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DIELECTRIC PROPERTIES OF AURIVILLIUS-TYPE $Bi_{4-x}Gd_xTi_3O_{12}$ CERAMICS

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The present work is aimed for dielectric investigation of undoped and gadolinium-substituted Aurivillius-structure bismuth titanates $Bi_4Ti_3O_{12}$ (BIT) and $Bi_{2.5}Gd_{1.5}Ti_3O_{12}$ (BGT). The measurements were performed as a function of both frequency and temperature in the frequency range of 20 Hz – 1 MHz and in the temperature range of 30–1100 K. Obtained results can be divided into two parts: the low temperature part, where the glass like dispersion occurs, and the high temperature part, where high electrical conductivity dominates. The activation energies for the presumably oxygen vacancies migration-related conductivity is $E_A = 0.73$ eV for $Bi_4Ti_3O_{12}$ and $E_A = 0.98$ eV for $Bi_{2.5}Gd_{1.5}Ti_3O_{12}$ [1].

Keywords: Aurivillius structure, ferroelectrics, ceramics

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1. Introduction

Complex oxides with the Aurivillius structure [2] appear to be a promising family for searching for novel functional materials. Indeed, the bismuth layer-structured ferroelectrics can be successfully used in nonvolatile random access memories (NVRAM), actuators, sensors, and piezoelectric components [2, 3]. The Aurivillius phases are composed of the $(Bi_2O_2)^{2+}$ sheets interleaved by perovskite-type blocks $(A_{n-1}B_nO_{3n+1})^{2-}$ of variable thickness corresponding to the natural n to form a "mica-like" $Bi_2A_{n-1}B_nO_{3n+3}$ structure [4]. Because of their ionic structural framework, Aurivillius phases exhibit a great variability with respect to A and B cation substitution; accordingly, these compounds have high potential for systematic property control [5]. Nevertheless, no comprehensive study allowing to reveal common tendencies of changes of crystal structure, magnetic and ferroelectric properties of the Aurivillius-type compounds upon introducing magnetically active 4f and 3d ions has been performed yet, so the Aurivillius-family ferroelectrics remain attractive from the viewpoint of multiferroic investigations [6]. One of the most recently reported examples of applications of this research strategy is $Bi_{4-x}Gd_xTi_3O_{12}$, which was proven to demonstrate the ferroelectric domain structure at ambient temperature (for $x \le 1.5$) and possess a high magnetic susceptibility in a low temperature range [6]. In this paper, we continue investigations of this series and report on its dielectric behaviour.

2. Experiment

Polycrystalline samples $Bi_{4-x}Gd_xTi_3O_{12}$ ($x = 0, 1.5$) were prepared by a two-stage solid-state reaction method using the oxides Bi_2O_3, Gd_2O_3, and TiO_2 taken in a stoichiometric ratio [6]. The heat treatment was carried out in air at 1073 K for 5 h and at 1123 K (BIT) or 1198 K (BGT) for 24 h with heating/cooling rates of 5 K/min. The measurements of the complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ were performed using a Hewlett Packard 4284A LCR meter in the 20 Hz – 1 MHz frequency range. To obtain a continuous metallic contact, three layers of platinum paste were deposited on the surface of the ceramics. Each layer was dried up by heating from the room temperature up to 1100 K at a constant rate of 15 K/min and cooled down at the same speed. All the measurements were made on heating with a rate of 1 K/min.

3. Results and discussion

The results of dielectric measurements are presented in Figs. 1–4. A dielectric anomaly is observed in $Bi_4Ti_3O_{12}$ ceramics at low temperatures (Figs. 1(a), 2(a)). At low temperatures the position of maximum of the real part of complex dielectric permittivity is frequency dependent (Fig. 1(a)). On the other hand, the temperature dependence of imaginary part of complex dielectric permittivity exhibit two overlapped and frequency dependent maxima (Fig. 2(a)). Both these maxima shift to higher temperatures with the increase of the frequency. Such behaviour of complex dielectric permittivity can be attributed to ferroelectric domain dynamic [7] or dipolar glass type behaviour [8]. At higher temperatures (above 500 K) the phenomena of electrical conductivity are observed in the dielectric spectra of BGT ceramics (Figs. 3(b) and 4(b)) [1]. The value of the imaginary part of complex dielectric permittivity of BGT

