SUPERCONDUCTIVITY

# High-Temperature Heat Capacity of $BaFe_{12}O_{19}$ and $BaSc_{0.5}Fe_{11.5}O_{19}$

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**Abstract**—Data on the heat capacity of $BaFe_{12}O_{19}$ (373–1450 K) and $BaSc_{0.5}Fe_{11.5}O_{19}$ (408–1000 K) have been obtained. In the temperature dependences of the heat capacity of these oxide compounds, the existence of extrema in the region of the Curie temperature $T_C$ has been established.

## 1. INTRODUCTION

Owing to their properties, hexaferrites of structural type $M$ ($BaFe_{12}O_{19}$) have been attracting for a long time interest of researchers [1–8]. The only magneto-active ions they contain are $Fe^{3+}$ ions located at sites with octahedral ($4f_2$, $2a$, $12k$), tetrahedral ($4f_1$), or bipyramidal ($2b$) oxygen environment [3]. Such ferrites feature anisotropy energy constants two orders of magnitude larger than is typical of the ferrite garnets, which likewise have only $Fe^{3+}$ magnetoactive ions in their composition [9]. Such values of the constants and, accordingly, of the anisotropy fields of the $M$-type hexaferrites are essential prerequisites for their broad application. Therefore, investigation of the various physical properties of these materials is of both pure scientific and applied interest. Nevertheless, available data relate primarily to investigation of their magnetic properties. We have not been able to find any information on the thermodynamic characteristics of $BaFe_{12}O_{19}$ and $BaSc_{0.5}Fe_{11.5}O_{19}$ at high temperatures. One has to bear in mind that, depending on the degree of doping and temperature, these materials undergo phase transitions accompanied by ordering of different types [6, 7]. Experimental data on their heat capacity permit one to establish in certain cases the specific features of these phase transitions [10].

The present study was aimed at investigating the high-temperature heat capacity of $BaFe_{12}O_{19}$ and $BaSc_{0.5}Fe_{11.5}O_{19}$.

## 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Information on the phase diagram of the $BaO–Fe_2O_3$ system can be found in [4, 11]. These data differ from one another both in the number of the compounds formed and in the phase equilibrium temperatures. Of all the chemical compounds formed in this system, the most interesting is $BaO \cdot 6Fe_2O_3$ ($BaFe_{12}O_{19}$). It features at the same time the highest melting temperature, a factor creating certain issues with its production. Therefore, some authors resort to low-temperature synthesis of $BaFe_{12}O_{19}$ [4–6, 8, 12] by using, for instance, water-soluble compatible salts $Fe(NO_3)_3 \cdot 9H_2O$ and $Ba(NO_3)_2$ [12], while others employ the melt solution technique [2, 3, 7, 9, 12]. Because the latter approach permits growing single crystals, it is this technique of fabrication of $BaFe_{12}O_{19}$ and $BaSc_{0.5}Fe_{11.5}O_{19}$ that seemed to us preferable.

Single crystals of $BaFe_{12}O_{19}$ and $BaSc_{0.5}Fe_{11.5}O_{19}$ were grown from the melt-solution using, as in [3, 7, 9], $BaO–B_2O_3$ as the solvent. The maximum size of the samples was ~3.5 mm for $BaFe_{12}O_{19}$ and 4.0 mm for $BaSc_{0.5}Fe_{11.5}O_{19}$. The phase composition of the crystals was monitored by the X-ray diffraction technique. The parameters of the crystal lattice obtained approach those reported in the literature.

The heat capacity $C_p$ was measured in platinum crucibles with an STA 449 C Jupiter instrument (NETZSCH). Because the grown single crystals did not match the instrument specifications in geometric dimensions, they were preliminarily ground, and subsequently pelletized to produce tablets 6.0 mm in
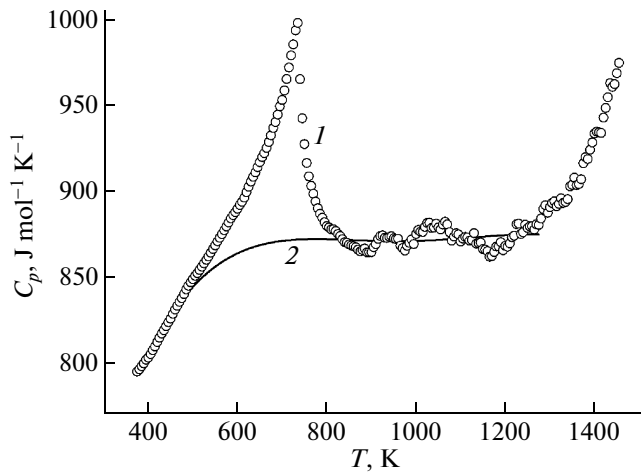
**Fig. 1.** Temperature dependence of the heat capacity of the $BaFe_{12}O_{19}$ hexaferrite: (*1*) our data and (*2*) base line.



**Fig. 2.** Temperature dependence of the heat capacity of $BaSc_{0.5}Fe_{11.5}O_{19}$: (*1*) our data and (*2*) base line.

diameter and ~2 mm high. In all the other details, the technique used in $C_p$ measurements was similar to that employed in [14, 15].

## 3. RESULTS AND DISCUSSION

The effect of temperature on the heat capacity $C_p$ of $BaFe_{12}O_{19}$ crystals is visualized in Fig. 1. As follows from the graphs, the $C_p = f(T)$ dependence exhibits a fairly complex pattern. A clearly pronounced extremum at $T = 734$ K stands out in the plot. Various authors cite 730 K [6] and $724 \pm 1$ K [7] as the Curie temperature for $BaFe_{12}O_{19}$. This difference between the values of $T_C$ obtained by us and in [6, 7] is in no way unexpected, because the critical temperature is known not to coincide, as a rule, with the maxima in the heat capacity $C_p$ and magnetic susceptibility [16].

