Thermodynamic Properties and Phase Transitions of Microcrystalline and Nanostructured SmFeO₃ Ceramics

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Abstract—The heat capacity and dielectric properties of microcrystalline and nanostructured SmFeO₃ ceramics obtained by solid phase synthesis are studied. The ceramics is synthesized by the treatment of the batch at room temperature in Bridgman anvils by forceful action combined with shear deformation followed by sintering. It is established that the mechanoactivation results in noticeable broadening antiferromagnetic—ferroelectric transition and shifting the temperature of phase transition in the low-temperature area. The phase transition having typical for relaxation oscillator frequency dependent character is found at 558 K. It is shown that the defect structure can take a dominant place in the formation of the physical properties of ceramics.

INTRODUCTION

Samarium ferrite SmFeO₃ (SFO) is rare-earth orthoferrite with the perovskite-like crystalline structure of $PPnma/Pbnm$, D_{2h}^{16}) [1]. SFO has a high coefficient of magnetostriction, temperatures of magnetic ordering (~670 K), and spin reorientation (480 K), which make it a promising candidate for magnetoelectric applications [2, 3]. However, the ability of improper ferroelectricity in SFO single crystals was controversial [3]. Recently, increased scientific attention has been paid to this material due to finding the extrinsic ferroelectric polarization at a $T_C = 670$ K ($P_s = 100$ μC/m²) [4]. The coincidence of Curie and Neel points ($T_C = T_N$) allows one to attribute this compound to multiferroics of the second type in which the ferroelectric (FE) phase is induced by the magnetoelectric (ME) interaction [5].

It is reported in a number of studies [4, 6, 7] that SFO demonstrates a complex character of temperature-induced spin dynamics of magnetoactive cations, which lead to slight ferromagnetism and phase transition due to competing interactions between Sm (f-sublattice) and Fe (d-sublattice). In particular, the spin reorientation transition occurs in a temperature area of $T_{SR} = 450$–480 K, which leads to change in magnetic symmetry of d-sublattice.

In recent years, it has been found during studies of micro- and nanocrystalline SFO samples that decreasing particle size results in significant changes structural and physical (magnetic and ferroelectric) properties [8, 9]. Nanoscaled effects on the structure and physical properties of multiferroics have been the focus of much recent research in materials science. This interest is caused by the potential ability of practical application of such nanostructures oxides. Moreover, the structure and properties of such compounds and their changes under external influences have been discussed recently. All these factors stimulate further detailed studies of oxide ceramic materials with nanoscale structures in both scientific and applied approaches.

In this work, we studied the heat capacity and dielectric properties of micro- and nanocrystalline SFO in a wide temperature range of 300–800 K including areas of phase transitions.

EXPERIMENTAL

Samples of SmFeO₃ ceramics were studied. Sm₂O₃ and Fe₂O₃ (reagent grade) oxides were used as the starting reagents for SFO synthesis; the oxides were mixed in an agate mortar with ethanol for 2 h. The obtained batch was sintered in a platinum crucible at a temperature of 1200°C for 2 h. Then, the material was
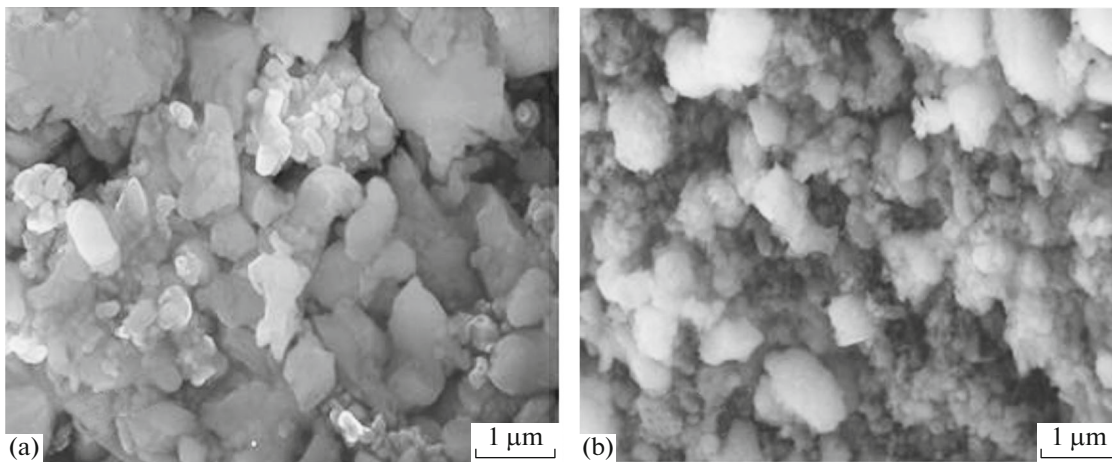
Fig. 1. Microscopic images of original (a) and mechanoactivated (b) samples of $SmFeO_3$.

