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The influence of sintering time on microstructure and dielectric properties of $K_{0.5}Bi_{0.5}TiO_3$ ceramics

Abstract: *Potassium-bismuth titanate $K_{0.5}Bi_{0.5}TiO_3$ ceramics were prepared by the conventional method using different sintering times. The obtained lead-free ceramics of $K_{0.5}Bi_{0.5}TiO_3$ show high density determined by the Archimedes method at about of 84-98% of the theoretical value. The microstructure investigations were performed using a scanning electron microscope (SEM). When sintering time equal to 4 and 5 hours was applied, the grains of $K_{0.5}Bi_{0.5}TiO_3$ are similar. However, for the sintering time of 8 hours, an increase of the grain size and their inhomogeneity was observed. The X-ray diffraction studies showed that the obtained samples have pure perovskite structure with tetragonal symmetry. The dielectric measurements showed differences in relative permittivity (ε) depending on the sintering time. The conclusions about influence of the sintering time on the properties of $K_{0.5}Bi_{0.5}TiO_3$ may be the starting point for the targeted technology and specific application*

Streszczenie: *Tytanian potasu i bizmutu K0,5Bi0,5TiO3 wytworzono metodą konwencjonalną z zastosowaniem różnych czasów spiekania. Otrzymana ceramika bezołowiowa K0,5Bi0,5TiO3 wykazuje wysoką gęstość wyznaczoną metodą Archimedesa na poziomie około 84-98% wartości teoretycznej. Badania mikrostruktury przeprowadzono przy użyciu skaningowego mikroskopu elektronowego (SEM). Gdy zastosowano czas spiekania równy 4 i 5 godzin, ziarna K0,5Bi0,5TiO3 są podobne. Jednak przy czasie spiekania wynoszącym 8 godzin zaobserwowano wzrost uziarnienia i jego niejednorodność. Badania dyfrakcji rentgenowskiej wykazały, że otrzymane próbki mają czystą strukturę perowskitu o symetrii tetragonalnej. Pomiary dielektryczne wykazały różnice w przenikalności względnej (ε) w zależności od czasu spiekania. Wnioski dotyczące wpływu czasu spiekania na właściwości K0,5Bi0,5TiO3 mogą być punktem wyjścia dla docelowej technologii i konkretnego zastosowania. (**Wpływ czasu spiekania na mikrostrukturę i właściwości dielektryczne ceramiki** $K_{0.5}Bi_{0.5}TiO_3$)*

Keywords: $K_{0.5}Bi_{0.5}TiO_3$,, perovskite structure, ferroelectric, lead free material preparation.
Słowa kluczowe: : $K_{0.5}Bi_{0.5}TiO_3$ struktura perowskitu, ferroelektryk, przygotowanie materiału bezołowiowego.

Introduction and literature review

Lead containing compounds, widely applied in the electronics industry exhibit some danger to the natural environment, causing its pollution due to volatilization of lead oxide (PbO). This can also cause instability of electrical characteristics of the electronic components (Rödel 2009, Shrout 2007, Seifert 2010, Aksel 2010, Zhang 2007, Suchanicz 2008). These effects are just two of a few disadvantages of the commonly used lead-based compounds in electronics.

In order to reduce the danger caused by lead, the European Union Directives limiting the use of this metal have been issued. The most important recommendations include: RoHS (Restriction of hazardous substances in electrical and electronic equipment) and WEEE (waste of electrical and electronic equipment). The RoHS directive sets the maximum concentration of lead in a homogeneous element to 0.1% (WWW, Directive 2011).

At present it is difficult to find a lead free material which could replace the most popular Pb - based materials (Sawaguchi 1953, Yamamoto 1996, Qu 2014). A very prospective material seems to be sodium-bismuth titanate $Na_{0.5}Bi_{0.5}TiO_3$ (hereinafter referred as NBT), a compound with the perovskite structure. Numerous research works on NBT related to its preparation and modification of its properties show widespread interest in this compound in the world's leading research laboratories (Vakhrushev 1985, Park 1996, Suchanicz 2002, Jones 2002, Barick 2011, Zannen 2012). However, due to some disadvantages like: high dielectric loss, large conductivity and high coercive field (~ 73 kV/cm) (Zannen 2016, Suchanicz 2017) researchers are still looking for new lead-free compounds whose properties will be comparable or better to lead zirconate titanate (PZT).

One of the most prospective lead-free materials analyzed in the recent years is potassium-bismuth titanate $K_{0.5}Bi_{0.5}TiO_3$ (hereinafter referred to as KBT), which has undergone a real renaissance among this kind of materials. The material that has been obtained in the recent years, is interesting mainly because of its rather high density - above 95% of the theoretical density (Rao 2010, Köenig 2015, Suchanicz 2018, Czaja 2018, Czaja 2019).

