

Features of the Ferro Ceramics Synthesis by Flux of Concentrated Solar Radiation

Muhammade-Sultahan Payzullakhanov

Institute of Material Sciences of the Academy of Sciences Republic of Uzbekistan

Abstract: *Synthesized ferroceramic material based on barium titanate melted in a solar furnace. A non monotonic character of the influence of doping of barium titanate with iron oxide Fe₂O₃, which consists in an increase in the dielectric constant of BaTiO₃, is revealed. The optimum concentration of iron oxide doping - 6 mole%, is determined, beyond which saturation of the curves of the dependences of the dielectric properties of barium titanate is observed.*

Keywords: *ferroelectric ceramic material, barium titanate, alloying, fused material, solar furnace, dielectric constant*

1. INTRODUCTION

It is known that barium titanate BaTiO₃ perovskite structure at room temperature is a dielectric with a specific resistance of 10⁸ Ohm. The tetragonal distortion of the barium titanate crystal lattice (a = 3.994, c = 4.038) promotes the manifestation of ferroelectric and piezoelectric properties, which makes it possible to widely use it in electronic engineering. Analysis shows that the specific electric resistance of barium titanate can be varied by isovalent or heterogeneous substitution of titanium ions (Ta, Zr, Hf) [1,2] or barium (Zn, Ni, Sr, Sb, Y, Fe) [3, 4]. According to [3], the introduction of ZnO increases the density of sintered samples of BaTiO₃ and degrades the dielectric properties. In [4], the influence of NiO was studied and it was shown that the presence of NiO leads to a decrease in the density of sintered samples and the grain size.

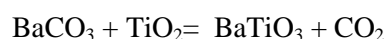
In this paper, we present the results of an investigation of the dielectric and mechanical properties of barium titanate doped with iron oxide synthesized from a melt obtained from a solar furnace.

2. EXPERIMENTAL RESULTS

At the first stage of the experiments for the synthesis of barium titanate, titanium oxide TiO₂, barium carbonate BaCO₃, was used. From stoichiometric mixtures of raw materials ground to fin 063 by the method of semi-dry pressing with a force of 50 MPa, with the use of PVA glue as a binding material, pellet samples with a diameter of 3 mm and a thickness of 2 mm were prepared. Samples-tablets were placed on the focal plane of the solar furnace and melted under the action of concentrated solar radiation at different light flux densities (100-300 W / cm²). The castings were cooled in water.

Castings obtained after cooling the melt were subjected to grinding in an agate mortar, then pellets with a diameter of 8 mm and a thickness of 2 mm were prepared by semi-dry pressing. The resulting tablets were sintered in a silitic oven at a temperature of 1350 ° C for 2 hours, cooled at 100 ° C / min (A-type samples).

The curves of differential thermal analysis (DTA) (Fig. 1) of a mixture of BaCO₃ + TiO₂ showed an endothermic peak at 8250 ° C, corresponding to a solid-phase reaction



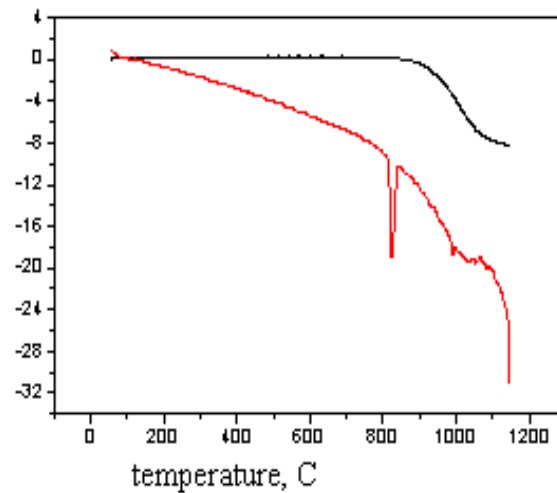


Fig1. DTA curves of mixture $BaCO_3 + TiO_2$

X-ray phase analysis performed on sintered samples on a DRON-3M apparatus with copper radiation indicated the formation of the tetragonal phase of $BaTiO_3$ (Fig. 2).

As a control on the basis of the initial mixture, the samples were sintered at a temperature of $1350\text{ }^\circ\text{C}$ with an exposure time of 2h, cooled at a rate of $100\text{ }^\circ\text{C} / \text{min}$ (B-type samples).

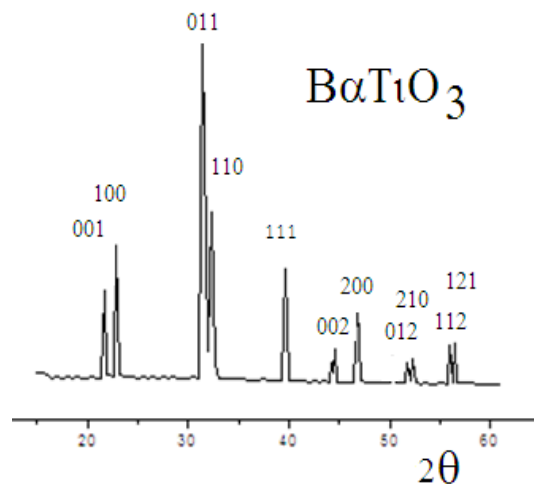


Fig2. X-ray diffraction patterns.