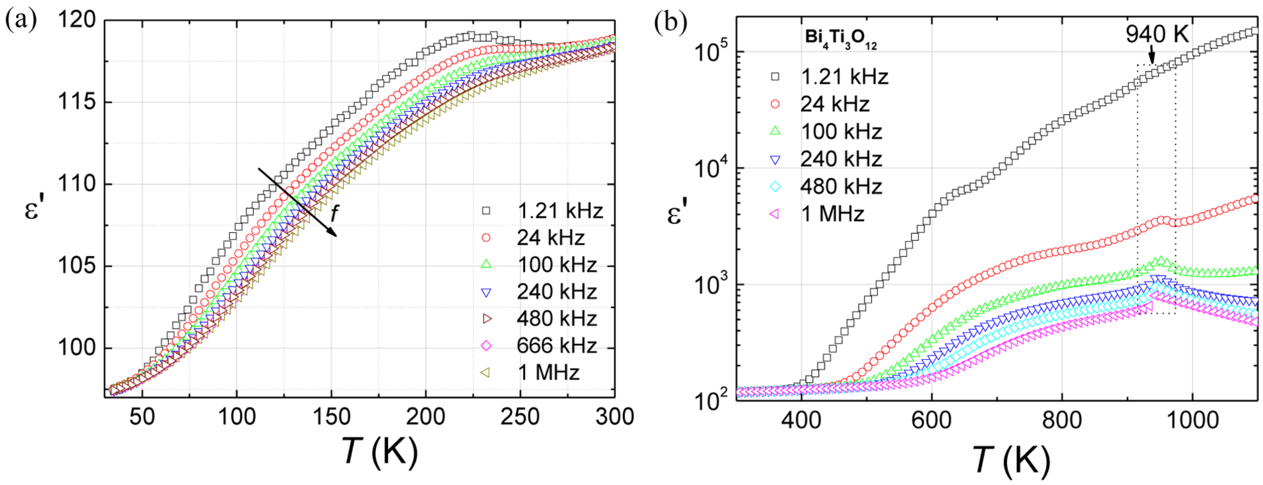

Fig. 1. Temperature dependence of the real (ε') part of complex dielectric permittivity of $Bi_4Ti_3O_{12}$ at different frequencies at (a) lower and (b) higher temperatures.

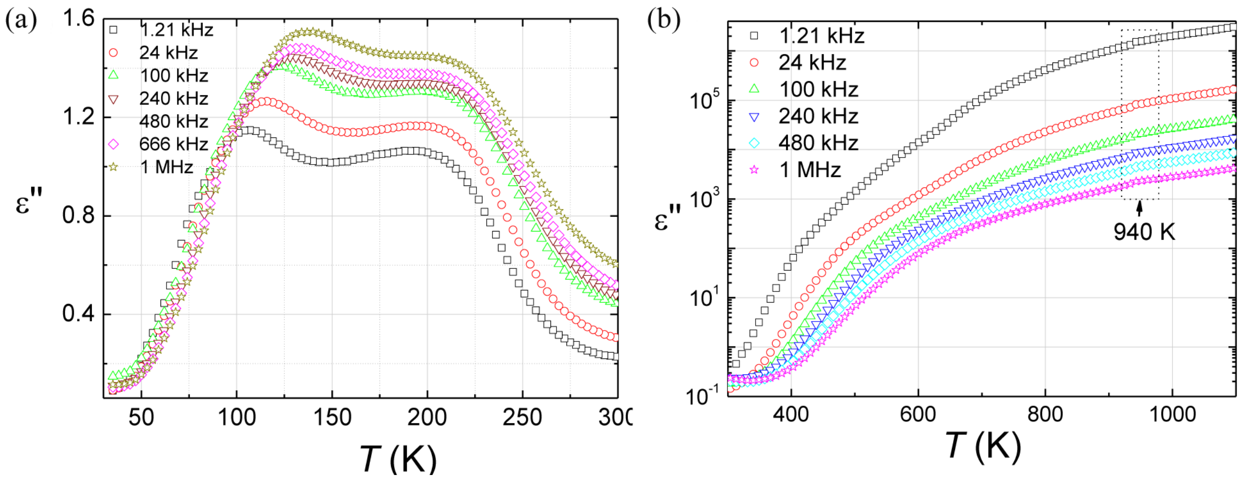

Fig. 2. Temperature dependence of the imaginary (ε'') part of complex dielectric permittivity of $Bi_4Ti_3O_{12}$ at different frequencies at (a) lower and (b) higher temperatures.

ceramics at temperatures higher than 800 K is bigger than that of the real part [1]. Therefore, the increase of the real part of complex dielectric permittivity is influenced by the same processes of electrical conductivity. The anomaly of electrical conductivity at 940 K in BIT ceramics is related with the ferroelectric phase transition reported in [3, 6].

