

Effect of sintering temperature on dielectric properties of barium titanate ceramics and composite

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Abstract

The structure and dielectric properties of barium titanate ceramics samples sintered at 1100, 1150, 1200, 1250 and 1350 °C have been compared with the dielectric properties of 80 vol.% barium titanate + 20 vol.% barium ferrite composite samples sintered at 1150, 1200 and 1250 °C. It has been shown that polarization sufficient for existence of the piezoelectric effect is only achieved in barium titanate samples sintered at 1250 and 1350 °C. Furthermore the pyroelectric coefficient and reversal polarization of these samples are far higher than those of samples sintered at lower temperatures. Analysis of the sample structures has confirmed that the dielectric properties of barium titanate ceramics depend on grain size and therefore on sintering temperature. Based on the experimental results we have selected the optimum sintering temperature for 80 vol.% barium titanate + 20 vol.% barium ferrite composite to be 1250 °C. Further increase in sintering temperature to 1300 °C showed that this composite has a eutectic. The temperature dependence of the permittivity of the barium titanate / barium ferrite composite sintered at 1250 °C is similar to that of BaTiO₃ ceramics samples sintered at 1350 °C. The room temperature permittivity of the composite samples also proves to be far higher than that of barium titanate ceramics samples sintered at the same temperatures. Barium ferrite addition to barium titanate increases the permittivity of the composite and also diffuses the ferroelectric phase transition and shifts the permittivity maximum temperature by 10 °C towards higher temperatures.

Keywords

piezoelectric ceramics, barium titanate, magnetoelectric composite, permittivity, Curie temperature, spontaneous polarization, pyroelectric effect, piezoelectric coefficient.

1. Introduction

The design of fundamentally new materials differing from currently used ones by composition and, more importantly, by functionality is critical for the development of intellectual technologies [1–4]. The composite materials possessing various useful properties are of special interest since their properties can be varied over a greater range as compared with single-component materials. The good

perspective for the practical application of functional ceramics based composite materials is explained by the possibility of varying their physical properties by modifying the raw material. Combinations of multiple components possessing different electrical and magnetic properties in a single material show good promise for providing fundamentally new materials possessing a magnetoelectric bond [3–5]. Composite structures may contain inhomogeneities caused by the presence of micro- and macroin-

clusions of ferroelectric and magnetic phases, porosity, bulk charge layers, “dead” layers etc. Therefore an important research task is not only to provide novel composite structures possessing ferroelectric and magnetic properties but also to study their physicochemical properties and identify a correlation between the formation conditions of inhomogeneous polar features and the appearance of their physical properties. These materials are composites with various types of bonds, the properties of these structures depending on the phase concentrations in the material and the electrophysical parameters of each constituent phase. Their response to external effects (electric or magnetic fields, temperature variation etc.) is an overall one contributed to by the responses of each system component, or is determined by a specific property not inherent to any of the constituent phases.

The basic material possessing ferroelectric and magnetic properties which is widely studied nowadays is bismuth ferrite [6]. For improving the multiferroic properties bismuth ferrite can be modified with various additives [7, 8].

In the meantime composite materials in which a bulk combination of ferroelectric and magnetic materials is implemented are more promising from practical viewpoint because controlling the composition of magnetoelectric composites allows one to design compositions with practically desirable dielectric and magnetic permeability figures. These composites are currently designed following two directions:

- layered composites in which layers of ferroelectric and magnetic materials interchange [9, 10];
- polymer magnetic materials containing ferroelectric ceramics [11].

Research efforts have been started recently aimed at designing magnetoelectric composites containing magnetic and piezoelectric ceramics [12, 13]. Controlling the composition of these magnetoelectric composites allows one to design compositions with practically desirable dielectric and magnetic permeability figures.

Barium titanate ceramics pertain to piezoelectric materials finding wide practical application. It is safe to assume that combining barium titanate with barium ferrite will produce a composite having electromagnetic properties. The authors have studied this composite [14, 15]. It is currently believed that the optimum synthesis temperature of barium titanate ceramics is the 1300–1350 °C range [16, 17], though there are indications [18] that it can be synthesized at below 1130 °C. Since solid state synthesis of barium ferrite / barium titanate composite at $T = 1300$ °C proved to be impossible due to the presence of a eutectic (compacted raw materials melted during synthesis) we synthesized the composite at the sintering temperature $T_{\text{sint}} = 1100$ °C. Although this composite has both magnetic and ferroelectric properties [14] its dielectric permeability proved to be lower than that of barium titanate ceramics [16]. Therefore, we carried out further experiments to study the effect of barium titanate

ceramics sintering temperature on its ferroelectric and dielectric properties.

