

## DIELECTRIC CHARACTERIZATION OF THE $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ CERAMICS

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Dielectric properties of the  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics synthesized under high pressure were investigated in a broad frequency range (20 Hz – 1 GHz) between 200 and 500 K. It was revealed that the ceramics exhibit electrical conductivity above 300 K. Below 300 K, a dielectric dispersion caused by ferroelectric domains was observed. It was found that the conductivity follows the Almond–West law, which allowed us to determine a DC contribution ( $\sigma_{\text{DC}}$ ). From the  $\sigma_{\text{DC}}$  values obtained at different temperatures, the activation energy ( $E_A = 0.302 \pm 0.006$  eV) was calculated using the Arrhenius law.

**Keywords:** ceramics, spectroscopy, ferroelectric materials

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### 1. Introduction

Oxide multiferroic materials that contain lone-pair cation(s) and transition metal cation(s) attract scientific interest because they may exhibit polar and magnetic ordering in a single phase. Bismuth ferrite,  $\text{BiFeO}_3$  (BFO), is one of the best-known type-I multiferroic materials. Moreover, BFO is the only Bi-containing simple perovskite, which can be manufactured in the bulk form via conventional techniques at ambient pressure. BFO shows a ferroelectric ordering and a complex magnetic ordering with a long-period cycloid, both remaining well above room temperature [1]. Its Curie temperature is as high as  $T_C = 1103$  K and the Néel temperature is  $T_N = 643$  K [1]. In the ferroelectric state, the perovskite structure of BFO is rhombohedral with the space group  $R3c$ .

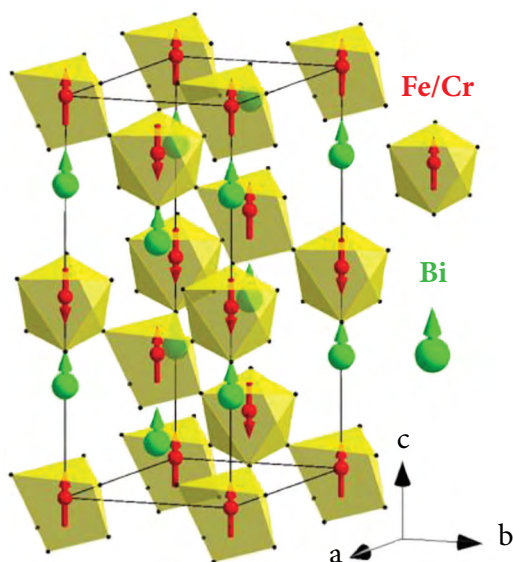
Synthesis of single-phase perovskite  $\text{BiCrO}_3$  using a high-pressure high-temperature method was first reported by Sugawara et al. in 1968 [2].

The first measurements showed that the material is an antiferromagnet with a weak parasitic ferromagnetic contribution below 123 K [2]. Forty years ago,  $\text{BiCrO}_3$  was studied in more detail using neutron diffraction in the temperature range between 7 and 490 K [3]. It was found that  $\text{BiCrO}_3$  is monoclinic (space group  $C2/c$ ) below 420 K, while above this temperature it exhibits a non-polar orthorhombic ( $Pnma$ ) structure. Four magnetic anomalies were revealed at temperatures of 40, 75, 109 and 111 K, respectively [4].

$\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ( $\text{Bi}_2\text{FeCrO}_6$ ) is an equimolar solid solution between the end members of the binary  $\text{BiFeO}_3$ - $\text{BiCrO}_3$  system. Based on the *ab initio* calculation reported in 2005, it was predicted that this perovskite composition would demonstrate the properties that would far surpass any known multiferroic: a polarization of  $80 \mu\text{C}/\text{cm}^2$  along the [111] axis and magnetization of  $160 \text{ emu}/\text{cm}^3$  [5, 6]. Polarization arises from a single bismuth atom (as in  $\text{BiFeO}_3$  or  $\text{BiCrO}_3$ ) and ferrimagnetism from the exchange

of iron and chromium atoms. The structure of this material was considered to be similar to BFO with iron cation replaced by chromium cation in every second place of the [111] axis [5, 6].