ground for 0.5 h and mechanoactivated under the pressure of 200 MPa between vertically Bridgman anvils the lower of which rotated with an angular velocity of $\Omega = 0.3$ rad/min. The sample of a disc shape was prepared from the powder activated at the constant pressure and shear strain. The sample was sintered without binders at $T = 1000°C$ for 2 h.

X-ray diffraction analysis of the obtained materials was carried out using an HZG-4B powder diffractometer. The crystalline structure of the original material and mechanoactivated $SmFeO_3$ ceramics at room temperature is attributed to the *Pnma* symmetry group [10]. Impurity phases were not detected in the X-ray diffraction sensitivity limits.

The permittivity and heat capacity were measured on ceramic samples with a diameter of 5 mm and a thickness of 1 mm. Ag-containing paste was used as an electrode.

RESULTS AND DISCUSSION

Figure 1 presents the microphotographs of the original and mechanoactivated samples; the images were obtained using a SUPRA 25 (Zeiss) scanning electron microscope. As it is seen, the mechanoactivated sample has a more "loose" structure. The distribution of grain size in the sample has a multimodal character in a range of 20–600 nm.

Figures 2, 3, and 4 demonstrate the results of the heat capacity (C_p) and permittivity (ε) studies of the original polycrystalline and nanostructured samples of $SmFeO_3$. It is seen from Fig. 2 that an anomalous behavior characteristic for the phase transitions is observed on the temperature dependence of C_p of SFO multiferroic at temperatures of $T_{NC} \approx 675$ K, $T^* \approx 558$ K, and $T_{SR} \approx 460$ K. According to [4], an antiferromagnetic and extrinsic ferroelectric phase transition occurs at T_{NC}. For the nanostructured sample, the

transition temperature T_{NC} shifts to the area of low temperatures on 9 K (Fig. 1). A slight anomaly is observed on the C_p temperature dependences of the original (microcrystalline) and nanostructured samples (Fig. 1, insert) in the area of spin-oriented transition $T_{SR} \approx 460$ K. The anomalous behavior of magnetic and dielectric properties was observed in this temperature area (450–480 K) elsewhere [6, 7].

As it is seen from Fig. 2, λ-anomaly is found on the C_p temperature dependence at $T^* \approx 558$ K, which is observed on the ε temperature dependence as a "dome" (Figs. 3 and 4). It should be noted that a wide "hump" characteristic for structural changes was observed on the permittivity temperature dependence in a temperature range of 500–600 K in [11]. The nature of this anomaly is not clear yet.
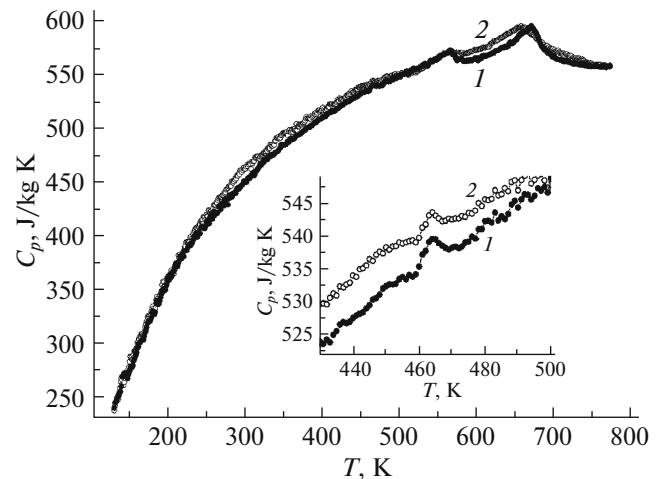