The aim of this work is to production barium titanate ceramics and barium titanate / barium ferrite composite at different sintering temperatures, compare their dielectric properties and identify the optimum sintering temperatures.

2. Experimental

We produced and studied samples of the barium titanate (BaTiO_3) ceramics and a barium ferrite (BF) / barium titanate (BaTiO_3) composite. BF and BaTiO_3 ceramics were synthesized using standard technologies [13, 16, 19]. The BaTiO_3 ceramics samples were sintered in a muffle furnace at 1100, 1150, 1200, 1250 and 1350 °C. The BF– BaTiO_3 samples were sintered at 1150, 1200 and 1250 °C. The raw components were taken in the 20 vol.% BF / 80 vol.% BaTiO_3 ratio.

We studied the structure and dielectric properties of the BaTiO_3 samples (temperature dependence of permittivity, dielectric hysteresis loop and presence of pyroelectric and piezoelectric effects).

The structure of the samples was examined under a JEOL 6510LV scanning electron microscope. The temperature dependence of the permittivity of the samples was tested on a special temperature equipment with heating rate control option. The equipment included a low-voltage furnace and a furnace control unit consisting of a programmable thermal controller (Miniterm) with a power amplifier and a computer with control software. The sample capacity was measured with a E7-20 imittance meter. Spontaneous polarization measurements were carried out based on the experimental dielectric hysteresis loops using the Sawyer–Tower circuit, the pyroelectric coefficient was measured using a dynamic method [20] and the piezoelectric modulus was measured using a resonance–antiresonance method [21].

3. Results and discussion

3.1. BaTiO_3 ceramics.

The surface structure of the barium titanate ceramics samples was examined using scanning electron microscopy (SEM). The results showed that the shape and size of barium titanate grains depend strongly on sintering temperature (Fig. 1). The samples sintered at 1100, 1150 and 1200 °C contained two types of grains. This can be accounted for by the fact that some of grains were not formed during the sintering process. One type of grains consisted of coalesced raw particles from which the sample was pressed and the second type were grains in which recrystallization was in progress. The grain structures in the samples sintered at 1250 and 1350 °C were quite similar with the only exception that medium sized grains were absent for the higher sintering temperature.