At higher temperatures (above 500 K) low-frequency permittivity is dominated by conductivity effects.

To distinguish the grain conductivity from intergrain conductivity, the specific resistance has been calculated according to

$$\rho^{*}=\frac{1}{\sigma^{*}(\omega)}=\rho^{'}(\omega)-i\rho^{''}(\omega)=\frac{\varepsilon^{'2}-i\varepsilon^{''2}}{\varepsilon_0\omega(\varepsilon^{'2}+\varepsilon^{''2})}, \quad (1)$$

where $\omega = 2\pi\nu$, ν is the measurement frequency, ε_0 is the vacuum permittivity. The results are presented in Fig. 5. One can clearly see that there are two semicircles, which can be attributed to the grain, intergrain conductivity, and blocking contacts effect. The semicircle at higher frequencies (and lower values of resistance) are usually caused by the volume conductivity of ceramics, while the higher value of ρ^* accounts for intergrain processes and can also be influenced by blocking contacts. From the left semicircle, the grain specific resistance ρ_g at different temperature was calculated. Bulk activation energy of the grains E_A was calculated from the obtained temperature dependence of $\sigma_g = 1/\rho_g$ according to the Arrhenius law:

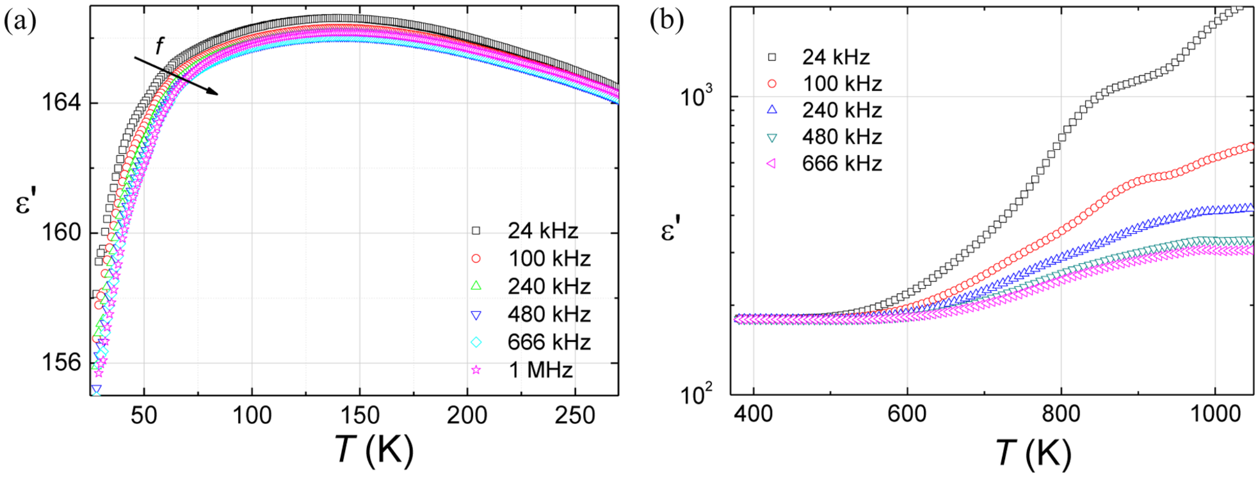

Fig. 3. Temperature dependence of the real (ε') part of complex dielectric permittivity of $Bi_{2.5}Gd_{1.5}Ti_3O_{12}$ at different frequencies at (a) lower and (b) higher temperatures.