KBT belongs to the perovskite family. It has a tetragonal structure at room temperature (the ratio c/a is about 1.01-1.02) (Ivanov 1962, Czaja 2018). During heating, the following phase transitions were noted in this material: from tetragonal phase to pseudocubic phase at about 533 K and from pseudocubic phase to cubic phase at about 683 K (Ivanov 1962). This material shows a relatively high Curie temperature T_c = 653 K (Smolenskii 1961, Buhrer 1962). In the literature some controversy connected with KBT's ferroelectric relaxor properties can be noticed. According to papers Czaja 2018, Czaja 2019, Buhrer 1962, Li 2003, Hiruma 2005, Yang 2007, Guo 2017) KBT shows ferroelectric relaxor features. However, the authors of (Suchanicz 2018) claim, the material does not have these properties. These discrepancies may result from the application of various processing conditions, which significantly affect the properties of the obtained materials (Suchanicz 2018, Czaja 2018). The aim of the paper is to compare microstructure and dielectric properties of KBT ceramics obtained at the same temperature, but at different sintering times.

Experimental

KBT ceramics were obtained by a solid-state reaction from a mixture of simple oxides and carbonates according to the equation (Czaja 2018):

$$0.25K_2CO_3+0.25Bi_2O_3+TiO_2 \rightarrow (K_{0.5}Bi_{0.5})TiO_3+0.25CO_2\uparrow \quad (1)$$

The samples were obtained in the same way as in Ref. (Czaja 2018) at the same temperature 1303 K for different sintering time: for 4 hours (*KBT* 1), for 5 hours (*KBT* 2), for 8 hours (*KBT* 3).

The apparent density of obtained ceramic materials was determined using the Archimedes method. Their microstructure was observed using a SEM (JEOL JSM-

7100F TTL LV). The chemical composition and distribution of all elements throughout the grains were examined by the standard method, using an energy dispersive spectrometer (EDS).

The crystallographic structure was examined using an Empyrean PANalytical diffractometer in the Bragg-Brentano geometry with the Cu radiation ($\lambda_{K\alpha}$ = 1.5418 Å) and PIXcell counter.

The dielectric measurements were performed using the Gwinstek Precision LCR 8110G meter in a wide range of temperature: from 293 K to 873 K at a constant rate of temperature change of 4K/min. The frequency range tested was taken from 10 kHz to 2 MHz. Before measurements the samples were polished, silver electrodes were superimposed, then the samples were heated at 873 K for 120 minutes.

Results and discussion

All samples (*KBT* 1, *KBT* 2, *KBT* 3) have a pure perovskite structure without any additional phase (PDF 4+: 01-072-8121). A typical X-ray diffraction pattern of *KBT* 2 ceramics in room temperature is shown in Fig. 1.

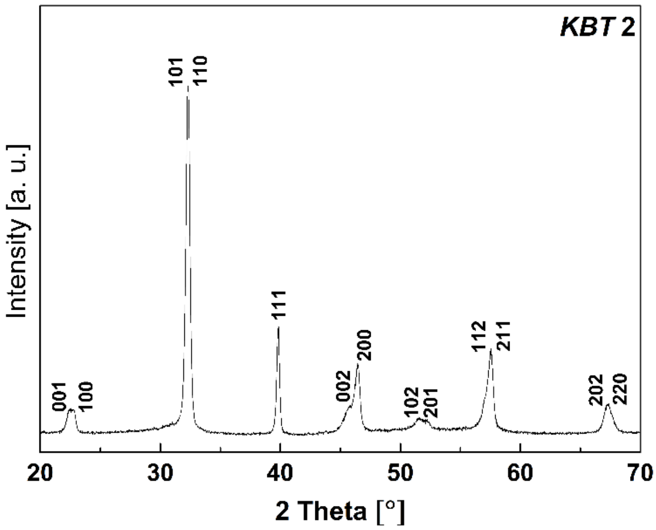


Fig. 1. X-ray diffraction pattern of KBT ceramic sintered at 1303 K for 5 hours (*KBT* 2)

Table 1 shows the values of the theoretical density (calculated on the basis of X-ray measurements) and the apparent density for the discussed ceramics.

Table 1. The theoretical and apparent densities of $K_{0.5}B_{0.5}TiO_3$.

The sample	Theoretical density [g/cm^3]	Apparent density [g/cm^3]
KBT 1	5.96	5.00±0.06
KBT 2	5.96	5.87±0.08
KBT 3	5.96	5.66±0.05

The experimentally determined densities of samples depend on the time of sintering and changes from 5.00 g/cm^3 (for KBT 1) to 5.87 g/cm^3 (for KBT 2), which is approximately 84% and 98% of the theoretical density, respectively. Figure 2 a-f shows SEM micrographs of KBT ceramics (KBT 1, KBT 2; KBT 3) in room temperature.

