THERMAL PROPERTIES

High-Temperature Heat Capacity of the BiFeO₃ Multiferroic

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Abstract—Data on the heat capacity of the $BiFeO_3$ multiferroic have been obtained within a broad temperature interval. Correlation has been established between the composition of the $Bi_2O_3-Fe_2O_3$ pseudobinary system and the specific heat capacity of the oxide compounds.

1. INTRODUCTION

The specific feature of the $Bi_2O_3-Fe_2O_3$ system is the existence of three intermediate compounds: $Bi_{25}FeO_{39}$, $BiFeO_3$, and $Bi_2Fe_4O_9$ [1–4]. Of most interest among them is $BiFeO_3$ as offering considerable potential for use as a working medium in information storage and processing devices. This compound is one of the first multiferroics studied [5]. The high Curie temperature of $BiFeO_3$ offers great promise for application as a ferroelectric capable of operating at high temperatures, an attractive feature of a material for possible use in MRAM (Magnetic Random Access Memory), sensors, and actuators [6, 7]. The multiferroic $BiFeO_3$ stands out with its high critical temperatures of ferroelectric and antiferromagnetic ordering ($T_C = 1043$ K, $T_N = 643$ K) [8]. The magnetic structure below T_N is defined by *G*-type helicoidal spin ordering of Fe^{3+} ions, which makes possible use of this material under normal conditions [9]. Despite the intense interest expressed in oxide compounds of the $Bi_2O_3-Fe_2O_3$ system, particularly in $BiFeO_3$ [5–12], information available on the thermodynamic properties of the latter is inadequate. The scanty relevant data that can be found in publications are rather poorly correlated.

The goal of the present work was to study the heat capacity of the $BiFeO_3$ multiferroic over a broad temperature range.

2. EXPERIMENT

The difficulties associated with preparation of single-phase $BiFeO_3$ were identified in literature [9, 13]. The results summed up in [2, 14–16] led to the con-
clusion [17] that single-phase $BiFeO_3$ cannot be produced by solid-phase synthesis.

To prevent formation of $Bi_2Fe_4O_9$ in solid-phase synthesis of $BiFeO_3$ from pure oxides, the process is conducted in the presence of excess Bi_2O_3 [9, 18]. Nevertheless, impurity phases are formed in these conditions too, including antiferromagnetic $Bi_2Fe_4O_9$ and paramagnetic $Bi_{25}FeO_{39}$, the latter being very difficult to separate from $BiFeO_3$ even by leaching in dilute nitric acid.

Following solid-phase synthesis from Bi_2O_3 and Fe_2O_3 at 1133–1183 K, $BiFeO_3$ samples contain an impurity of the paramagnetic phase $Bi_{25}FeO_{39}$ in amounts of up to ~3 wt % [9].

The above factors formed a basis for our decision to prepare $BiFeO_3$ from melt solutions of nonstoichiometric composition. Our technique is similar to the one accepted in [19], the only difference being that we abandoned the second heating, and the cooling rate was 2 K/h. The X-ray powder diffraction pattern of the crystals thus obtained was consistent with the data available for $BiFeO_3$.

The heat capacity C_P was measured in platinum crucibles on STA 449 Jupiter (NETZSCH) equipment. The technique employed in the measurements was similar to the one described in [20].

3. RESULTS AND DISCUSSION

The influence of temperature on the heat capacity of $BiFeO_3$ crystals is shown graphically in Fig. 1. The $C_P = f(T)$ graph is seen to follow a fairly complex pattern. One immediately notices two extrema, a small one at 549 K and a more clearly pronounced one at
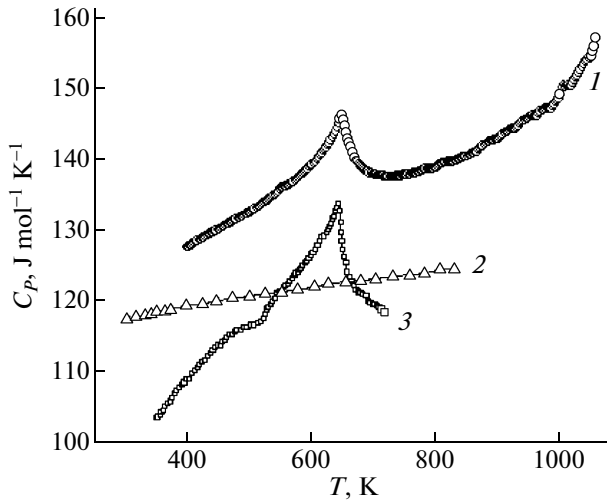
Fig. 1. Effect of temperature on the heat capacity of BiFeO$_3$: (*1*) our data, (*2*) [21], and (*3*) [5].

