

Functional properties of barium titanate ceramics alloyed with nickel ferrite

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Abstract

The paper studies the effect of nickel ferrite addition and sintering temperature on the density, dielectric and piezoelectric characteristics of barium titanate ceramics. A density jump is detected, when with an increase in the ferrite content the density first increases and then drops sharply. Moreover, if at a sintering temperature of 1200 °C the maximum density (5.38 g/cm³) occurs at a ferrite concentration of 0.05 mol.%, then at a sintering temperature of 1300 °C the maximum density (5.62 g/cm³) shifts to the region of higher ferrite concentrations and is 0.1 mol.%. Thus, it can be stated that at a sintering temperature of 1300 °C the ferrite addition in an amount of 0.1 mol.% acts as a sintering activator. X-ray phase analysis showed that in alloyed barium titanate the tetragonal splitting of lines is expressed more strongly, and the calculated lattice parameters *a* and *c* differ significantly from the parameters of pure barium titanate. The addition of 0.1 mol.% ferrite lowers the Curie temperature of the phase transition from the cubic phase to the tetragonal phase from 117 to 108.5 °C. Activation of the sintering process with the addition of ferrite up to ~0.1 mol.% makes it possible to reduce the sintering temperature to 1300 °C and obtain ceramics with high functional characteristics. Relative density is 93%, specific resistance is ~10¹⁰ Ohm·m, permittivity is 1500, piezoelectric modulus *d*₃₁ is 85 pC/N, electromechanical coupling coefficient is 0.37.

Keywords

barium titanate, nickel ferrite, resistivity, permittivity, piezoelectric modulus, electromechanical coupling coefficient, Curie temperature

1. Introduction

Currently, barium titanate is one of the most widely used materials in modern electronic and technical devices [1]. Since its dielectric characteristics depend significantly on the production technology, it is of interest to study the influence of modifying additions on its properties. We used

nickel ferrite as such an addition. There are many publications devoted to the study of physical properties in materials of the barium titanate – nickel ferrite system [2–4]. The combination of piezoelectric and magnetostrictive phases in one sample allows us to create a qualitatively new composite structure with a magnetoelectric bond [5–7]. In such materials, the content of the magnet-

ic phase is 10–60 mol.%. At the same time, it is known that the interaction of barium titanate and nickel ferrite in the region of small ferrite addition (~ 0.1 mol.%) has a eutectic character, which allows us to obtain ceramics at temperatures below 1300 °C [8]. However, no detailed studies have been done in this area. Therefore, the purpose of this work is to study the influence of the additions of nickel ferrite and sintering temperature on the density, dielectric and piezoelectric characteristics of barium titanate ceramics.

2. Experimental

Barium titanate ceramics doped with nickel ferrite were obtained using a standard technique by sintering mixtures of single-phase components [9]. For this purpose, powder mixtures of six compositions with the following molar ratios of ferrite to ferroelectric were prepared: 0:100, 0.05:99.95, 0.1:99.9, 0.15:99.85, 0.2:99.8, 0.3:99.7. Nickel ferrite NiFe_2O_4 , synthesized from chemically pure nickel oxide (NiO) and chemically pure iron oxide (Fe_2O_3) at a temperature of 1100 °C, was used as an alloying addition. Barium titanate BaTiO_3 synthesized from titanium oxide (TiO_2) of special purity grade and barium carbonate (BaCO_3) of chemically pure grade at a temperature of 1150 °C was selected as a ferroelectric. The powder mixtures were mixed with a solution of a plasticizer based on polyvinyl alcohol and pressed under a pressure of $2 \cdot 10^8$ Pa. The briquettes were sintered in air at temperatures of 1200, 1220, 1240, 1260, 1280 and 1300 °C for two hours. The resulting ceramics were subjected to plane-parallel grinding. The samples were in the form of disks with a diameter of 8.8–9.5 mm and a thickness of 0.8–1.0 mm. The density of the composites was calculated based on the ratio of the sample mass to its volume, determined from the linear dimensions of the samples (diameter and thickness). The method ensures an accuracy of density measurement of up to 0.4% with an accuracy of volume measurement of 0.3% and mass measurement of 0.1%. To study the dielectric and piezoelectric characteristics, electrodes were applied to the ceramics by burning silver paste at a temperature of 700 °C for 0.5 h. The samples were polarized at a temperature of 105 °C for one hour in an electric field of 1.5 kV/mm, followed by cooling in this field to room temperature for half an hour. The dielectric characteristics were studied using an E7 – 8 device at a frequency of 1 kHz and an E6-13A teraohmmeter. The resonance – antiresonance method was used to find the piezoelectric modulus d_{31} and the electromechanical coupling coefficient for radial oscillations [10]. X-ray diffraction studies were performed on a DRON-3M automated diffractometer in monochromatic CuK_α radiation at room temperature. The diffraction spectra were recorded point by point with a step of 0.04 deg. by 2 θ with an exposure of 2 s at each point. For a more qualitative analysis, the profiles of some lines were recorded with an exposure of up to 8 s.