Microstructure of *KBT* 1 and *KBT* 2 ceramics is characterized by very fine grains with a characteristic well-shape. The grain size changes from 220 nm (*KBT* 1) to 270 nm (*KBT* 2). Grains of both materials have a uniform shape and size. However, in the *KBT* 1 sample (Fig. 2 a-b) the binding between grains is weaker than the one observed in *KBT* 2 sample (Fig. 2 c-d). The significantly larger changes in the microstructure are observed in the case of *KBT* 3 ceramics (Fig. 2 e-f). The heterogeneity of grains size can be observed. A fraction of the grains have larger size in comparison to the ones observed in *KBT* 1 and *KBT* 2 ceramics.

The increase of sintering time may cause volatility of elements, e.g. bismuth and/or potassium. In order to assess the impact of the volatilization process of these elements the quantitative EDS X-ray microanalysis was carried out. Fig. 3 shows exemplary spectra of EDS analysis for a *KBT* 2 (a) and *KBT* 3 (b) samples. The obtained results indicate that the impact of volatilization process is negligibly small. Moreover the mentioned results confirm the assumed share of the specific components and it showed that the materials do not contain any impurities.

The temperature dependences of relative permittivity ε(T) measured at frequency of 100 kHz are presented in Fig. 4a. The measurements give not only information about temperature evolution of relative permittivity, but also allow to determine the temperature of phase transitions occurrence and gives some information about its type.

The presented data is concerned with the real part of relative permittivity and shows a broadened maximum at temperature T_m, with clear dependence on the time of sintering (Table 2). It can be seen that increasing in the sintering time affects also the maximum value of relative permittivity (Table 2). The mentioned broadening of the ε(T) maximum indicated the diffuse character of the phase transition, which is commonly described using the degree of diffuseness (γ). The value of the γ parameter could be estimate from the modified Curie-Weiss law:

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_{\max}} = \frac{\left(T - T_{\max}\right)^{\gamma}}{C} \qquad (2)$$

where $\varepsilon'_{\max}$ is the maximum value of relative permittivity at the transition temperature (T_m), C is a constant and γ is the degree of diffuseness. The value of γ is limiting to the range from 1 to 2, which reduces the expression to the Curie-Weiss law valid for the linear and quadratic dependence. Fig. 4b shows the plot of $\ln(1/\varepsilon - 1/\varepsilon_{\max})$ versus $\ln(T - T_m)$ for the *KBT 2*, as an example. The value of γ increases with increasing of sintering time, which may be related to the creation of additional defects (Table 2).

Table 2. Transition temperature T_m, maximal relative permittivity at transition temperature ε_{max}, degree of diffusion γ.

Sintering time [h]	$T_{m100\,kHz}$ [K]	$\varepsilon_{max100\,kHz}$
4	637	2960
5	632	2963
8	624	4544

