

Heat capacity of CoFe_2O_4 and $0.3\text{CoFe}_2\text{O}_4-0.7\text{PbTiO}_3$ composite

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The temperature dependence of the heat capacity of the CoFe_2O_4 ferromagnet and the $0.3\text{CoFe}_2\text{O}_4-0.7\text{PbTiO}_3$ multiferroic composite in the temperature range 150–820 K has been studied. Heat capacity over a wide temperature range. It is noted that the additional component of the heat capacity is due to the transition of cobalt or iron ions to higher energy levels, as well as due to the distortion of the lattice parameters due to the appearance of three coexisting phases.

Keywords: heat capacity, multiferroic composite, Schottky effect.

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1. Introduction

Development of composites is to a great extent promoted by the demand of the modern electronics for new compounds whose properties are not available in single-phase materials with improved characteristics [1]. The search for new multiferroics is explained by their special properties associated with simultaneous implementation of electrical and magnetic structure which have high application potential of utilization in multifunctional devices (spintronics, memory elements, magnetic sensors, etc.) [2–5]. Composite materials are formed by combinations of two or more single-phase compounds. Their physical properties are defined by the properties and quantities of phases included in them and by interaction of these phases [6,7]. Composites shall maintain the properties of the initial phase and obtain new functionalities. Due to multiple publications devoted to magnetoelectric (ME) composites formed by ferrites, there is deeper understanding of processes responsible for magnetoelectric coupling, development of magnetically induced ferroelectricity, interaction between spin, charge and lattice degrees of freedom, and property control methods. Nevertheless, complex problems of multifunctional ME-coupled two-phase composites are far from solution and their investigation still requires high efforts.

For this purpose, we have investigated the heat capacity of CoFe_2O_4 ferromagnet and $0.3\text{CoFe}_2\text{O}_4-0.7\text{PbTiO}_3$ composite. CoFe_2O_4 (CF) cobalt ferrite is well known for its highest magnetostriction constant among all known ferrite spinels with moderate saturation magnetization, chemical resistance, high mechanical hardness and high magnetic phase transition temperature ($T_C \sim 793$ K) [8]. PbTiO_3 (PT) is one of the most important ferroelectrics in perovskite

family having high Curie temperature ($T_C \sim 563$ K), high pyroelectric coefficient ($250 \text{ mC/cm}^2 \cdot \text{K}$), low permittivity ($\epsilon \sim 150$) and high spontaneous polarization [9,10]. This material is widely used in electronics (capacitors, ultrasonic transducers, thermistors) and in optoelectronics [11]. Thanks to high pyroelectric coefficient and low permittivity, PbTiO_3 is a promising material for applications such as infrared pyroelectric detectors. $x\text{CoFe}_2\text{O}_4-(1-x)\text{PbTiO}_3$ multiferroic composites were primarily investigated in film structures [12] and only a few publications report the investigations of electrical properties for several selected compositions [13,14]. Thus, calorimetric testing of $x\text{CoFe}_2\text{O}_4-(1-x)\text{PbTiO}_3$ ceramic composites is of interest for deep understanding of physical processes in these materials. As far as we know, no such investigations have been carried out before.

2. Specimens and experiment

The CF specimens tested herein were obtained by the solid-phase method. CF were produced by mixing CoO and Fe_2O_3 ($\text{CoO} \geq 99.9\%$, $\text{Fe}_2\text{O}_3 \geq 99.9\%$ and Sigma-Aldrich) in stoichiometric proportions. Then the prepared mixture was ground in an agate mortar in presence of ethanol during 2 h, then the compound was placed into a closed platinum crucible. The synthesis was carried out in a high-temperature furnace with thermal stabilization at 1000°C during 4 h in air. After cooling down, the synthesized CF powder was ground in an agate mortar during 1 h and tested by X-ray diffraction analysis (XRDA) method, no impurity phase was found.

We have prepared PT specimens by means of solid-state reaction synthesis. For this, TiO_2 and PbO ($\text{TiO}_2 \geq 99.9\%$,

PbO \geq 99.9%, Sigma-Aldrich) were taken and mixed in stoichiometric ratios. Then the prepared mixture was ground in an agate mortar in presence of ethanol during 1 h, then the compound was compacted into a pellet at 200 MPa and placed into a closed platinum crucible. The synthesis was carried out in a high-temperature furnace with thermal stabilization at 900°C during 2 h. Then the furnace was turned off and cooled down by inertia to room temperature. Then the synthesized PT was ground in an agate mortar. The X-ray diffraction test has shown no impurity phase.

