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SEMICONDUCTORS

High-Temperature Heat Capacity of $Y_{2.9}Ho_{0.1}Al_5O_{12}$

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Abstract—This paper presents data on the heat capacity of $Y_{2.9}Ho_{0.1}Al_5O_{12}$ as a function of temperature (360–1020 K). The experimental data obtained are used to derive the thermodynamic functions of the oxide compound.

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1. INTRODUCTION

Single crystals of complex oxide compounds with garnet structure are widely employed as working substance in optical quantum generators [1, 2], acoustoelectronics equipment [3], and other optoelectronics devices. Of particular interest proved to be single crystals of solid solutions based on $Y_3Al_5O_{12}$ garnet, which revealed the existence of magnetic field-mediated polarized luminescence [4]. It was assumed that this phenomenon could be strongly amplified if combined with the "mixing" effect the Tb^{3+} and Ho^{3+} non-Kramers ions demonstrate in garnets. The information available on the heat capacity and other thermodynamic properties of these phases provides a basis for thermodynamic calculations aimed at optimization of the process of their synthesis. This relates in the first place to garnet-based solid solutions. One should take here into account both the high melting temperature of the yttrium aluminum garnet [5] and the difficulties encountered in its preparation in the form of single crystals [6].

The heat capacity of $Y_3Al_5O_{12}$ was measured in the temperature interval 4.3–300 K [7] by stepped heating in an adiabatic calorimeter. In the domain of higher temperatures (350–610 K) the heat capacity was determined with the use of differential scanning calorimeter [8]. One can find in the literature the following values of C_p (J/mol K) at 298 K: 351.6 [8], 348.13 [9], and 352.5 [10]. Studies of the solid solutions based on rare-earth aluminum garnets were also reported [8, 11].

The present work was aimed at measuring the high-temperature heat capacity, to be subsequently employed as a basis for deriving the thermodynamic properties of $Y_{2.9}Ho_{0.1}Al_5O_{12}$.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The heat capacity C_p of $Y_{2.9}Ho_{0.1}Al_5O_{12}$ garnets was measured by the technique described elsewhere [12, 13]. Pressed powder samples were employed. All measurements were conducted in platinum crucibles by differential scanning calorimetry with STA 44 C Jupiter equipment (NETZSCH).

The $Y_{2.9}Ho_{0.1}Al_5O_{12}$ single crystals used in the studies were grown from the solution-melt [14, 15]. The unit cell parameters obtained for $Y_{2.9}Ho_{0.1}Al_5O_{12}$ (12.0077 Å) fit fairly well those reported for $Y_3Al_3O_{12}$ (12.0081 [7] and 12.0070 Å [16]).

3. RESULTS AND DISCUSSION

The effect of temperature on the heat capacity of $Y_{2.9}Ho_{0.1}Al_5O_{12}$ crystals is shown graphically in Fig. 1. As the temperature increases, the values of C_p are seen to grow regularly, to reach only at $T = 1020$ K the classical Dulong–Petit limit $3Rs$, where R is the universal gas constant, and s is the number of atoms in the garnet unit cell. The $C_p = f(T)$ curve reveals near 860 K a weak extremum whose origin remained unclear. Significantly, its presence was demonstrated in all the samples studied. If one disregards this extremum, the temperature dependence of the heat capacity can be described with a correlation coefficient of 0.9976 by the following equation (in units J/mol K):

$$C_p = 315.067 + 0.278T - 4.063\times10^{-6}T^2 - 9.275\times10^{-8}T^3. \quad (1)$$

Converting these data into the Maier–Kelly equation $C_p = a + bT - cT^{-2}$ [17] yields the value $r = 0.9942$.

