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## Heat capacity of nanostructured SmFeO<sub>3</sub>

© R.G. Mitarov<sup>2</sup>, S.N. Kallaev<sup>1</sup>, Z.M. Omarov<sup>1</sup>, M-Sh.C. Khizriev<sup>2</sup>, K.G. Abdulvakhidov<sup>3</sup><sup>1</sup> Amirkhanov Institute of Physics, Dagestan Federal Research Center, Russian Academy of Sciences, Makhachkala, Russia<sup>2</sup> Dagestan State Technical University, Makhachkala, Russia<sup>3</sup> Southern Federal University, Rostov-on-Don, Russia

E-mail:kallaev-s@rambler.ru

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The temperature dependence of the heat capacity of nanostructured SmFeO<sub>3</sub> ceramics obtained by mechanical activation in the temperature range of 120–800 K has been studied. It has been shown that the excess heat capacity of mechanically activated ceramics is due to: displacements of iron and samarium ions and with a change in the angle between FeO<sub>6</sub> oxygen octahedra.

**Keywords:** multiferroics, heat capacity, samarium ferrite, Schottky heat capacity, nanostructured ceramics, mechanical activation.

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### 1. Introduction

Samarium ferrite SmFeO<sub>3</sub> (SFO) belongs to the rare-earth orthoferrite family with perovskite-like crystalline structure (*Pnma/Pbnm*,  $D_{2h}^{16}$ ) [1]. SFO has a high magnetostriction coefficient, high magnetic ordering temperature  $\sim 670$  K and spin-flip temperature 480 K which make it a potential candidate to magnetoelectric applications [2,3]. In recent time, a keen interest of researchers to this material is associated with the extrinsic ferroelectric polarization at  $T_C = 670$  K ( $P_s = 100 \mu\text{C}/\text{m}^2$ ) found in this material [4]. Coincidence of the Curie and Neel points ( $T_C = T_N$ ) gives reasons to assign this compound to multiferroics of the second kind where ferroelectric (FE) phase is induced by magnetoelectric (ME) interaction [5].

Some publications [4,6,7] report that SFO demonstrates a complex temperature-induced spin behavior of magnetoactive cations which leads to low ferromagnetism and phase transformations as a result of competing interactions between Sm (*f*-sublattice) and Fe (*d*-sublattice). In particular, within the temperature range  $T_{SR} = 450\text{--}480$  K, a spin-flip transition takes place as a result of which magnetic symmetry of *d*-sublattice is changed.

In recent years, the study of micro- and nanocrystalline SFO samples has detected that the decrease in the particle size leads to pronounced changes in structural and physical properties [8,9]. Many recent materials science investigations have been focused on the nanoscale effects on the multiferroic structure and physical properties of multiferroics. This focus is attributed to potential opportunities of practical applications of such nanostructured oxides.

Earlier in [10], we have presented the experimental data on heat capacity and permittivity of samarium ferrite

SmFeO<sub>3</sub> in a wide temperature range from 130 K to 800 K. It has been found that mechanoactivation of a ceramic SmFeO<sub>3</sub> sample causes phase transition (PT) smearing and phase transition temperature  $T_{CN}$  shift to the low temperature region and the observed phase transition at  $T = 558$  K has a frequency-dependent behavior typical of ferroelectrics. However, the authors have not analyzed the temperature dependence of SmFeO<sub>3</sub> and have not discussed the contribution of various heat capacity components. A detailed analysis of the temperature dependence of the heat capacity of nanostructured SmFeO<sub>3</sub> in a wide temperature range 120–800 K.

### 2. Experimental procedure

Ceramic SmFeO<sub>3</sub> samples were the targets of research. Chemically pure Sm<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> were used as precursors for SFO synthesis. They were mixed during two hours in an agate mortar with addition of ethanol. The charge was ignited in a platinum crucible at  $T = 1200^\circ\text{C}$  during 2 h. Then the obtained material was ground during 30 minutes and mechanically activated at 200 MPa between the vertical Bridgman anvils with the lower of them rotating at an angular speed  $\Omega = 0.3$  rad/min. A disc-shaped sample was prepared from the powder activated at fixed pressure and shear strain. The sample was baked without any bonding additives during two hours at  $T = 1000^\circ\text{C}$ .

X-ray diffraction analysis of the obtained materials was carried out using HZG-4B X-ray powder diffractometer. Crystalline structure of the initial and mechanoactivated ceramic SmFeO<sub>3</sub> at room temperature belongs to symmetry group *Pnma* [11]. No impurity phases were detected within the X-ray diffraction analysis sensitivity limits.

