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Heat and electrical properties of composite ceramic with a perovskite structure, doped with magnetic ions

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Abstract. In this paper, ceramics of pure barium titanate and barium titanate doped with manganese have been investigated. The temperature dependences of capacitance and heat capacity were measured. A comparison of the positions of the temperature maxima was carried out. Excess heat (ΔQ) and excess entropy (ΔS) of phase transitions were determined. The types of phase transitions for different samples were determined. An estimate of the spontaneous polarization of the samples was obtained by calorimetric measurements.

1. Introduction

Recently, there is a heightened interest in the investigation of multiferroics - materials with simultaneous electrical, magnetic, and electromechanical ordering. If there are at least two types of ordering coexisting in the material, it is usually called a multiferroic. The doping of barium titanate ceramics (BaTiO_3 -BTO) with a high concentration of manganese (5-30 mol %) opens up new possibilities for applying this classical ferroelectric [1-3] due to the ferromagnetic properties of manganese (Mn). At a certain concentration of Mn in BTO or BSTO structures can exhibit not only ferroelectric properties, but also give a response to a magnetic field, i.e. demonstrate the properties of multiferroics [3]. The thermophysical properties of BTO with a large concentration of Mn ions have not been studied yet. Information of the dielectric characteristics, in particular, of the polarization of barium titanate with manganese is not enough. In the paper, the thermal and dielectric properties of barium titanate (BTO) ceramics doped with manganese magnetic ions of high concentration were investigated.

2. Experimental

Ceramics were prepared by conventional solid state reaction method [4] with sintering in the air. The manganese content (Table 1) was chosen so that the components interact weakly with each other at the sintering temperature. This allows to preserve the ferroelectric properties of BTO and the ferromagnetic properties of the impurity. The synthesis was carried out in two stages with intermediate grinding and granulation of the samples. Ceramic samples of pure BTO possessed the value of relative densities (84- 94)%, which are close to the maximum (90-95)%. The relative densities of manganese doped samples were significantly lower – (77-83)%. Silver electrodes were coated on the surface of ceramic discs to measure dielectric characteristics. The thickness of the samples was $h = 0.25 - 1.35$ mm. Temperature dependences of capacitance were measured by the Agilent E4980A Precision LCR Meter.



The samples were fixed in a special holder, placed in a climatic chamber. The measurements were carried out in the temperature range from $-60\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$ at a temperature change rate of $0.001 \dots 200\text{ K/min}$. Capacitance measurement error was 0.05% pF. The heat capacity was measured in aluminum crucibles with differential scanning calorimeter DSC 204 Phoenix F1. The rate of heating and cooling was 10 K/min in the temperature range ($-30\text{ }^{\circ}\text{C} - 180\text{ }^{\circ}\text{C}$). The error in the heat capacity measuring was $\pm 3\%$.

3. Results and discussion

Figure 1 shows the temperature dependences of the electrical capacitance $C(T)$ for BTO samples with different concentrations of Mn.

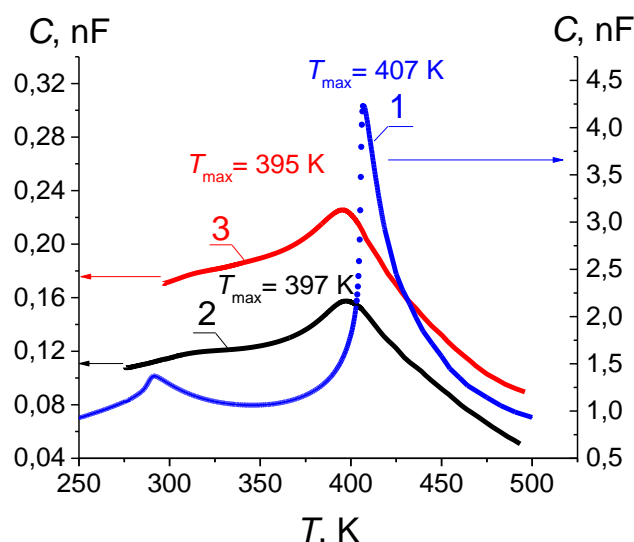


Figure 1. Temperature dependences of the capacity of barium titanate ceramics doped with Mn: 1 - ceramics of pure BTO; 2 - ceramics BTO + 5 mol. % Mn; 3 - ceramics BTO + 10 mol. % Mn.