The thermodynamic functions of $Y_{3-x}Lu_xAl_5O_{12}$ (x = 0, 0.5, 0.75, 1.0, 1.5, 2.0, 2.5, 3.0) were studied in [7]. It was found that as the temperature increases (starting from 65 K and up to the room level), the difference in C_p between the samples with the lowest and highest compositions falls off, to become at room temperature comparable to the measurement error. Assuming the same to be true in our case, one can compare the values of C_p obtained for $Y_{2.9}Ho_{0.1}Al_5O_{12}$ with the data available for $Y_3Al_5O_{12}$. These results are presented graphically in Fig. 1. We readily see that the data derived on the heat capacity of the $Y_{2.9}Ho_{0.1}Al_5O_{12}$ garnet fit, on the whole, those available for $Y_3Al_5O_{12}$. This provides supportive evidence for some results reported for the $Y_{3-x}Lu_xAl_5O_{12}$ system [7].

Equation (1) can be used to derive from the thermodynamic equations available for $Y_{2.9}Ho_{0.1}Al_5O_{12}$ the changes in enthalpy $H_T^0 - H_{360}^0$ and entropy $S_T^0 - S_{360}^0$. The results of the calculations are listed in the table.

To calculate the temperature dependences of the heat capacity of $R_3M_5O_{12}$ (R^{3+} = Y, Bi, rare-earth metals; M^{3+} = Al, Ga, Fe), the following equation was proposed in [10]:

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

where $x = T \times 10^{-4}$ K. The results of the calculation performed with Eq. (2) for $Y_{2.9}Ho_{0.1}Al_5O_{12}$ are compared in Fig. 2 with the experimental values of C_p. The values of the coefficients φ_2, φ_3, φ_5, φ_6, φ_7 can be found in [10]. As follows from Fig. 2, the calculated values of C_p fit satisfactorily the experiment.

Figure 2 plots also the values of C_p calculated from the Debye model [18]. We used the value of the Debye characteristic temperature Θ_D = 750 K obtained by us, which coincides with the data reported [19] for $Y_3Al_5O_{12}$. The calculations allowed for the following points. First, in the Debye model one calculates C_v rather than C_p. Second, Debye's theory of heat capacity should be considered only as an approximate approach for a number of garnet crystals, with the corresponding Grüneisen coefficient depending in an intricate way on temperature [20]. Therefore, the assumption of the heat capacities C_v and C_p for garnets being close offers in the first approximation a possibility of comparing the values calculated with Debye's model with experiment. As seen from Fig. 2, starting from ~650 K, a certain difference between the calculated and experimental values of C_p appears, which grows with increasing temperature.

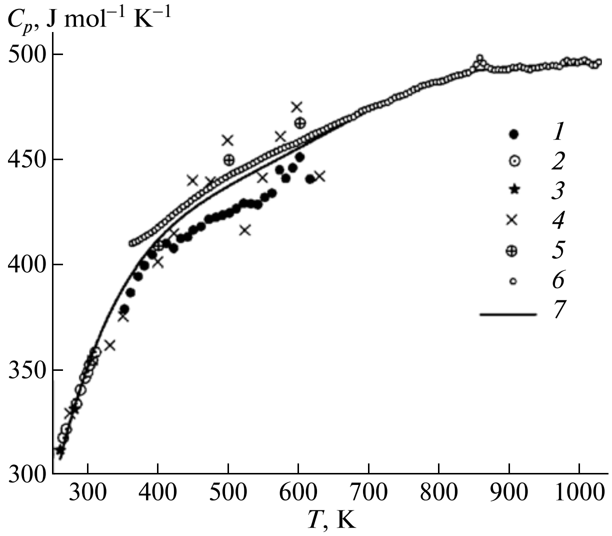

Fig. 1. Temperature dependences of the heat capacity: (*1–5*) $Y_3Al_5O_{12}$ [8], (*6*) $Y_{2.9}Ho_{0.1}Al_5O_{12}$ (our data), and (*7*) approximating curve.