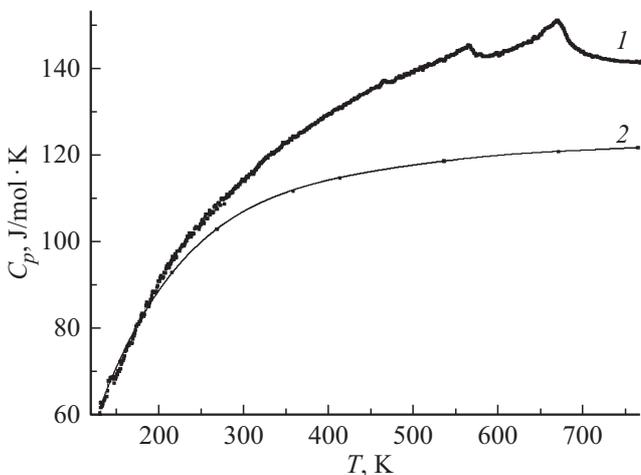
In SEM images [11] made using FE-SEM Zeiss SUPRA 25 electron microscope, the mechanoactivated sample is characterized by a „loose“ structure and the grain size distribution in the sample is of a multimodal type within 20–600 nm.

Heat capacity was measured by NETZSCH DSC 204 F1 Phoenix® differential scanning calorimeter. The heat capacity measurement sample was a plate with a diameter of 4 mm and a thickness of 1 mm, respectively. The rate of temperature change was 5 K/min. Heat capacity measurement error was lower than 3

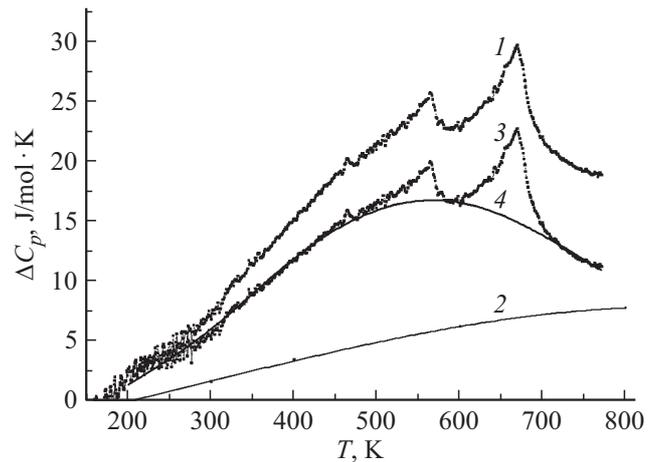
### 3. Results and discussions

As shown in Fig. 1, the experimental heat capacity values for SmFeO<sub>3</sub> within 130–800 K exceed the heat capacity of the samarium ferrite crystal lattice which is indicative of the presence of additional heat capacity components. To calculate the crystal lattice heat capacity, the Debye model was used, and to assess the anharmonic heat capacity component, the linear expansion coefficient Bi<sub>1-x</sub>La<sub>x</sub>FeO<sub>3</sub> [12] and volume compressibility modulus of ceramics Pb(TiZr)O<sub>3</sub> reported in [13] for structurally similar SmFeO<sub>3</sub> were used. The calculations show that the anharmonic heat capacity component is lower than 2% of the total heat capacity of SmFeO<sub>3</sub>, and therefore  $C_p = C_V$  may be assumed. Phonon heat capacity of SmFeO<sub>3</sub> calculated according the Debye model is shown with a solid line in Fig. 1. Excessive heat capacity  $\Delta C$  was defined as a difference of experimental phonon heat capacity  $C_p$  and heat capacity calculated using the Debye model  $C_0$ :  $\Delta C = C_p - C_0$  (curve 1 in Fig. 2).

The presence of 4*f*-shells that are partially occupied and lie deep in the atom is an important feature of paramagnetic rare earth (RE) ions. Crystal lattice vibrations can bring RE ions to the overlying layers and this leads to a decrease in



**Figure 1.** Temperature dependences of heat capacity of nanostructured SmFeO<sub>3</sub> multiferroic: 1 — experiment, 2 — phonon heat capacity approximation by the Debye function.



**Figure 2.** Temperature dependence of abnormal heat capacity component  $\Delta C_p$  SmFeO<sub>3</sub>: 1 —  $\Delta C = C_p - C_0$ , 2 — approximation result using expression (2), 3 —  $C_{add} = \Delta C - C_{msch}$ , 4 — approximation result using expression (3).

the heat capacity due to thermal excitation of 4*f*-electrons of rare earth elements (REE), i.e. to Schottky effect and reduction of crystal lattice heat capacity as a result of resonant phonon scattering on paramagnet RE ions [14]. Therefore, the presence of an additional heat capacity component in samarium ferrite can be associated with transition of RE ion 4*f*-electrons to higher levels.

The Schottky heat capacity  $C_{sch}$  may be written in the form of a sum [15]:

$$C_{sch} = C_{fsch} + C_{msch}, \quad (1)$$

where  $C_{fsch}$  and  $C_{msch}$  are heat capacities attributed to Stark ground-state structure and multiplet term structure of RE ions, respectively.

