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Effect of Ce and La substitution on dielectric properties of bismuth titanate ceramics

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Abstract

Effect of Ce and La substitution on the microstructure and dielectric properties of bismuth titanate (BT) ceramics was investigated. Bismuth titanate ceramics ($Bi_{4-x}A_xTi_3O_{12}$) (A = Ce or La; $x = 0$, 0.5, 1) were processed by sintering of pressed pellets, prepared from nanopowder synthesized by the modified sol–gel method. Pure and La modified bismuth titanate ceramics have single $Bi_4Ti_3O_{12}$ phase of Aurivillius type, whereas a small amount of $Bi_2Ti_2O_7$ pyrochlore phase appears in Ce modified bismuth titanate ceramics. In the same time addition of La and Ce improved sinterability of BT ceramics. The results of the measurement of dielectric constant and loss tangent at different frequencies (100 Hz–1 MHz) as a function of temperature reveal that Ce modified ceramics has a diffuse phase transition. Temperature T_m, corresponding to the maximum value of the dielectric constant, is shifted to higher temperature and the maximum value of the dielectric constant is decreased with increasing frequency, which indicate that relaxor behavior is caused by Ce substitution.

Keywords: A. Sol–gel processes; A. Sintering; C. Dielectric properties; D. Perovskites

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1. Introduction

Piezoelectric ceramics such as lead zirconate titanate PZT have been widely used in sensors and actuators because they have excellent piezoelectric properties [1]. On the other hand this material possesses some shortcomings such as fatigue endurance and significant amount of toxic lead. As the new environmental protection laws become very strict, lead-free materials are receiving considerable attention.

Among many lead free compositions that have been used in order to overcome the fatigue problems existing in PZT ceramics [2], bismuth layered perovskite metal oxide materials, such as $SrBi_2Ta_2O_9$ (SBT) and $Bi_4Ti_3O_{12}$ (BT) are considered as the promising solutions. One of the most intensively studied lead-free ferroelectrics includes compounds based on layered bismuth oxides belonging to the class of Aurivillius type structure ferroelectric materials. Structure of these ferroelectrics consists of $[Bi_2O_2]^{2+}$ layers interleaved with perovskite-like $[A_{n-1}B_nO_{3n+1}]^{2-}$ units stacked along *c*-axes. In the general formula of Aurivillius family, n is number of BO_6 octahedra, (i.e. $n = 1–5$), A represents 12-fold cation sites [3] which can be occupied by Ba^{2+}, Ca^{2+}, Sr^{2+}, Bi^{3+} and the rare earth cations, while on 6-fold *B*-sites belonging to BO_6 octahedra Ti^{4+}, Ta^{5+}, Nb^{5+} and W^{6+} can be found [4–6]. The three-layer member ($n = 3$) of Aurivillius phase is bismuth titanate, $Bi_4Ti_3O_{12}$. Its lead-free content, high Curie temperature ($T_c = 675$ °C), excellent fatigue endurance and electrooptic switching behavior make it potential candidate for various applications such as memory storage, optical display, piezoelectric transducers or pyroelectric devices [7]. The ferroelectric phase transition in $Bi_4Ti_3O_{12}$ is characterized by the change in symmetry of the crystal structure from paraelectric tetragonal to orthorhombic state exhibiting ferroelectric properties, which is accompanied by the lattice distortion and internal stresses [8].

In order to control dielectric and ferroelectric properties of bismuth titanate it is possible to substitute cations of the proper ionic radii and valence for *A* and/or *B*-sites of perovskite like slabs. The influences of Bi^{3+} site substitution with isovalent La^{3+}, Nd^{3+}, Pr^{3+} and Sm^{3+} cations and Ti^{4+}site substitution with

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higher-valent Nb^{5+}, V^{5+} and W^{6+} cations on dielectric and ferroelectric properties have been well studied [4,9,10]. Pure bismuth titanate materials have p-type conductivity and a relatively low electrical resistivity. As expected in p-type material, acceptor dopants increase the BT electrical conductivity, whereas doping with donor cations decreases BT conductivity [11]. In addition, it is reported [12] that substitution with proper ionic radii of lanthanoid elements enhances polarization, which is in this system much lower than in PZT. In this paper we report on influence of Ce and La substitution on microstructure and dielectric properties of bismuth titanate ceramics.

