

BROADBAND DIELECTRIC SPECTROSCOPY OF CALCIUM MODIFIED BaZrTiO_3 RELAXOR CERAMICS

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In this work, we present the broadband dielectric spectroscopy results of Ca-modified $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0.5; 0.6$). The goal of the work is to understand if the relaxor ferroelectric properties of BZT are affected by the calcium substitution at the A-site of the perovskite lattice. The tolerance factor of calcium ions is below 1 so they are supposed to introduce a larger lattice distortion.

Thus, we carefully investigate two BZT (BZT50 and BZT40) compositions with 10% of calcium. To assess the influence of the substitution, we analyze the dielectric spectra and Vogel–Fulcher behaviour of mean relaxation time. This data is compared with the data of parental compositions that are available in the literature.

Keywords: relaxors, broadband dielectric spectroscopy, perovskites

1. Introduction

Relaxors are a subclass of disordered materials that are closely related to ferroelectrics. The origin of relaxor behaviour is one of the most intriguing topics in solid-state physics. These materials are not only relevant from the standpoint of fundamental physics but also are of significant technological importance. The primary applications are related to their superior piezoelectric properties [1, 2]. Such materials like $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) and $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$ (PMN-PT), are on the frontiers of medical ultrasound, piezoelectric energy harvesting, sensing and actuating applications.

Relaxor behaviour can occur only in compositionally disordered materials. The disorder arises from the site/charge disorder. In PMN, the effect stems from the B-site charge disorder of perovskite lattice. Due to the presence of different valence ions at the B-site, the random fields emerge in the materials [3, 4]. The random fields are the cornerstone of the relaxor behaviour. However, recent studies revealed that in lead-based relaxors, Pb^{2+} ions residing at the A-site of perovskite lattice play an im-

portant role for the unique properties of lead-based relaxors [5, 6]. It was proven that the lone-pair electron of lead tends to hybridize with the oxygen electrons [7]. This causes huge lattice distortions in the Pb-based perovskites. All in all, it is a multiple local phenomenon like random-fields and local distortions, that contribute to unique dielectric/piezoelectric (i.e. macroscopic) properties.

Despite the significant understanding of relaxor phenomenon in Pb-based perovskites, there is another family of materials based on BaTiO_3 (BT). It exhibits a typical dielectric behaviour associated with relaxor ferroelectrics. However, the relaxor behaviour in BaTiO_3 -based systems occurs with isovalent ion substitution. Such ions as Zr, Sn and Ce replacing titanium at the B-site suppress the BT phase transitions and enhance relaxor properties. Usually, the dielectric anomaly shifts towards lower temperatures [8–10]. Contrary to lead-based relaxors, the electric-field induced phase transition has not been clearly observed. It is one of the most important differences between such relaxors as $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ (BZT). Very often, BaTiO_3 -based relaxors are referred to as dipolar/cluster glasses [11–14].

The Vogel–Fulcher freezing phenomenon in BT-based relaxors is also a little vague compared to lead-based relaxors. The unique features of these materials are due to nanometre-scale polarization inhomogeneities caused by the displacement of ferro-active ions. These nanometre regions, the so-called polar nanoregions, emerge at the T_b temperature [15, 16] and grow upon cooling. At higher temperatures, they are dynamic entities but undergo a slowing down until it freezes at the freezing temperature T_f [17]. The freezing in classical relaxors manifests as the slowing down of relaxation dynamics observed in broadband dielectric spectroscopy [18–20]. However, the dynamics of BT-based relaxors very often shows almost Arrhenius behaviour (i.e. T_f is close to 0 K) [14, 21, 22]. This might be related to the fact that only Ti-ions are involved in the polar response of these relaxors. Thus, they can be considered as interacting dipoles in a very complicated, fractal-like potential well [23]. This situation, as pointed out by Sherrington, is an electrical equivalent of spin glasses. Indeed, the presence of dipolar-glass state can be justified by the order–disorder nature of Ti ions in barium titanate [24]. By introducing non ferro-active ions, like zirconium, cerium or tin, the potential well becomes non-regular for Ti-dipoles. That might be the source of competing interactions that are necessary for the dipolar glass state to appear.

The double-well potential model, that is applicable to dipolar glasses [25], has been successfully implemented to the $\text{BaTi}_{0.7}\text{Ce}_{0.3}\text{O}_3$ solid solutions [23]. In contrast, that model fails when applied to PMN or other lead-based relaxor ferroelectric systems. This is a strong evidence that BT-based relaxors have similarities to dipolar glasses. Furthermore, it seems that glassiness in these materials is dependent on the ionic radius of substituents that replace titanium.

