

DIELECTRIC RELAXATION OF MANGANESE MODIFIED $\text{Bi}_5\text{Fe}_2\text{Ti}_3\text{O}_{18}$ AURIVILLIUS TYPE CERAMICS

The five-layer Aurivillius type structures with the general chemical formula $\text{Bi}_5\text{Fe}_{2-x}\text{Mn}_x\text{Ti}_3\text{O}_{18}$, where $x = 0, 0.6, 1.2$ have been synthesized and tested. The SEM studies showed a significant increase in grain size in the manganese-modified Aurivillius type ceramic material (for $x = 1.2$). The increase in the amount of manganese ions (Mn^{3+}) affects the decrease in the temperature at which the relaxation processes take place. Namely from 525 K (1 kHz) and 725 K (1 MHz) for BFT sample ($x = 0$) to 355 K (1 kHz) and 565 K (1 MHz) for BFM12T sample ($x = 1.2$).

Using the Arrhenius's law and the Vogel-Fulcher's relationship the activation energy (E_a) and the relaxation time have been calculated. The value of E_a increases with the increase of the Mn amount from 0.737 eV (for $x = 0$) to 0.915 eV (for $x = 1.2$).

Keywords: activation energy, Aurivillius phase, dielectric constant, dielectric relaxation, Vogel-Fulcher law

Introduction

Aurivillius type materials have been attracting substantial attention during the last decade. This type of materials shows a perovskite-like structure with multiferroic properties. The first description of bismuth oxides with perovskite – like layered structures was given by Aurivillius, therefore these materials are called Aurivillius phases [1]. Aurivillius phases are described by the general chemical formula which was proposed by Subbaro: $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, where m means a number of perovskite – like layers $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ which are separated by fluorite – like layers $(\text{Bi}_2\text{O}_2)^{2+}$, A is a mono-, di-, or trivalent element while B is a transition element [2]. In recent years, there has been an increase in interest in Aurivillius type structures that exhibit the features of multiferroic materials. Materials that belong to the group of multiferroics are characterized by at least two ferroic features, namely ferroelectric, ferromagnetic, ferroelastic or ferrotoroidic [3-5]. Multiferroic materials may find potential applications as sensors, storage or random access memory [6-7]. A promising group of materials for this purpose are Aurivillius type materials. Among the multiferroic Aurivillius type materials, magnetoelectric materials i.e. materials that exhibit both magnetic and electrical properties, deserve special attention [8]. There are many published papers presenting the results of research of multiferroic Aurivillius type materials, but research on these type structures is poorly advanced. The subject of research that was presented in this paper, were manganese (Mn^{3+}) doped five – layer Aurivillius type structures with a general chemical formula: $\text{Bi}_5\text{Fe}_{2-x}\text{Mn}_x\text{Ti}_3\text{O}_{18}$, where

$x = 0, 0.6, 1.2$. The purpose of this work was obtaining Aurivillius type ceramics (BFT-type materials) doped with manganese ions (Mn^{3+}) and investigating its dielectric properties. In this paper was presented conditions of the technological process of obtaining Aurivillius type ceramics and results of researches the effect of influence of manganese ions on dielectric properties and dielectric relaxation.

1. Experimental

The research subject was Aurivillius type ceramic material modified by manganese ions with a general chemical formula $\text{Bi}_5\text{Fe}_{2-x}\text{Mn}_x\text{Ti}_3\text{O}_{18}$, where $x = 0, 0.6, 0.12$. The Aurivillius type materials were obtained by conventional solid state reaction from simple high-purity oxides: Bi_2O_3 (99.999%, Sigma-Aldrich), Fe_2O_3 (99%, Chempur), Mn_2O_3 (99.9%, Sigma-Aldrich) and TiO_2 (99.9%, Merck). The stoichiometric oxide mixtures were wet milled for 24 h in ethyl alcohol using zirconia-milling balls and then the powders were calcined at 1113 K/4 h. After calcination powder mixtures were milling again for 12 h and pressed into pellets of 10 mm in diameter and 1 mm in thickness under the pressure of 300 MPa. Then obtained pellets were sintered at 1213 K/4 h and next polished. The last step of technological process was applied platinum paste on both surfaces as electrodes for electric measurements. Three different Aurivillius type ceramic materials with chemical formulas: $\text{Bi}_5\text{Fe}_2\text{Ti}_3\text{O}_{18}$ (BFT), $\text{Bi}_5\text{Fe}_{1.4}\text{Mn}_{0.6}\text{Ti}_3\text{O}_{18}$ (BFM6T), $\text{Bi}_5\text{Fe}_{0.8}\text{Mn}_{1.2}\text{Ti}_3\text{O}_{18}$ (BFM12T) were obtained in the technological process discussed above.