3. Results and discussion

Figure 1 shows the results of studying the influence of ceramic composition on the density of samples obtained at sintering temperatures of 1200, 1240, 1260 and 1300 °C. A characteristic feature of the dependencies is the presence of a density jump, when with an increase in the concentration of ferrite the density first increases and then drops sharply. Moreover, if for the curves obtained at sintering temperatures of 1200 and 1240 °C the maximum density value (5.38 g/cm^3) occurs at a ferrite concentration of 0.05 mol.%, then for the curves obtained at sintering temperatures of 1260 and 1300 °C the maximum density (5.62 g/cm^3) is observed at a ferrite concentration of 0.1 mol.%. With an increase in the sintering temperature, the maximum density shifts to the region of higher ferrite concentrations. The specified density value for barium titanate ceramics can only be obtained by sintering at a temperature of ~ 1360 °C [9]. Such an anomalous dependence of the ceramic density on ferrite additives indicates structural changes occurring in the ceramics and the eutectic nature of the interaction of barium titanate and nickel ferrite [11, 12].

It follows from the obtained data that barium titanate ceramics doped with nickel ferrite in the amount of 0.05 mol.% and 0.1 mol.% are of interest for further study, since it was in these materials that a density of over 5 g/cm^3 was obtained. Let us consider in more detail the functional properties of these compositions in comparison with the properties of pure barium titanate.

Permittivity, specific resistance, piezoelectric modulus, and electromechanical coupling coefficient are important indicators of functional ceramics. Therefore, studies were carried out to investigate the influence of sintering temperature on these characteristics.

The results of the studies for specific resistance are presented in Fig. 2. It was found that with an increase in sintering temperature, a tendency to a decrease

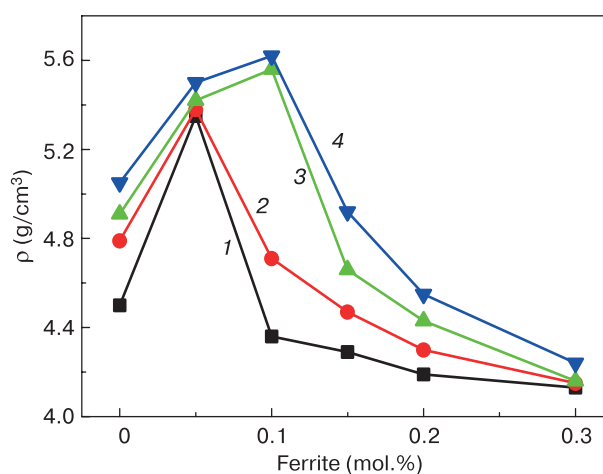


Figure 1. Dependence of ceramic density on nickel ferrite concentration obtained at sintering temperatures: (1) 1200 °C, (2) 1240 °C, (3) 1260 °C, (4) 1300 °C

in specific resistance is observed. The obtained values for most compositions are in the range from 10^{10} Ohm·m to 10^{11} Ohm·m. For barium titanate alloyed with 0.1 mol.% ferrite at sintering temperatures of 1200, 1220 and 1240 °C, the specific resistance exceeds 10^{11} Ohm·m. Apparently, this is due to the low density of the samples obtained at these temperatures.

