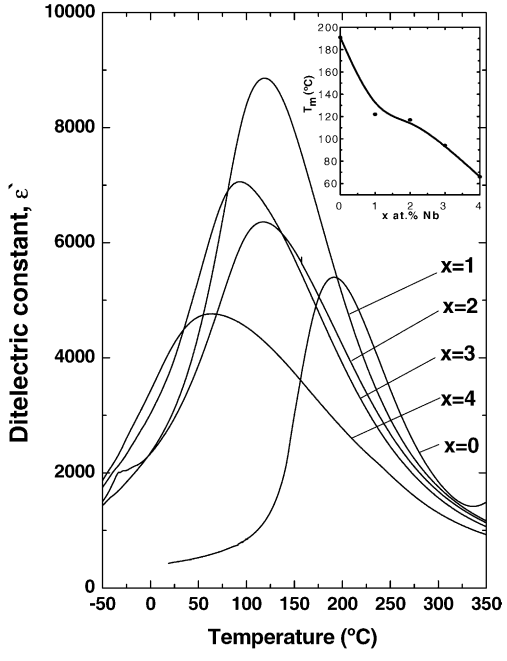

Fig. 3. Dielectric constant as a function of temperature, measured at frequency 1 kHz, for PBZT 25/70/30 ceramics with various Nb contents. The dependence of temperature T_m, corresponding to ε'_{max} on the Nb concentration is shown in the inserted plot.

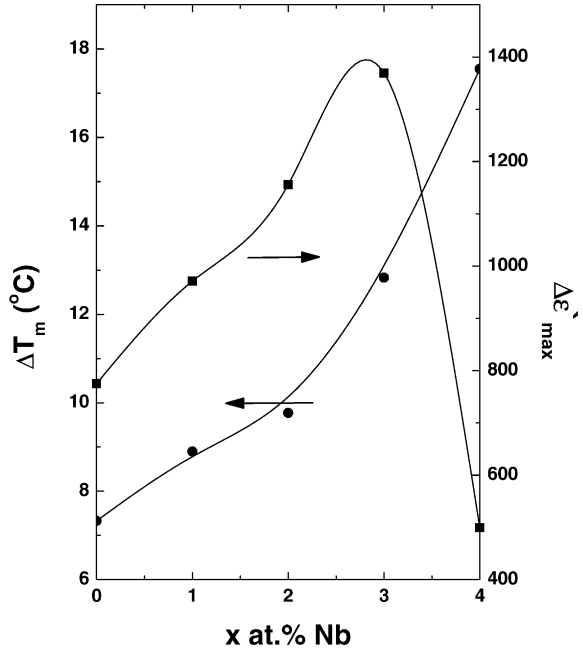

Fig. 4. Degree of frequency dispersion of $\Delta T_m = T_m$ (20 kHz) $- T_m$ (0.1 kHz) and $\Delta\varepsilon'_{max} = \varepsilon'_{max}$ (0.1 kHz) $- \varepsilon'_{max}$ (20 kHz) as a function of Nb concentration.

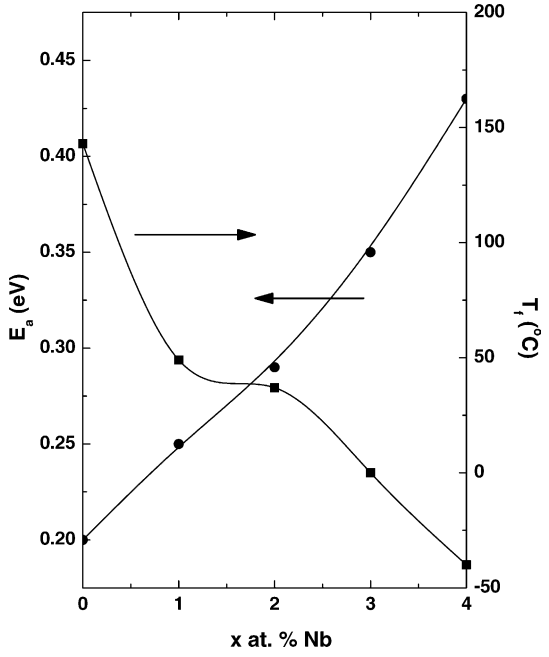

Fig. 5. Activation energy (E_a) and freezing temperature (T_f) as a function of Nb content for PBZT 25/70/30 ceramics.