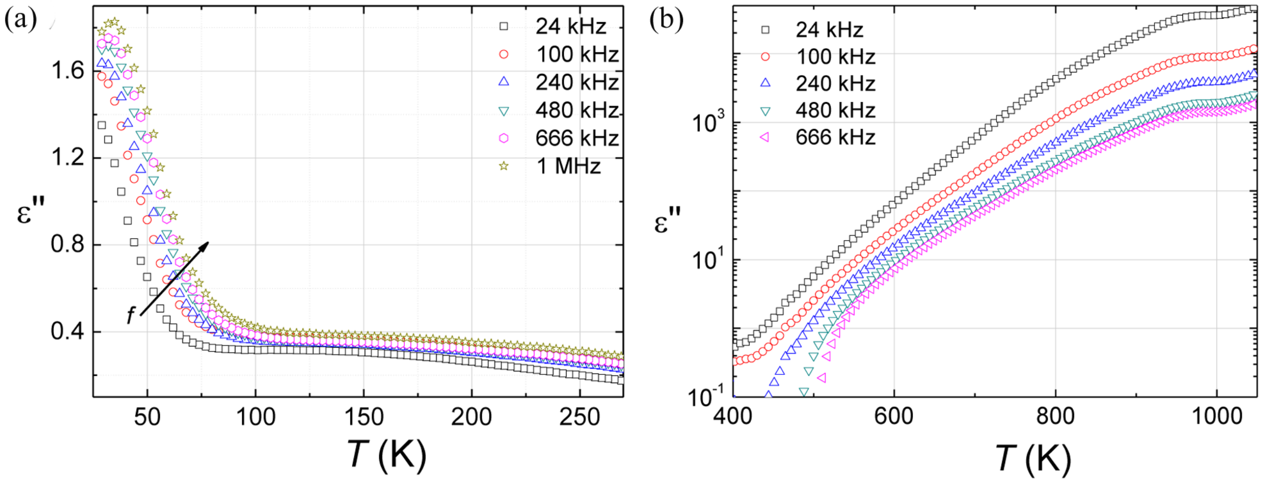

Fig. 4. Temperature dependence of the imaginary (ε") part of complex dielectric permittivity of $Bi_{2.5}Gd_{1.5}Ti_3O_{12}$ at different frequencies at (a) lower and (b) higher temperatures.

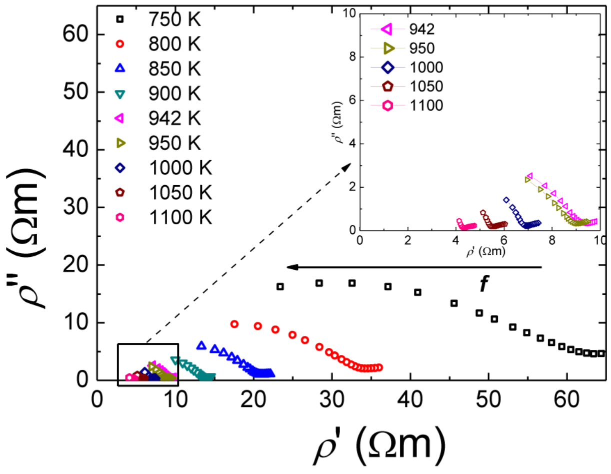

Fig. 5. Nyquist diagram for specific resistance of $Bi_4Ti_3O_{12}$.

$$\sigma_g = \sigma_{g0}\exp(-E_A/kT). \tag{2}$$

The fracture at 940 K and the change of activation energies are visible in Fig. 6. Above 940 K the activation energy decreases and is equal to 0.39 eV.

The conductivity effect may be treated in terms of electrical modulus. The conductivity of mobile ions is related to the electrical modulus $M^*(\omega)$ using complex dielectric permittivity by the following expression:

$$M^* = \frac{1}{\varepsilon^*(\omega)} = M'(\omega) + iM''(\omega), \tag{3}$$

The frequency dependences of real (M') and imaginary (M'') parts of a complex electric modulus at several temperatures are shown in Fig. 7. Taking into account the values of activation energies obtained above, oxygen vacancies should be the most probable electrical charge carrier [1]. In such a case, dispersion of the electrical modulus in the BIT and BGT are related to the oxygen vacancies caused conductivity process. The low-frequency value of M' is close to zero and represents a lack of the restoring force for the electric-field-induced mobile oxygen vacancies. As frequency increases, each vacancy moves within a reducible range until the electric field changes become too rapid to induce the vacancy oscillations outside the confinement of their potential energy wells. As a result, M' increases to a maximum asymptotic value $M(\infty) = 1/\varepsilon(\infty)$. The spectra of M'' show a slightly asymmetric peak centred in the dispersion region of M', which is typical of hopping ion conductivity [9].

The frequency of the peak (ω_{max}) is related to the most probable ionic conductivity relaxation time τ by the relation of $\omega_{max}\tau = 1$. The obtained temperature dependence of the relaxation time is plotted in Fig. 8. It shows that the relaxation time of the

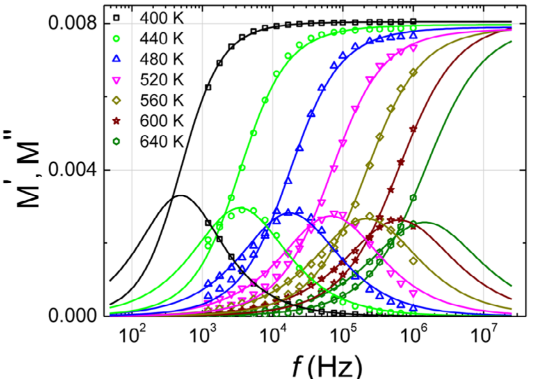

Fig. 7. Frequency dependencies of real (M') and imaginary (M'' parts of electrical modulus at different temperatures for $Bi_4Ti_3O_{12}$.