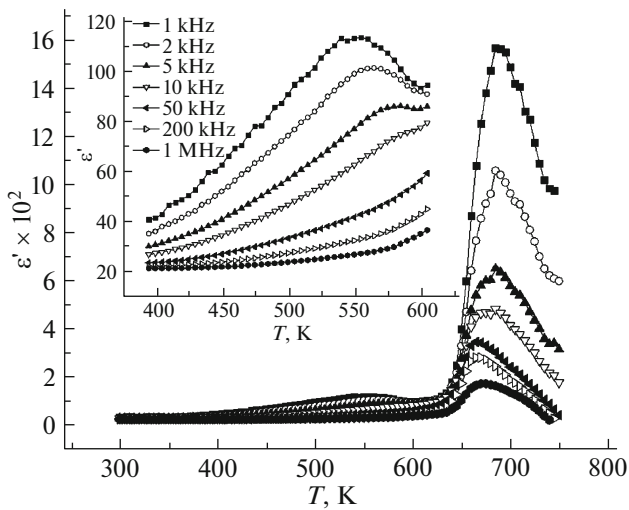**Fig. 2.** Temperature dependence of heat capacity of microcrystalline (*1*) and nanostructured (*2*) $SmFeO_3$.

Fig. 3. Temperature dependence of permittivity of micro-crystalline SmFeO$_3$ sample.

Fig. 4. Temperature dependence of permittivity of nano-structured SmFeO$_3$ sample.

Figures 3 and 4 demonstrate the results of studying dielectric dependence of original and nanostructured SmFeO$_3$ ceramics in a high-temperature area. As it is seen from Figs. 3 and 4, the anomalies on the $\varepsilon(T)$ and $C_p(T)$ dependencies are observed at the same temperatures. Strong frequency dependence $\varepsilon(\omega)$ is caused by the fact that the ferroelectric phase transition occurs in the area at T_N as it was noted in [4]. The mechano-activation results to the broadening of the antiferromagnetic–ferroelectric transition T_{NC}, noticeable decreasing ε in a wide temperature range, and shifting T_{NC} to the low-temperature area on the value of $\Delta T \approx 7$ K. Such behavior is connected with the fact that the mechanical activation leads to a high concentration of point defects and dislocations in the nanostructured ceramics [10]. The high concentration of defects [12] and the deformation field created by dislocations [13] can significantly affect the features of thermodynamic values of the sample in the area of the phase transition. According to [12], the high concentration of defects can result in increasing the value of heat capacity and broadening thermodynamic properties in the phase transition area which is observed in the experiment (Figs. 2 and 4). It is shown in [13] that the ordered regions near dislocation lines can appear at temperatures significantly higher than the transition temperature in an "ideal" crystal. The ordered regions form a complex random framework consisting of ordered domains (electrical and magnetic) in different crystallites which penetrating the whole crystal although occupying a small fraction of its volume. The correlation length of such areas is very small. At a specific temperature $T > T_{NC}$, such a structure can transform into the state with the predominant number of domains with a certain polarization sign or direction of magnetization; i.e., the phase transition in the dis-
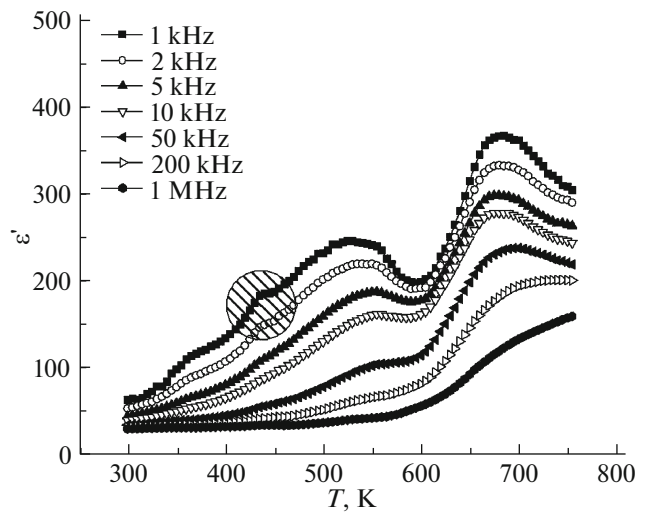
location framework occurs. When the temperature decreases, the thickness of the ordered areas increases and rather large ordered clusters occupying many dislocations should appear at $T = T_{NC}$. As the result, the ordering extends over the total volume of the crystal in the $T \approx T_{NC}$ area; it should appear during the experiment as the broadened phase transition of the second type.