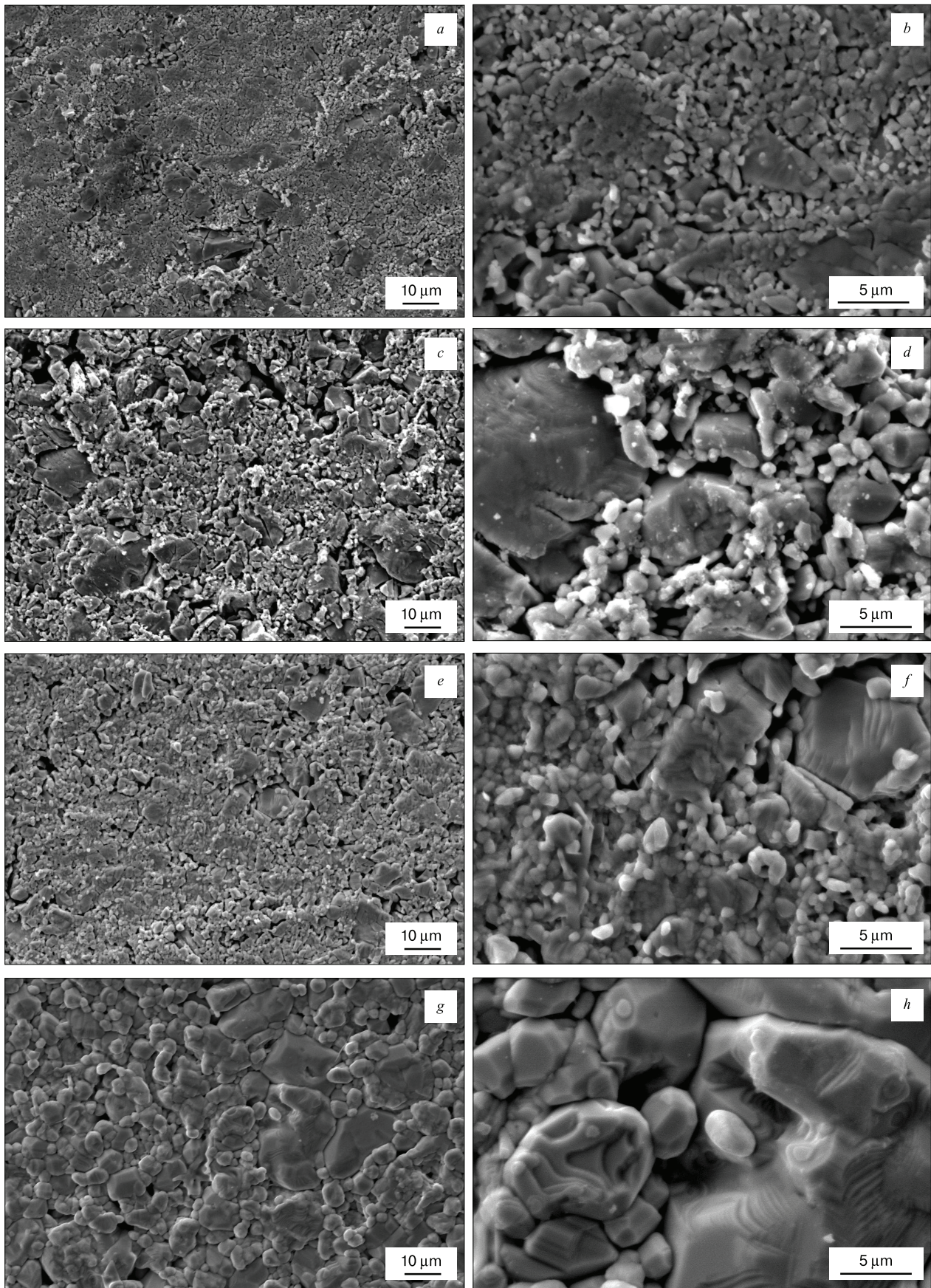


Figure 1. Different magnification SEM images of BaTiO₃ sample structure for sintering temperatures of (a and b) 1100, (c and d) 1150, (e and f) 1200, (g and h) 1250 and (i and j) 1350 °C.

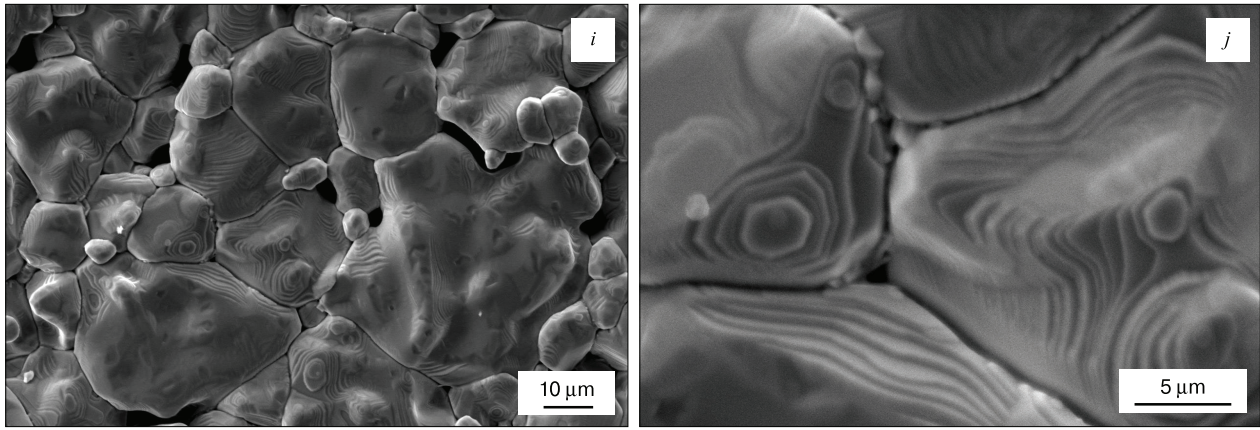


Figure 1. Continued.