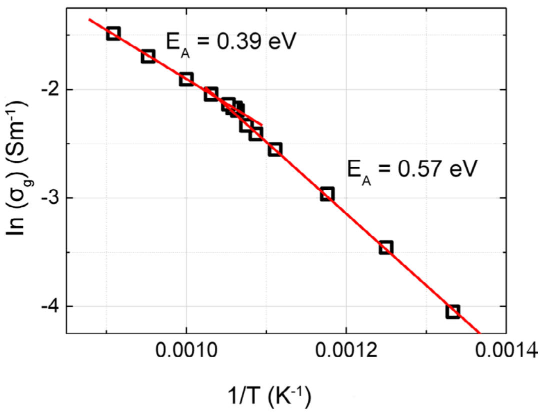

Fig. 6. Electrical conductivity of grains in $Bi_4Ti_3O_{12}$.

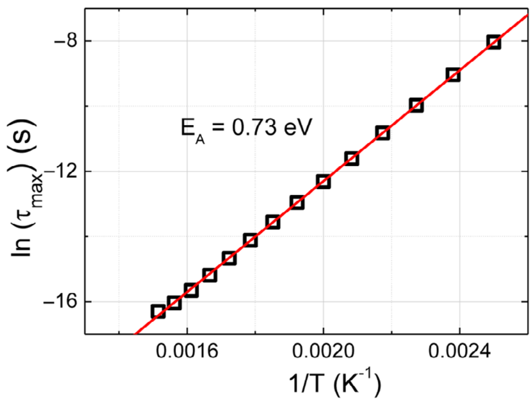

Fig. 8. Relaxation time obtained from the electrical modulus spectra of $Bi_4Ti_3O_{12}$.

vacancies is thermally activated and can be described by the Arrhenius law $\tau = \tau_0 \exp(E_A/kT)$. The value of activation energy for BIT is E_A = 0.73 eV.

4. Conclusions

Results of dielectric investigation of BIT and BGT revealed two different temperature regions of dielectric dispersion. At high temperatures (above 500 K) the dielectric spectra are dominated by electrical conductivity. From the dielectric data, the electrical modulus was calculated. The activation energy for conductivity was found to be ΔE_A = 0.73 eV (BIT). In the low temperature region (20–500 K) in BIT, dielectric dispersion was observed, which is related with two dielectric anomalies: the one at lower temperatures is similar to dielectric anomaly of dipolar glasses and the other at higher temperatures is related with ferroelectric domains dynamics. In the BGT, the behaviour at low temperatures is completely different – the dielectric anomaly, which could be associated with the domain like behaviour, is not observed, and only dielectric dispersion similar to dipolar glasses [8] is observed at very low temperatures.

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AURIVILIJAUS SANDAROS $Bi_{4-x}Gd_xTi_3O_{12}$ KERAMIKŲ DIELEKTRINĖS SAVYBĖS

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Santrauka

Naujos Aurivilijaus struktūros multiferoinės medžiagos yra perspektyvūs junginiai. Aurivilijaus struktūrą turinčios medžiagos yra labai svarbios dėl plataus jų pritaikymo feroelektriniams, pjezoelekriniams, mikroelektromechniniams įtaisams. Viena iš tokių medžiagų yra $Bi_4Ti_3O_{12}$ (BIT). Buvo pabandyta į BIT struktūrą įterpti magnetinių savybių turintį retųjų žemių metalą gadolinį (Gd). Šiame darbe publikuojami $Bi_4Ti_3O_{12}$ (BIT) ir $Bi_{4-x}Gd_xTi_3O_{12}$ (x = 1,5) (BGT) dielektriniai tyrimai.

Tyrimai atlikti dielektrinės spektroskopijos metodu 20 Hz – 1 MHz dažnių diapazone esant 30 K – 1 100 K temperatūrai. Žemų dažnių srityje, aukštoje temperatūroje, BGT ir BIT keramikose aiškiai matyti dominuojantys laidumo reiškiniai. Apskaičiuota aktyvacijos energija yra lygi E_A = 0,73 eV ($Bi_4Ti_3O_{12}$).