2. Experimental

Bismuth titanate nanopowders ($Bi_{4-x}A_xTi_3O_{12}$) (A = Ce or La; $x = 0, 0.5, 1$; corresponding to the samples BT, BCT-y and BLT-y where $y = 100\cdot x$) were synthesized by the modified sol–gel method in a two-step process: first by controlled hydrolysis of titanium-butoxide with distilled water, and then by further reaction of the formed hydrated titania gel particles with corresponding ions (Bi^{3+} and La^{3+} or Ce^{3+}) [13,14]. Metal ions precursors in these syntheses are tetrabutyl-orthotitanate ($Ti(OC_4H_9)_4$, Fluka), bismuth(III)-nitrate pentahydrate ($Bi(NO_3)_3 \times 5H_2O$, Fluka), cerium(III)-nitrate hexahydrate ($Ce(NO_3)_3 \times 6H_2O$, Merck) and lanthanum(III)-nitrate hexahydrate ($La(NO_3)_3 \times 6H_2O$, Riedel-de Haen).

After calcination at 600 °C for 1 h powders were uniaxially pressed into disk of 10 mm diameter at pressure of 125 MPa. The pellets were sintered at temperatures up to 1100 °C for 2 h in the Bi_2O_3 rich atmosphere in closed crucible. The $Bi_4Ti_3O_{12}$ powder, placed in the crucible, was used as a source of bismuth oxide in order to minimize the bismuth loss during high-temperature sintering.

The phase structure of the bismuth titanate based ceramics is analyzed by X-ray diffraction (Philips 70, Cu Kα) for 2θ in the range of 20° to 60° and the microstructure is observed by scanning electron microscope, SEM (JEOL JSM-6460LV). Density of sintered samples is measured by Archimedes method using distilled water. Samples with gold/palladium electrodes, sputtered on polished pellets, were used for conductivity measurements at Novocontrol Alpha-AN. In order to examine the dielectric properties, silver paste is coated to form electrodes on both major sides of the sample, and then subsequently fired at 850 °C for 60 min. The capacitance and dielectric losses of the samples are measured as a function of temperature using HP 4294A impedance analyzer.

3. Results

X-ray diffraction patterns of samples sintered at 1050 °C for 2 h are illustrated in Fig. 1. XRD data for the ceramic sample BT ($Bi_4Ti_3O_{12}$) revealed the existence of single bismuth titanate phase of Aurivillius type, similar as the ceramics with La addition, BLT ($Bi_{3.5}La_{0.5}Ti_3O_{12}$ and $Bi_3LaTi_3O_{12}$). However, the Ce modified bismuth titanate ceramics, BCT ($Bi_{3.5}Ce_{0.5}Ti_3O_{12}$ and $Bi_3CeTi_3O_{12}$), besides bismuth titanate phase, consists of small amount of $Bi_2Ti_2O_7$ pyrochlore phase. The presence of small portion of pyrochlore phase is expected as it was shown that stability of $Bi_2Ti_2O_7$ phase in BT powders was increased with Ce addition [13].

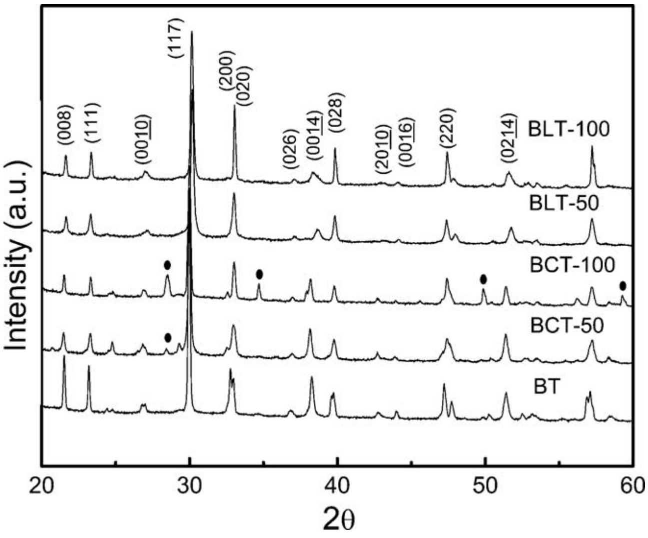

Fig. 1. X-ray diffraction patterns of BT, BCT-50, BCT-100, BLT-50 and BLT-100 sintered at 1050 °C (● pyrochlore phase).