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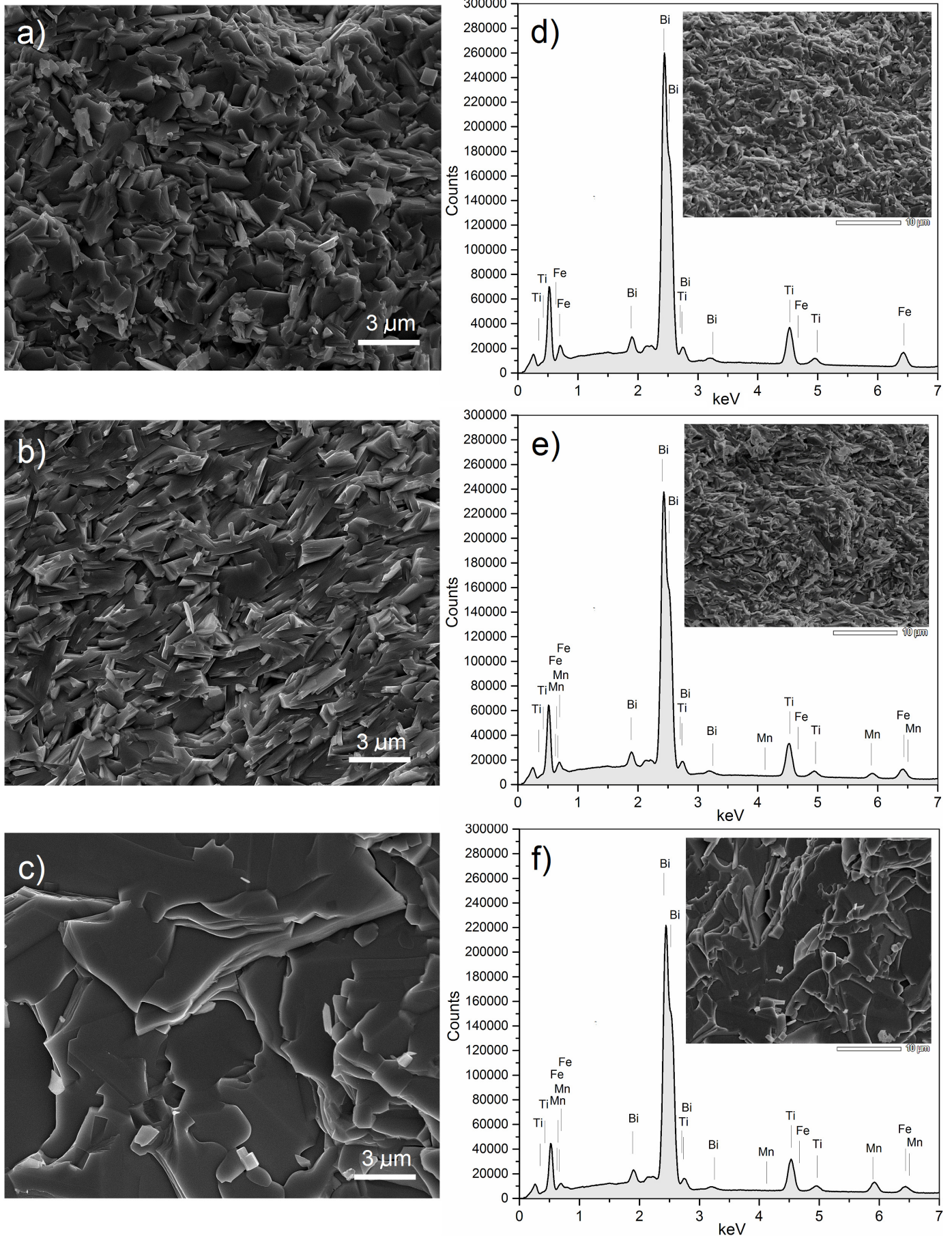


