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THERMAL PROPERTIES

High-Temperature Heat Capacity of $CuGeO_3$ and $Cu_{0.9}Yb_{0.1}GeO_3$

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Abstract—Data on the heat capacity of $CuGeO_3$ and $Cu_{0.9}Yb_{0.1}GeO_3$ have been obtained in a wide temperature range. Their thermodynamic properties have been calculated from experimental data.

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1. INTRODUCTION

The very first measurements of the magnetic and resonance properties which revealed the low-temperature anomaly in magnetic susceptibility at $T_{SP} = 14$ K (the spin-Peierls (SP) transition) [1] propelled interest in the oxide compound $CuGeO_3$. A large number of publications address primarily investigation of its magnetic properties [2–6]. It was demonstrated that growth of $CuGeO_3$ single crystals produces crystals of green and blue colors due to different degrees of oxygen nonstoichiometry, which, in its turn, depends on the actual conditions of synthesis [2]. The former reveal oxygen deficiency δ transforming their chemical formula to $GuGeO_{3-\delta}$ [3]. The magnetic susceptibility was shown [2] to depend strongly on oxygen content in the sample both above and below T_{SP}. It is believed [3] that oxygen nonstoichiometry may cause a change of the effective valence of both Cu and Ge, as well as stimulate formation of cation vacancies. It was also suggested that substitution of copper by ions of other valence may become manifest not only as a mechanism underlying diamagnetic dilution but as variation of the degree of oxygen nonstoichiometry in a sample.

Despite such interest in $CuGeO_3$, its thermodynamic properties in the high-temperature domain have not, as far as we know, been studied. At the same time, to optimize the conditions of its fabrication, one has to conduct a thermodynamic study of the phases. Significantly, thermodynamic investigation of the conditions favoring synthesis of a substance becomes possible only if one has adequate information on its thermodynamic properties, which is often lacking. The goal of the present work was to investigate the high-temperature heat capacity of $CuGeO_3$ and $Cu_{0.9}Yb_{0.1}GeO_3$ and to derive their thermodynamic properties from these data.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

All measurements were performed on single crystals of blue color grown by the technology described elsewhere [2]. The technique employed in the experimental study of the effect of temperature on the heat capacity of the samples is similar to the one used by us earlier [7, 8]. The measurements of C_p were conducted in platinum crucibles with the STA 449 C Jupiter (NETZSCH) system.

The phase diagram of the $CuO–GeO_2$ system exhibits the presence of the $CuGeO_3$ compound revealing a smeared melting maximum at 1446 K, after which CuO transforms to Cu_2O [9]. The temperature interval covered (360–1030 K) was chosen in view of this factor, as well as on the basis of the differential thermal analysis performed with the STA 449 C Jupiter.

3. RESULTS AND DISCUSSION

Our calorimetric measurements show (Fig. 1) that within the temperature interval studied the values of C_p increase regularly, and that the $C_p(T)$ dependence has no extrema. The temperature dependence of the heat capacity obtained for $CuGeO_3$ can be fitted by the following relation (in units of J/mol K)

$$C_p = 107.24 + 12.10 \times 10^{-3} T - 17.18 \times 10^5 T^{-2}. \quad (1)$$

The well-known thermodynamic relations and equation (1) have been used to calculate the changes of

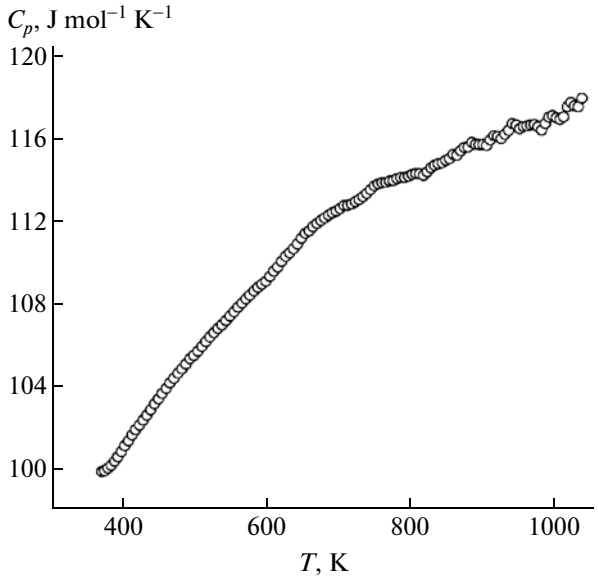

Fig. 1. Effect of temperature on the heat capacity of $CuGeO_3$.