Another intriguing question related to BT-based relaxors is the role of charge disorder. Since most of these relaxors have isovalent substitution, no charge disbalance is supposed to appear. Recently, extensive studies of Nb and Zr substituted barium titanate were conducted [26]. Niobium has 5+ valance and thus should strengthen random fields in the system. Due to the charge disbalance, some compensation mechanism should be present, thus complicating the situation. Indeed, the temperature dependence of complex dielectric permittivity differs drastically. Nb-doped barium titanate showed relaxor-like dispersion only at low temperatures, while at higher

temperature some charge separation related process dominated the dielectric spectra.

In this contribution, we investigate how the presence of different calcium ions at the A-site of perovskite lattice affects the relaxor behaviour of widely studied BZT50 and BZT40 solid solutions. The study will concentrate on broadband dielectric spectroscopy and a detailed analysis of dielectric spectra.

2. Experimental methods

For obtaining $\text{Ba}_{0.9}\text{Ca}_{0.1}(\text{Ti}_{0.4}\text{Zr}_{0.6})\text{O}_3$ and $\text{Ba}_{0.9}\text{Ca}_{0.1}(\text{Ti}_{0.5}\text{Zr}_{0.5})\text{O}_3$ (BCZT40 and BCZT50), the Pechini method was used. The Pechini method is a variation of the sol–gel technique dedicated to simple titanates and niobates of alkali metals using mainly nitrates and alcoholates as reagents. The key advantage is atomic-scale homogeneity. The process is valuable for creating complex materials with a uniform atomic-scale distribution of elements, such as superconductors, supercapacitors and fuel cell components.

The measured volumes of titanium (IV) and zirconium (IV) alkoxides were first mixed together and then vigorously stirred with a solution of ethylene glycol. The temperature of the resulting clear solution was raised to 80°C, while simultaneously adding a portion of a previously prepared saturated citric acid solution. A precipitate was formed and redissolved after a few minutes. Separately, weighed powders of barium and calcium carbonates were gradually dissolved in small portions in a saturated aqueous solution of citric acid heated to 100°C. Subsequently, the resulting barium and calcium citrate solution was added dropwise in stoichiometric amounts to the vigorously stirred solution of titanium Ti^{4+} and zirconium Zr^{4+} citrates prepared earlier. A yellowish semi resin solution was obtained, which was stirred while maintaining the temperature at 120°C for approximately 1 h to achieve the complete homogenization. This obtained solid resin is then heated to combust the organic matrix, resulting in a highly pure, finely crystallized oxide powder.

The calcination temperature was optimized by calcining the as-synthesized powders at 700°C for 4 h to get the BCZT phase formation confirmed by X-ray diffraction studies. The calcined powders were mixed with polyvinyl alcohol (PVA) and compacted into pellets of 10 mm diameter and 2 mm thickness using a uniaxial press at an applied pressure

of 375 MPa. The final sintering was performed at 1400°C for 2 h at a heating rate of 5°C/min.

The samples were measured by three different dielectric spectroscopy techniques in the 5–400 K temperature range. The conventional flat capacitor setup was used to investigate the temperature dependences of complex dielectric permittivity in the 20 Hz – 1 MHz frequency range. The capacitance and loss tangent was measured by a HP4824A LCR meter. The temperature was measured by a 100-ohm platinum resistor connected to a *Keithley* Integra 2700. A *Solartron* Modulab XM MTS system was used to measure capacitance and loss tangent to cover the 1 mHz – 1 MHz frequency range. The temperature was measured with a *Lakeshore* model 335 temperature controller.

Higher frequency region (1 MHz – 1 GHz) experiments were conducted by measuring the complex reflection coefficient from the end of short-circuited coaxial line that was loaded with the specimen. The complex reflection coefficient was measured with an *Agilent* 8714ET vector network analyzer. The multi-mode capacitor model was used to calculate the complex dielectric permittivity from the ex-

perimental results [27]. The temperature was measured by a 100-ohm platinum resistor connected to a *Keithley* Integra 2700.

The 26–35 GHz frequency range was covered by measuring scalar reflection and transmission coefficients inside the rectangular waveguide. The rod-shaped sample was placed perpendicularly in the middle of a wider wall of the waveguide. The dimension of waveguide was set so only the fundamental H10 mode could propagate. Scalar transmission/reflection coefficients were measured with an *Elmika* R2400 scalar network analyzer. The complex permittivity was then obtained by solving a set of nonlinear equations by the optimized Newton method. The temperature was measured with a T-type thermocouple connected to a *Keithley* Integra 2700 multimeter.

