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Dielectric properties of BT–LMT mixed ceramics

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Abstract

Two types of ceramics of $(1-x)$BaTiO$_3$–xLa(Mg$_{1/2}$Ti$_{1/2}$O$_3$) with $x = 0.025$ (0.975BT–0.025LMT) were dielectrically investigated over the extended frequency range. Dielectric studies have been performed in the frequency range from 20 Hz to 10 GHz within the temperature interval of −170–230 °C. It is shown, that in these ceramics BT-type three phase transitions become diffuse and typical relaxor type dispersion is observed. Maxima of both imaginary and real parts of the dielectric permittivity are shifted to lower temperatures in comparison with pure BT and in the temperature ranges close to the phase transitions show a strong frequency-dependent behaviour. The distribution function of the relaxation times $g(\tau)$ was calculated from dielectric measurements for both measured ceramics—homogenous and non-homogenous. Dynamics of the phase transitions are discussed.

Keywords: Barium titanate; Dielectric properties; Perovskites

1. Introduction

Lead-free perovskite relaxors were not investigated as widely as more conventional lead-containing compounds, e.g. PMN and PLZT. In spite of the similar characteristic features of the dielectric behaviours observed in lead-based and lead-free relaxors, these are believed to be rather different.[1] It is generally accepted that short-range correlated displacements of the A-site cation (Pb^{2+}) induced by the chemical disorder are the origin of polar nanoregions (PNR) in lead-based materials.[2] The microscopic origin of PNR in lead-free perovskites has not been fully elucidated yet. At the same time, the key source for relaxor behaviour in these environment-friendly relaxors is mainly supposed to be a perturbation the B–O bond oscillations caused by a chemical inhomogeneity.[3]

Appearance of PNR and their dynamics in lead-based perovskite relaxors have been thoroughly investigated by a wide range dielectric spectroscopy.[4–7] As regards lead-free relaxors, no complete data on their dielectric spectra were reported and analysed so far.

It has been shown[8] that relaxor state in barium titanate (BT) can be readily induced by both A- and B-site heterovalent substitutions with "non-ferroelectric" cations. Indeed, solely relaxor behaviour was observed in the system BT–La(Mg$_{1/2}$Ti$_{1/2}$)O$_3$ at as low as 7.5 mol% doping with lanthanum magnesium titanate (LMT).[9] At the same time, the BT ceramics doped with 2.5 mol% of LMT (BT–0.025LMT) were found to exhibit the features typical of both ferroelectrics and relaxors.[10]

Till present there was no experimental data of dielectric dispersion of these ceramics. Only low frequency measurements have been performed.[9,10] The aim of the present paper was investigation of the dielectric dispersion up to microwave frequency range and calculation of the dispersion parameters of these BT–0.025LMT ceramics.

2. Experimental

Both the conventional mixed oxides method and the chemical method based on the Pechini route[11] were used for the powder processing. A stoichiometric mixture of the respective reagent-grade oxides and carbonates was ball-milled in ethanol and calcined at 1200 °C for 4 h. Following the latter (chemical) procedure, nitrates of lanthanum and magnesium as well as barium carbonate in proper ratio were dissolved in titanium citrate. The resulting solution was then dried and calcined at 750 °C (2 h) to obtain a fine powder of the desired composition. This preparation route was shown to allow the production of more uniform and

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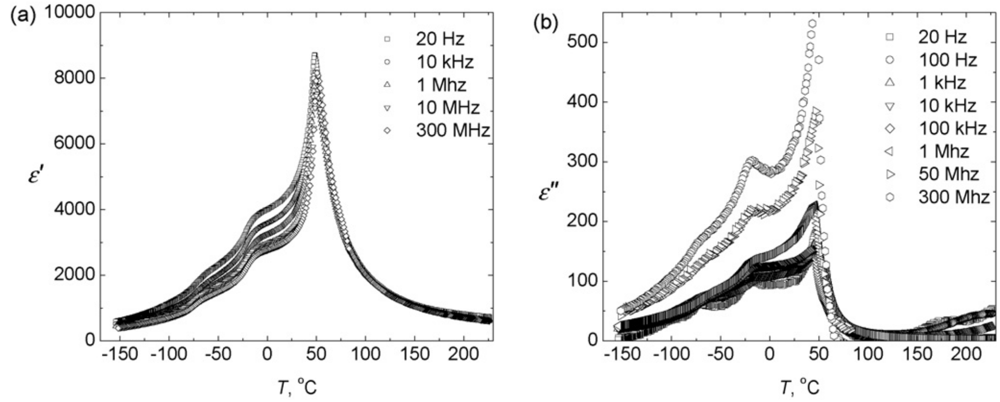

Fig. 1. Temperature dependence of the real (a) and imaginary (b) parts of dielectric permittivity at different frequencies of BT–0.025LMT (homogenous).

fine-grain ceramics in comparison with those processed by the conventional method.