Fig. 1. SEM images of the microstructure of fractures (a-c) and the EDS analysis of chemical elements (d-f) of the BFT materials. The samples of the BFT (a, d), BFM6T (b, e) and BFM12T (c, f)

Microstructure of the fracture of ceramic materials was characterized using a scanning electron microscope (SEM – JEOL JSM-7100F TTL LV). The studies of chemical composition were performed by standard method, using an energy dispersive spectrometer (EDS). The SEM and EDS studies were carried out at the accelerating voltage 15-20 kV and low vacuum, with Au sputtering on the surface of samples. Values of dielectric constant were measured using LCR meter (QuadTech 1920 Precision) at temperature range from room temperature (RT) to 820 K, for several frequencies of measurement field, range from 1 kHz to 1 MHz.

2. Results and discussion

The SEM images of undoped BFT material as well as manganese-doped BFM6T, BFM12T ceramic samples are shown in Figs 1a-1c, respectively.

The microstructure of fracture of the BFT-type materials consists of platelet-like grains. This shape of grains is characteristic of bismuth perovskite-like layers Aurivillius type [9]. The microstructure of BFT (Fig. 1a) and BFM6T samples (Fig. 1b) are very similar. For both ceramic materials the grains have similar sizes. In the case of the BFM12T ceramic materials the grain size is much bigger (Fig. 1c). On the basis of SEM tests, it can be assumed that the manganese doping influences on the grain sizes of the microstructure in BFT-type ceramics.

The qualitative EDS analysis used to investigate the chemical composition of the BFT-type materials are presented in Figs 1d-1f. The microanalysis of the BFT, BFM6T and BFM12T ceramics was performed at micro-areas on the fractures of samples (inset in Figs 1d-1f). The qualitative EDS investigations confirmed the assumed share of the individual components.

The results of dielectric investigations obtained for undoped BFT Aurivillius type ceramic material is shown in Fig. 2. In the case of the BFT ceramic sample ($x = 0$), the values of dielectric constant rise with increasing temperature as shown in the Fig. 2a.

On the $\varepsilon'(T)$ graph the first anomaly, i.e. the maximum of dielectric constant, appears at a temperature of about 525 K for 1 kHz (Fig. 2a). As the frequency increases, the maximum value of the dielectric constant becomes lower, and the location of this maximum, moves towards higher temperatures. For the highest frequency of measuring field, i.e. for a 1 MHz, the maximum dielectric constant occurs at 725 K (Fig. 2b). These results are consistent with results of the research presented in the paper of Zuo et al. [10].

The dielectric constant (ε') as a function of temperature for manganese doped BFT-type samples are presented in Fig. 3. In the case of the BFM6T sample (Fig. 3a) the dielectric constant rises with increasing temperature. The maximum dielectric constant occurs at 367 K for 1 kHz. As the measurement field frequency increases, the position of maximum moves towards higher temperatures, and for 1 MHz the maximum occurs at 600 K. The height of maximum of the dielectric constant decreases with the increasing of the measuring field frequency.

The temperature dependencies of dielectric constant $\varepsilon'(T)$ for BFM12T ceramic sample ($x = 1.2$) are presented in Fig. 3b. As the temperature increases, the dielectric constant increases, too. The dielectric constant achieves a maximum value at different temperatures for different frequencies i.e. at 355 K for 1 kHz and at 565 K for 1 MHz (Fig. 3b). The position of the maximum of dielectric constant depends on the frequency of measuring field for all materials tested. The height of this maximum decreases with increasing of the electric field frequency. The shift the position of the dielectric constant maximum towards higher temperatures, for increasing frequency of measuring field, is a hallmark of the dielectric relaxation phenomenon [11]. The oxygen vacancies or oxidation charges of Fe ions may be the source of the maximum of dielectric relaxation [12].