3. Results and discussion

Figure 1 depicts the temperature dependence of complex dielectric permittivity for BCZT50 and BCZT40 ceramics. The decrease of titanium in solid solutions shifts the dielectric anomaly towards

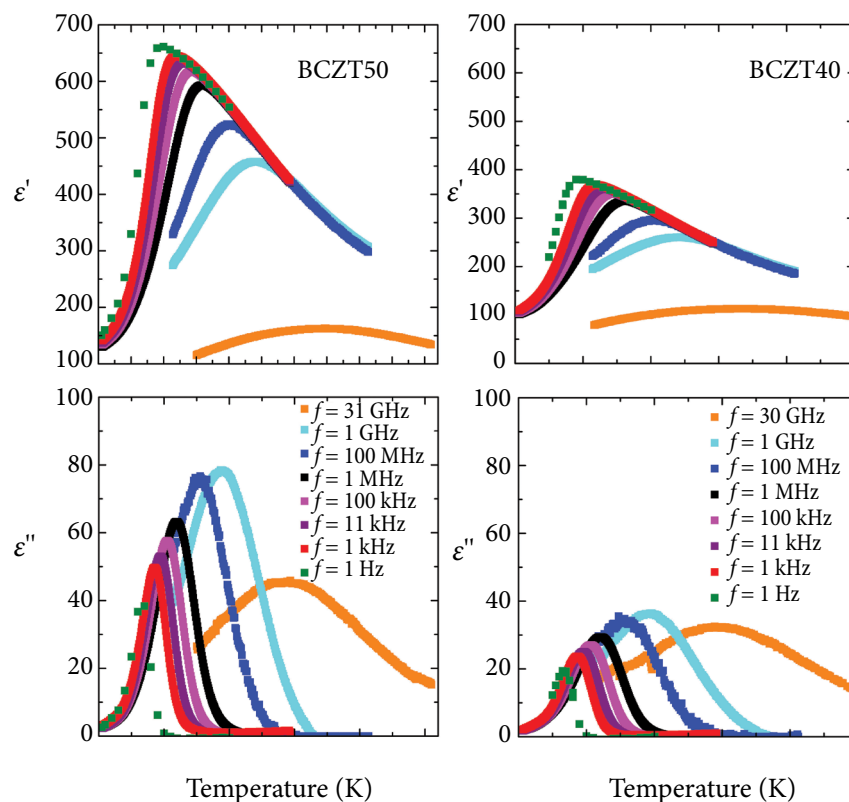


Fig. 1. Temperature dependences of the complex permittivity of BCZT50 and BCZT40 ceramics. The top panel depicts a real part, and the bottom panel shows an imaginary part.

lower temperatures. Additionally, the dielectric strength of relaxation decreases. According to the theoretical studies, it is related to the fact that Zr^{4+} barely contributes to dielectric permittivity. Most of the dielectric response stems from the dipoles containing Ti^{4+} ions [28]. This is a typical behaviour that is observed in ceramics without calcium [21].

The dielectric properties BZT50 and BZT40 have been extensively studied in literature [10, 13, 14, 21, 22, 29]. The calcium impact will be extracted by comparing our data to the ones that can be found in the literature. Calcium ions have the same valance as barium ions; they tend to occupy the A-site of the perovskite lattice. Furthermore, calcium titanate is non-ferroelectric in all the temperature range. However, the tolerance factor of CaTiO_3 is less than 1 [30], meaning that a strong lattice distortion is present. So, the substitution of barium by calcium should increase the local stress in the lattice. Thus, these distortions might contribute to the relaxor behaviour of BZT solid solutions.

BCZT50 and BCZT40 ceramics have a lower permittivity relative to their counterparts in the BZT family. The peak loss and permittivity in our investigation corresponds to nearly the same temperature as in the BZT samples [22]. A more detailed description of the shift of anomaly will be given when analyzing the temperature dependences of the mean relaxation time.

Figure 2 represents the frequency dependences of complex dielectric permittivity for BCZT50 ceramics. Only one sample is presented, because qualitatively the results are very similar for both samples. At low temperatures, the dielectric spectra are very broad. The peak of imaginary part of permittivity lies at the lower frequency range. This peak shifts outside the measurable frequency range and cannot be observed below ~ 40 K. Other important feature of the dielectric spectra is the obvious asymmetry at low temperatures. The asymmetry of the dielectric spectra gradually disappears as the sample is heated.