Whatever the powder processing way was used, all the ceramics were sintered in oxygen gas flow at 1450–1500 °C for 2–4 h.

Two types of ceramics have been obtained. After measurements they were classified into two types: homogeneous one, which showed all three phase transitions of BT type, and non-homogeneous, in which only two phase transitions have been observe.

The dielectric measurements of BT–0.025LMT ceramics were performed by a computer controlled LCR meter HP 4284A in the frequency range 20 Hz–1 MHz, by the coaxial (frequency range 300 kHz–3 GHz) and the waveguide (8–12 GHz) dielectric spectrometers.[12] All measurements were made at cooling with a rate of 1 °C/min in the temperature interval of 230–(−170) °C. Samples of different size, satisfying technical requirements were used for every mentioned frequency range. Silver paste was used for contacts.

3. Results and discussion

Temperature dependence of the real and imaginary parts of the dielectric permittivity of BT–0.025LMT ceramics are presented in Fig. 1. As it is possible to see, there are three phase transitions as in pure BT. Only these phase transitions are shifted to lower temperatures, compared with BT. Also, below the first phase transition at 50 °C, typical relaxor properties are observed. The real part of dielectric permittivity is strongly frequency dependent below 50 °C and imaginary part at low frequencies is nearly frequency independent. This is also confirmed by frequency dependence of the real and imaginary parts of dielectric permittivity (Fig. 2). From the results presented in Figs. 1 and 2, we see, that we have relaxor, which in the low temperature phase shows another two phase transitions. In Fig. 3 the temperature dependence of the real and imaginary parts of dielectric permittivity of non-homogeneous sample are presented. These temperature dependences differ significantly from the results presented in Fig. 1. As we can see, in the temperature dependence of the real part of dielectric permittivity we can clearly distinguish only two phase transitions: at about 100 and 30 °C. The first one most probably is caused by BT regions, the other one by the rest volume of the ceramics. Due to that we classify this ceramics as non-homogeneous. This ceramics below the phase transition at 30 °C shows typical relaxor behaviour as PLZT and other well investigated relaxors.[7] The frequency dependence of the real and imaginary parts of dielectric permittivity of non-homogeneous ceramics confirm typical relaxor behaviour (Fig. 4). The real part of the dielectric permittivity shows linear behaviour with frequency, the imaginary part up to microwaves also is frequency nearly independent.

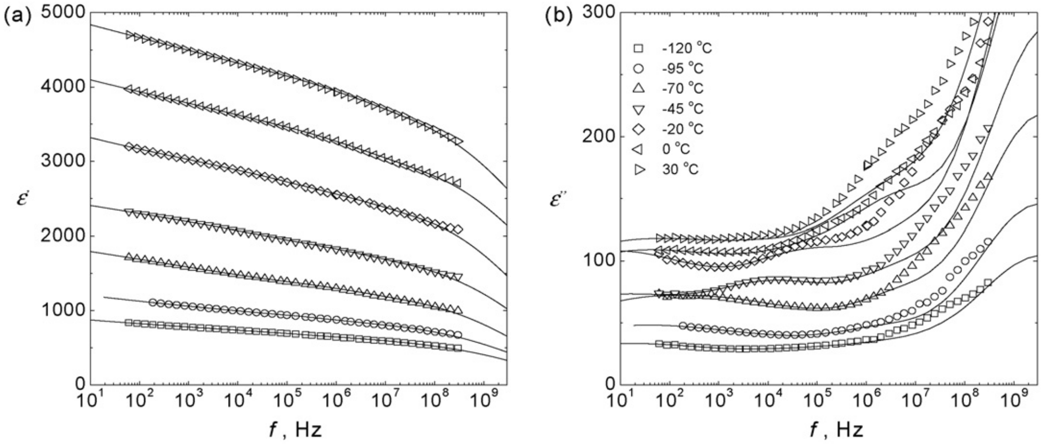

Fig. 2. Frequency dependences of the real (a) and imaginary (b) parts of the dielectric permittivity measured in different temperatures. Lines are the best fits with the obtained distribution of the relaxation times (BT–0.025LMT homogenous).