We measured the grain sizes using a special option of the scanning electron microscope (*scaler*). Grain size was analyzed for the second type of grains in which recrystallization started. The dependence of average grain size r on sintering temperature is shown in Fig. 2. The grain size for the samples sintered at 1300 °C was borrowed from an earlier work [22]. It can be seen from Fig. 2 that for sintering temperatures of below 1250 °C the grain size grows linearly with an increase in sintering temperature but then it exhibits an abrupt growth.

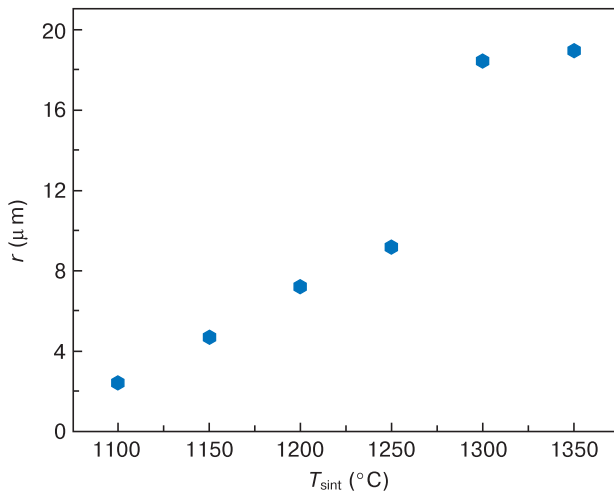


Figure 2. Average grain size dependence on BaTiO₃ sample sintering temperature.

One can therefore conclude that recrystallization during which grains coalesce and grow ends at 1250 °C following which the grain size increases only due to the grain growth. This is also confirmed by the appearance of growth steps in the samples sintered at 1250 °C and higher temperatures (Fig. 1g–j [22]).

The temperature dependence of the permittivity of the BaTiO₃ ceramics samples are shown in Fig. 3a. All the samples have a clear maximum at the Curie temperature (approx. 130 °C). However the permittivity maximum values depend on sintering temperature. The higher the sintering temperature the higher the permittivity of the

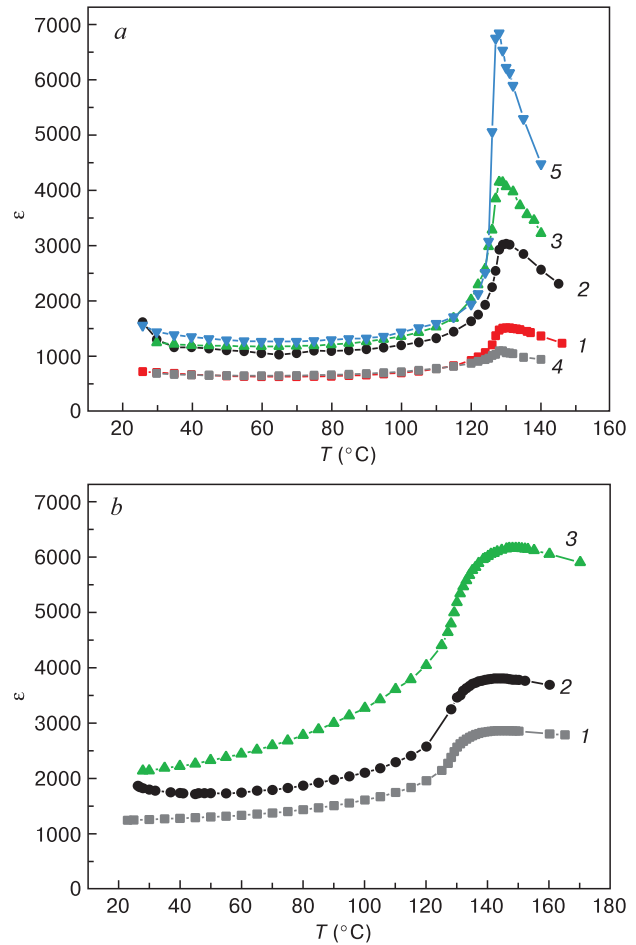


Figure 3. Temperature dependences of permittivity for (a) BaTiO₃ and (b) BF20 – BaTiO₃ 80 samples sintered at (4) 1100, (1) 1150, (2) 1200, (3) 1250 and (5) 1350 °C.

samples at the Curie temperature. The room temperature permittivity are close for the samples sintered at 1100 and 1150 °C and for the samples sintered at 1200, 1250 and 1350 °C. This regularity agrees with earlier data [23] based on which the authors concluded on a relationship between the dielectric properties and grain size of BaTiO₃ ceramics.