The microstructure of the bismuth titanate based ceramics sintered at 1050 °C is shown in Fig. 2. In the micrographs of the fracture surface of the samples BT, BCT-50 and BLT-50 platelike grains with the grain size of ~5 μm are observed. Density of the pure bismuth titanate ceramics is ~92% of theoretical density, while density of the Ce and La modified ceramics are higher (above 95% of theoretical density). Another distinct feature of the samples with Ce observed in the micrographs is that the fracture occurs through the large number of grains. The existence of transgranular fracture is probably due to preferable distribution of Ce in the boundary region [14].

The frequency dependence of electrical conductivity measured at room temperature for the BCT-50 and BLT-50 samples was studied in the frequency range from 1 Hz to 1 MHz, Fig. 3. Conductivity in bismuth titanate ceramics is a mixture between ionic and electronic conduction and strongly influenced by defects, such as bismuth and oxygen vacancies, which can be trapped at sites like grain boundaries and grain-electrode interfaces and create space charges [15]. Thus, the observed reduction in electrical conductivity in the La substitute BT ceramics (sample BLT-50) with regards to pure BT could be explained by the fact that La substitution suppresses the volatility of Bi and decreases concentration of oxygen and bismuth vacancies [16]. The conductivity value for the BLT-50 is a little bit higher compared to the BCT-50 sample at low frequencies, but two orders of magnitude lower at frequencies above 100 kHz. It has been reported [17,18] that activation energy for electrical conduction in bismuth titanate ceramics is different at high, intermediate and low frequencies and also that at high frequencies grain rather than grain boundary and grain-electrode effects has stronger influence on electrical properties. Thus, as the grain size of the samples BLT-

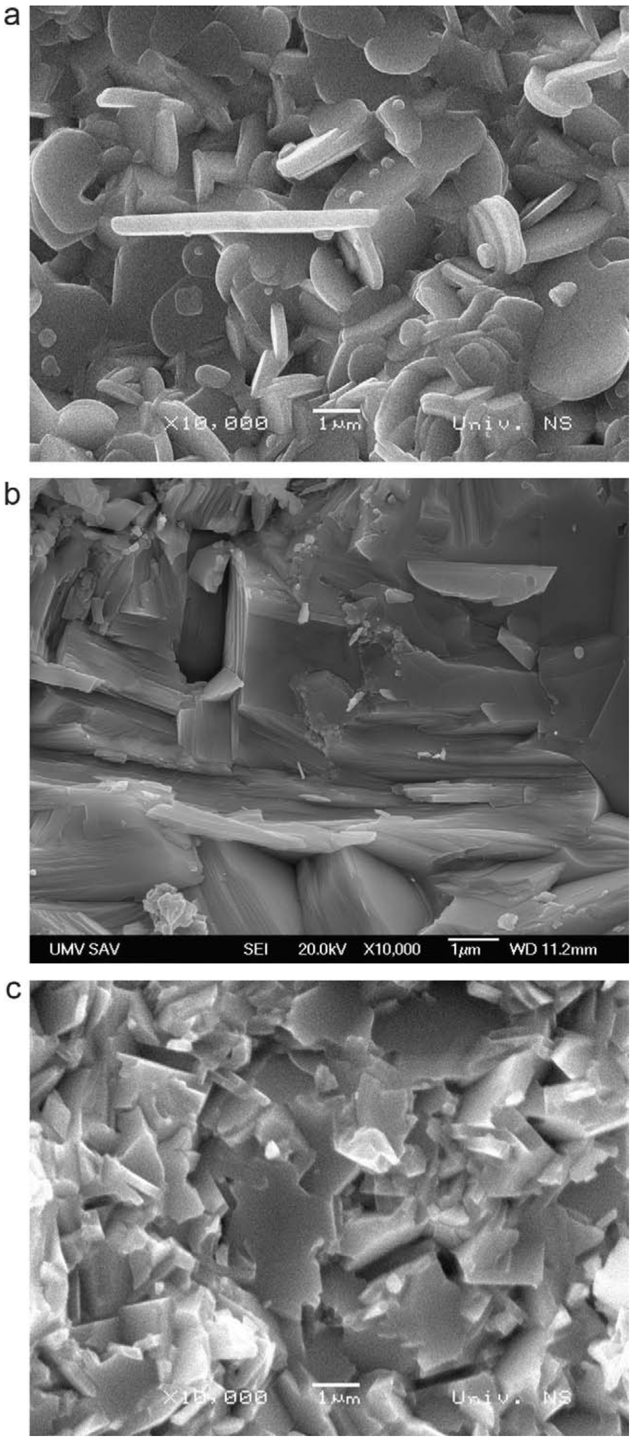

Fig. 2. SEM micrographs obtained for the fracture surfaces of (a) BLT-50, (b) BCT-50 and (c) BT sintered at 1050 °C/2 h.