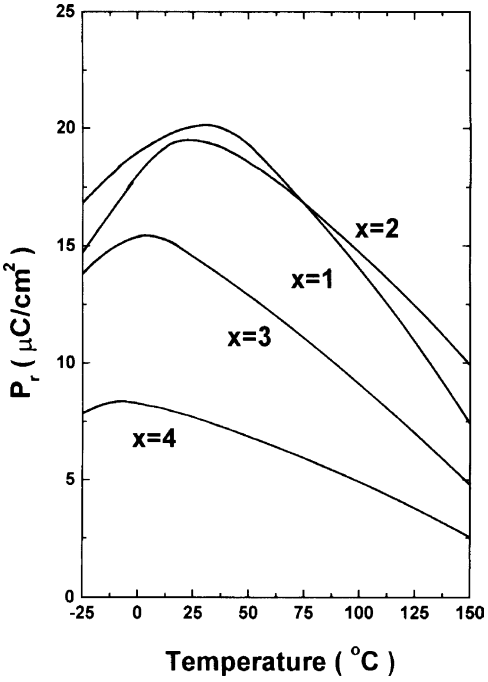

Fig. 6. Remanent polarisation as a function of temperature, determined on heating from histeresis loop measurements at field of strength 10 kV/cm for the PBZT 25/70/30 ceramics with various Nb content.

modified by Sherrington and Kirkpatric:[11]

$$\varepsilon' = \frac{C\{1 - q(T)\}}{T - \theta\{(1 - q(T)\}} \tag{3}$$

where θ is the Curie–Weiss temperature, C is the Curie–Weiss constant and $q(T)$ is the temperature-dependent local order parameter, which is equal to zero at the temperature where the polar clusters begin to appear on cooling (T_B). The temperature T_B calculated on the basis of the Eq. (3) did not reveal any systematic changes. For the ceramics with $x \leq 2$ the temperature T_B increased, but for larger concentration of niobium the T_B decreased to the value of $T_B = 330\,^{\circ}C$ for $x = 4$.

The temperature dependence of remanent polarisation (P_r) was determined from the histeresis loop measurements in the field of frequency 50 Hz and strength 10 kV/cm. The $P_r(T)$ curves are shown in Fig. 6. These curves differ significantly from the ones for normal ferroelectrics with the first order FE–PE phase transition. It concerns both the surroundings of the temperature T_m and temperature range below the maximum in $P_r(T)$ curves. The behaviour of $P_r(T)$ in the range of low temperatures points to the strong influence of screening processes of P_s by ion and electron–hole space charges and associated with ageing process. It is observed in all the investigated ceramics. In the case of undoped PBZT ceramics the maximum value of P_r is relatively small ($P_r \approx 6\,\mu C/cm^2$).[3] This value, with change of niobium concentration firstly increases to $P_r \approx 19\,\mu C/cm^2$ (for ceramics with $x = 1$ at.% of Nb) and then gradually decreased.