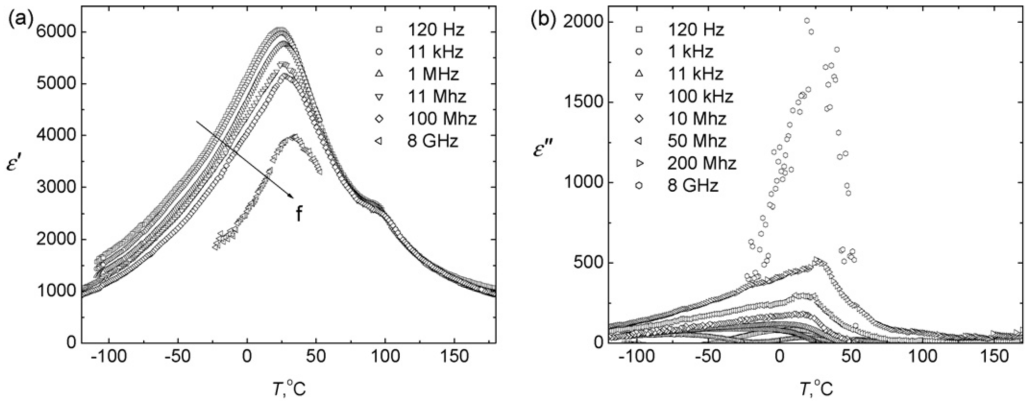

Fig. 3. Temperature dependence of the real and imaginary parts of dielectric permittivity at different frequencies of BT–0.025LMT (non-homogenous).

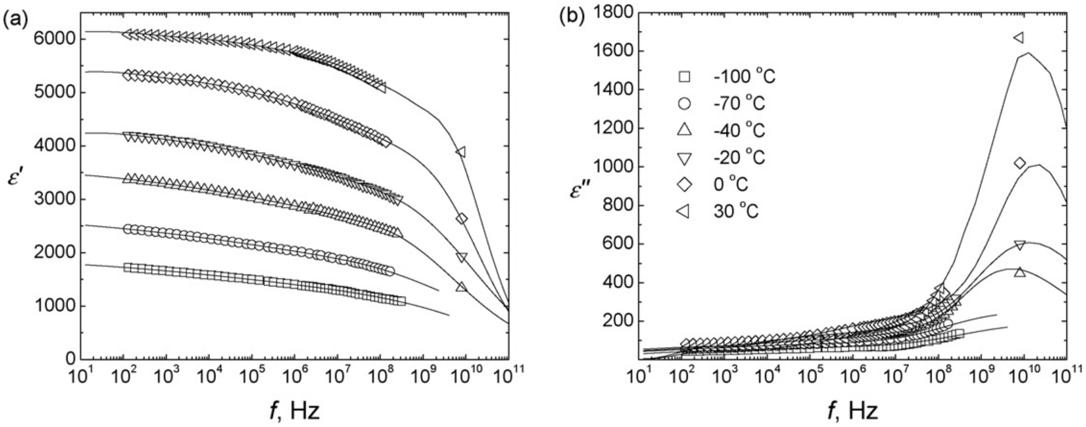

Fig. 4. Frequency dependences of the real (a) and imaginary (b) parts of the dielectric permittivity measured in different temperatures. Lines are the best fits with the obtained distribution of the relaxation times (BT–0.025LMT non-homogenous).

Usual evaluation of the dielectric dispersion parameters is performed with Cole–Cole or Havriliak–Negami formulas. Unfortunately, these formulas have defined shape of the distribution of the relaxation time function. As we can see from Figs. 2 and 4 in our case we have extremely broad and non-symmetrical shape of the frequency dependence of the imaginary part of the dielectric permittivity. Also, after careful examination of the frequency dependence of the imaginary part we can see, that there are at least two maxima, so there is no possibility to describe dispersion with single Cole–Cole or Havriliak–Negami process (Fig. 2). In such case, only one possibility is to extract the real distribution of the relaxation times from the dielectric spectra.

From the frequency dependence of the real and imaginary parts of dielectric permittivity the distribution of relaxation times is treated as the ensemble of independent Debye-like processes:

$$\varepsilon'(f) = \varepsilon_\infty + \int_{-\infty}^{\infty} \frac{g(\tau)}{1+(2\pi f\tau)^2}\,\mathrm{d}(\ln\tau) \qquad (1)$$

$$\varepsilon''(f) = \int_{-\infty}^{\infty} \frac{2\pi f\tau g(\tau)}{1+(2\pi f\tau)^2}\,\mathrm{d}(\ln\tau) \qquad (2)$$

These integral equations have been numerically solved. The Tikhonov regularization method has been used. This method and calculation technique is described in detail elsewhere.[13]