Figs 3a and 3b show that further increase in temperature causes decreasing of the dielectric constant for all frequencies of measuring field except for the frequency of 2 kHz. Such behavior of the dielectric constant may indicate the influence of the measuring field frequency on the change of the electric

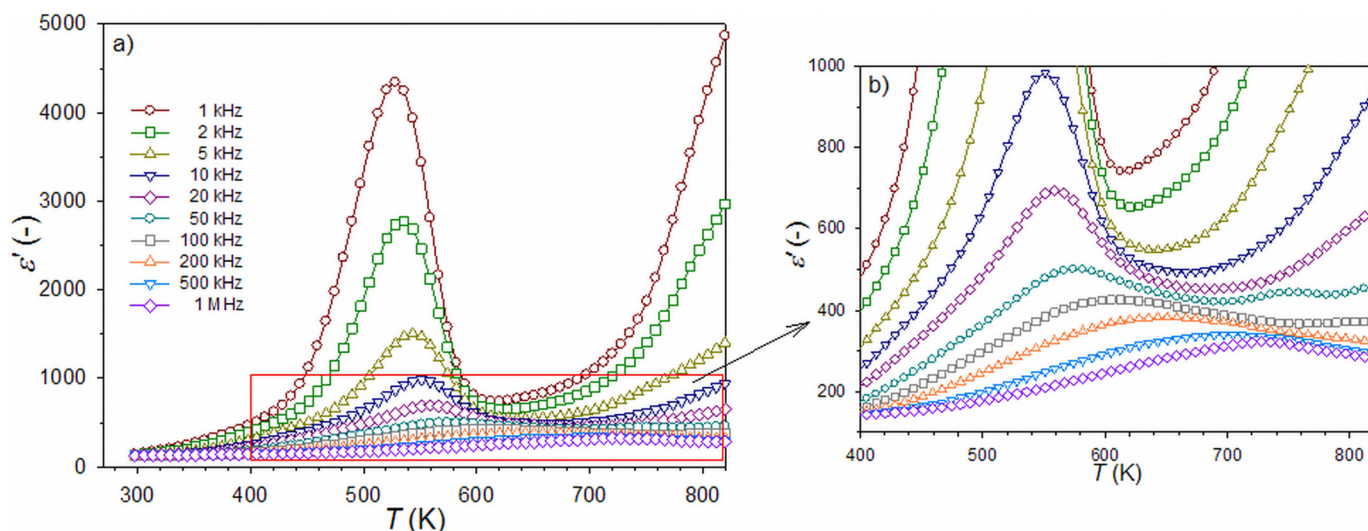


Fig. 2. The dielectric constant ε' in BFT ceramics as a function of temperature (a), an enlarging the area marked with a red rectangle (b)