In 2007, Suchomel et al. reported the successful preparation of  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics using a high-pressure synthesis method [7]. Indeed, the crystal structure of the obtained  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  perovskite was found to be rhombohedral ( $R3c$ ) at room temperature (Scheme 1). The material turned out to be paramagnetic at room temperature due to the structural disorder of the  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  cations. No dielectric properties have been reported.



Scheme 1. Polyhedral representation of the  $R3c$  polar structure of  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ .

Still, in 2007, an epitaxial thin layer of  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  deposited on  $\text{SrTiO}_3$  substrate using a pulsed laser deposition technique was reported [8, 9]. The material was shown to be ferroelectric with a high polarization ( $60 \pm 1 \mu\text{C}/\text{cm}^2$ ) at 77 K and with antiferromagnetic ordering. It was also found that the magnetic hysteresis in  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  occurs at room temperature and its magnetization value is one order of magnitude higher than that of the BFO film of the same thickness [8, 9]. Two years later, the same group of scientists observed a magnetic phase transition in the  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  film between 600 and 800 K, but the exact critical temperature has not been determined [10].

In summary, the perovskite composition  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  has not been extensively studied, but the available results lead to the conclusion that it

is a ferroelectric with a probable phase transition above room temperature.

Here we report the results of dielectric characterization of chromium-substituted bismuth ferrite ( $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ ) ceramics in a wide temperature range using impedance spectroscopy.

## 2. Experiment

The  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics were prepared under high-pressure and high-temperature conditions as described in Ref [11]. The thickness of the samples was 0.6–0.7 mm and the area was between 1.2 and 3.4  $\text{mm}^2$ . The samples were electrodes with silver paint. Dielectric measurements were performed in the wide frequency range from 20 Hz to 1 GHz over the temperature interval of 200–500 K. In the 20 Hz – 1 MHz range, a *Hewlett Packard* 4284 LCR-meter was used to measure the capacitance and the loss tangent of samples, and a model of the flat dielectric capacitor was used to calculate the complex dielectric permittivity. Measurements of complex transmission and reflection coefficients were performed using an *Agilent* 8714ET network analyzer in the 1 MHz – 1 GHz range. In this case, a multimode capacitor model was used to obtain complex dielectric permittivity.

## 3. Results and discussion

The temperature dependence of the real and imaginary parts of the dielectric permittivity of  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics is shown in Fig. 1. In the

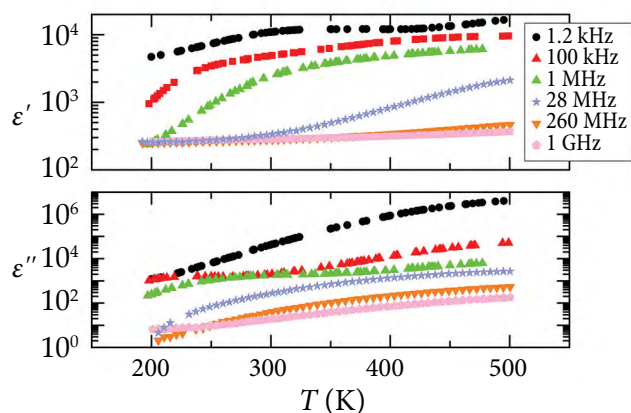


Fig. 1. The temperature dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the complex dielectric permittivity of  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics at different frequencies.

region of relatively high temperatures, a growth of both parts with temperature is observed, which is caused by the conductivity. The rise of the real part of the dielectric permittivity at the lowest frequency can be influenced by Maxwell–Wagner polarization, that is a phenomenon where the charges in the material accumulate near the electrodes until they reach a critical total value and new charges are injected from the electrode layer.

Figure 2 shows the dependence of the real and imaginary parts of the dielectric constant on the frequency at different temperatures. As the frequency is increased, both  $\epsilon'$  and  $\epsilon''$  decrease, which is a property of ferroelectrics [12]. At low temperatures, 300 K and below, there is a visible dielectric dispersion that can be associated with ferroelectric domains [13]. The dispersion maximum shifts to higher frequencies with increasing temperature. At low frequencies (less than 1 MHz), a conductivity pot is visible.