Sintering time [h]	γ	ΔTm [K]
4	1.90	9
5	1.99	11
8	2.00	12

Sintering time [h]	$\Delta\varepsilon_{max}$
4	736
5	372
8	947

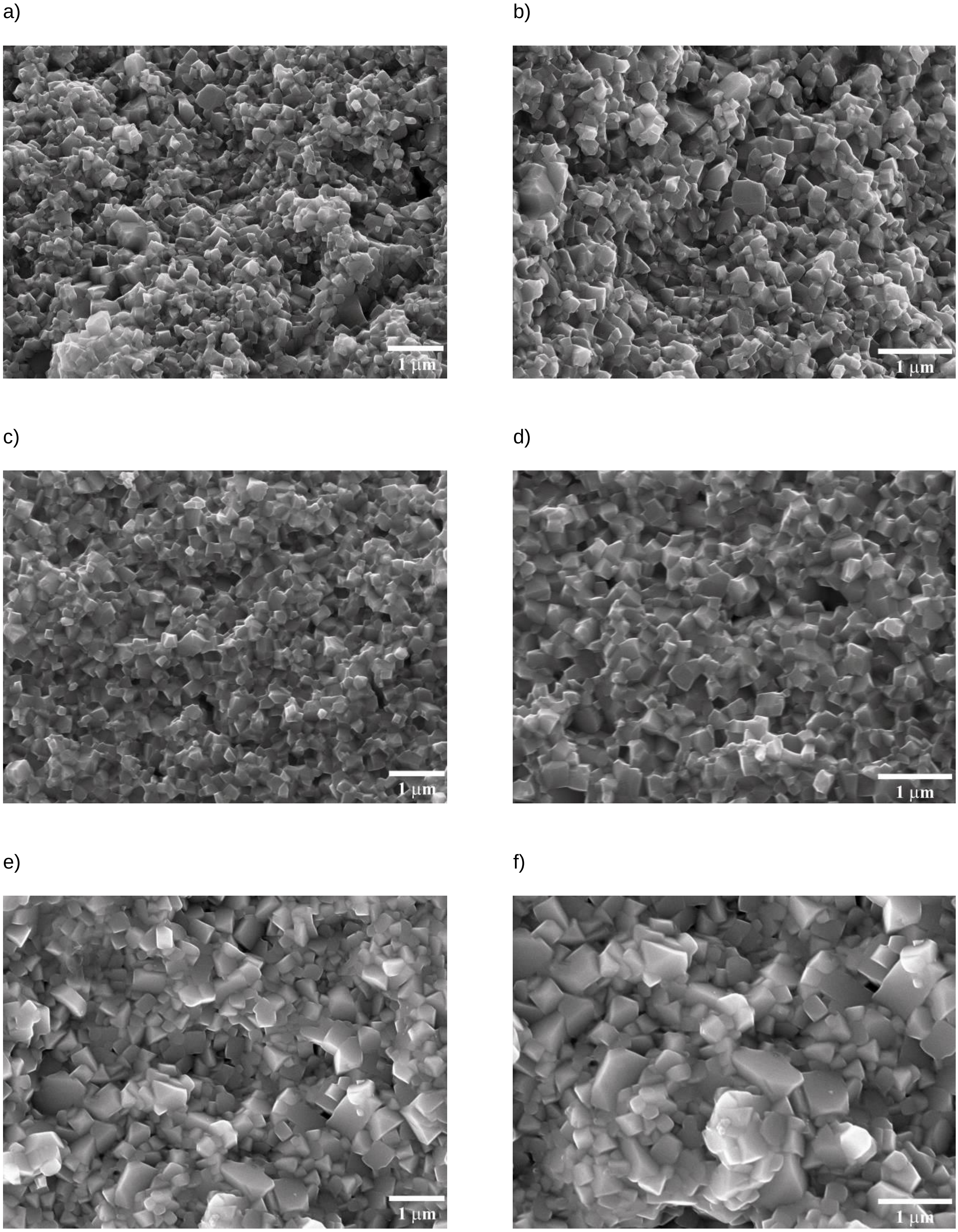


Fig. 2. SEM micrographs of KBT ceramics sintered at:
a) 1303 K for 4 hours (*KBT* 1 - 15 000 magnification),
b) 1303 K for 4 hours (*KBT* 1 - 20 000 magnification),
c) 1303 K for 5 hours (*KBT* 2 - 15 000 magnification),
d) 1303 K for 5 hours (*KBT* 2 - 20 000 magnification),
e) 1303 K for 8 hours (*KBT* 3 - 15 000 magnification),
f) 1303 K for 8 hours (*KBT* 3 - 20 000 magnification)

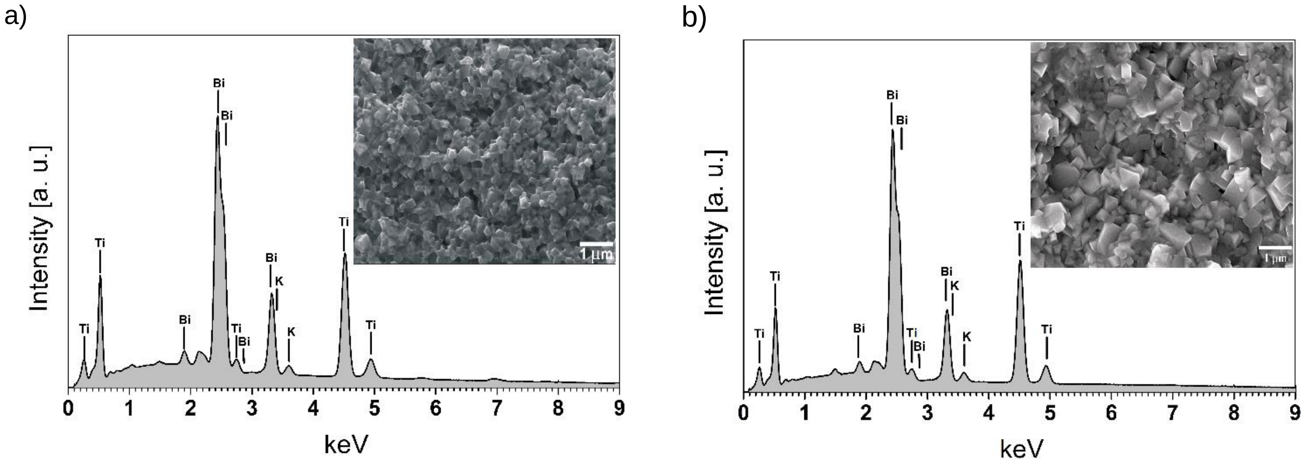


Fig. 3. EDS analysis of the elemental distribution of a KBT ceramic sintered at 1303 K for: a) 5 hours (*KBT* 2), b) 8 hours (*KBT* 3)