The dielectric spectra were modelled by the Havriliak–Negami equation [31, 32] to consider the spectral asymmetry,

$$\varepsilon^*(\omega) = \varepsilon(\infty) + \frac{\Delta\varepsilon}{(1 + (i\omega\tau_{\text{HN}})^{1-\alpha})^\beta}. \quad (1)$$

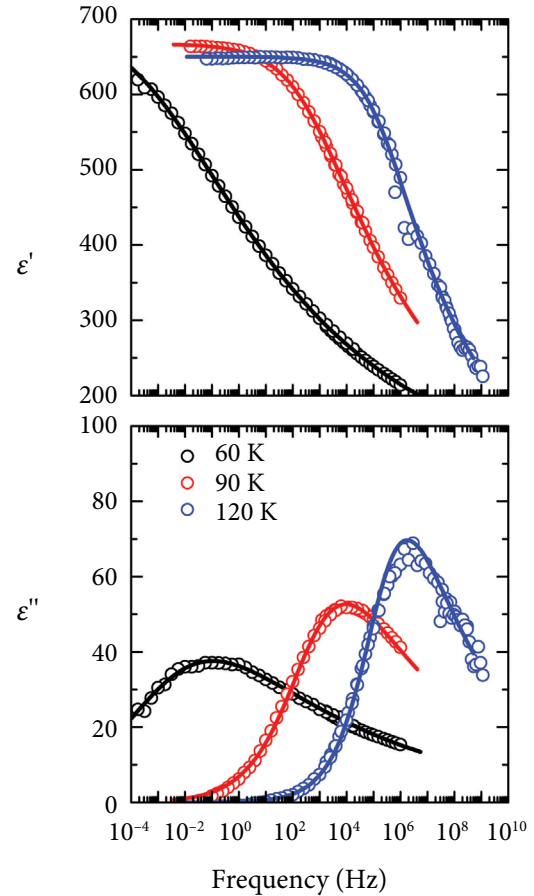


Fig. 2. Frequency dependences of the complex dielectric permittivity of BCZT50 ceramics at selected temperatures.

In the latter formula, $\varepsilon(\infty)$ depicts the phonon and electron contribution to the dielectric permittivity, $\Delta\varepsilon$ is the dielectric strength (i.e. contribution of relaxational entities to the dielectric process), ω is the angular frequency, τ_{HN} is the Havriliak–Negami relaxation time, α is the parameter that determines the breadth of dielectric spectra, and β is the asymmetry parameter.

The real and imaginary parts of permittivity were fitted simultaneously by Eq. (1). The aim of the procedure is to extract the parameter τ_{HN} . It is related to the Havriliak–Negami relaxation time, and it is a parameter that helps understand the behaviour of the thermally activated relaxation process.

The temperature dependence of Havriliak–Negami relaxation time (τ_{HN}) is depicted in Fig. 3 for both samples. The solid curves represent the fitting of the data by the Vogel–Fulcher relation [33]. The parameters of the fitted curves are summarized in Table 1. Both curves show a very similar

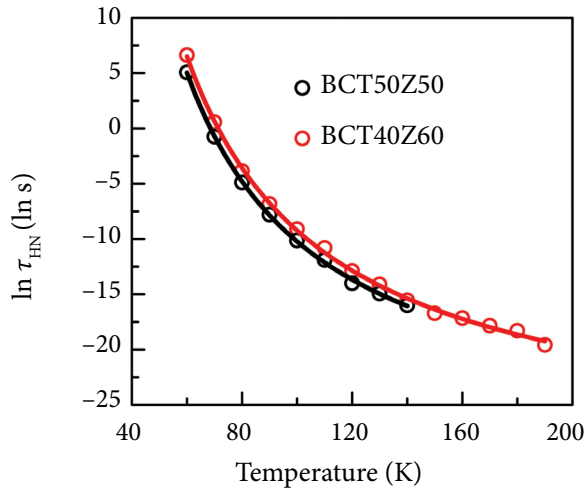


Fig. 3. Temperature dependence of relaxation time for both investigated ceramics.

Table 1. Vogel–Fulcher parameters for all the concentrations. The values of BZT ceramics are taken from the literature.