Fig. 2. Standard heat capacity as a function of the composition of the Bi$_2$O$_3$–Fe$_2$O$_3$ system: (*1*) [24], (*2*) our data, (*3*) [25], (*4*) [5], and (*5*) [26].

651 K. We note that the second maximum can be identified with the antiferromagnetic phase transition at T_N. A similar $C_P = f(T)$ curve in this temperature region was demonstrated in [5] as well (Fig. 1). At the same time, the values of C_P obtained by us are smaller (the measurements were conducted in the temperature interval of 350–720 K on ceramic samples). The first extremum at 533 K was assigned in [5] to the onset of structural changes, and the second one, at 642 K, to termination of the transition.

As follows from our data (Fig. 1), the magnitude of C_P of the multiferroic begins to grow continuously starting approximately from 800 K. One cannot exclude the possibility that this is actually the result of ferroelectric ordering (different authors place T_C at 1083 K [5], 1043 [8], ~1100 K [9]).

The heat capacity C_P of the BiFeO$_3$ ceramic was measured also in the 313–911-K interval with a Calvet calorimeter by the sample drop technique [21]. These results are also displayed in Fig. 1 for comparison. The values of C_P for BiFeO$_3$ reported in [21] are seen to increase weakly with increasing temperature, and the $C_P = f(T)$ graph does not exhibit any extrema. This certainly seems surprising, because heat capacity is a very sensitive probe of phase transitions occurring in a solid. Thus, for instance, the effect of ordering on the heat capacity was reliably identified in nonstoichiometric samples of carbides and oxides [22].

An earlier study established a correlation between the composition of the oxides in the GeO$_2$–PbO system and their standard heat capacity [23]. This relation is shown graphically for the Bi$_2$O$_3$–Fe$_2$O$_3$ system in Fig. 2. We readily see that this correlation is observed to exist, on the whole, for this system as well. Note, however, the following point. The lowest value
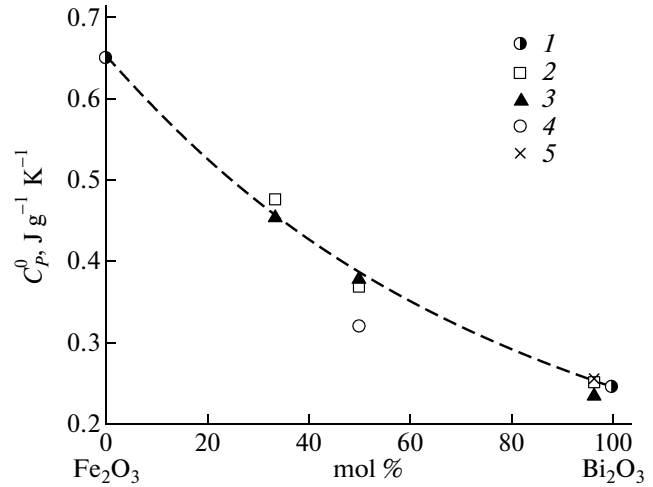
of C_P^0 for BiFeO$_3$ was obtained in [5]. Low values for Bi$_{25}$FeO$_{39}$ were reported in [21, 25]. Significantly, in the latter case the values of C_P^0 for Bi$_{25}$FeO$_{39}$ turned out to be even lower than those for pure Bi$_2$O$_3$.

Disregarding the additional contribution to C_P in the vicinity of T_N, the data obtained within the 298–510-K region can be presented in the form of the following relation (in units of J(mol K))

$$C_P = 141.12 + 1.412 \times 10^{-3}\,T - 23.09 \times 10^{5}\,T^{-2}. \quad (1)$$

Thermodynamic functions of BiFeO$_3$

T, K	C_P, J mol^{-1} K^{-1}	$H_T^0 - H_{298}^0$, kJ mol^{-1}	$S_T^0 - S_{298}^0$, J mol^{-1} K^{-1}
298	115.54	–	–
300	115.89	0.335	0.774
310	117.53	2.00	4.601
330	120.38	5.28	12.04
350	122.77	8.51	19.20
370	124.78	11.70	26.07
390	126.49	14.86	32.69
410	127.96	17.98	39.05
430	129.24	21.07	45.18
450	130.35	24.15	51.08
470	131.33	27.20	56.77
490	132.20	30.24	62.26
510	132.96	33.26	67.56