50 and BCT-50 is similar preferable distribution of Ce in boundary region could be responsible for the observed difference in conductivity in low and high frequency region.

Dielectric constant and loss tangent as a function of temperature, measured at different frequencies for the samples BCT-50 and BLT-50 sintered at 1050 °C for 2 h are shown in Figs. 4 and 5. With temperature increasing dielectric constant for both, Ce and La modified ceramics increases and reaches maximum at around 540 and 525 °C, respectively, which is considerably lower than the value of 675 °C for pure BT. This is a consequence of the incorporation of La and Ce in the $Bi_4Ti_3O_{12}$ lattice and slightly diminution of the crystal lattice

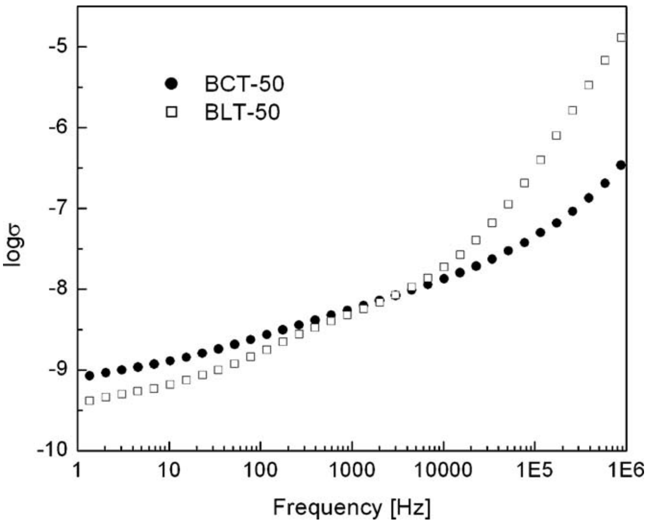

Fig. 3. Conductivity as a function of frequency at room temperature for BLT-50 and BCT-50.

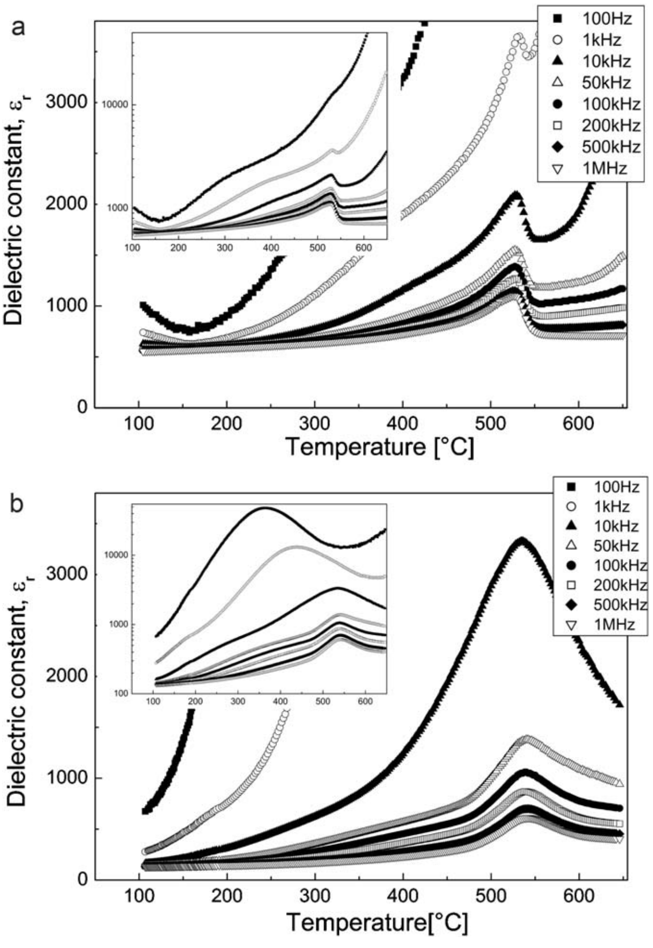

Fig. 4. Dielectric constant of (a) BLT-50 and (b) BCT-50, as a function of temperature, for eight frequencies. Inset note semilogarithmic scale.