Component  $C_{fsch}$  can be observed at low temperatures (below 100 K), and component  $C_{msch}$  can be observed at moderate and high temperatures [16]. Therefore transitions of samarium 4*f*-electrons to higher multiplet levels results in the increase in heat capacity of SmFeO<sub>3</sub>. The distance between the multiplet levels of samarium ion Sm<sup>3+</sup> (<sup>6</sup>H<sub>5/2</sub>, <sup>6</sup>H<sub>7/2</sub>, <sup>6</sup>H<sub>9/2</sub>, <sup>6</sup>H<sub>11/2</sub> — 0, 1100, 2300, 3600 cm<sup>-1</sup>) [16,17] is comparable with the phonon energy and transitions between these samarium ion levels lead to the increase in the total heat capacity of SmFeO<sub>3</sub>.

Equation for the Schottky heat capacity  $C_{sch}$  can be obtained by temperature differentiation of the energy-level average particle energy [17]:

$$C_{sch} = N \frac{\partial}{\partial T} \left[ \frac{\sum_{i=0}^m E_i g_i \exp(-\frac{E_i}{k_0 T})}{\sum_{i=0}^m g_i \exp(-\frac{E_i}{k_0 T})} \right]. \quad (2)$$

Since the position of RE ion multiplet levels in various crystals remains virtually unchanged, the Schottky heat capacity attributed to transitions between the multiplet levels may be calculated using the equation (2) [18]. Fig. 2 shows

the dependence  $C_{\text{msch}}(T)$  (solid line 2) for  $\text{SmFeO}_3$ . As shown in Fig. 2, the excessive heat capacity  $\Delta C$  exceeds the Schottky heat capacity attributed to transitions between the samarium multiplet levels. This is indicative of the presence of other heat capacity components in samarium ferrite.

According to [19], high concentration of defects leads to the increase in the heat capacity of nanostructural  $\text{SmFeO}_3$  and thermodynamic property smearing in the phase transition region. Mechanoactivation of  $\text{SmFeO}_3$  leads to point defects and dislocations [10]. If the crystal lattice defects are generated thermally, then the defect generation energy also provides additional contribution to the heat capacity of  $\text{SmFeO}_3$  ceramic crystal lattice. Therefore, it can be assumed that the excessive heat capacity in samarium ferrite is caused by thermal generation of point defects and dislocations.

Presence of another heat capacity component in samarium ferrite may be associated with ions that can take various (several) structurally equivalent positions separated by energy barriers  $\Delta E_1$ ,  $\Delta E_2$ . Authors [20] associate the occurrence of such states separated by energy barriers  $\Delta E_1$  and  $\Delta E_2$  from the ground state with the change in crystal lattice parameters due to polar ionic displacements of iron and samarium and to the angle variation between oxygen octahedra of  $\text{FeO}_6$  with the increase in temperature.

Analysis of the temperature dependence of the additional heat capacity  $C_{\text{add}} = \Delta C - C_{\text{msch}}$  (curve 3 in Fig. 2) makes it possible to interpret it as a Schottky abnormality for three-level states. For a three-level system, the equation (2) is as follows [4]:

$$C_{\text{sch}} = R \left[ D_1 (\Delta E_1/kT)^2 \exp(-\Delta E_1/kT) + D_2 (\Delta E_2/kT)^2 \exp(\Delta E_2/kT) \right] / \left[ 1 + D_1 \exp(\Delta E_1/kT) + D_2 \exp(-\Delta E_2/kT) \right]^2, \quad (3)$$

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

By comparison of heat capacity calculated using the equation (3) (solid line 4 in Fig. 2) and experimentally obtained excessive heat capacity  $C_{\text{add}}$ , model parameters  $\text{SmFeO}_3$ :  $D_1 = 16.246$ ,  $D_2 = 0.557$ ,  $\Delta E_1 = 0.450$  eV and  $\Delta E_2 = 0.193$  eV were derived. The experimentally obtained abnormal heat capacity  $C_{\text{add}}$  matches well with the heat capacity calculated using the equation (3)  $C_{\text{sch}}$  (Fig. 2). It should be noted that the observed  $\lambda$ -abnormalities in the range of 670K and 558K are caused by structural phase transitions.

## 4. Conclusion

Thus, based on the experimental study of the samarium ferrite heat capacity in a wide temperature range, it has been found that the excessive heat capacity is attributed to: 1) transitions of samarium ion  $4f$ -electrons to

higher multiplet levels; 2) thermal generation of point defects and dislocations appearing during mechanoactivation; 3) transitions between energy levels associated with polar ionic displacements of iron and samarium as well as with angular change between the oxygen octahedra of  $\text{FeO}_6$  with the increase in temperature.

## Conflict of interest

The authors declare that they have no conflict of interest.

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