Dielectric permittivity jump in the of pure barium titanate at $T_m = T_c = 407\text{ K}$ indicates a first-order phase transition. At a lower temperature of $\sim 287.6\text{ K}$, a second phase transition was observed. This corresponds to the literature data [1, 5]. Further in the article, the temperature maximum at 400 K is considered and discussed. It corresponds to a ferroelectric phase transition. With increasing concentration of Mn, the temperature of the maxima decreased by $10\text{--}12$ degrees, the values of the capacitance and permittivity also decreased, and the temperature dependences were smoothed out. From the temperature dependences of the doped samples capacity, it is impossible to establish the nature of the phase transitions. The dielectric permittivities corresponding to the temperature maxima for various ceramics samples were within the range of $\epsilon(T_m) = 400\text{--}4400$. The characteristics of the investigated samples are given in Table 1, where: h is the thickness of the samples, S is the area of the electrodes; T_m is the temperature of the maximum capacity; ϵ is the relative permittivity.

Table 1. Characteristics of the samples

Material	Sintering temperature ($^{\circ}\text{C}$)	h (mm)	s (m^2)	T_m (K)	$\epsilon(T_m)$
BTO	1400	1.27	$7.85 \cdot 10^{-5}$	407	4400
BTO+5% Mn	1350	1.85	$7.85 \cdot 10^{-5}$	397	421
BTO+10% Mn	1350	1.35	$7.85 \cdot 10^{-5}$	395	436

Figure 2 shows the temperature dependences of the heat capacity of the samples $C_p(T)$.

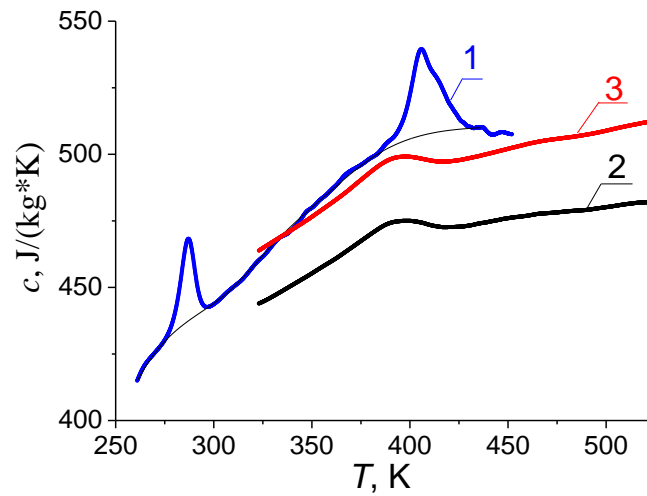


Figure 2. Temperature dependences of the heat capacity of barium titanate ceramics doped with Mn: 1 - ceramics of pure BTO (a thin continuous line shows the approximating dependence of $C_p(T)$); 2 - ceramics BTO + 5 mol % Mn; 3 - ceramics BTO + 10 mol % Mn.

The temperatures of the heat capacity maxima correspond to the temperatures of the maxima of the electric capacity (T_m) to within 1-2 degrees. The values of the heat capacity and its temperature dependence for pure BTO corresponded to the literature data [1, 5, 6]. The heat capacities of manganese-doped samples were significantly lower than for pure BTO. In addition, the temperature of the phase transition upon heating was 5 degrees higher than upon cooling for doped samples. This is characteristic of first-order transitions [7]. According to the results of the measurement of specific heats (Fig. 2) in Table 2: C is the Curie-Weiss constant (calculated from the dielectric measurements in Fig. 1); T_c is the Curie temperature, which coincided with T_m for dielectric measurements; ρ is the sample density, ΔQ is the excess heat of the transition; ΔS excess transition entropy; P is the value of spontaneous polarization.