To verify the existence of spontaneous polarization at a macroscopic level we studied the dielectric hysteresis loops

for the samples in a 900 V/mm AC field. Based on the dielectric hysteresis loops we calculated the reversal polarization for BaTiO₃ ceramics samples sintered at different temperatures. The calculation results are presented below.

$T_{\text{sint}}, ^\circ\text{C}$	$P_{\text{rev}}, \text{C/m}^2$
1100	0.002
1150	0.005
1200	0.005
1250	0.016
1350	0.031

Before measuring the pyroelectric and piezoelectric parameters we poled the samples in a 1500 V/mm DC electric field.

The square-modulated heat flow source for the pyroelectric measurements was a 960 nm IR laser. The pyroelectric current was measured in short circuit mode with an OR297 operational amplifier having a 2.5×10^8 V/A current to voltage conversion ratio. The pyroelectric coefficient calculation results are presented in Fig. 4. Since the dynamic pyroelectric effect method used allows determining spontaneous polarization direction in samples [20] the measurements were conducted at both sample sides corresponding to the positive ($+P_s$) and negative ($-P_s$) spontaneous polarization vector orientations.

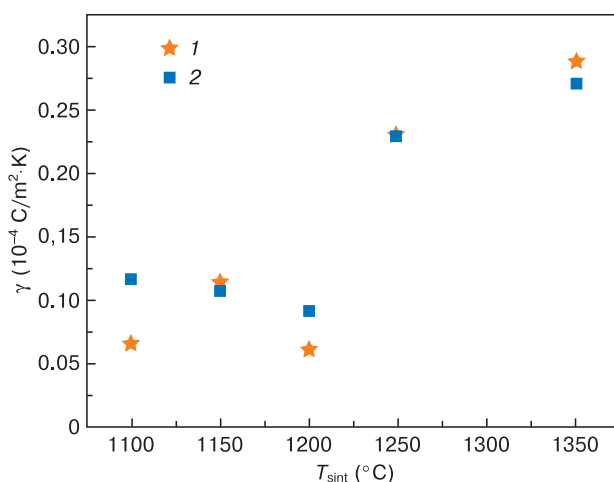


Figure 4. Pyroelectric coefficient dependence on sintering temperature for different BaTiO₃ sample sides: (1) $+P_s$ and (2) $-P_s$.

The resonance and antiresonance frequency measurements for piezoelectric coefficient study by a resonance method showed that piezoelectric resonance only exists in the samples sintered at 1250 and 1350 °C. The experimentally measured piezoelectric moduli d_{31} and d_{33} (Table 1) for the samples were in agreement with the industry standard despite that the reversal polarization P_{rev} (see above) and the pyroelectric coefficient (Fig. 4) of the sample sintered at 1250 °C were lower than those for the sample sintered at 1350 °C.

Table 1. Piezoelectric modules of BaTiO₃ samples sintered at different temperatures.

Sintering temperature, °C	$d_{31}, 10^{-12} \text{ C/N}$	$d_{33}, 10^{-12} \text{ C/N}$
1250	32	191
1350	31	210

3.2. Barium ferrite/barium titanate composite.

The studies of the dielectric properties for BaTiO₃ ceramics showed that only the sample sintered at 1350 °C has the true ferroelectric properties. Although the sample sintered at 1250 °C had high piezoelectric moduli, its pyroelectric coefficient and spontaneous polarization were inferior to those of the sample sintered at 1350 °C. However the experiments for obtaining barium ferrite / barium titanate composite (BF – BaTiO₃) revealed a eutectic in this mixture that renders impossible sample sintering at temperature 1300 °C. It was therefore of interest to compare the temperature dependence of the permittivity of the BaTiO₃ ceramics samples with those of BF – BaTiO₃ composite.