In the second stage of the experiments, we prepared samples based on a mixture of $(1-x) BaTiO_3 + xFe_2O_3$ ($0 < x < 10$ mole%). From this mixture (50Mpa) samples were pressed, which were sintered at a temperature of $1350\text{ }^\circ\text{C}$ with a holding time of 2 hours (C-type samples). Measurements of the dielectric constant were carried out at the LCR (PM 6303) setup at a frequency of 1 KHz on samples with ohmic contacts deposited by vacuum deposition of aluminum.

Figure 3 shows the dependences of the permittivity of barium titanate doped with Fe_2O_3 synthesized at various densities of the concentrated light flux.

It can be seen from Fig. 3 that the dielectric constant of a sample of barium titanate sintered in an electric furnace (A-type sample) is 480-500, while B-type samples obtained from castings on a solar furnace exhibit twice the dielectric Permeability (1000). As can be seen from Fig. 3, with an increase in the molar Fe_2O_3 content, an increase in the permittivity of barium titanate is observed. Apparently, this phenomenon is associated with the chemical interactions of Fe_2O_3 with barium titanate. Iron ions Fe^{3+} (0,064 nm) replace barium ions Ti^{4+} (0.042nm) in octahedral positions B, resulting in the formation of oxygen vacancies in the crystal lattice. Double acceptor traps are formed, which are formed as a result of the formation of a bond between two Fe^{3+} ions at neighboring positions of the crystal lattice and a titanium vacancy. An increase in the concentration of iron is accompanied by an increase in the concentration of such traps and a corresponding decrease in the number of free electrons[4,5].

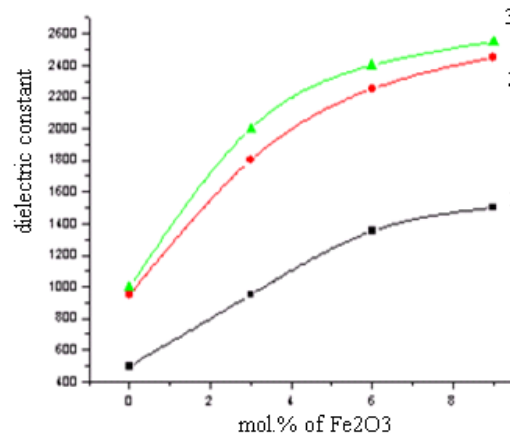


Fig3. The dielectric constant of barium titanate doped with Fe₂O₃ as a function of the solar flux density: 1- 0 W/cm², 2 - 200W/cm², 3 - 300 W/cm².

As the concentration of iron oxide increases, the density of the sintered sample increases. Apparently, the iron oxide distributed at the grain boundaries promotes the bonding of the neighboring grains of barium titanate and thus causes an increase in their size. In addition, superficial energy states of acceptor character are formed at the grain boundaries, which capture the electrons lower the conductivity of the ceramic.

It is known that the increase in the permittivity of barium titanate in comparison with other perovskite-type titanates is due to the fact that in barium titanate, the distance between titanium and oxygen ions $L_{Ti-O} = 1.99 \text{ \AA}$ is greater than the sum of their radii $R_{Ti} + R_O = 1.82 \text{ \AA}$. [6]. If an iron ion with a radius of $R_{Fe^{3+}} = 0.064 \text{ nm}$ replaces the titanium ion Ti^{4+} ($R = 0.042 \text{ nm}$), the lattice will expand, causing additional tetragonal distortion of the lattice.

Figure 4 shows the temperature dependences of the permittivity $(1-x) BaTiO_3 + xFe_2O_3$ ($0 < x < 10$ mole%) at a frequency of 100 and 500 kHz.

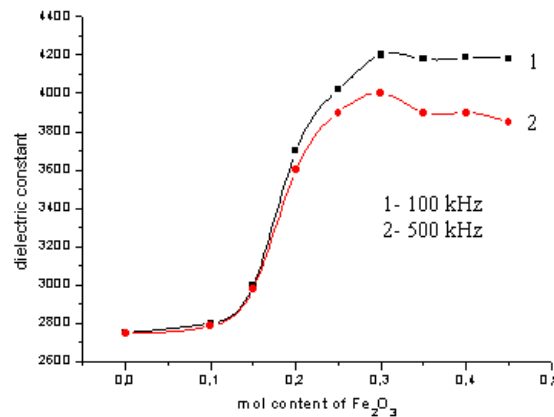


Fig4. The dielectric constant of barium titanate doped with Fe₂O₃ as a function of the frequency: 1- 100kHz, 2 – 500 kHz.

As the content of iron oxide increases, the dielectric constant of barium titanate increases. And at values of iron oxide content greater than 0.3 mole the dielectric constant remains constant in the range 3800 - 4200. It can also be noticed that with increasing frequency from 100 to 500 kHz the dielectric constant decreases.