4. Pyroelectric and thermally stimulated depolarisation currents

The measurements of pyroelectric and thermally stimulated depolarisation currents (TSDC) were carried out for better understanding the unusual behaviour of dielectric characteristics, shown above. The samples were first polarised at DC field applied for 10 min at temperature $T_p = 200\,^{\circ}C$ and then cooled in the field to $-20\,^{\circ}C$ at which the field was switched off. The samples were then heated with constant rate of 5 K/min. through the diffuse FE–PE phase transition to the temperature 450 °C. The both currents were recorded numerically as a function of temperature and time during heating. The temperature changes of these currents, in the case of undoped ceramics, were widely discussed in our previous paper.[3] It is worth noting that in the undoped ceramics we observed great value of thermally stimulated depolarisation current with broadened maximum occurred at temperature on range 250–270 °C (depending on the temperature T_p) in which background appeared the distinct peaks of pyroelectric current. This peak occurred in temperature T_f calculated from Vogel–Fulcher relationships.[9] Addition 1 at.% of niobium to investigated ceramics caused increased value of pyroelectric peak, which also was less broaden (see Fig. 7). Moreover, the value of maximum of TSDC (J_{max}) reminded unchanged. The both peaks are separated by wide minimum. For both (doped and undoped) ceramics J_{max} was range of 10^{-9} A/cm^2. When the content of niobium increased, the value of peak of pyroelectric current decreased as well as the thermal depolarisation cur-

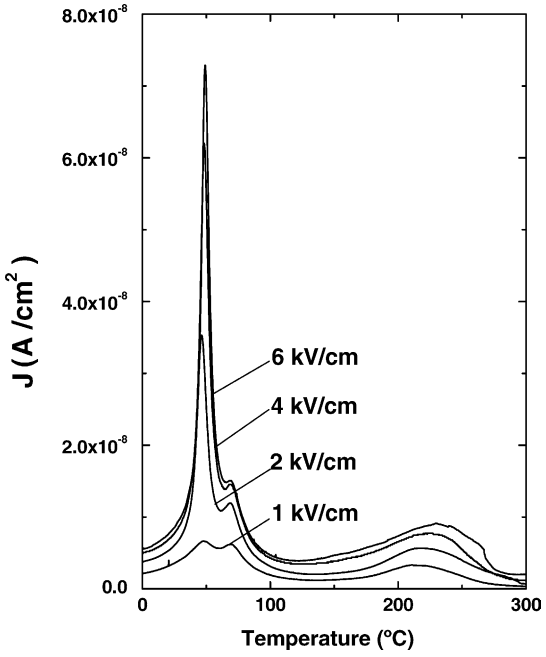

Fig. 7. Pyroelectric and thermally stimulated depolarisation currents vs. temperature, for Nb modified ($x = 1$) ceramics pre-polarised by applying electric field of various strength at constant temperature $T_p = 200\,^{\circ}C$.

rent. In the ceramics with 4 at.% of Nb the TSDC disappears completely.

5. Discussion

The obtained experimental data show that the Nb dopant strongly influences on all the investigated characteristics of PBZT 25/70/30 ceramics. The undoped and Nb-modified ceramics show the features typical for the relaxor ferroelectrics such as reducing ε'_{max} and shift of the corresponding temperature T_m towards higher temperatures with the increasing of frequency of the measuring field. Admixture of niobium caused not only a shift in the temperature T_m (Fig. 3) but also a considerable improvement of the relaxor properties (Fig. 4). It can be understood based on the well-known interpretation models describing the dielectric properties of the relaxor ferroelectrics.[15]

It is commonly known that the dielectric behaviour of Pb containing the relaxor ferroelectrics are generally explained in the literature in terms of small regions of local spontaneous polarisation (so called polar-regions) with a nanometer scale size.[12,16] The regions appear on cooling at the temperature T_B, much higher than T_m and their density increases with decreasing temperature. The decreasing temperature causes the increase of both: the number of polar-regions, as well as their size. Distribution of the relaxation times depends on the distribution of the size and polarisation strength of the polar-regions. The Nb-dopant probably reduces not only the grain size (Fig. 1) but also the size of polar-regions. It is very possible, that the size of regions is diverse. It leads to the broadening of relaxation time and increases the degree of frequency dispersion (Fig. 4).