Figure 3 shows the dependences of the permittivity values on the sintering temperature of the ceramics. For barium titanate alloyed with 0.05 mol.% nickel ferrite, the permittivity values are in the range from 1300 to 1400. For barium titanate alloyed with 0.1 mol.% nickel ferrite, a jump in permittivity is observed from 1000 at a sintering temperature of 1240 °C to 1500 at a temperature of 1260 °C. The permittivity of pure barium titanate increases approximately linearly from 1000 at a sintering temperature of 1200 °C to 1100 at a temperature of 1300 °C. This behavior of the curves qualitatively reflects

the dependences of the density of the studied compositions on the sintering temperature (see Fig. 1).

Figures 4 and 5 show the dependences of the piezoelectric modulus d_{31} and the electromechanical coupling coefficient on the sintering temperature of the ceramics for the compositions under consideration. The obtained dependences qualitatively coincide with each other. This is due to the fact that the piezoelectric modulus is proportional to the electromechanical coupling coefficient. The maximum values of the piezoelectric modulus and the electromechanical coupling coefficient were obtained for the composition containing 0.1 mol.% nickel ferrite at a sintering temperature of 1300 °C. They were 85 pC/N and 0.37, respectively.

The obtained values of specific resistance, permittivity, piezoelectric modulus and electromechanical coupling coefficient correspond to the best characteristics of conventional barium titanate ceramics [13].

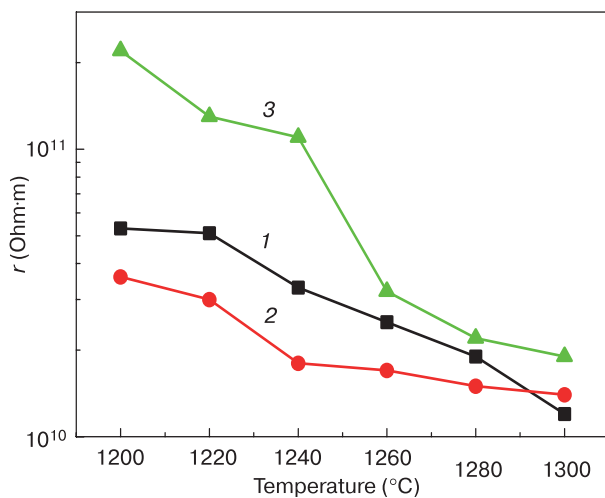


Figure 2. Dependence of the specific resistance of ceramics on its sintering temperature, with the addition of nickel ferrite: (1) 0, (2) 0.05 mol.%, (3) 0.10 mol.%

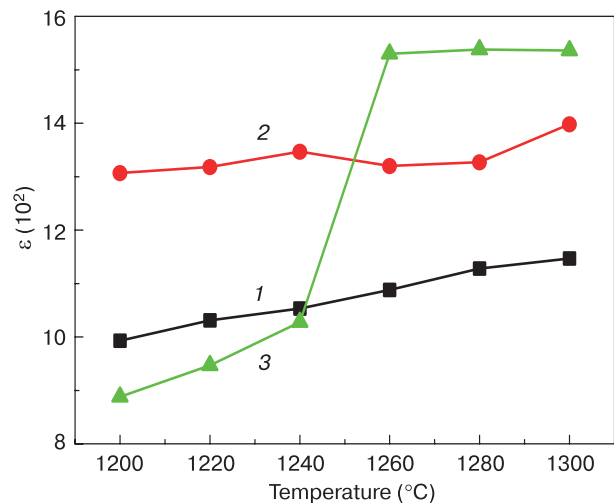


Figure 3. Dependence of the values of the permittivity at room temperature of ceramics on its sintering temperature, with the addition of nickel ferrite: (1) 0, (2) 0.05 mol.%, (3) 0.10 mol.%