The data on the temperature dependence of the permittivity of the 20 % barium ferrite 80% + barium titanate composite samples sintered at 1150, 1200 and 1250 °C are shown in Fig. 3b. As can be seen from Fig. 3b barium ferrite addition to barium titanate diffuses the ferroelectric phase transition. However the permittivity of the BF – BaTiO₃ composite samples was higher than that of the BaTiO₃ samples sintered at the same temperatures (Fig. 3). Thus barium ferrite addition to barium titanate increases the dielectric permeability of BF – BaTiO₃ composite.

4. Conclusion

Study of the effect of BaTiO₃ ceramics sintering temperature showed that the ferroelectric properties of the samples are the better the higher the sintering temperature. This regularity shows itself in the value of the reversal polarization and pyroelectric response, presence or absence of piezoelectric effect in poled samples and value of the permittivity at the Curie temperature. The phase transition temperature does not depend on sintering temperature and the maximum permittivity of all the samples is observed at 130 °C. However the permittivity maximum values depend on sintering temperature: the higher the sintering temperature the higher the permittivity of the samples at the Curie temperature.

Although the BaTiO₃ ceramics sample sintered at 1350 °C has the best ferroelectric properties, the pyroelectric and piezoelectric properties of the samples sintered at 1250 °C are but slightly inferior to it. This shows a theoretical possibility of reducing sintering temperature of barium titanate based composite to 1250 °C.

Indeed experiments showed that a sintering temperature of 1250 °C is below the eutectic one but on the other hand allows production BF – BaTiO₃ composite samples with a permittivity temperature dependence similar to that of BaTiO₃ ceramics samples sintered at 1350 °C. Barium

ferrite addition to barium titanate ceramics increases the permittivity of the sample and diffuses the phase transition. The permittivity maximum temperature shifts by 10 °C towards higher temperatures.