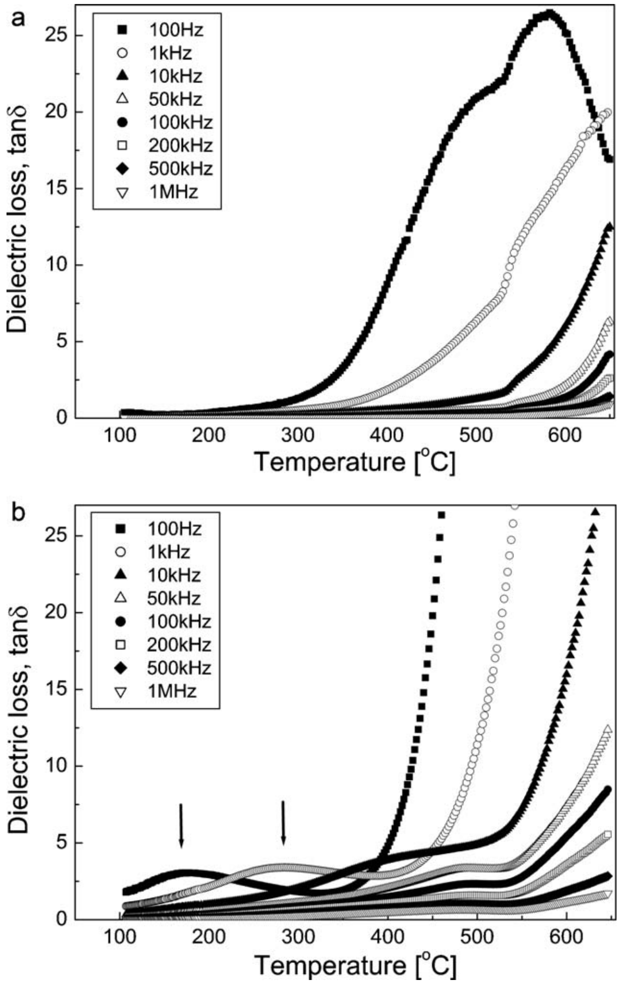

Fig. 5. Dielectric loss tangent of (a) BLT-50 and (b) BCT-50, as a function of temperature, for eight frequencies.

distortion. Addition of La improves dielectric properties of bismuth titanate as it suppresses the volatility of Bi and reduces the oxygen vacancies in the ceramics. However, it can be seen (Fig. 4) that dielectric constant of the sample BCT-50, at the same frequency, is lower than for the sample BLT-50. There are a few possible reasons for this behavior: (i) characteristic nature of Ce which can change its oxidation states easily between +3 and +4 and thus has different role in creation of structural defects, (ii) the presence of a small amount of the secondary $Bi_2Ti_2O_7$ phase (Fig. 1), etc.

Loss tangent (tan δ) decreases with frequency and increases with temperature, with the obvious change in slope at temperature of dielectric maximum (Fig. 5). The loss tangent at 150 °C and frequency range between 50 kHz and 1 MHz is <0.02 for the BLT-50 and much higher (<0.15) for and the BCT-50 ceramics. The increase in the dielectric loss with temperature is correlated with the increased electric and ionic conduction [8]. However, specifically for the BCT ceramics there are broad peaks at low temperatures, clearly visible in low-frequency curves, indicated by arrows in Fig. 5b. It is shown that this low-frequency dielectric dispersion at low temperature could be correlated with high concentration of defects such as bismuth and oxygen vacancies [4,16,19].

It should also be noted that strong frequency dispersion is observed around the dielectric constant peak for the Ce modified sample (Fig. 4b). The temperature T_m, corresponding to the maximum value of the dielectric constant, is shifted to higher temperature and the maximum value of the dielectric constant is decreased with increasing frequency. The observed diffuse phase transition and frequency dispersion of the dielectric constant in the BCT ceramic, characteristic of the relaxor ferroelectrics behavior, are not typical dielectric behavior of pure and La modified bismuth titanate ceramics [4,10,20]. Unlike in normal ferroelectric phase transitions whose permittivity above the Curie point should obey the Curie-Weiss law ($\varepsilon = C/(T - T_{CW})$), where C is the Curie constant and T_{CW} is the Curie-Weiss temperature, in relaxor ferroelectric materials this law is valid only at temperatures much higher than temperature of maximum relative dielectric constant T_m (typically by hundreds of degrees) [21]. Fig. 6 shows the variation of reciprocal dielectric constant of the BCT-50 and BLT-50 with temperature at 200 kHz. It was found that dielectric constant of bismuth titanate ceramics with addition of Ce obviously deviates from the Curie-Weiss law. For the

