

Heat Capacity and Thermodynamic Properties of GaFeO₃ in the Range 330–900 K

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Abstract—The heat capacity of multiferroic GaFeO₃ has been measured in a wide temperature range and the results have been used to evaluate its thermodynamic functions (enthalpy increment and entropy change).

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INTRODUCTION

Multiferroic GaFeO₃ has attracted researchers' interest as a potentially attractive magnetoelectric material. The optical, magneto-optical, and other physical properties of this multiferroic have been the subject of extensive studies [1–6]. At the same time, there are no data on its thermophysical properties.

The purpose of this work was to investigate the high-temperature heat capacity of GaFeO₃ in a wide temperature range.

EXPERIMENTAL

The heat capacity C_p of the multiferroic was measured as described elsewhere [7, 8]. Our experiments were carried out in platinum crucibles using a Netzsch STA 449 C Jupiter thermoanalytical system. To calculate the heat capacity, we performed DSC scans of three materials—a base, sapphire (reference), and a sample—at heating rates of 5, 10, 15, and 20 K/min. The temperature range examined was chosen based on differential thermal analysis (DTA) data obtained with the STA 449 C Jupiter.

The phase diagram of the Ga₂O₃–Fe₂O₃ system is characterized by the presence of a chemical compound with the composition GaFeO₃, which has a wide homogeneity range [9]. Because of this, its formula is often represented in the form Ga_{2–x}Fe_xO₃ [1, 2]. As pointed out by Kalashnikova et al. [2], a distinctive feature of this material is that its crystal structure and physical properties depend on x . The most important compositions are those in the range $0.7 \leq x \leq 1.4$, which crystallize in a noncentrosymmetric, pyroelectric structure with space group $Pc2_1n$. Moreover, the Curie temperature T_C of this material depends on both the concentration of Fe³⁺ magnetic ions (increases

with increasing x) and the preparation procedure (increases in the following order: ceramic samples < single crystals grown by the floating zone (FZ) technique < single crystals grown from high-temperature solutions) [1, 2].

In this paper, we present data for $x = 1$ single crystals. The GaFeO₃ single crystals were prepared by a high-temperature solution growth technique similar to that described by Kalashnikova et al. [2]. The lattice parameters of the crystals differed little from those reported by Arima et al. [1].

RESULTS AND DISCUSSION

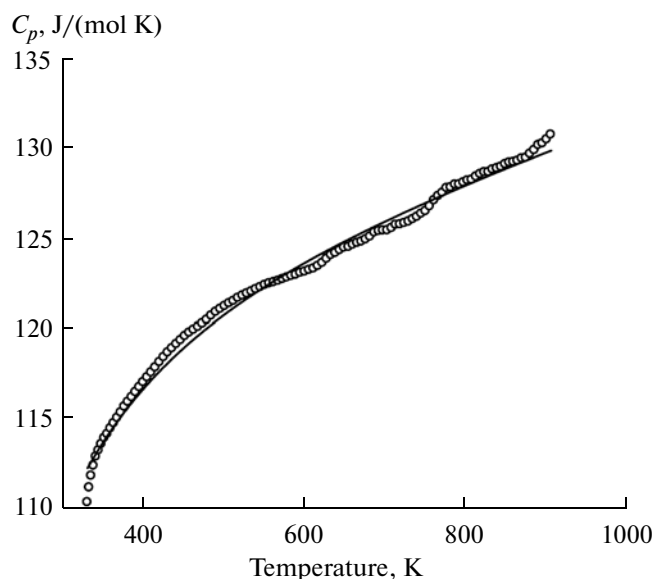
It follows from the temperature-dependent C_p data for multiferroic GaFeO₃ (figure) that its C_p increases systematically with increasing temperature. For $T > 640$ K, it exceeds the Dulong–Petit (classical) limit $3Rs$, where R is the gas constant and s is the number of atoms per formula unit ($s = 5$ for GaFeO₃).

In data processing, we used licensed SYSTAT SigmaPlot 12 graphing software. The largest deviation of data points from the best fit curve was within 0.5%. The $C_p(T)$ data obtained for GaFeO₃ in the temperature range 330–900 K can be represented by the following polynomial (at low temperatures, C_p decreases much more rapidly in comparison with the proposed relation):

$$C_p = 118.46 + 14.5 \times 10^{-3}T - 11.56 \times 10^5 T^{-2}. \quad (1)$$

This makes it possible to find the enthalpy increment ($H_T^0 - H_{330}^0$) and entropy change ($S_T^0 - S_{330}^0$) using known thermodynamic relations. The results are presented in the table.

The C_p data obtained for GaFeO₃ cannot be compared to previous data because there are no such data.



Temperature dependence of heat capacity for GaFeO₃. The open circles represent the experimental data and the solid line represents smoothing results.

Nevertheless, it is worth pointing out the following: According to our data, the temperature-dependent heat capacity of BiFeO₃, another ferromagnet, can be represented in the range 400–540 K by the following equation [10]:

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

Heat capacity and thermodynamic functions of GaFeO₃

T , K	C_p , J/(mol K)	$H_T^0 - H_{330}^0$, kJ/mol	$S_T^0 - S_{330}^0$, J/(mol K)
330	112.6	—	—
350	114.1	2.67	6.67
370	115.4	5.32	13.05
390	116.5	7.96	19.15
410	117.5	10.59	25.00
450	119.3	15.83	36.03
500	121.1	22.35	48.69
550	122.6	28.87	60.31
600	124.0	35.38	71.03
650	125.2	41.91	81.00
700	126.3	48.44	90.32
750	127.3	55.00	99.06
800	128.3	61.58	107.3
850	129.2	68.19	115.1
900	130.1	74.82	122.5

It follows from Eqs. (1) and (2) that, at a given temperature, the C_p of BiFeO₃ is somewhat higher. The molar mass of BiFeO₃ exceeds that of GaFeO₃ and, accordingly, its C_p is higher.

It is worth pointing out that multiferroic BiFeO₃ has high ferroelectric and antiferromagnetic ordering temperatures ($T_C = 1043$ K, $T_N = 643$ K), which shows up in its $C_p(T)$ curve. The T_C reported for multiferroic GaFeO₃ is lower than that in our experiments (260–345 K, depending on doping [2]). For this reason, its $C_p(T)$ curve has no extrema (figure).

CONCLUSIONS

Experimental heat capacity data for GaFeO₃ were used to determine its main thermodynamic functions. The heat capacities of multiferroic GaFeO₃ and BiFeO₃ were compared and BiFeO₃ was found to have higher C_p .

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