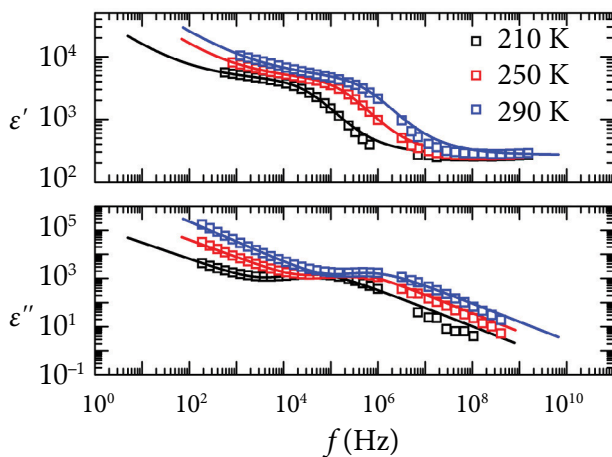


Fig. 2. The frequency dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the complex dielectric permittivity of  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics at different temperatures. The solid curve describes the Cole–Cole equation [14].

From the approximation of the frequency dependences by the Cole–Cole equation [14], the relaxation times were obtained, which are shown in Fig. 3. Based on the obtained data, the activation energy was calculated using the Arrhenius law  $\tau = \tau_0 \exp(E_A/kT)$ . The value of activation energy for  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  is  $E_A = 0.181 \pm 0.002$  eV and  $\tau_0 = 22.5 \pm 0.1$  ps.

In the considered  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics, electrical conductivity is visible at high (over 300 K)

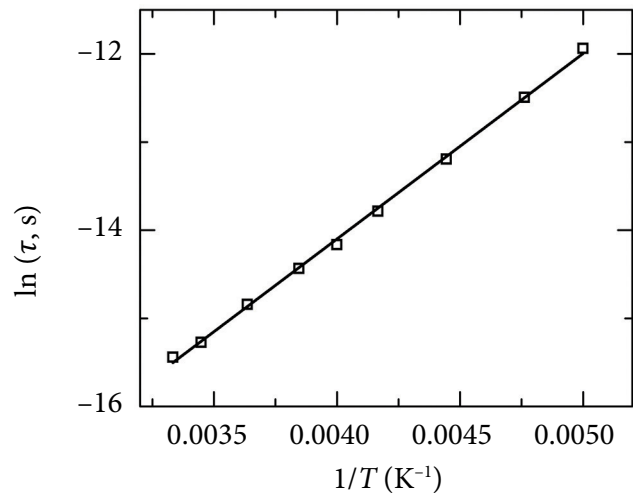


Fig. 3. Dependence of the relaxation times of  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics on the inverse temperature. The solid line describes the Arrhenius law.

temperatures. The dependence of the electrical conductivity on the frequency at different temperatures is shown in Fig. 4. One can see from the obtained dependences that the static part of the conductivity is observed from room temperature.

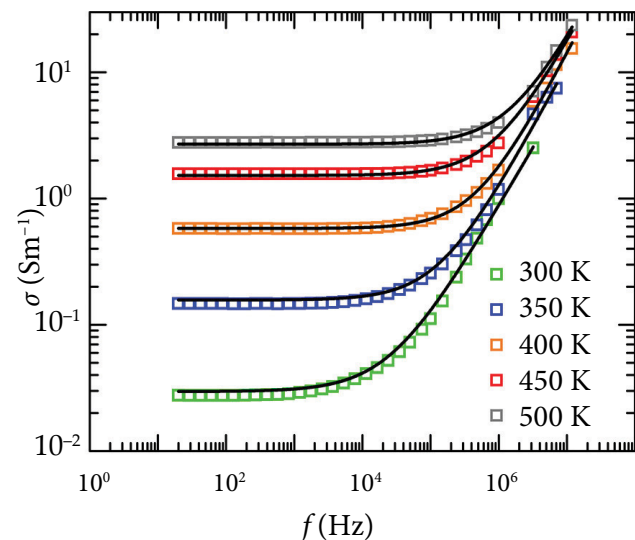


Fig. 4. The frequency dependence of the electrical conductivity of  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics at different temperatures. The solid curve describes the Amond–West law [15].