Sample	Vogel–Fulcher freezing temperature T_{VF} , K	Activation energy of the relaxation process E_a , eV	Attempt time τ_0 , s
BCZT50 (τ_{HN})	10.6 ± 2.4	0.14 ± 0.01	$(2.3 \pm 1.6) \times 10^{-13}$
BCZT50 ($\langle \tau \rangle$)	16 ± 6	0.09 ± 0.02	$(1.1 \pm 1.1) \times 10^{-13}$
BCZT40 (τ_{HN})	8.9 ± 1.5	0.16 ± 0.01	$(1.8 \pm 0.6) \times 10^{-13}$
BCZT40 ($\langle \tau \rangle$)	11 ± 5	0.09 ± 0.01	$(8 \pm 6) \times 10^{-15}$
BZT50 [22]	0	0.19	3.5×10^{-14}
BZT40 [22]	0	0.178	3.2×10^{-14}
BZT50 [14]	9.5 ± 1.2	0.19 eV (2225 K)	4.08×10^{13} Hz

behaviour, but the one with a higher Zr^{4+} concentration is shifted towards lower temperatures. However, the activation energy and freezing temperature for both compositions are very similar. The freezing temperature is roughly 10 K, indicating that it is close to the Arrhenius behaviour. Petzelt et al. found that a low frequency relaxation can be fitted by using the Arrhenius law in BZT40 and BZT50 ceramics. Thus, the freezing temperature in Table 1 for BZT compositions is 0 K. The parameters of BCZT samples are very close to the ones provided by Petzelt et al. [22]. It is an indication that calcium barely alters the dielectric relaxation, which is mostly governed by Ti^{4+} ions within the octahedral cage.

Another notable work on the freezing phenomenon in BZT50 was performed by Filipič et al. [14]. They did an extensive analysis of dielectric data of BZT50. They showed that the different methods to extract the Vogel–Fulcher parameters can yield different results. Depending on the analysis method, the activation energy and freezing temperature can differ. In this work, we focused on τ_{HN} relaxation time. The meaning of this parameter is a little bit vague, but its temperature dependence can be representative of thermally activated process. BCZT samples and BZT50 and BZT40 samples all exhibit an asymmetric dielectric spectrum. Thus, different approaches to analyzing relaxation times can be carried out. Very often three types of temperature dependence of relaxation are analyzed: the shortest and longest edges of distribution of relaxation times and the mean value of relaxation time. Filipič et al. showed that for all these three cases results can be different.

We also compare the different analysis methods from our data. For this purpose, we have calculated the temperature dependences of mean relaxation time, that is related to Havriliak–Negami fitting parameters [31]:

$$\langle \ln \tau \rangle = \ln \tau_{HN} + \frac{\Psi(\beta) - \Psi(1)}{1 - \alpha}, \quad (2)$$

where Ψ is the digamma function, and α and β are Havriliak–Negami parameters from Eq. (1).

The fitting parameters that we obtained from mean relaxation data are presented in Table 1 (i.e. they are denoted as $\langle \tau \rangle$). These two approaches give slightly different results as well. However, the values observed by Filipič et al. [14] show similar discrepancies.

4. Conclusions

The broadband dielectric investigation revealed that 10% calcium-modified BZT40 and BZT50 ceramics have a similar behaviour to those of original compositions. There are no significant temperature shifts in dielectric anomaly. The only visible change is the decrease of the dielectric strength of relaxation. Thus, the permittivity in both investigated compositions is lower.

The analysis of dielectric spectra showed that relaxation mechanisms have not been altered as well. Due to its larger ionic radius, it just suppresses

the total contribution of Ti-ion hopping to the dielectric permittivity of BCZT ceramics. The comparison of the Vogel–Fulcher/Arrhenius fitting parameters justify this assumption that calcium ions barely contribute to the nature of dielectric relaxation. The parameters of Vogel–Fulcher fitting are almost the same as in BZT40 and BZT50. Thus, to enhance the dielectric and/or piezoelectric properties of BZT, it is necessary to search for different chemical approaches.

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KALCIU MODIFIKUOTŲ BaZrTiO_3 KERAMIKŲ PLAČIAJUOSTĖ DIELEKTRINĖ SPEKTROSKOPIJA

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Santrauka

Tirtos kalciumu modifikuotų $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0,5; 0,6$) keramikų dielektrinės savybės. Darbo tikslas – išsiaiškinti, kaip netvarka perovskito gardelės A srities mazge keičia BZT dielektrines savybes. Kadangi kalcio jonų tolerancijos faktorius yra mažesnis nei 1, pakeitus bario jonus kalciumu turėtų padidėti gardelės deformacija.

Šiame darbe detalai išnagrinėtos dvi BZT (BZT50 ir BZT40) kompozicijos su 10 % kalcio. Kalcio įtaka buvo vertinama nagrinėjant dielektrinius spektrus. Šie duomenys lyginami su literatūroje publikuotais BZT50 ir BZT40 keramikų tyrimų rezultatais.