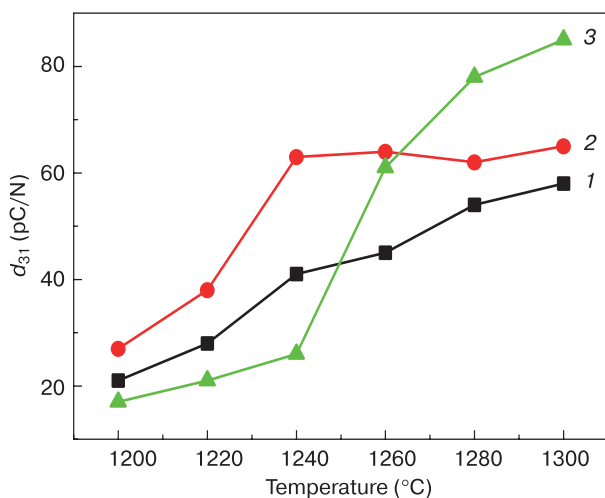


Figure 4. Dependence of the piezoelectric modulus of ceramics on its sintering temperature, with the addition of nickel ferrite: (1) 0, (2) 0.05 mol.%, (3) 0.10 mol.%

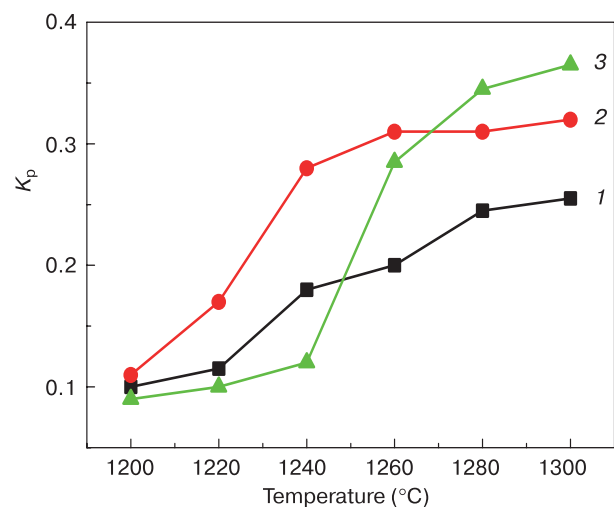


Figure 5. Dependence of the electromechanical coupling coefficient of ceramics on its sintering temperature, with the addition of nickel ferrite: (1) 0, (2) 0.05 mol.%, (3) 0.10 mol.%

The dielectric properties of barium titanate ceramics are sensitive to various impurities. This is especially evident during phase transitions. For this purpose, the temperature dependences of the permittivity of the obtained samples were studied during the transition from the cubic paraelectric to the tetragonal ferroelectric phase. Samples of all compositions obtained at a sintering temperature of 1300 °C were selected as objects of study. From the obtained data presented in Fig. 6 it follows that the addition of nickel ferrite up to 0.1 mol.% leads to an increase in the permittivity in the phase transition region. Its growth in our case can be explained by an increase in the density of the obtained ceramics. A further increase in the concentration of nickel ferrite is accompanied by a sharp decrease in the permittivity value at the Curie point and blurring of the phase transition, which is probably due to the formation of the nickel ferrite phase, leading to a change in the dielectric properties and a decrease in the density of the ceramics.

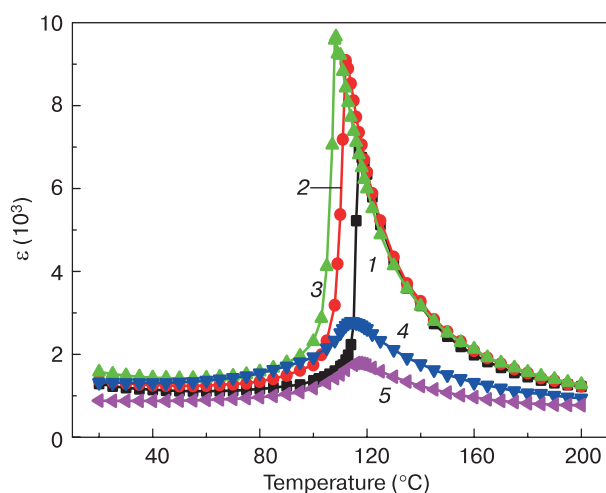


Figure 6. Temperature dependence of the permittivity of samples with the addition of nickel ferrite: (1) 0, (2) 0.05 mol.%, (3) 0.1 mol.%, (4) 0.15 mol.%, (5) 0.3 mol.%