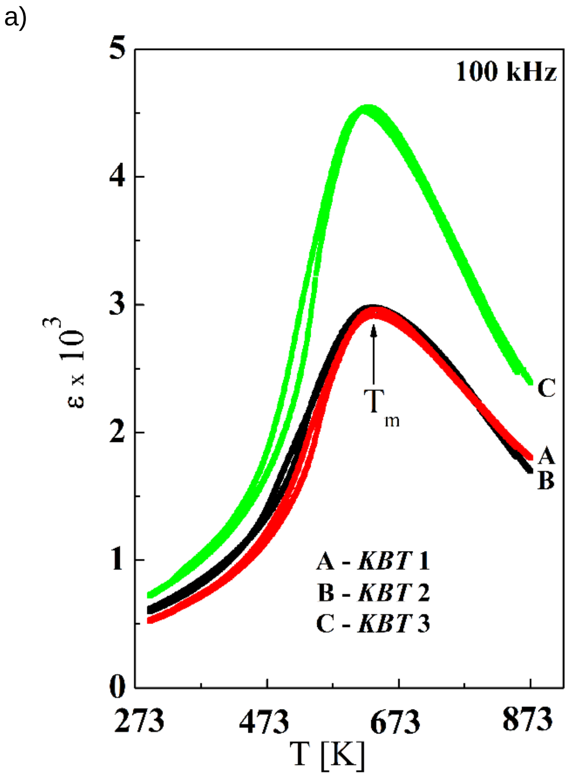


Fig. 4a. Temperature/frequency dependence of the relative permittivity (ε) for: *KBT* 1, *KBT* 2 and *KBT* 3 for 100 kHz

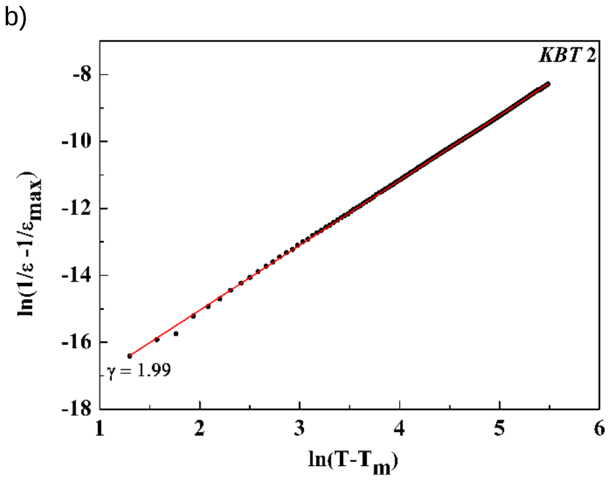


Fig. 4b. Plot of $\ln(1/\varepsilon - 1/\varepsilon_{max})$ versus $\ln(T - T_m)$ for the *KBT 2* ceramics