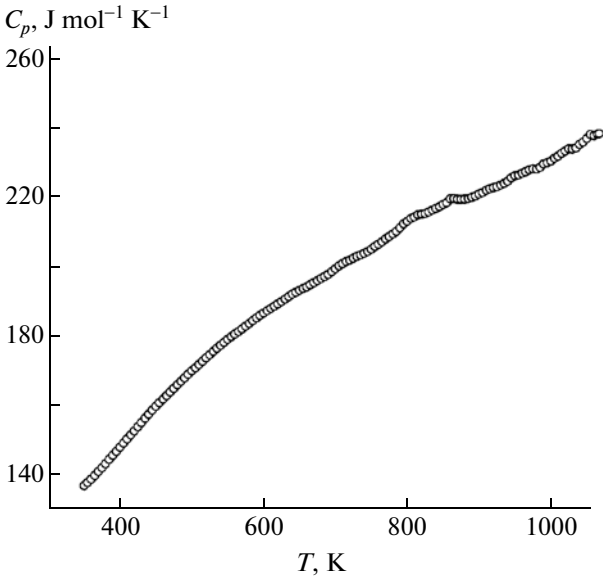

Fig. 2. Temperature dependence of the heat capacity of $Cu_{0.9}Yb_{0.1}GeO_3$.

the enthalpy $H_T^0 - H_{360}^0$ and entropy $S_T^0 - S_{360}^0$. The results are presented in Table 1.

It can be noted that, for all the temperatures studied, the heat capacity C_p does not exceed the classical Dulong–Petit limit $3R_s$, where R is the universal gas constant, and s is the number of atoms in the $CuGeO_3$ formula unit ($s = 5$).

Figure 2 displays graphically the temperature dependence of the heat capacity of $Cu_{0.9}Yb_{0.1}GeO_3$. In this case, just as for pure $CuGeO_3$, the $C_p(T)$ graph is a smooth function. Note the larger values of C_p for the doped crystal. Note that this difference is larger than that could be expected considering the contribution to the molar heat capacity deriving from the increase of the molar mass of the material under study. These data are fitted by the following equation (in units of J/mol K)

$$C_p = 151.12 + 87.30 \times 10^{-3}T - 55.35 \times 10^5 T^{-2}. \quad (2)$$

Doping $CuGeO_3$ with gallium (Ga^{3+}) is suggested [3] to drive two mechanisms mediating the magnetic properties of germanium cuprate, namely, diamagnetic dilution itself and variation of the degree of effective oxygen nonstoichiometry. In the latter case, doping with trivalent gallium ions increases the effective nonstoichiometry even if oxygen deficiency δ is left unchanged.

The influence of doping by various elements produced on the properties of $CuGeO_3$ was reported in a number of publications: Li, Ga [3], Co [6, 10, 11], Fe [12], Zn [13], Zn, Mg, Ni, Mn, Si [14], and Si, Mg, Al, Ni [15]. Most of the interest centered on substitution of Cu^{2+} with divalent ions. At the same time substitution of copper ions in $CuGeO_3$ with ions in valence states other than 2 attracted much less attention.

Assuming that doping of $CuGeO_3$ with trivalent ions of ytterbium acts on it in the way similar to that

Table 1. Heat capacity and thermodynamic functions of $CuGeO_3$

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}
360	98.34	–	–
400	101.34	3.995	10.52
440	103.69	8.095	20.30
480	105.59	12.28	29.40
520	107.17	16.53	37.92
560	108.54	20.85	45.91
600	109.73	25.21	53.44
640	110.79	29.62	60.56
680	111.75	34.07	67.30
720	112.64	38.55	73.72
760	113.46	43.07	79.83
800	114.23	47.62	85.67
840	115.00	52.20	91.26
880	115.66	56.81	96.62
920	116.34	61.45	101.78
960	116.99	66.11	106.72
1000	117.62	70.80	111.54
1030	118.08	74.33	115.02

Table 2. Heat capacity and thermodynamic functions of $Cu_{0.9}Yb_{0.1}GeO_3$

T, K	C_p, J mol^{-1} K^{-1}	$H_T^0 - H_{343}^0$, kJ mol^{-1}	$S_T^0 - S_{343}^0$, J mol^{-1} K^{-1}
343	134.01	–	–
350	136.49	0.947	2.733
400	151.44	8.163	21.98
450	163.07	16.04	40.52
500	172.63	24.44	58.21
550	180.84	33.28	75.05
600	188.12	42.50	91.11
650	194.76	52.08	106.43
700	200.93	61.97	121.09
750	206.75	72.17	135.15
800	212.31	82.64	148.68
850	217.66	93.39	161.71
900	222.86	104.4	174.3
950	227.92	115.8	186.5
1000	232.88	127.2	198.3
1050	237.76	139.0	209.8

produced by trivalent ions of gallium [3], the larger values of C_p for $Cu_{0.9}Yb_{0.1}GeO_3$ compared with $CuGeO_3$ could be attributed to the increase of oxygen nonstoichiometry. The latter suggestion is supported also by the data [16] indicating that violation of stoichiometry may result in a change of high-temperature heat capacity.

Relation (2) was used to calculate $H_T^0 - H_{343}^0$ and $S_T^0 - S_{343}^0$ for $Cu_{0.9}Yb_{0.1}GeO_3$. These values are listed in Table 2.

4. CONCLUSIONS

The high-temperature heat capacity of $CuGeO_3$ (360–1030 K) and of $Cu_{0.9}Yb_{0.1}GeO_3$ (343–1050 K) has been measured. The values of C_p obtained are linked with oxygen nonstoichiometry.

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