Origin of the mentioned regions is caused by the structural disorder. In lead containing relaxor ferroelectrics of the perovskite structure (ABO_3) two kinds of the structural disorder are taken into consideration: chemical disorder of A- and B-sites and A-site dynamical disorder, caused by the anharmonic motion of the Pb atoms.[13] The Nb^{5+} addition to PBZT ceramics changes both types of disorder. It has already been shown that the substitution of Nb^{5+} ions for Zr^{4+}/Ti^{4+} ions is the most likely phenomena.[8] Due to the large difference between the coordination numbers (coordination numbers for Nb^{5+} and Pb^{2+} are 6 and 12, respectively), it is unlikely that Nb^{5+} ions substitute for Pb^{2+}. This process should be accompanied by the effect of an increase of Pb-position vacancy concentration. In our previous paper[17] we have shown that the degree of frequency dispersion for PBZT 25/70/30 ceramics also depends on the Pb-vacancies.

The presence of Pb and O vacancies exerts a strong influence on the balance of charge carriers transport process. As it is known from earlier studies[8] the PZT ceramics exhibit electric conductivity of p-type caused by Pb vacancy, which act as the acceptor centres. The Nb^{5+} ions substituted for Zr/Ti play the role of donors. This leads initially to the decrease of electric conductivity, due to compensation of the already existing holes by electrons from donor dopant.[8] Additionally, we investigated DC electric conductivity for Nb-modified PBZT 25/70/30 ceramics (Fig. 8). In fact, it was noticed that the value of the electric conductivity decreases significantly from 9×10^{-7} (at 360 °C) to $9 \times 10^{-10}\ \Omega^{-1}\ cm^{-1}$ for the undoped and Nb (3 at. %) doped ceramics, respectively. The additional

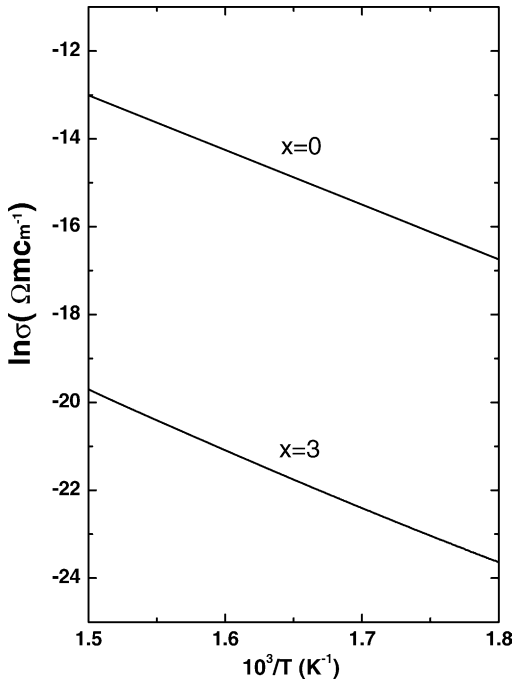

Fig. 8. Temperature dependence of DC electric conductivity as $\ln\sigma = f(1/T)$ measured on heating for undoped ($x = 0$) and Nb-modified ($x = 3$) ceramics.

low frequency dielectric dispersion which appears in the PE phase range in undoped ceramics, described in greater detail in our earlier papers,[2,9,14] depends on ion defects and electron-hole carriers which compensate, by screening, the dipole moments of polar-regions. After the disappearance of dipole moments of polar-regions the liberated carriers and ion defects give rise to the observed anomalies of ε' and TSDC in the PE phase. The screening process plays much smaller role in the case of Nb-modified PBZT 25/70/30 ceramics, with the electric conductivity reduced by three orders of magnitude. Therefore, the low frequency dispersion is not observed and the wide maximum of TDS current gradually disappeared for Nb-modified ceramics.

It is worth mentioned, that admixture of niobium causes also the change of the temperature T_B and the markedly decrease of the T_f. It leads to widening of the temperature range in which the relaxor properties occur. The similar influence on dielectric behaviour was observed for La-modified PBZT 25/70/30 ceramics.[9]

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