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SEMICONDUCTORS

High-Temperature Heat Capacity of $Y_{2.93}Ho_{0.07}Fe_5O_{12}$

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Abstract—This paper presents data on the heat capacity of $Y_{2.93}Ho_{0.07}Fe_5O_{12}$ obtained in the temperature range 343–1000 K. A correlation between the composition of the Fe_2O_3–Y_2O_3 pseudobinary system and the specific heat capacity of oxide compounds is pointed out.

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1. INTRODUCTION

Single crystals of complex compounds with garnet structure are employed in electronics as substrates for storage devices with cylindrical magnetic domains, active working medium in quantum oscillators, etc. [1, 2]. Ferromagnetic garnet $Y_3Fe_5O_{12}$ enjoys the largest popularity among them [3]. It possesses a high optical transparency, high specific Faraday rotation in the IR range and reveals good microwave characteristics [4]. Despite the large area of applications of $Y_3Fe_5O_{12}$ and a large number of publications dealing with investigation of its physical properties, one can locate in literature only a limited number of publications bearing on studies of the thermodynamic properties of this material. The behavior with temperature of the molar heat capacity C_p of the $Y_3Fe_5O_{12}$ garnet was studied in the following intervals: 1–20 [5], 80–390 [6], and 200–673 K [7]. These data were summarized [8] and used to calculate the thermodynamic functions for $Y_3Fe_5O_{12}$. Data available on the high melting temperature of $Y_3Fe_5O_{12}$, which depends on the partial pressure of oxygen [9], stresses the need for information on the $C_p = f(T)$ dependence at temperatures higher than those covered in [7, 8]. This information would permit optimization of the conditions of synthesis and suggest recommendations concerning the regimes appropriate for the use of the materials obtained [10].

This paper reports on a study of the high-temperature heat capacity of $Y_{2.93}Ho_{0.07}Fe_5O_{12}$.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

We used $Y_{2.93}Ho_{0.07}Fe_5O_{12}$ single crystals grown from a melt solution by the technique described in [11, 12]. The largest size of the single crystals was ~10 mm.

The heat capacity C_p of the garnet was measured by the method described earlier [13]. We employed compacted powder samples. All the measurements were performed in platinum crucibles. The differential scanning calorimeter data were obtained with a STA 449 C Jupiter instrument (NETZSCH).

3. RESULTS AND DISCUSSION

The influence of temperature on the heat capacity of $Y_{2.93}Ho_{0.07}Fe_5O_{12}$ crystals is displayed graphically in Fig. 1. As seen from these data, the $C_p = f(T)$ dependence follows a fairly complex pattern. At $T = 559$ K, the curve exhibits a clearly pronounced peak. The distinct λ-shape of the heat capacity peak and its continuous variation in the region of the transition may suggest that it is a second-order phase transition [14, 15]. The jump of C_p in the region of the phase transition is $\Delta C_p(T_{max}) \approx 45$ J/(mol K), with the width of the transition $\Delta T \approx 160$ K. We note that, according to [8], one observes near 560 K another anomaly in C_p, which was assigned to a magnetic transformation at the Curie point ($T_C = 560 \pm 10$ K).

The transition entropy ΔS can be estimated from the excess heat capacity ΔC_p near T_C with the relation $\Delta S = \int \Delta C_p dT/T$ [16, 17]. To find ΔC_p, we apply an approach similar to the one described in [18]. The

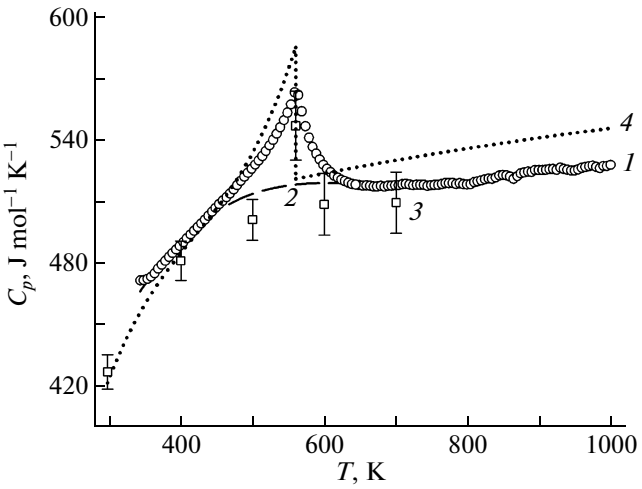

Fig. 1. Temperature dependence of C_p of the $Y_{2.93}Ho_{0.07}Fe_5O_{12}$ compound according to (*1*) our data, (*2*) base line, (*3*) [8], and (*4*) [10].