For cosynthesis of 0.3CFO–0.7PTO, different molar fractions were mixed and ground in an agate mortar in presence of ethanol. Then the mixture was compacted at 120 MPa into discs with a diameter of 6 mm and a thickness of 1 mm. Then each compound was placed into a closed platinum crucible and baked at 900°C during 4 h. Standard ceramic CF and PT specimens were prepared in the same way. Design density of compounds varies within 5.25–5.52 g/cm³. The pore volume is on average \sim 10% of the total specimen volume. Phase analysis of compounds was carried out using D2 Phaser X-ray diffractometer with CuK α -radiation. It has been found that hard-phase baking of CoFe₂O₄ spinel and PbTiO₃ ferroelectric is accompanied by formation of additional phases — PbFe₁₂O₁₉ [15] hexaferrite.

Heat capacity was measured by NETZSCH DSC 204 F1 Phoenix[®] differential scanning calorimeter. A plate with a diameter of 4 mm and thickness of 1 mm, respectively, was used as a heat capacity test specimen C_p . Heat capacity measurement error was lower than 3%.

3. Findings and discussion

Measured heat capacity C_p of ferromagnet CoFe₂O₄ of 0.3CoFe₂O₄–0.7PbTiO₃ multiferroic composite in the temperature range 150–820 K is shown in Figure 1. When lead titanate ferroelectric is added to cobalt ferrite ferromagnet, phase transition (PhT) drops from 793 to 744 K, PhT heat also decreases.

In most cases, quantitative analysis of heat capacity-temperature dependence and separation of phonon and abnormal contributions used a simple model describing a phonon heat capacity of Debye functions $C_p^0 \sim D(\theta_D/T)$, where θ_D is the Debye temperature. Analysis of our heat capacity data for CoFe₂O₄ and 0.3CoFe₂O₄–0.7PbTiO₃ gives $\theta_D \approx$ 610 K and $\theta_D \approx$ 542 K. It is known that the Debye temperature depends on coupling forces between ions in the crystal lattice. Therefore, reduction of θ_D when lead titanate is added to cobalt ferrite indicate that coupling forces between crystal lattice ions become lower.

Phonon heat capacity calculations within the Debye model are shown with a solid line in Figure 1. Within 250–650 K, deviation of measured points from the calculated phonon heat capacity is observed and is indicative of excessive heat capacity (Figure 1). Abnormal heat capacity component was calculated as the difference of the measured and calculated phonon heat capacity

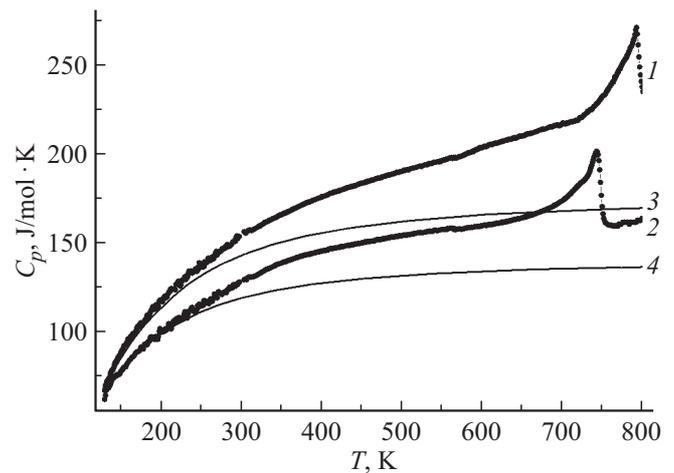


Figure 1. Heat capacity-temperature dependence of CoFe₂O₄ (1) ferromagnet and 0.3CoFe₂O₄–0.7PbTiO₃ (2) composite; approximation of phonon heat capacity by the Debye function for CoFe₂O₄ (3) and for 0.3CoFe₂O₄–0.7PbTiO₃ (4).

$\Delta C = C_p - C_p^0$. Abnormal heat capacity — temperature dependence $\Delta C(T)$ is shown in Figure 2.

For analysis of measured heat capacity within a wide temperature range, consider the anharmonic contribution to phonon heat capacity that can result in visible difference of C_p and C_v in high temperature range. This heat capacity component can be calculated using the measured compressibility (K_T) and thermal expansion coefficient (α): $C_p - C_v = V\alpha^2 T / K_T$ [16], where V is the molar volume. No thermal expansion and compressibility were reported for 0.3CoFe₂O₄–0.7PbTiO₃ multiferroic composite, therefore we used the known Einstein and Lindeman–Gruneisen equations for the calculations [17]:

$$\theta_D = 1.8 \cdot 10^{-3} A^{1/3} \rho^{-1/6} K_T^{-1/2},$$

$$\theta_D = 19.37 (AV_a^{2/3} \alpha)^{-1/2},$$

where θ_D is the Debye temperature, ρ is the density, A is the mean atomic weight, V_a is the molar volume, α is the linear expansion coefficient.