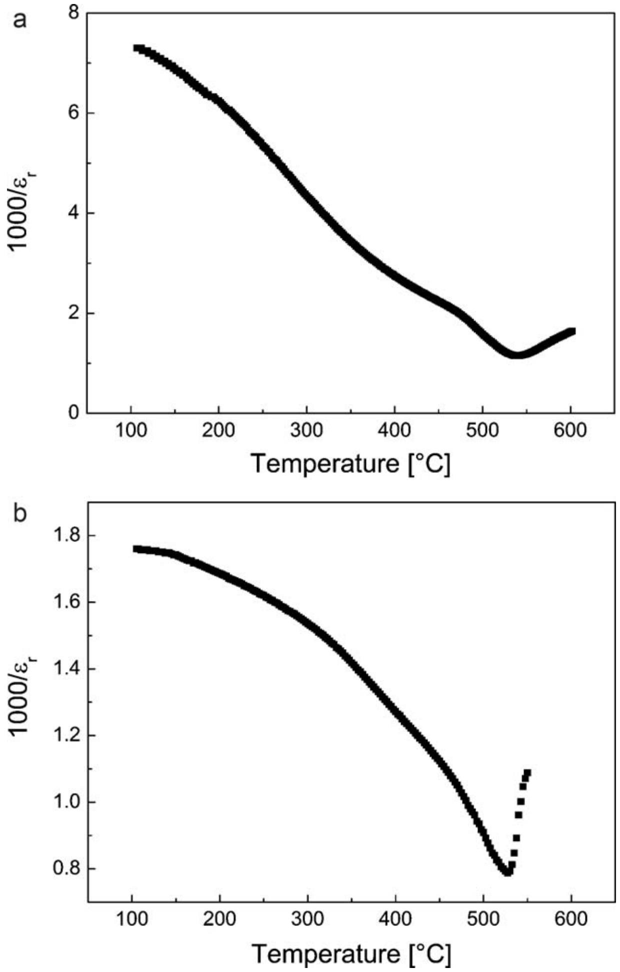

Fig. 6. Inverse dielectric constant at 200 kHz as a function of temperature for: (a) BCT-50 and (b) BLT-50.

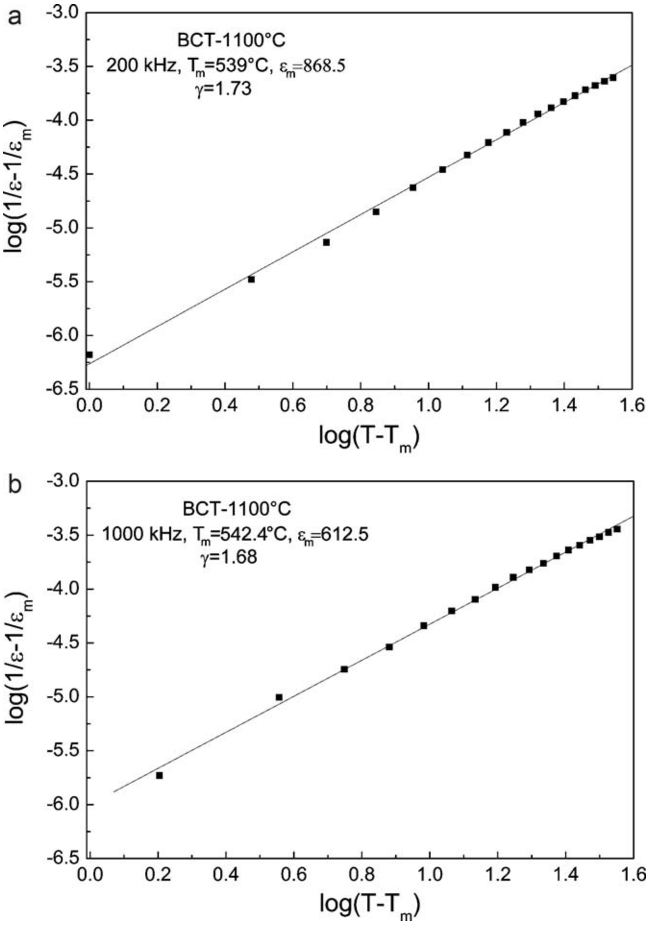

Fig. 7. Relation $\log(1/\varepsilon - 1/\varepsilon_m)$ and $\log(T - T_m)$ for BCT-50 sample at: (a) 200 kHz and (b) 1000 kHz.