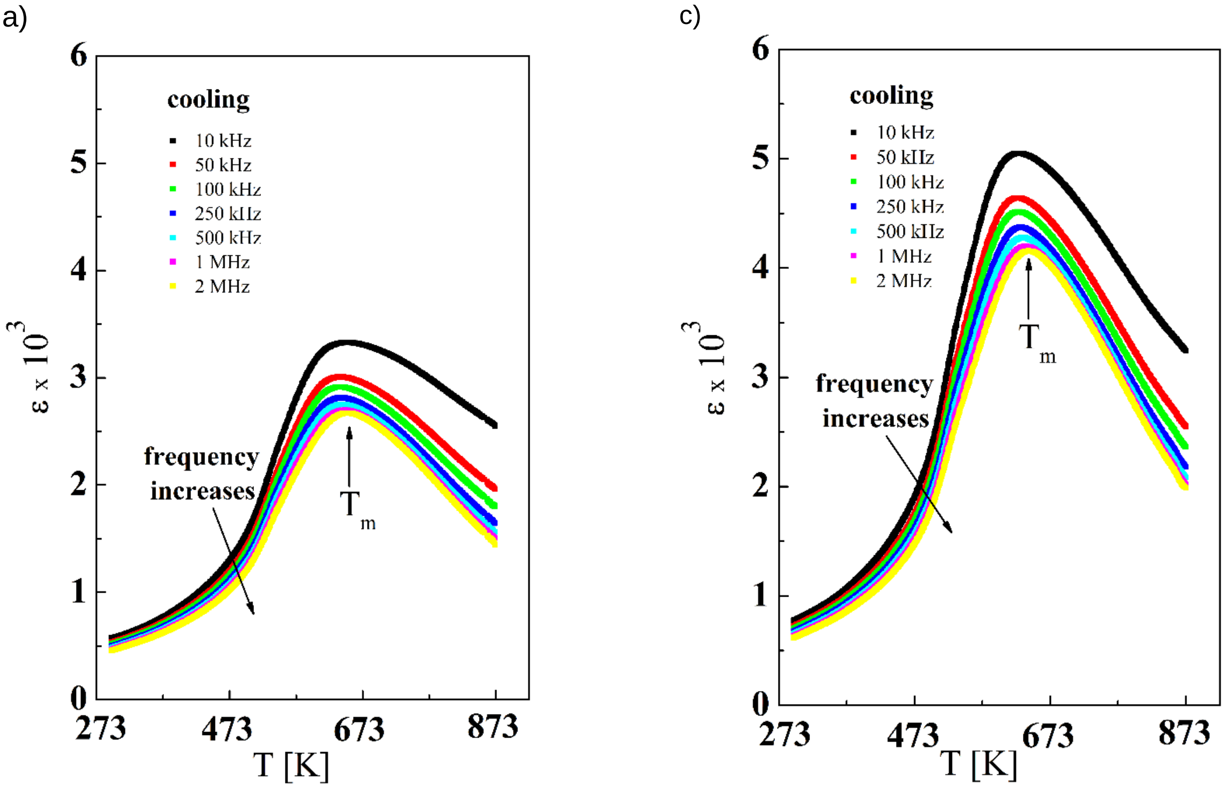
The real part of relative permittivity obtained for all discussed ceramic materials shows frequency dispersion with regard to ε_{max} (Fig. 5). Namely the value of ε_{max} decreases with increasing frequency and the corresponding temperature shifts towards higher values. The degree of dispersion of $\Delta\varepsilon_{max}$, defined as $\Delta\varepsilon_{max} = \varepsilon_{max}(10\ kHz) - \varepsilon_{max}(2\ MHz)$, changes considerably from 372 for the *KBT 2* ceramics to 947 for *KBT 3* ceramics, whereas the degree of dispersion of ΔT_m ($\Delta T_m = T_m(2\ MHz) - T_m(10\ kHz)$) remains practically unchanged (Table 2).

The relative permittivity values at room temperature (ε_{RT}) and at a temperature at which the maximum relative permittivity occurs (ε_m) for the samples studied at selected frequencies: 10 kHz, 100 kHz, 1 MHz, 2 MHz are shown in Table 3.

Table 3. The values of relative permittivity at the room temperature (ε_{RT}) and maximum temperature (ε_m) for KBT ceramics for selected frequencies: 10 kHz, 100 kHz, 1 MHz and 2 MHz.

	Frequency							
	10 kHz		100 kHz		1 MHz		2 MHz	
The sample	ε_{TR}	ε_m	ε_{RT}	ε_m	ε_{RT}	ε_m	ε_{RT}	ε_m
*KBT*1	572	3323	520	2960	469	2695	458	2699
*KBT*2	669	3199	610	2963	537	2849	523	2836
*KBT*3	770	5049	704	4544	635	4204	619	4162

Analysis of relative permittivity values at room temperature (ε_{RT}) and maximum temperature (ε_{max}) allowed us to determine relative changes, defined as: (($\varepsilon_{RT\text{-}KBT\ 3}/\varepsilon_{RT\text{-}KBT\ 1\ or\ 2}$) and ($\varepsilon_{max\text{-}KBT3}/\varepsilon_{max\text{-}KBT\ 1\ or\ 2}$)). These values are: ~ 1.35 for ($\varepsilon_{RT\text{-}KBT\ 3}/\varepsilon_{RT\text{-}KBT\ 1}$), ~ 1.16 for ($\varepsilon_{RT\text{-}KBT\ 3}/\varepsilon_{RT\text{-}KBT\ 2}$), ~ 1.55 for ($\varepsilon_{max\text{-}KBT\ 3}/\varepsilon_{max\text{-}KBT\ 1}$), ~ 1.53 for ($\varepsilon_{max\text{-}KBT\ 3}/\varepsilon_{max\text{-}KBT\ 2}$), respectively.