The calculations show that anharmonic component accounts for less than 2% of the phonon heat capacity. Therefore, due to its smallness, the difference between C_p and C_v may be ignored ($C_p \approx C_v$) during further analysis of phonon heat capacity-temperature dependence. Low anharmonic contribution is due to rather low heat expansion coefficient of the tested compounds.

Abnormal heat capacity — temperature dependence $\Delta C(T)$ is shown in Figure 2. By adding the second component, the excessive heat capacity decreases (Figure 2) and this is probably due to lower concentration of ions (cobalt, iron) whose transitions between levels result in appearance of this heat capacity component, and to lattice parameters distortion by occurrence of three coexisting phases (structures) [15,18,19].

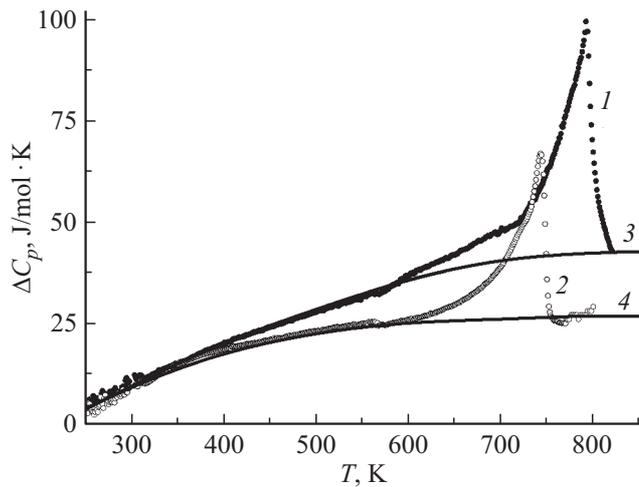


Figure 2. Abnormal heat capacity component-temperature dependence of CoFe_2O_4 (1) ferromagnet and $0.3\text{CoFe}_2\text{O}_4-0.7\text{PbTiO}_3$ (2) composite; solid lines — approximation (2) for CoFe_2O_4 (3) and $0.3\text{CoFe}_2\text{O}_4-0.7\text{PbTiO}_3$ (4).

Analysis of the excessive heat capacity-temperature dependence ΔC makes it possible to interpret it as a Schottky abnormality for three-level states. The Schottky heat capacity expression generally can be obtained by differentiating the average particle energy at energy levels [20]:

$$C_W^T = (kT^2)^{-1} (\langle \Delta E_i^2 \rangle - \langle \Delta E_i \rangle^2). \quad (1)$$

For the three-level system, the equation is as follows

$$C_W^T = R [D_1 (\Delta E_1/kT)^2 \exp(-\Delta E_1/kT) + D_2 (\Delta E_2/kT)^2 \exp(-\Delta E_2/kT)] / [1 + D_1 \exp(-\Delta E_1/kT) + D_2 \exp(-\Delta E_2/kT)]^2, \quad (2)$$

where D_1 and D_2 are the relations of level degeneracy multiplicities.

By comparison of heat capacity calculated using equation (2) and measured excessive heat capacity ΔC , CoFe_2O_4 model parameters were derived: $D_1 = 8.155$, $D_2 = 1.324$, $\Delta E_1 = 4.127$ eV and $\Delta E_2 = 1.036$ eV, and for $0.3\text{CoFe}_2\text{O}_4-0.7\text{PbTiO}_3$ compound: $D_1 = 15.369$, $D_2 = 0.715$, $\Delta E_1 = 1.678$ eV and $\Delta E_2 = 0.061$ eV. The measured abnormal heat capacity ΔC adequately meets the value calculated using equation (2) ΔC (Figure 2).

4. Conclusion

Therefore, based on the experimental investigation of heat capacity of CoFe_2O_4 and $0.3\text{CoFe}_2\text{O}_4-0.7\text{PbTiO}_3$ multiferroic composite in the range of 150–820 K, it has been found that, when lead titanate was added to cobalt ferrite, PhT temperature decreased from 793 to 744 K and PhT heat decreased. Additional heat capacity component in CoFe_2O_4 and $0.3\text{CoFe}_2\text{O}_4-0.7\text{PbTiO}_3$ can be interpreted as a Schottky abnormality for three-level states.

Conflict of interest

The authors declare that they have no conflict of interest.

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