Table 2. Characteristics of the samples

Material	C (K)	T_m (K)	ρ (kg/m ³)	ΔQ (J/kg)	ΔS (J/kg·K)	P (C/cm ²)
BTO	$0.88 \cdot 10^5$	407	$5.65 \cdot 10^3$	584	1,434	$11.2 \cdot 10^{-6}$
BTO+5% Mn	$0.8 \cdot 10^4$	397	$5.05 \cdot 10^3$	246	0,620	$2.1 \cdot 10^{-6}$
BTO+10% Mn	$0.15 \cdot 10^5$	395	$4.65 \cdot 10^3$	258	0,653	$2.83 \cdot 10^{-6}$

The Curie-Weiss constant for pure BTO almost coincides with the literature data for the ceramic samples [5, 6]. For doped samples, the Curie-Weiss constant is much lower. There are no literature data on the evaluation of the the Curie-Weiss constant for manganese-doped samples.

The excess energy (ΔQ) and the excess entropy (ΔS) of the phase transition for ceramics were determined by graphical integration between the temperatures T_1 and T_2 :

$$\Delta S = \int_{T_2}^{T_1} \frac{\Delta C}{T} dT \quad (1)$$

In accordance with the thermodynamic theory of ferroelectricity, the entropy increment is associated with a change in polarization [5, 8]:

$$\Delta S = \frac{\Delta P^2}{2C\rho\epsilon_0} \quad (2)$$

where $\Delta P^2 = P(T_1)^2 - P(T_2)^2$.

Since $T_2 > T_1$ then $P(T_2) = 0$ and expression (2) is equal to the square of the polarization at temperature T_1 . Thus, using relation (1) in the form:

$$\Delta S = \frac{P^2}{2C\rho\epsilon_0} \quad (3)$$

the value of the spontaneous polarization can be estimated (Table 2). Preliminary results of direct measurement of spontaneous polarization give the value of spontaneous polarization an order of magnitude smaller than the one obtained from measurements of the heat capacity. The same discrepancy in the polarization estimate from the results of calorimetric measurements was observed for other ferroelectric and multiferroic materials [6-8].

4. Conclusions

The temperature dependences of the electric capacity and the heat capacity of the samples have anomalies that correspond to phase transitions. The positions of the temperature maxima of these dependences coincided with an accuracy of (1 – 2) K. The anomalies of the heat capacity and the dielectric properties of the doped samples shifted toward low temperatures compared to pure BTO. Calorimetric measurements of BTO samples doped with a large concentration of magnetic ions were carried out for the first time. The excess heat (ΔQ) and entropy (ΔS) of phase transitions are determined (Table 2). For samples with 10 mol % Mn, these values are slightly higher than for samples with 5 mol % Mn, but significantly less than for pure BTO ceramics. Low values of a phase transition excess entropy are usually associated with a displacive transition [7]. Combined measurements of the heat capacity and dielectric characteristics correspond to the literature data [1, 5, 6]. It is possible to say that a first-order phase transition is observed in pure BTO ceramics. An estimate of the spontaneous polarization of the samples was obtained by calorimetric measurements. The value of spontaneous polarization of pure BTO coincides with the results of the literature data [1, 5, 7]. The polarization estimate for the doped samples with 5 mol % Mn and with 10 mol % Mn was obtained for the first time (to the best of our knowledge). It is 3-5 times less than in pure BTO (Table 2), however such a value of polarization is sufficient for the application of ceramics as elements of electrocaloric or multicaloric [9] cooling. Comparison of dielectric (Table 1) and thermal (Table 2) characteristics of the samples allows to say that the values of the electrical capacity, dielectric constant, heat capacity and spontaneous polarization for samples with 10 mol % Mn are always slightly higher than for samples with 5 mol % Mn. Therefore, samples with 10 mol % Mn are more preferable for practical applications.

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