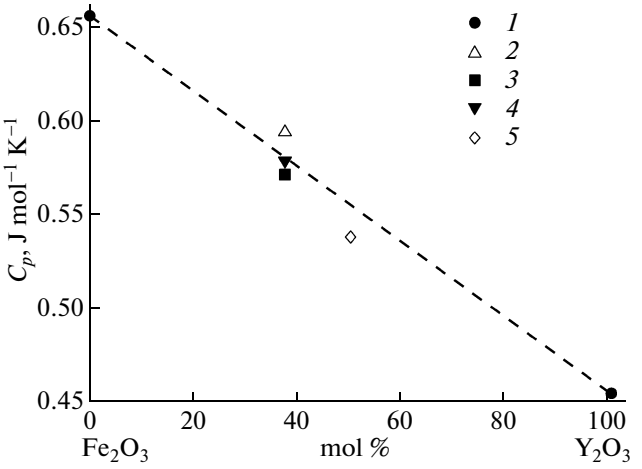

Fig. 2. Dependence of the standard heat capacity on the composition of the Fe_2O_3–Y_2O_3 pseudobinary system according to (*1*) [19], (*2*) our data, (*3*) [10], (*4*) [8], and (*5*) [23].

excess heat capacity is derived in this case by subtracting from the experimental heat capacity its regular part C_{pn} defined by the base line of the $C_p = f(T)$ relation. The base line was found by extrapolating the heat capacity from the temperature region above T_C (649–774 K) to that lying below T_C (344–464 K), with the exclusion of the phase transition region. The base line obtained for these conditions is shown in Fig. 1. With the data thus obtained, we came to $\Delta S = 5.57$ J/(mol K). This value is practically equal to $\Delta S = R\ln 2 = 5.76$ J/(mol K), the value predicted for the order/disorder-type transitions [16]. The base line was used to determine the heat capacity at 298 K. It turned out to be equal to $C_p^0 = 438.21$ J/(mol K). This result is slightly larger than the one presented in [8], $C_p^0 = 426.77 \pm 8.36$ J/(mol K). One cannot exclude the possibility that this is connected with the garnet being doped in our case with holmium, because for $Ho_3Fe_5O_{12}$ and $C_p^0 = 451.52$ J/(mol K) [19]. Besides, the properties of the crystals grown may be affected by the deviation of the garnet composition from stoichiometry, formation of vacancies, antisites and other defects [4, 10, 12]. It was reported [10] that formation of antisite defects in the course of exchange of ions occupying different sites of the garner structure may bring about a change in magnetic order in ferrite garnets and, hence, cause a change in the heat capacity and enthalpy as well. While partial or complete replacement of yttrium in $Y_3Fe_5O_{12}$ with a rare-earth element does not affect noticeably the anisotropy of the Fe^{3+} ions, the rare-earth ion (REI) adds to it a contribution [3]. We note that the effect of magnetic "dilution" on exchange interactions and ferrimagnetism is considered in sufficient detail in [20]. The above factors were found to cause a difference between thermodynamic properties measured by different methods, as well as between the properties of samples with different prehistories [10]. Indeed, nanostructural samples of $Y_3Fe_5O_{12}$ obtained by nonequilibrium methods have defects on the surface and in the bulk of crystals and vacancies in the cation and oxygen sublattices, and this is believed [21] to be capable of affecting the physical properties.

The above considerations may be viewed as corroboration for the influence of garnet doping with holmium, although the T_C points on the $C_p = f(T)$ curve obtained by us and reported in [8] coincide in position.

It was proposed [10] to calculate the temperature dependences of the heat capacities of the $R_3M_5O_{12}$ garnets ($R^{3+} \equiv$ Y, Bi, REI; $M^{3+} \equiv$ Al, Ga, Fe) with polynomials of the kind

$$C_p(T) = \varphi_2 + 2\varphi_3 x^{-2} + 2\varphi_5 x + 6\varphi_6 x^2 + 12\varphi_7 x^3,$$

where $x = T \times 10^{-4}$ [K]. The data obtained using this equation for $Y_3Fe_5O_{12}$ are plotted in Fig. 1. Note that for $T < T_C$ this equation describes satisfactorily the experimental $C_p = f(T)$ relations, whereas for $T > T_C$ no such agreement is seen. The required values of φ_2, φ_3, φ_5, φ_6, φ_7 were taken from tables [10]. Note that they are different for $T < T_C$ and $T > T_C$. Calculations made with the use of this equation yield $C_p^0 = 421.3$ J/(mol K), which is slightly smaller than our data presented in this paper and reported in [8].