The direct current conductivity values were obtained using the Amond–West law [15]. Figure 5 shows the dependence of  $\sigma_{\text{DC}}$  on the inverse temperature. The value of activation energy for  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  calculated according to the Arrhenius law [16] is  $E_A = 0.302 \pm 0.006$  eV.

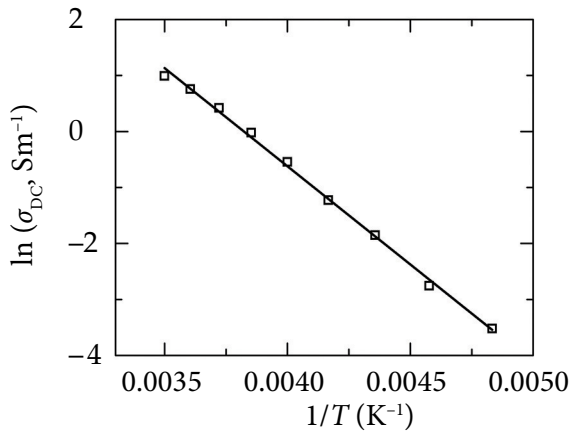


Fig. 5. The  $\sigma_{DC}$  value for  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics versus inverse temperature. The solid line describes the Arrhenius law [16].

Figure 6 shows the frequency dependence of the real and imaginary parts of the complex resistivity of  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics at 400 and 500 K.

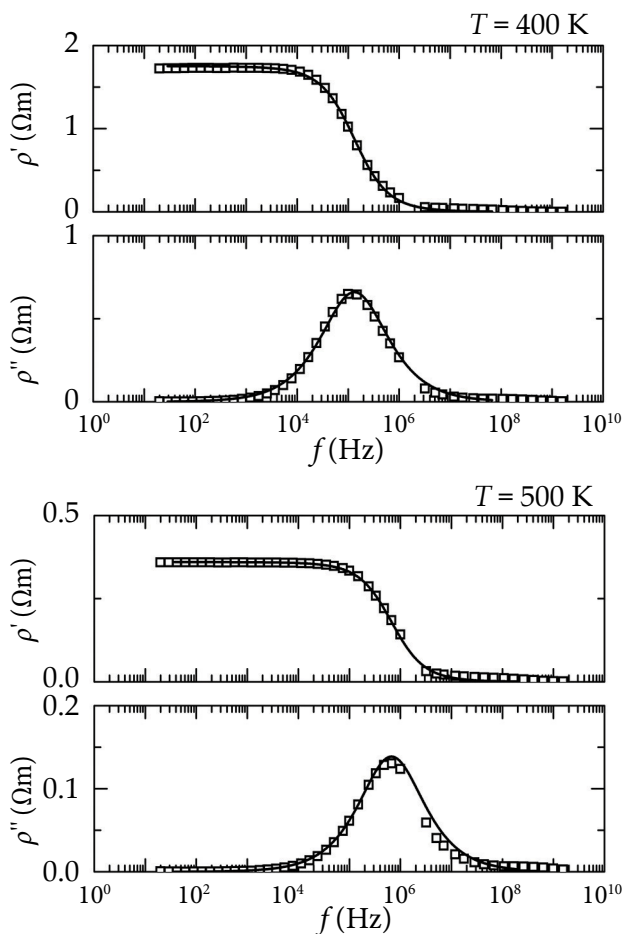


Fig. 6. The frequency dependence of the real ( $\rho'$ ) and imaginary ( $\rho''$ ) parts of the complex resistivity of  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics at 400 K (top panel) and at 500 K (bottom panel). The solid curve represents the approximation using the Cole–Cole equation [14].