The continuous variation of the heat capacity of $BaFe_{12}O_{19}$ in the region of the transition implies it to be second order [16–18]. At the same time, the well pronounced λ-shaped contour of the heat capacity peak suggests influence of thermodynamic fluctuations on the heat capacity of $BaFe_{12}O_{19}$ in the region of the transition. The magnitude of the jump in $C_p$ in the region of the phase transition is $\Delta C_p(T_{max}) \sim$ 126 J/(mol K) and the width of the transition, $\Delta T \approx$ 355 K. The latter value ($\Delta T$) is quite large, which likewise suggests a second-order transition (the heat capacity peak for first-order transitions is very narrow, with its width being usually less than 10 K [18]). It is believed [18] that the large width of the peak may be caused by slow transition kinetics, because heat capacity measurements are conducted in some cases with a step of 5 K at a heating rate of 20 K/min. At the same time, the diffuse contour of the peak is assumed to reflect changes in short-range order evolving gradually near the phase transition temperature. It was also sug-
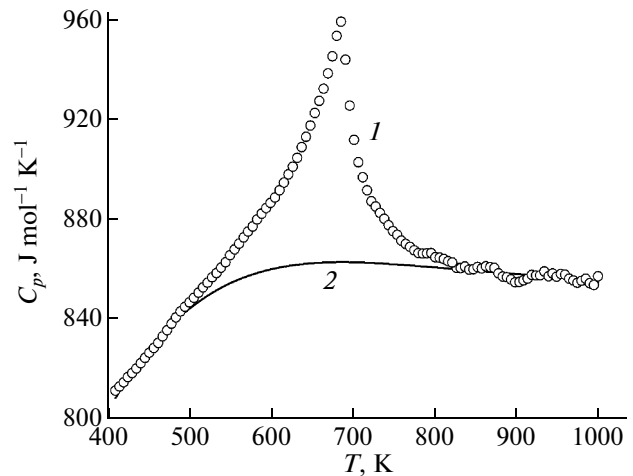
gested [18] that to reveal the effect produced by experimental conditions on the peak width, $C_p$ measurements in the vicinity of the phase transition temperature should be conducted with a heating rate of 0.2 K/min and with a step of 0.5 K. In our case, the $C_p$ measurements were performed at rates of 5, 10, 15, and 20 K/min with a step of 0.5 K. The results obtained coincided.

Measurements of the magnetic susceptibility of $BaFe_{12}O_{19}$ [7] led to a conclusion that at the Curie temperature $T_C = 724$ K a ferrimagnet–paramagnet phase transition is observed.

The entropy of a phase transition is derived from measurements of $C_p = f(T)$ within a broad temperature interval including the phase transition point [19]. The excess heat capacity $C_{pi}$ associated with the phase transition and needed for this purpose is found by subtracting from the measured heat capacity its regular part $C_b$ set by the base line of the $C_p = f(T)$ function [20]. The base line was determined by extrapolating the heat capacity from the region lying above $T_C$ (833–1273 K) to the low-temperature domain below $T_C$ (381–478 K). Just as in [20], the phase transition region was not included. Estimation of the entropy of the phase transition $\Delta S$ from the excess heat capacity in the region of $T_C$ yields $\Delta S = \int (C_{pi} - C_b) dT/T \approx 20$ J/(mol K).

Figure 2 displays data on the temperature dependence of the heat capacity of $BaSc_{0.5}Fe_{11.5}O_{19}$. We readily see that in this case the $C_p = f(T)$ curve likewise has a clearly pronounced extremum at $T = 685$ K, which can also be assigned to a second-order transition. For $BaSc_{0.5}Fe_{11.5}O_{19}$, the magnitude of the jump in the region of the phase transition is $\Delta C_p(T_{max}) \approx$ 97 J/(mol K), and the width $\Delta T \approx 338$ K. Estimation

of the phase transition entropy in the region of $T_C$ yields $\Delta S = 14.4$ J/(mol K).

A comparison of the data obtained for $BaFe_{12}O_{19}$ and $BaSc_{0.5}Fe_{11.5}O_{19}$ suggests that introduction of scandium into the hexaferrite results in a decrease of the jump $\Delta C_p(T_{max})$ in the phase transition entropy $\Delta S$. In both cases, one observes a fairly large transition width $\Delta T$. This may be associated both with delayed transition kinetics [18] and with second-order phase transitions being related, as a rule, with a change in the degree of order in the crystal. It is known that $T_C$ specifies the limiting temperature at which ordering disappears. Nevertheless, a certain degree of short-range order involving only a small number of close-located atoms in the crystal may still persist [21].

The above difference in some properties between the $BaFe_{12}O_{19}$ and $BaSc_{0.5}Fe_{11.5}O_{19}$ crystals studied here may stem from magnetic "dilution" which affects exchange interactions and ferrimagnetism [21]. To cite an example, $T_C$ for the first crystal, is, according to our data, 734 K, whereas for the second one it is 685 K. A comparison of the values of $\Delta S$ obtained with the value $\Delta S = R \ln(2s + 1) \approx 14.9$ J/(mol K), where $s = 5/2$ for the $Fe^{3+}$ ion [22], which is predicted for the order-disorder transitions [19], indicates that for $BaFe_{12}O_{19}$ the experimental value is larger than the theoretical one, while for $BaSc_{0.5}Fe_{11.5}O_{19}$ they are practically equal.

## 4. CONCLUSIONS

The temperature responses of the heat capacity of $BaFe_{12}O_{19}$ and $BaSc_{0.5}Fe_{11.5}O_{19}$ have been studied. It has been shown that doping the hexaferrite with scandium changes strongly the properties of the compound.

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