Smoothed values of the molar heat capacity and the thermodynamic functions derived from them

T, K	C_p, J mol^{-1} K^{-1}	$H_T^0 - H_{360}^0$, kJ mol^{-1}	$S_T^0 - S_{360}^0$, J mol^{-1} K^{-1}
380	415.03	33.22	98.39
420	424.24	50.01	140.4
460	433.06	67.16	179.4
500	441.46	84.65	215.8
540	449.40	102.5	250.1
580	456.84	120.6	282.5
620	463.76	139.0	313.4
660	470.11	157.7	342.4
700	475.86	176.6	370.2
740	480.98	195.8	396.8
780	485.42	215.1	422.2
820	489.15	243.6	446.6
860	492.15	254.2	470.0
900	494.36	273.9	492.4
940	495.76	293.7	513.9
980	496.30	313.6	534.6
1020	495.97	333.4	554.5

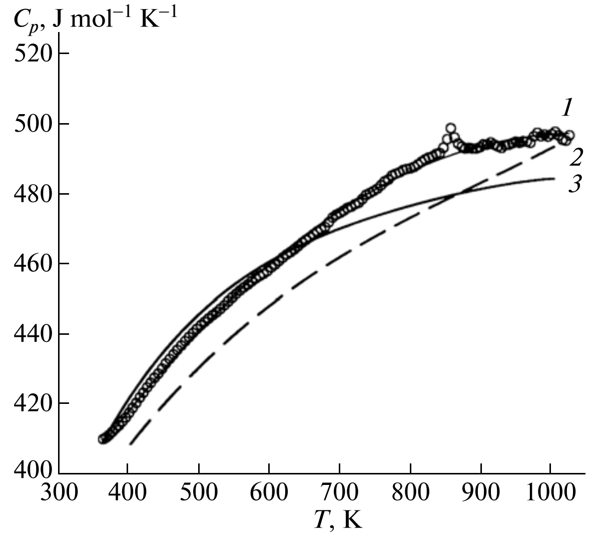

Fig. 2. Comparison of (*1*) experimental values of C_p and (*2*, *3*) values calculated using (*2*) Eq. (2) and (*3*) Debye model.

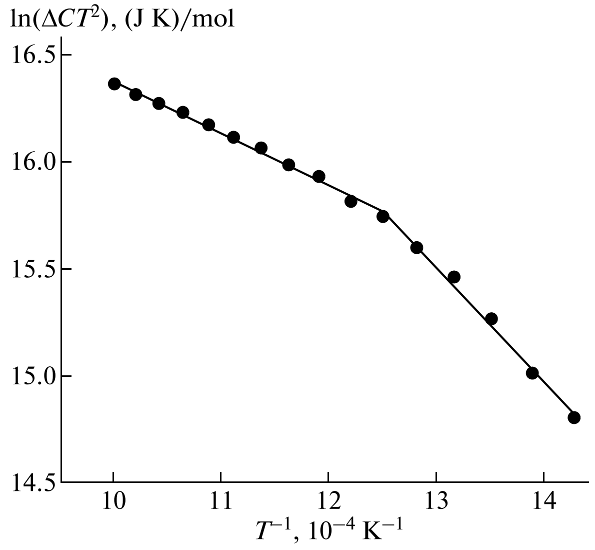

Fig. 3. Approximation of the excess heat capacity by Einstein's function at $T \ll \Theta_E$.

We analyze these results along the lines followed in [21], more specifically, assuming that the excess heat capacity within the temperature interval studied is described by the relation

$$\Delta C = R\left(\frac{\Theta_E}{T}\right)^2 \exp\left(-\frac{\Theta_E}{T}\right), \qquad (3)$$

where Θ_E is Einstein's characteristic temperature. Representing ΔC in ln(ΔCT^2)$-1/T$ coordinates yields a straight line with a kink at ~800 K, with the correlation coefficients 0.9939 and 0.9928 for the high- and low-temperature intervals, respectively (Fig. 3). Observation of contributions of the type of (3) suggests [21] that the vibrational spectrum of the compound under analysis has a localized optical mode, which forms in ordered systems if the masses of component atoms are essentially different. Note that this contribution, being excessive relative to the Dulong–Petit law, cannot be of the lattice origin.

4. CONCLUSIONS

The temperature dependence of the heat capacity of $Y_{2.9}Ho_{0.1}Al_5O_{12}$ has been studied. It has been established that the Debye model does not describe the experimental values of C_p throughout the temperature interval covered.

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