One can see that the peak of the real part shifts to higher frequencies with increasing temperature. Besides, the lower the temperature, the higher the real and imaginary parts of the resistance are observed. A high value of specific resistance can also be influenced by electrical contacts. The measured resistivity was fitted using the modified Cole–Cole equation for resistivity processes, that is represented by the solid curve in Fig. 6. The relaxation time values were also obtained from the fit. Figure 7 shows the dependence of the relaxation time of the  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics on the inverse temperature. The value of activation energy for  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  calculated using the Arrhenius law [16] is  $E_A = 0.319 \pm 0.005$  eV.

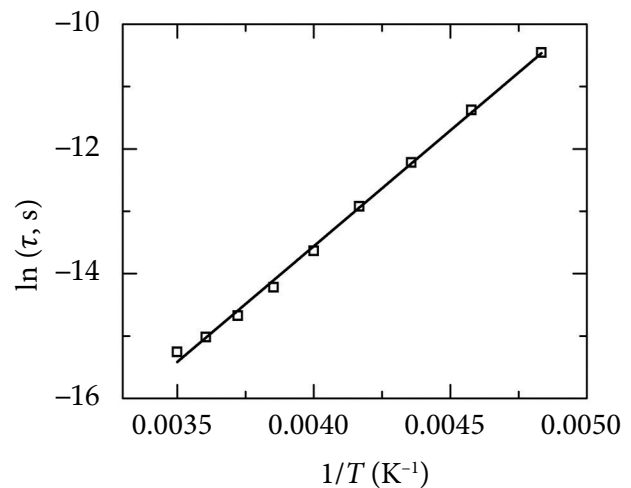


Fig. 7. The relaxation time of  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics versus inverse temperature. The solid line describes the Arrhenius law [16].

#### 4. Conclusions

Dielectric properties of the  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics synthesized under high pressure have been studied using broad-band dielectric spectroscopy over the temperature range of 200–500 K. It was revealed that the  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  ceramics exhibit electrical conductivity above about 300 K. Below 300 K, a dielectric dispersion caused by ferroelectric domains is observed. The measured complex dielectric permittivity and the complex resistivity were fitted using the Cole–Cole equation. The electrical conductivity was approximated with the Almond–West law and a DC contribution was estimated. Activation energy values were found via the Arrhenius law.

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**DIELEKTRINĖ  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  KERAMIKOS CHARAKTERISTIKA**

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**Santrauka**

Multiferoikas – medžiaga, turinti ir feroelektrinių, ir feromagnetinių savybių. Viena tokių medžiagų yra bismuto ferito keramika (BFO), kuri turi feroelektrinių bei feromagnetinių savybių kambario temperatūroje, todėl sulaukė didelio tyrinėtojų dėmesio. Dėl paprastos gardelės struktūros ir savybių kitimo kambario temperatūroje dauguma naujų keramikų yra sintetamos su šios medžiagos elementais: bismutu, geležimi ir deguonimi. Viena tokių medžiagų – bismuto ferumo chromo oksidas ( $\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3$ ), apie kurią žinoma mažai, tačiau tikimasi, kad tai bus aukštos temperatūros multiferoikas. Dėl feroelektrinių ir feromagnetinių savybių tikėtina, kad multiferoikai bus plačiai pritaikomi elektronikoje, pavyzdžiui, mag-

netinei atminčiai kontroliuoti elektriniu lauku arba atvirksčiai.

Šiame darbe publikuojami  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  keramikos dielektriniai tyrimai. Tyrimai atlikti plačiajuostės dielektrinės spektroskopijos metodu 20 Hz – 1 GHz dažnių diapazone esant 200–500 K temperatūrai.  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  keramikos dielektriniamis spektrams daugiausia įtakos turi elektrinis laidumas, kurio temperatūra yra daugiau nei 400 K ir dažnis žemesnis nei 100 Hz.  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  keramikoje žemose temperatūrose (žemiau 300 K) matoma dielektrinė dispersija, kurią nulemia feroelektriniai domenai.  $\text{BiFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$  keramikoje žemose dažniuose stebimi elektrinio laidumo indukuoti procesai, aukštuose dažniuose – dipolinė relaksacija.