As is known, the permittivity ϵ is defined as the ratio of charges on the capacitor plates when replacing plates from a given dielectric by vacuum. Such a change in the capacity of the capacitor occurs as a result of the phenomenon of polarization of the dielectric. Polarization is the process of displacement of structural elements (electrons, atoms, ions, etc.) of a crystal lattice from its normal position under the influence of an electric field. As a result of interaction with an external electric

field, the electrostatic forces acting inside the crystal are disrupted and redistributed, while maintaining its overall neutrality. The mechanism of polarization can be different depending on which structural elements are involved in the polarization process. The following basic types of polarization are observed in ceramic materials: electronic, ionic, electron- and ion-relaxation, spontaneous. The degree of polarization of the ceramic dielectric and its polarizability as a whole is the sum of the polarizations of each species. The magnitude of the permittivity reflects the polarizability of this type of ceramics.

Electronic polarization is the elastic displacement of the center of gravity and the deformation of a negatively charged electron cloud under the influence of an electric field. Electronic polarization proceeds almost instantaneously and is not associated with energy loss. Electronic polarization for most types of ceramics is not typical.

Ionic polarization is the relative displacement of ions. This kind of polarization is inherent in ceramics containing ionic crystals. Ionic polarization also proceeds instantaneously. If, on the return of electrons or ions, any appreciable time interval is required, then the electron and ion-relaxation polarization are distinguished. Substances with electron-relaxation polarization have a large dielectric constant. Spontaneous polarization is an orientation directed toward the external electric field of electric moments located chaotically in individual regions of the crystal (domains) prior to the imposition of an electric field. Spontaneous polarization is associated with significant energy dissipation. A feature of spontaneous polarization is the nonlinear dependence of the dielectric constant on the magnitude of the electric field strength and the presence of a maximum at a certain temperature. Spontaneous polarization has a number of crystals of a certain structure, for example BaTiO₃ and some other substances. In most cases, the electrical conductivity of the ceramic is ionic. The ions that enter the crystal lattice, as well as those in a less ordered state in the vitreous matter, have a certain mobility. It is the smaller, the stronger the intracrystalline bonds. Those ions that are in the interstices and defective positions of the crystal lattice, as well as the ions of the impurity compounds and the vitreous phase ions are always more mobile than the ions of the crystalline phase. They are the main source of electrical conductivity of ceramics.

Apparently, with increasing frequency, the ionic and orientational polarization decreases and disappears due to the inertia of molecules and ions. As the content of ferrite exceeds the percolation limit, a sharp drop in the resistivity occurs, leading to an exchange of electrons between Fe²⁺ ↔ Fe³⁺ in the ferrite phase causing electronic polarization.

Figure 5 shows the change in the tangent of the loss angle. This behavior is due to the presence of two types of charge carriers for polarization. Local displacement of the charge of the p-type charge occurs in the opposite direction from n-type charge carriers, which reduces the polarization at lower frequencies.

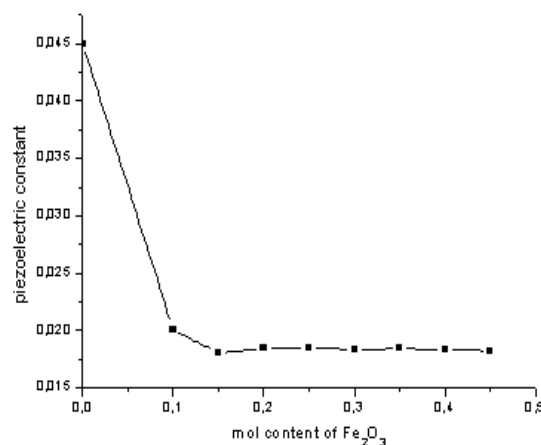


Fig5. Loss angle tangent of barium titanate doped with Fe₂O₃

3. SUMMARY

Thus, the non monotonic character of the effect of doping of barium titanate with iron oxide Fe₂O₃, which consists in an increase in the dielectric constant of BaTiO₃, has been revealed. There is an optimum concentration of doping of iron oxide –4,5 mole%, beyond which, the curves of the dependences of the dielectric properties of barium titanate are saturated.

REFERENCES

- [1] K. Okazaki. Semiconductors based on barium titanate. Energoizdat. M. (1982)
- [2] IT Sheftel. Thermoresistors. The science. M. 1973.
- [3] A. C. Caballero, J. F. Fernandez, C. Moore and P. Duran, ZnO-Doped BaTiO₃: Microstructure and electrical properties, Journal of the European ceramic society 17 (1997) 513-523.
- [4] W.H. Tzing, W.H. Tuan, Effect of NiO addition on the sintering and grain growth behavior of BaTiO₃, Ceramics International 25 (1999) 69-75.
- [5] Srinivas, V., Raghavender, A.T. And Vijaya Kumar, K. (2016) Effect of Ba Substitution on the Structural and Magnetic Properties of BiFeO₃. World Journal of Nano Science and Engineering, 6, 38-44. <http://dx.doi.org/10.4236/wjnse.2016.61004>
- [6] B. M. Bul. Substances with high and super high dielectric permittivity. Successes of Physical Sciences, Vol. 93, Issue 3