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References

1. Bataev A.A. *Kompozitsionnye materialy* [Composite materials]. Moscow: Logos, 2006: 397 (In Russ.)
2. Grashchenkov D.V., Chursova L.V. Development strategies of composite and functional materials. *Aviacionnye Materialy and Tekhnologii*, 2012: 231–242. (In Russ.)
3. Titov S.V., Titov V.V., Shabanov V.M., Aleshin V.A., Shilkina L.A., Reznichenko L.A. Multifractal studies of active ceramic composite materials. *Design of Composite Materials*, 2014; (3): 46–52. (In Russ.)
4. Ortega N., Kumar A., Scott J. F., Katiyar R.S. Multifunctional magnetoelectric materials for device applications. *J. Phys.: Condens. Matter*, 2015; 27(50): 504002 (24pp.). <https://doi.org/10.1088/0953-8984/27/50/504002>
5. Petrov V.M. *Magnetoelectric properties of the ferrite-piezoelectric composite materials*. Diss. ... Dr. Sci. (Eng.). Velikiy Novgorod, 2004: 186. (In Russ.)
6. *Segnetomagnitnye veshchestva* [Ferro-magnetic materials]. Eds. Yu.N. Venevtcev, V.N. Lyubimov. Moscow: Nauka, 1990: 184. (In Russ.)
7. Kallaev S.N., Omarov Z.M., Bakmaev A.G., Mitarov R.G., Reznichenko L., Bormanis K. Thermal properties of multiferroic $\text{Bi}_{1-x}\text{Eu}_x\text{FeO}_3$ ($x = 0-0.40$) ceramics. *J. Alloys and Compounds*, 2017; 695: 3044–3047. <https://doi.org/10.1016/j.jallcom.2016.11.347>
8. Kallaev S.N., Omarov Z.M., Mitarov R.G., Sadykov S.A., Khasbulatov S.V., Reznichenko L., Bormanis K., Kundzinsh M. Heat capacity and thermal conductivity of multiferroics $\text{Bi}_{1-x}\text{Pr}_x\text{FeO}_3$. *Integrated Ferroelectrics*, 2019; 196(1): 120–126. <https://doi.org/10.1080/10584587.2019.1591973>
9. Karpenkov D.Y., Bogomolov A.A., Solnyshkin A.V., Karpenkov A.Y., Shevyakov V.I., Belov A.N. Multilayered ceramic heterostructures of lead zirconate titanate and nickel-zinc ferrite for magnetoelectric sensor elements. *Sensors and Actuators A: Physical*, 2017; 266: 242–246. <https://doi.org/10.1016/j.sna.2017.09.011>
10. Grechishkin R.M., Kaplunov I.A., Ilyashenko S.E., Malyshkina O.V., Mamkina N.O., Lebedev G.A., Zalyotov A.B. Magnetoelectric effect in metglas/piezoelectric macrofiber composites. *Ferroelectrics*, 2011; 424(1): 78–85. <https://doi.org/10.1080/00150193.2011.623939>
11. Makarova L.A., Alekhina Yu.A., Perov N.S., Omelyanchik A.S., Rodionova V.V., Malyshkina O.V. Elastically coupled ferromagnetic and ferroelectric microparticles: new multiferroic materials based on polymer, NdFeB and PZT particles. *J. Magn. Magn. Mater.*, 2019; 470: 89–92. <https://doi.org/10.1016/j.jmmm.2017.11.121>
12. Kleemann W. Multiferroic and magnetoelectric nanocomposites for data processing. *J. Phys. D: Appl. Phys.*, 2017; 50(22): 223001. <https://doi.org/10.1088/1361-6463/aa6c04>
13. *Magnetic Oxides and Composites*. Vol. 31. Eds. R.B. Jotania, S.H. Mahmood. Millersville (PA, USA): Materials Research Foundations, 2018: 274.
14. Malyshkina O.V., Shishkov G.S., Ivanova A.I., Malyshkin Y.A., Alexina Y.A. Multiferroic ceramics based on barium titanate and barium ferrite. *Ferroelectrics*, 2020; 569(1): 215–221. <https://doi.org/10.1080/00150193.2020.1822679>
15. Ivanova A.I., Malyshkina O.V., Karpenkov A.Yu., Shishkov G.S. Microstructure of composite materials based on barium titanate and barium ferrite. *Ferroelectrics*, 2020; 569(1): 209–214. <https://doi.org/10.1080/00150193.2020.1822678>
16. Okadzaki K. *Tekhnologiya keramicheskikh dielektrikov* [Ceramic dielectric technology]. Moscow: Ehnergiya, 1976: 336. (In Russ.)
17. Patent 0002706275 (RF). A method of producing ceramics based on barium titanate. A.D. Smirnov, A.A. Holodkova, M.N. Danchevskaya, S.G. Ponomarev, A.A. Vasin, V.V. Rybalchenko, Yu.D. Ivakin, 2019. (In Russ.)
18. Patent 2646062 (RF). A method of manufacturing barium titanate (BaTiO_3) for multilayer ceramic capacitors with a dielectric sintering temperature of not more than 1130 °C. K.D. Gasyimov, I.K. Ezovskij, 2017. (In Russ.)
19. Slocari G. Phase equilibrium in the subsystem $\text{BaO-Fe}_2\text{O}_3 - \text{BaO-6Fe}_2\text{O}_3$. *J. Amer. Ceram. Soc.* 1973; 56(9): 489–490. <https://doi.org/10.1111/j.1151-2916.1973.tb12531.x>
20. Golovnin V.A., Kaplunov I.A., Malyshkina O.V., Ped'ko B.B., Movchikova A.A. *Fizicheskie osnovy, metody issledovaniya i prakticheskoe primeneniye p'ezomaterialov* [Physical foundations, research methods and practical application of piezomaterials]. Moscow: Tekhnosfera, 2016: 272. (In Russ.)
21. *Industry standard. Piezoceramic materials*. OST II 0444-87. (In Russ.)
22. Malyshkina O.V., Ivanova A.I., Karelina K.S., Petrov R.A. Structure features of barium and calcium titanate ceramics. *Physical and Chemical Aspects of the Study of Clusters, Nanostructures and Nanomaterials*, 2020; 12: 652–661. (In Russ.). <https://doi.org/10.26456/pcascnn/2020.12.652>
23. McNeal M.P., Jang S.-J., Newnham R.E. The effect of grain and particle size on the microwave properties of barium titanate BaTiO_3 . *J. Appl. Phys.*, 1998; 83(6): 3288–3297. <https://doi.org/10.1063/1.367097>