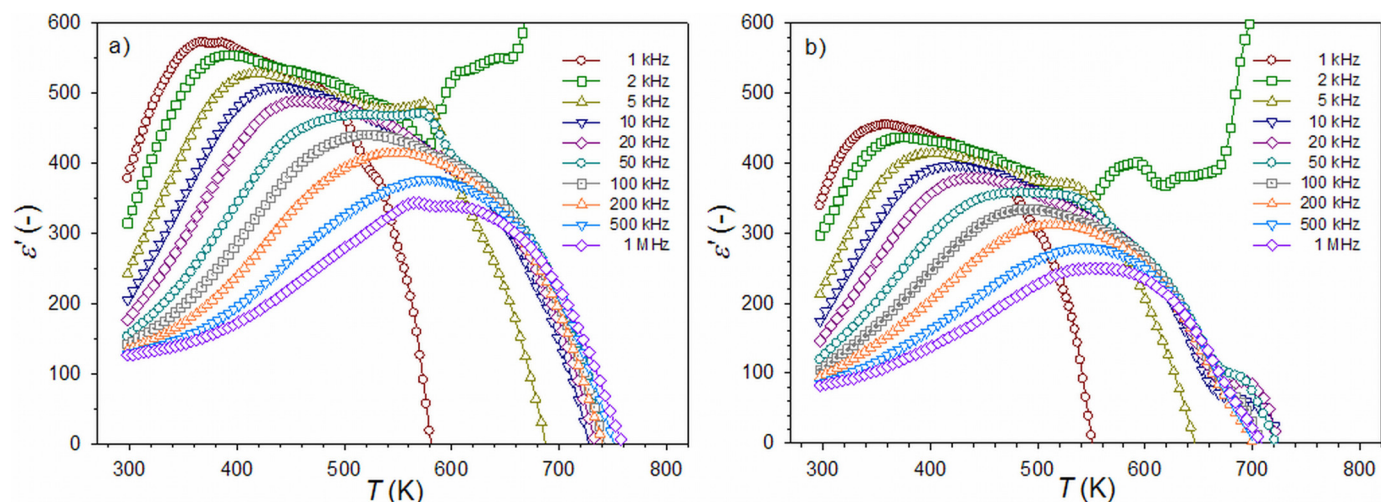


Fig. 3. The dielectric constant ϵ' as a function of temperature for BFM6T (a) BFM12T (b) samples

character of manganese doped BFT-type samples. In the case of frequencies different from 2 kHz there is a change of the electric character of material from capacitive to inductive, while for the 2 kHz the electric character of tested samples does not change [13]. Fig. 4a shows the Arrhenius plot of relaxation frequency, as a function of the reversal of temperature for the BFT, BFM6T and BFM12T ceramic samples. The phenomenon of dielectric relaxation, which occurs in the five-layer Aurivillius type ceramics, was described by using the Arrhenius plot (Fig. 4a) and Arrhenius law [14]:

$$f = f_0 \exp\left[-\frac{E_{a1}}{k_B T}\right] \quad (1)$$

where: f is the frequency of measuring field, E_{a1} is the activation energy, k_B is the Boltzmann constant. On the base of Arrhenius law the values of the activation energy (E_{a1}) were calculated and is 0.597 eV, 0.759 eV and 0.959 eV for BFT, BFM6T and BFM12T ceramic samples, respectively. The calculated values of the activation energy are consistent with the activation energy

values in analogous materials [15]. However, the fitted theoretical curve does not precisely describe the experimental data, as can be seen in Fig. 4a. Therefore another relationship was used to theoretical description of the dielectric relaxation phenomenon.

The phenomenon of dielectric relaxation, which occurs in the manganese-modified Aurivillius type ceramics, was also described using the relationship of Vogel-Fulcher (V-F) [16]:

$$\omega = \tau^{-1} \exp\left[-\frac{E_a}{T_m - T_{V-F}}\right] \quad (2)$$

where: $\omega = 2\pi f$ is the measurement frequency, τ^{-1} is the pre-exponential factor which has a meaning of the inverse minimum relaxation time, E_a is the activation energy, T_{V-F} is so-called Vogel-Fulcher temperature, which is the freezing temperature where the spectrum of the relaxation times becomes to infinitely broad.

Fig. 4b shows the dependencies of the logarithm of the inverse frequency on T_{\max} (T_{\max} means the temperature of the maximum of dielectric constant) for all Aurivillius type ceramic samples. This kind of plot is so-called the Vogel-Fulcher one.