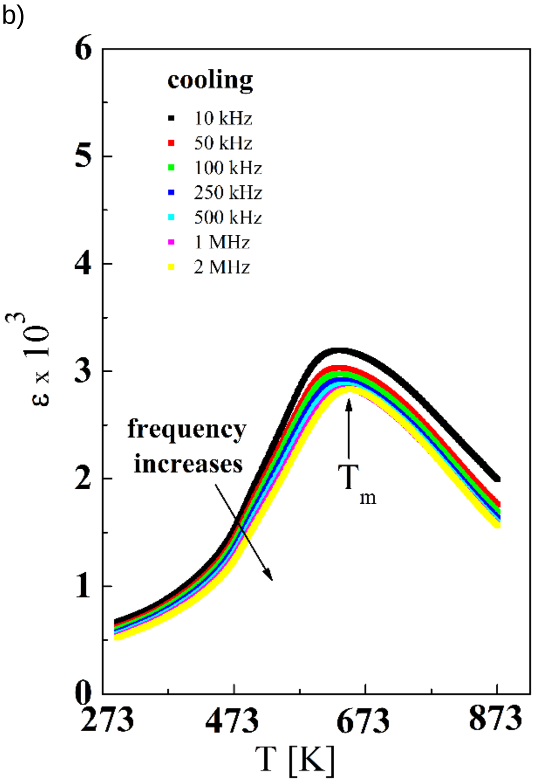


Fig. 5. Temperature/frequency dependence of the relative permittivity (ε) for: a) *KBT* 1, b) *KBT* 2 and c) *KBT* 3 ceramics

Summary and conclusion

Lead-free KBT ceramics have been produced using different sintering times by a solid-state synthesis method. The pure perovskite phase specimens demonstrate an apparent density from 84% (KBT 1) to 98% (KBT 2).

Microstructure research revealed that sintering time primarily affects the size and shape of KBT grains and, thereby, higher homogeneity. For example, KBT 1 (sintering time 4 hours) and KBT 2 (sintering time 5 hours) can be characterized as homogenous materials, while KBT 3 (sintering time 8 hours) exhibits a more microstructure inhomogeneity.

Also, the sintering time significantly influences the dielectric properties. The maximum permittivity (εmax) is about 1.5 times larger for KBT 3 than for KBT 1 and KBT 2, respectively. Furthermore, the dispersion degree of εmax demonstrates a substantial variability from 372 (KBT 2) to 947 (KBT 3). Therefore, the sintering time is an essential parameter of KBT ceramics as it initiates the specific behavior of dielectric permittivity.

The presented studies demonstrate that the appropriate density and microstructural homogeneity of samples, sintering temperature, and milling time of the ingredients are necessary for good-quality KBT fabrication and will be soon investigated in detail.

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REFERENCES

[1] Aksel E, Jones Jacob L., 2010. Advances in lead-free piezoelectric materials for sensors and actuators, Sensors, 10, 1935-1954; DOI:10.3390/s100301935.

[2] Barick BK, Misra KK, Arora AK et al., 2011. Impedance and Raman spectroscopic studies of $Na_{0.5}Bi_{0.5}TiO_3$, J. Phys. D., 44, 355402.

[3] Buhrer CF, 1962. Some properties of bismuth perovskites, J. Chem. Phys., 36, 798-803.

[4] Czaja P, Suchanicz J, Bochenek D, Dercz G, Piasecki M, Hudy W, 2018. High density lead free $K_{0.5}Bi_{0.5}TiO_3$ ceramics preparation mechanical and dielectric properties, Phase Transitions, 91(9-10), 1051-1059.

[5] Czaja P, Suchanicz J, Kluczewska K, Piasecki M, Hudy W, 2018. The influence of technological conditions on dielectric and optical properties of $K_{0.5}Bi_{0.5}TiO_3$ ceramics, Ferroelectrics, 538, 91-95.

[6] DIRECTIVE 2011/65/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment.

[7] Guo J, Zhu M, Li L, et al., 2017. Relaxor to ferroelectric crossover in KBT ceramics by prolonged annealing, J. Alloys Compd., 703, 448-453.

[8] http://ec.europa.eu/environment/waste /weee /index_en.htm.

[9] Hiruma Y, Aoyagi R, Nagata H, et al., 2005, Ferroelectric and piezoelectric properties of $K_{0.5}Bi_{0.5}TiO_3$ ceramics, Jpn. J. Appl. Phys., 44(7A), 5040-5044.

[10] Ivanov VV, Kapyshev AG, Venevcev YN, et al., 1962, Rentgenovskoye opredeleniye elementarnyh jacejek $K_{0.5}Bi_{0.5}TiO_3$ i $Na_{0.5}Bi_{0.5}TiO_3$ i wysokotemperaturnyh fazowyh perechodov v $K_{0.5}Bi_{0.5}TiO_3$, Izv. Akad. Nauk SSSR, 26, 354-356 (in Russian).