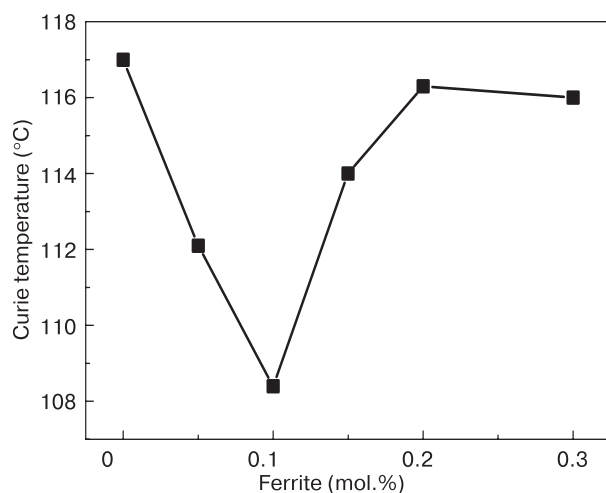


Figure 7. Dependence of the Curie temperature on the concentration of nickel ferrite in barium titanate ceramics

The study of the influence of the addition of nickel ferrite on the Curie temperature (Fig. 7) showed that at first the Curie temperature decreases from 117 °C for pure barium titanate to 108.5 °C for ceramics alloyed with nickel ferrite in an amount of 0.1 mol.%. A further increase in the ferrite concentration is accompanied by an increase in the Curie temperature, and with the addition of ferrite in an amount of 0.2 mol.% it is 116.3 °C. The obtained results confirm that small addition of nickel ferrite (up to 0.1 mol.%) dissolve in the original material, activating the sintering process, and lead to a decrease in the Curie temperature. With an increase in the ferrite concentration, a sharp drop in the density of the ceramics occurs due to the deterioration of its sinterability. As a result, the solubility of ferrite in barium titanate decreases, and the Curie temperature tends to the initial value.

Based on the obtained data, it can be assumed that the addition of nickel ferrite to barium titanate in an amount of up to ~0.1 mol.% leads to the formation of a single-phase structure that activating the sintering process. With a further increase in the concentration of ferrite, the density of the ceramics decreases sharply, which is probably due to the formation of a two-phase structure.

X-ray diffraction spectra were recorded from pre-polished samples obtained at 1300 °C with a ferrite content of 0 mol.%, 0.1 mol.% and 0.3 mol.%. Only lines corresponding to the perovskite structure are observed in the X-ray patterns (Fig. 8).

The unit cell parameters calculated by the least squares method were found to be equal for pure barium titanate $a = 0.3989$ nm, $c = 0.4032$ nm. For doped barium titanate with the addition of nickel ferrite in the amount of 0.1 mol.% and 0.3 mol.%, the unit cell parameters were $a = 0.3987$ nm, $c = 0.4042$ nm and $a = 0.3990$ nm, $c = 0.4032$ nm, respectively. The calculations were made under the assumption that the X-ray spectra correspond to a tetragonal structure with the $P4mm$ space group. The lattice parameters for pure barium titanate and with the addition of nickel ferrite in the amount of 0.3 mol.% practically coincide with each other, which indicates the correspondence of their phase composition. In the X-ray diffraction pattern of barium titanate with the addition of 0.1 mol.% nickel ferrite, the characteristic tetragonal splitting of the lines is expressed most clearly, and the calculated lattice parameters a and c differ significantly from the parameters of samples of other compositions. Such a change in the structural parameters is most likely caused by the formation of a single-phase structure and an increase in the grain size of the ceramics with an increase in the ferrite concentration from 0 to 0.1%, and the formation of a two-phase composition when the specified concentration is exceeded. The capabilities of the research method, unfortunately, do not provide an unambiguous picture of the formation of the second phase with an increase in the ferrite concentration above 0.1 mol.%, but the change in the lattice parameters is quite explainable by the described structural change. The indicated changes in the structure of the ceramics, obviously, cause