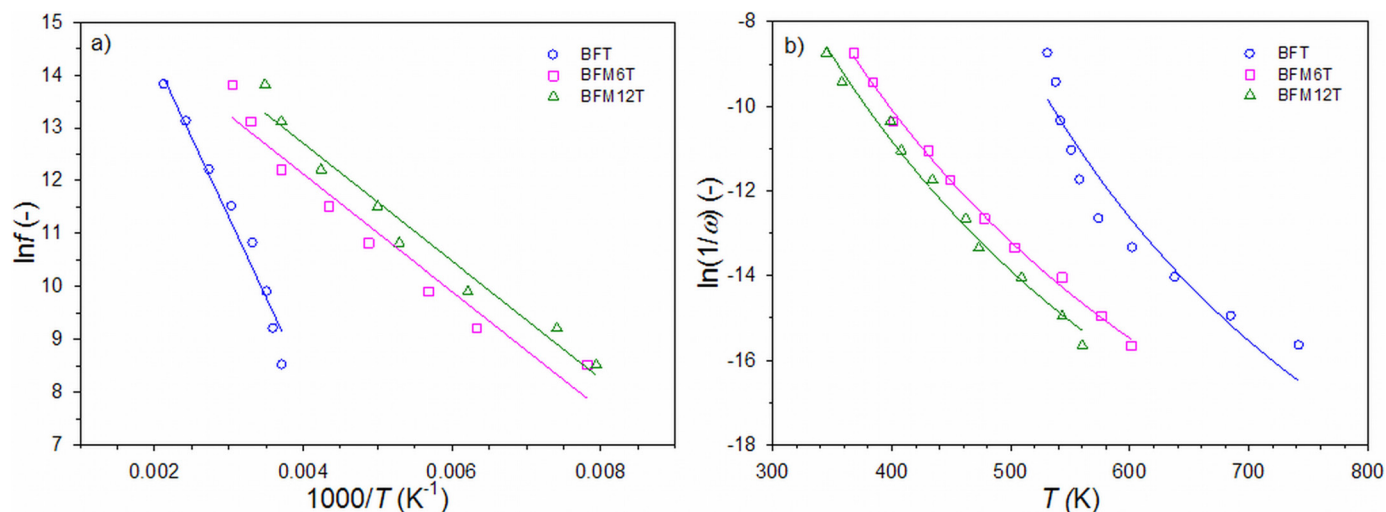


Fig. 4. The Arrhenius plot (a) and the Vogel-Fulcher plot (b) relating temperature of the dielectric maximum (T_{\max}) with measurement frequency for BFT, BFM6T and BFM12T samples. Solid lines mean the fitting results of Aurivillius and Vogel-Fulcher relationships

The Vogel-Fulcher relationship Eq. (2) was applied to fit the dielectric data presented in Fig. 4b. The values of fitting parameters were summarized in the Table 1.

TABLE 1

The values of fitting parameters for all studied manganese modified Aurivillius type ceramic samples

Fitting parameters	BFT	BFM6T	BFM12T
τ (s)	1×10^{-13}	1×10^{-13}	1×10^{-13}
E_a (eV)	0.737	0.862	0.915
T_{V-F} (K)	104	123	135

The calculated values of the activation energy (E_a) are in the range from 0.737 eV for BFT ($x = 0$) to 0.915 eV for BFM12T ($x = 1.2$), while the values of relaxation time are kept constant, regardless of the addition of manganese, for all Aurivillius type ceramic samples.

Conclusion

The manganese-modified Aurivillius type ceramic samples were successfully obtained used a conventional solid state technique. The microstructure of fracture of the BFT-type materials consists of platelet-like grains. The scanning electron microscope studies showed a significant increase in grain size in the manganese-modified Aurivillius type ceramic material ($x = 1.2$). A small amount of manganese ions (Mn^{3+}) does not clearly affect the grain size. The BFM6T material ($x = 0.6$) is characterized by microstructure fracture similar to BFT ceramic material ($x = 0$). The increase in the amount of manganese ions (Mn^{3+}) affects the decrease in the temperature at which the relaxation processes take place. Namely from 525 K (1 kHz) and 725 K (1 MHz) for BFT sample ($x = 0$) to 355 K (1 kHz) and 565 K (1 MHz) for BFM12T sample ($x = 1.2$). Using the Arrhenius law and the Vogel-Fulcher relationship, the dielectric relaxation phenomena

have been described. The results of the fitting shows, that the relaxation processes which takes place in the tested Aurivillius type materials, are better described by the Vogel-Fulcher model. The results of presented investigations have shown that the modification with the manganese of Aurivillius type ceramics affects the value of activation energy from 0.737 eV for BFT ($x = 0$) to 0.915 eV for BFM12T ($x = 1.2$).

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