[11] Jones GO, Thomas PA, 2002, Investigation of the structure and phase transitions in the novel A-site substituted distorted perovskite compound $Na_{0.5}Bi_{0.5}TiO_3$, Acta Crystallographica B, 58, 168-178.

[12] Köenig J, Suvorov D, 2015, Evolution of the electrical properties of $K_{0.5}Bi_{0.5}TiO_3$ as a result of prolonged sintering, J. Europ. Ceram. Soc., 35(10), 2791-2799.

[13] Li ZF,. Wang CL, Zhong WL, et al, 2003, Dielectric relaxor properties of $K_{0.5}Bi_{0.5}TiO_3$ ferroelectrics prepared by sol-gel method, J. Appl. Phys., 94, 2548-2552.

[14] Park SE, Chung SJ, 1996, Ferroic phase transitions in $Na_{0.5}Bi_{0.5}TiO_3$ crystals, J. Am. Ceram. Soc., 79, 1290-1296.

[15] Qu J, Huang S, Xu Y, et al., 2014, Fabrication and properties of PZT piezoelectric ceramics tubes with large length-diameter ratio, Ceramics International, 40(8), 13019-13024.

[16] Rödel J, Jo W, Seifert Klaus TP, Anton M, Granzow T, 2009, Perspective on the development of lead-free piezoceramics, J. Am. Ceram. Soc., 92(6), 1153-1177, doi: 10.1111/j.1551-2916.2009.03061.x.

[17] Rao Vijaya Bhaskar P, Sankaram Bhima T, 2010, Impedancy spectroscopy studies of $K_{0.5}Bi_{0.5}TiO_3$, J. Electroceram, 25, 60-69, DOI 10.1007/s10832-009-9589-4.

[18] Shrout TR, Zhang SJ, 2007, Lead-free piezoelectric ceramics; Alternatives for PZT ? Journal of Electroceramics, 19(1), 113-126.

[19] Seifert K, 2010, Lead-free piezoelectric ceramics [PhD thesis], Darmstadt.

[20] Suchanicz J, Sitko D, Kim-Ngan NTH, Balogh AG, 2008, Electric properties of soft PZT ceramics under combined electric and mechanic fields, J. Appl. Phys, 104, 094106-0941110.

[21] Sawaguchi E, 1953, Ferroelectricity versus antiferroelectricity in the solid solutions of $PbZrO_3$ and $PbTiO_3$, J. Phys. Soc. Jpn., 8, 615-629.

[22] Suchanicz J, Mercurio JP, Konieczny K, 2002, Electric properties of $(Na_{0.5}Bi_{0.5})_{0.86}Ba_{0.14}TiO_3$ single crystal, Ferroelectrics, 268, 357-362.

[23] Suchanicz J, Kluczewska K, Czaja P, Kania A, Konieczny K, Handke B, Sokołowski M, Trubitsyn MP, Kruzina TV, 2017, The influence of electric poling on structural, thermal, Dielectric and ferroelectric properties of $Na_{0.5}Bi_{0.5}TiO_3$ ceramics, Ceramic International, 43, 17194-17201.

[24] Suchanicz J, Kania A, Czaja P, et al., 2018, Structural, thermal, dielectric and ferroelectric properties of $K_{0.5}Bi_{0.5}TiO_3$ ceramics, J. Europ. Cer. Soc, 38, 567-574.

[25] Smolenskii GA, Isupov VA, Agranovskaya AI, et al., 1961, New ferroelectrics of complex compositions, Sov. Phys. Sol. Stat., 2, 2651-2654.

[26] Vakhrushev SB, Isupov VA, Kvyatkovsky BE, et al., 1985, Phase transitions and soft modes in sodium bismuth titanate, Ferroelectrics, 63, 153-160.

[27] 27 Yamamoto T, 1996, Ferroelectric properties of the $PbZrO_3$ and $PbTiO_3$. Jpn. J. Appl. Phys., 35(1), 5104.

[28] Yang J, Hou Y, Wang Ch, et al., 2007, Relaxor behavior of $K_{0.5}Bi_{0.5}TiO_3$ ceramics derived from molten salt synthesized single crystalline nanowires, Appl. Phys. Lett., 91, 023118.

[29] Zhang S, Xia R, Shrout T, 2007, Lead-free piezoelectrics ceramics v PZT ?, Journal of Electroceramics, 19(4), 251-257.

[30] Zannen M, Lahmar A,. Dietze M, et al., 012, Structural, optical and electrical properties of Nd-doped $N_{0.5}Bi_{0.5}TiO_3$, Mater. Chem.Phys., 134, 829.

[31] Zannen M, Lahmar A, Khemakhem H, et al., 2016, Energy storage property in lead free Gd doped $Na_{0.5}Bi_{0.5}TiO_3$ ceramics, Solid State Communications, 245, 1-4.