The composition of the oxides of the GeO_2–PbO system and their standard heat capacity were found to correlate [22]. This relation is demonstrated graphically in Fig. 2. We see that on the whole this relation is seen to hold for this system as well. We have not suc-

ceeded in finding data on the heat capacity for $YFeO_3$, therefore they were calculated by the Neumann–Kopp method [23].

4. CONCLUSIONS

The temperature dependence of the heat capacity of $Y_{2.93}Ho_{0.07}Fe_5O_{12}$ has been studied. The $C_p = f(T)$ dependence was found to have a distinct extremum corresponding to the ferrimagnetic–paramagnetic transition.

REFERENCES

1. V. V. Randoshkin and A. Ya. Chervonenkis, *Applied Magnetooptics* (Energoatomizdat, Moscow, 1990) [in Russian].
2. A. S. Malkova and A. S. Pashinkin, Neorg. Mater. **29** (2), 240 (1993).
3. S. Krupička, *Physik der Ferrite und der verwandten magnetischen Oxide* (Academia, Prague, 1973; Mir, Moscow, 1976), Vol. 2 [in German and in Russian].
4. I. D. Lomako, Crystallogr. Rep. **56** (3), 385 (2011).
5. A. B. Harris and H. Meyer, Phys. Rev. **127**, 101 (1962).
6. E. D. Devyatkova and V. V. Tikhonov, Sov. Phys. Solid State **9** (3), 604 (1967).
7. V. A. Shchelkotunov and V. N. Danilov, Izv. Akad. Nauk SSSR, Neorg. Mater. **9**, 682 (1973).
8. V. A. Shchelkotunov, V. N. Danilov, L. A. Reznitskii, and A. V. Korobeinikova, Izv. Akad. Nauk SSSR, Neorg. Mater. **11** (9), 1633 (1975).
9. N. A. Toropov, V. P. Barzakovskii, V. V. Lapin, and N. N. Kurtseva, *Handbook of Phase Diagrams of Silicate Systems*, Vol. 1: *Binary Systems* (Nauka, Leningrad, 1969; Israel Program for Scientific Translations, Jerusalem, 1972).
10. O. Yu. Goncharov and Yu. P. Vorob'ev, Russ. J. Phys. Chem. **73** (1), 27 (1999).
11. D. M. Bal'zamov, L. A. Dolomanov, V. D. Kudryavtsev, A. N. Ostroukhova, O. I. Rozhdestvenskaya, K. Ya. Turkina, and V. A. Fabrikov, *Physical and Physico-Chemical Properties of Ferrites* (Nauka i Tekhnika, Minsk, 1966) [in Russian].
12. I. D. Lomako, M. I. Danil'kevich, V. D. Karpinskii, and I. I. Makoed, Crystallogr. Rep. **53** (2), 278 (2008).
13. V. M. Denisov, L. T. Denisova, L. A. Irtyugo, and V. S. Biront, Phys. Solid State **52** (7), 1362 (2010).
14. S. V. Vonsovskii, *Magnetism* (Nauka, Moscow, 1971; Wiley, New York, 1974).
15. A. I. Gusev, *Nonstoichiometry, Disorder, Short-Range and Long-Range Order in Solid State* (Fizmatlit, Moscow, 2007) [in Russian].
16. B. A. Strukov and A. P. Levanyuk, *Ferroelectric Phenomena in Crystals: Physical Foundations* (Fizmatlit, Moscow, 1995; Springer, Berlin, 1998).
17. R. L. Carlin, *Magnetochemistry* (Springer, New York, 1985; Mir, Moscow, 1989).
18. A. A. Bush and E. A. Popova, Phys. Solid State **46** (5), 902 (2004).
19. J. Leitner, P. Chuchvalec, D. Sedmidubský, A. Strejc, and P. Abrman, Thermochim. Acta **395**, 27 (2003).
20. S. Krupička, *Physik der Ferrite und der verwandten magnetischen Oxide* (Academia, Prague, 1973; Mir, Moscow, 1976), Vol. 1 [in German and in Russian].
21. A. A. Makhnev, B. A. Gizhevskii, and L. V. Nomerovannaya, JETP Lett. **91** (2), 79 (2010).
22. V. M. Denisov, L. A. Irtyugo, and L. T. Denisova, Phys. Solid State **53** (4), 689 (2011).
23. G. K. Moiseev, N. A. Vatolin, L. A. Marshuk, and N. I. Il'inykh, *Temperature Dependences of the Reduced Gibbs Energy for Some Inorganic Substances* (Ural Branch of the Russian Academy of Sciences, Yekaterinburg, 1977) [in Russian].

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