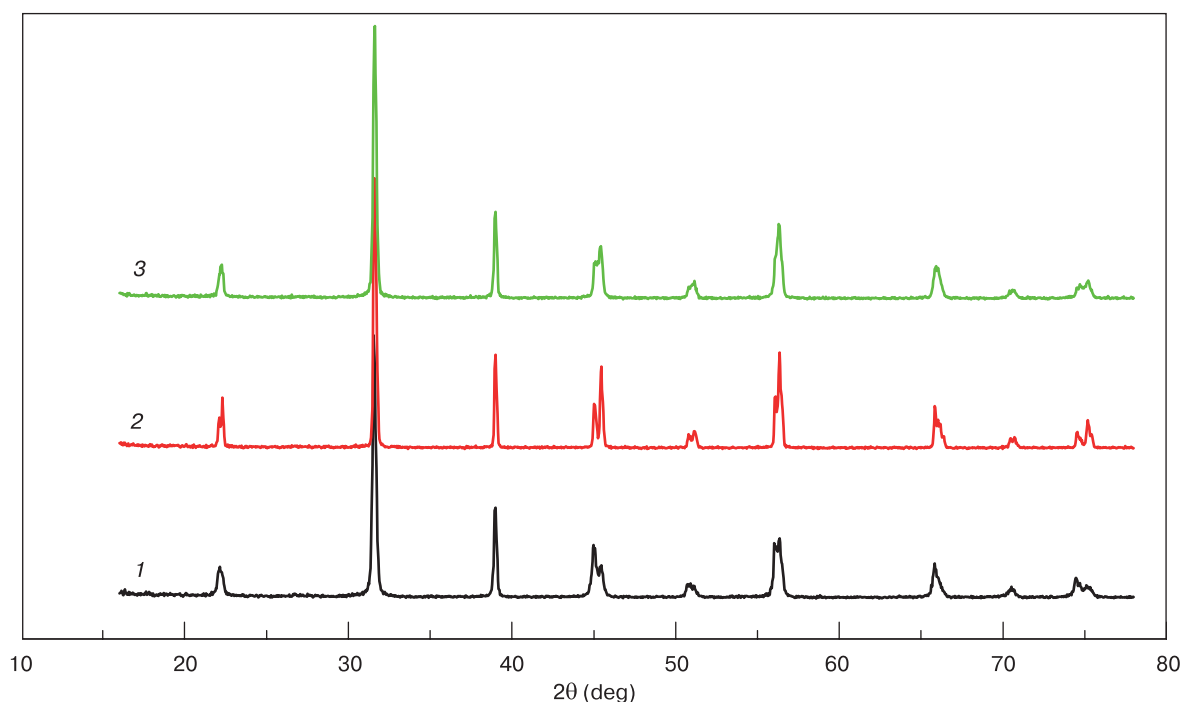


Figure 8. X-ray diffraction spectra of BaTiO₃ ceramics with the addition of nickel ferrite: (1) 0, (2) 0.1 mol.%, (3) 0.3 mol.%

a change in the functional properties that are most pronounced precisely at 0.1 mol. %.

4. Conclusion

Alloying barium titanate ceramics with nickel ferrite in an amount of up to ~0.1 mol. % leads to the formation of a single-phase solid solution, an increase in density, an increase in the permittivity and a decrease in the Curie temperature of barium titanate. With this addition, nickel ferrite acts as a sintering activator.

It is assumed that increasing the concentration of nickel ferrite above 0.1 mol. % leads to the formation of two-phase ceramics with a reduced value of dielectric constant and a diffuse ferroelectric – paraelectric phase transition.

The presence of a region activating the sintering process allows obtaining doped barium titanate ceramics at a temperature of 1300 °C, which is approximately 60–80 deg. lower compared to the usual sintering temperature of barium titanate ceramics. The properties of the obtained doped ceramics correspond to the best characteristics of ordinary barium titanate ceramics.

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