Thus, the high concentration of point defects, the formation of dislocation framework, and crystallite boundaries can be the physical causes of the experimentally observed T_{NC} phase transition in the nanostructured SmFeO$_3$. The shift of the phase transition of the mechanoactivated sample in the area of low temperatures can be connected with decreasing the crystallite size (size effect) [14, 15].

The anomalous behavior characteristic for the phase transition is observed on the temperature dependences of $C_p(T)$ and $\varepsilon(T)$ in the temperature area about 558 K for the all studied samples. As it is seen from Figs. 3 (insert) and 4, the characteristic for ferroelectric relaxation oscillator behavior is observed on the ε temperature dependence in the T^* area. The broadening phase transition in a wide temperature area, shifting ε maximum at T^* to the area of high temperature with increasing frequencies, and strong frequency dependence of ε occur. The transition at T^* completely broadens at frequencies $\omega \geq 50$ kHz and $\omega \geq 1$ MHz for the original and nanostructures samples respectively. Such relaxation oscillator behavior is usually attributed to the appearance of nanopolar areas in the matrix of the main structure. Namely, the phase with nanopolar areas (superdomain structure) likely exists together with the antiferromagnetic phase in this temperature area, and at high frequencies, this phase transits to ferroelectric domain structure.

As it is seen from Figs. 2 and 4, slight anomalies are seen on the $C_p(T)$ and $\varepsilon(T)$ dependences at the temperature of $T_{SR} \approx 460$ K for both microcrystalline and nanostructured $SmFeO_3$ ceramics. According to [4, 6, 7], the spin-reorientation transition leading to the weak ferromagnetism occurs in this temperature area due to competing interactions between the Sm (f-sublattice) and Fe (d-sublattice) sublattices. When the frequency is increased, the $\varepsilon(T)$ anomaly smoothes and disappears at frequencies $\omega > 2$ kHz. It should be noted that for the first time the dielectric anomaly (in the area of spin-reorientation transition) which is not associated with structural changes was found by Polomska in bismuth ferrite [16] at a temperature of 458 K.

CONCLUSIONS

Thus, the results of the studies of the thermodynamic properties of microcrystalline and nanostructured $SmFeO_3$ ceramics show that the mechanoactivation lead to the noticeable broadening of antiferromagnetic-ferroelectric transition T_{NC} and shifting transition temperature in the low-temperature region. The phase transition having frequency dependent character typical for ferroelectric relaxation oscillators occurs at $T^* = 558$ K. It was shown that defective structure makes a significant contribution to the formation of the physical properties of ceramics.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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