Obtained results are presented in Figs. 5 and 6. As we see, the distributions of the relaxation times for homogeneous and non-homogeneous ceramics are clearly different. In the case of homogeneous ceramics we observe one maxima at about 10^{-11} s, and broad maxima at longer relaxation times. Similar picture was already obtained for PMN-PSN-PZN relaxor ceramics.[7] With temperature decreasing, the maxima at 10^{-10} s decreases, and becomes comparable with long relaxation times broad maxima. We assume, that this maxima at

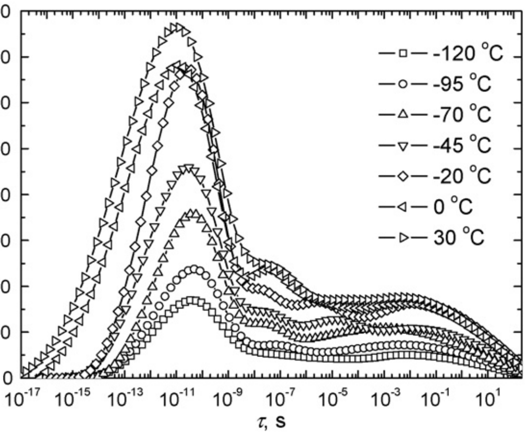

Fig. 5. Distribution of the relaxation times of BT–0.025LMT (homogenous).

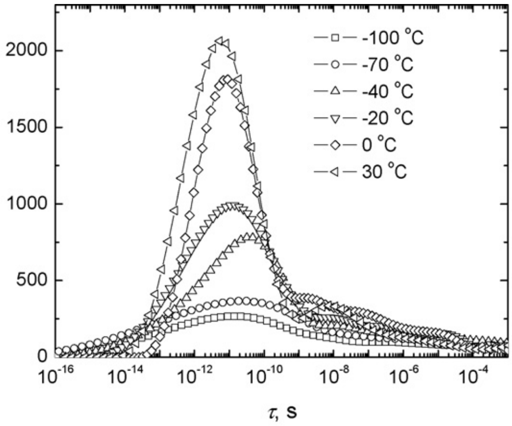

Fig. 6. Distribution of the relaxation times of 0.025LMT–BT (non-homogenous).

about 10^{-11} s is caused by non-polar matrix of relaxor and long relaxation times and broad maxima is caused by polar nano regions, which contribution increases with decreasing temperature. The main difference, compare with previous results for relaxors, is that the long relaxation time edge do not diverge according to Vogel–Fulcher law, but stays nearly constant at all temperatures at about 10 s. Such behaviour can be caused by the limits of our experimental frequency range. For exact characterization of the low frequency or long relaxation time limit further investigations at low frequencies are required.

The distribution of the relaxation times for non-homogeneous ceramics (Fig. 6) is different. As we can see, we do not observe clearly expressed long relaxation times maxima, instead of that, the maxima of non-polar matrix decreases with temperature and broadens. This result confirms non-homogeneous distribution of LMT in the sample—it does not behave as typical relaxor. It is more like ferroelectric phase transition, but with broad distribution of the relaxation times. As in previous sample, we were not able to check validity of Vogel–Fiulcher law of the long relaxation time edge.

4. Conclusions

From the broad band dielectric spectroscopy of two types of BT–0.025LMT ceramics the distribution of the relaxation times for both of them have been calculated. These distributions of the relaxation times differ from typical relaxor distribution of the relaxation times.[7] In the case of homogeneous ceramics (Fig. 5), distribution is more similar to the relaxor type, but the dynamics of polar nano regions is different—no Vogel–Fulcher law dependence of the long relaxation times has been observed. This can be caused by influence of the ferroelectric phase transition at 50 °C. Due to that, the dynamics of relaxor type polar nano regions is strongly influenced by ferroelectric order, and these regions, caused by substitution of LMT do not give the main contribution to the dielectric permittivity, and the dynamics of these regions is completely different from the relaxors. But the temperature and frequency dependencies look very similar to the relaxor ones. They even look more similar for the relaxor type for non-homogeneous sample. But after examination of the distribution of the relaxtion times (Fig. 6) we see, that this ceramics is even more different from realxors. We see, that main maxima of the distribution of the relaxation times only slightly shifts with temperature and significantly broadens, but we do not observe splitting of the distribution times caused by polar nano regions.

From these results we can conclude, that the BT–0.025LMT composition shows ferroelectric and nearly relaxor properties. In this composition we have bridging materials between ferroelectrics and relaxors.

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