relaxor ferroelectrics, the reciprocal of the dielectric constant vs. temperature follows a modified Curie-Weiss law [5]:

$$\frac{1}{\varepsilon}-\frac{1}{\varepsilon_m}=\frac{(T-T_m)\gamma}{A}$$

where A is a constant, and γ is called a diffusion coefficient ranging from 1 (normal ferroelectric) to 2 (an ideal relaxor ferroelectric). According to the plot of $\log(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\log(T - T_m)$ at 200 and 1000 kHz for the BCT-50 ceramics (Fig. 7) the slope of the fitting curve is used to determine the γ value [22]. It is found that the γ coefficient for the BCT-50 sample has a value of $\sim$1.7 which confirms that material shows relaxor behavior.

4. Discussion

The broadened ε maximum (in ε vs. temperature curve) and its deviation from the Curie-Weiss law are the main characteristics of a diffuse phase transition of a material and relaxor behavior. The broadness or diffusiveness in ε vs. temperature occurs mainly due to compositional fluctuation and structural disordering in the arrangement of cations in one or more crystallographic sites of the perovskite structure. This suggests a microscopic heterogeneity in the compound with different local Curie points [23].

Among lanthanide metals Ce can change its oxidation states easily between +3 and +4. It can be expected that Ce ions preferably occupy Bi-site in the bismuth titanate ceramics due a similar ionic radii and the fact that at higher temperature (>730 °C) Ce^{4+} cation is usually reduced to Ce^{3+}. In this valent state part of Ce ions enters crystal structure at Bi-site, similar to *A*-site substitution in perovskite oxides. However, in spite of a large difference in the ionic radii of Ce^{4+} (0.087 nm) and Ti^{4+} (0.0605 nm) ions, in some case Ce^{4+} ion can partially substitute the Ti^{4+} ion located at the center of the oxygen octahedron of perovskite type unite [24,25]. Thus, we assume that when Ce is added into bismuth titanate structure, it preferably substitutes Bi^{3+} ions, but could be introduced also into *B*-sites, i.e. on the Ti^{4+} position, depending on oxygen states of Ce ion. This increases off-center displacement because the radius of Bi^{3+} (0.093 nm) is smaller than that of Ce^{3+} (0.101 nm) and the radius of Ti^{4+} is much smaller than that of Ce^{4+} (0.087 nm). The increase of the off-center displacement gives rise to a local polar moment, which leads to the formation of more macropolar domains at room temperature. With the temperature increase, more macrodomains (long-range ordered regions) breakup into microdomains, then form polar microregions [22]. As it is mentioned above, heterogeneity which is due to existence of these microregions with different local Curie points in the compound leads to diffuse phase transition of Ce modified bismuth titanate ceramics.

5. Conclusion

Addition of La and Ce improved sinterability of bismuth titanate ceramics, but had different influence on microstructure. Thus, pure and La modified bismuth titanate ceramics have single $Bi_4Ti_3O_{12}$ phase of Aurivillius type, whereas a small amount of $Bi_2Ti_2O_7$ pyrochlore phase appears in Ce modified bismuth titanate ceramics. Microstructure of fracture surface of ceramics with Ce revealed the existence of fracture through the large number of grains, while ceramics with La consisted of well defined platelike grains as well as pure bismuth titanate compounds.

Addition of La improves dielectric properties of bismuth titanate as it suppresses the volatility of Bi and reduces the oxygen vacancies in the ceramics. On the other side, addition of Ce changes considerably dielectric behavior of bismuth titanate ceramics creating diffuse phase transition and frequency dispersion of the dielectric constant, characteristic for the relaxor ferroelectrics. The broadened ε maximum (in ε vs. temperature curve) and its deviation from the Curie-Weiss law in BCT ceramics are mainly due to compositional fluctuation and structural disordering in the arrangement of cations in one or more crystallographic sites of the perovskite structure.

Acknowledgements

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