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High-Temperature Heat Capacity of Erbium Cuprate

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Data on the molar heat capacity of $Er_2Cu_2O_5$ (359 – 974 K) were obtained by differential scanning calorimetry. The $C_p = f(T)$ experimental data were used to determine thermodynamic properties of this compound.

Keywords: thermodynamic properties, ·erbium cuprate.

Высокотемпературная теплоемкость купрата эрбия

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Методом дифференциальной сканирующей калориметрии получены экспериментальные данные по молярной теплоемкости $Er_2Cu_2O_5$ (359–974 K). По экспериментальным данным $C_p = f(T)$ рассчитаны термодинамические свойства оксидного соединения.

Ключевые слова: термодинамические свойства, купрат эрбия.

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Introduction

For a long time interest in metal oxide compounds including $Er_2Cu_2O_5$ crystals does not weaken [1-5]. In spite of the attention to this compound, many of its features have not been studied. In particular it applies to the thermal properties. The heat capacity of $Er_2Cu_2O_5$ was investigated at temperatures 2–30 K [3]. The information on the standard Gibbs free energy of formation of this compound is given in [2]. The optimization of obtaining conditions for such compounds presupposes thermodynamic studies which are feasible with the thermodynamic databases.

The purpose of this work is to measure the high-temperature heat capacity and to calculate the thermodynamic properties of $Er_2Cu_2O_5$ using the data obtained.

Experimental

The $Er_2Cu_2O_5$ samples were prepared by a solid-phase synthesis technique. Taking into account peculiarities of CuO behavior at high temperatures, the weighed Er_2O_3 and CuO samples were previously ignited at 1173 K [6]. On homogenization and following pressing, the tablets were annealed in air at 1273 K during 25 h with 5 intermediate grindings and pressings. XRD-spectra of the samples were collected on X'Pert Pro (PANalytical, CuKα radiation). From the X-ray diffraction patterns, we found the lattice parameters by the full-profile analysis without referring to the structure. The obtained data is shown in Fig. 1. The synthesized samples had an orthorhombic structure (space group $Pna2_1$) with the lattice parameters a = 10.777(1) Å, b = 3.4711(4) Å, c = 12.443(1) Å. These values are consistent with the data of [7]: a = 10.7839(2) Å, b = 3.4745(1) Å, c = 12.4434(3) Å, and coincide completely with the data of [8].

The heat capacity C_p was measured in platinum crucibles with an STA 449 C Jupiter instrument (NETZSCH). The used technique was similar to that employed in [9, 10]. The temperature range examined (359 – 974 K) was chosen based on differential thermal analysis (DTA) data obtained with the STA 449 C Jupiter.

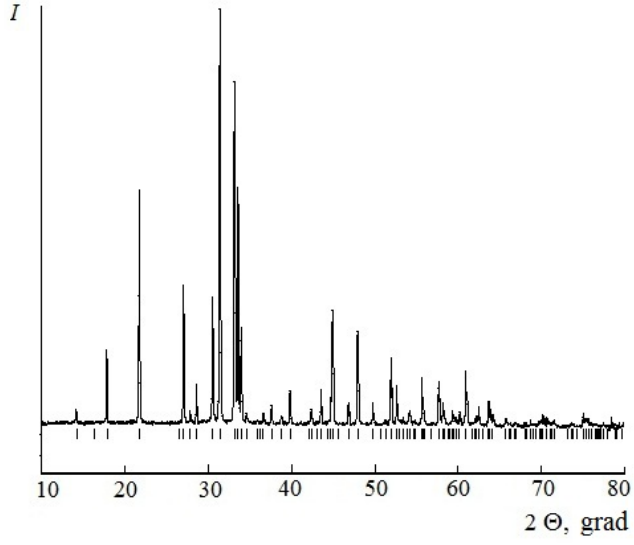

Fig. 1. X-ray diffraction pattern of $Er_2Cu_2O_5$ at 298 K

Results and discussion

The results of experiments on the measurements of the heat capacity of $Er_2Cu_2O_5$ are presented in Fig. 2. As follows from the graphs, C_p increases systematically with increasing temperature.

The $C_p = f(T)$ dependence was approximated by a Maier-Kelly-type equation:

$$C_p = a + b\cdot10^{-3} - c\cdot10^{5}T^{-2} = 200.50 + 34.50\cdot10^{-3}T - 7.38\cdot10^{5}T^{-2}. \quad (1)$$

This makes it possible to determine the enthalpy increment $(H_T^{\circ} - H_{359}^{\circ})$ and entropy change $(S_T^{\circ} - S_{359}^{\circ})$ using known thermodynamic relations. The results are presented in the Table 1.

At temperatures above 500 K, the heat capacity exceeds the classical Dulong-Petit limit $3Rs$, where R is the universal gas constant, and s is the number of atoms in the $Er_2Cu_2O_5$ formula unit ($s = 9$). Using the experimental data on C_p for $Er_2Cu_2O_5$ at low temperatures, we determined the Debye temperature. It was found to be 400 K.

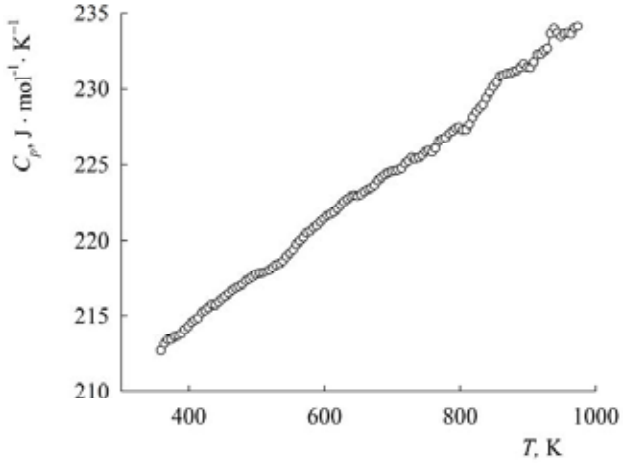

Fig. 2. Temperature dependences of the heat capacity of $Er_2Cu_2O_5$

Table 1. Thermodynamic properties of $Er_2Cu_2O_5$

T, K	C_p, J/(mole K)	$(H_T^{\circ} - H_{359}^{\circ})$, kJ/mole	$(S_T^{\circ} - S_{359}^{\circ})$, J/(mole K)
359	212.9	–	–
400	214.3	8.757	23.10
450	216.0	19.52	48.43
500	217.7	30.36	71.29
550	219.5	41.29	92.12
600	221.2	52.31	111.3
650	222.9	63.41	129.1
700	224.6	74.60	145.6
750	226.4	85.87	161.2
800	228.1	97.24	175.9
850	229.8	108.7	189.7
900	231.5	120.2	202.9
950	233.3	131.8	215.5

The obtained values of C_p cannot be compared with the results of other authors, since there is no such information in the literature. Nevertheless, taking into consideration a correlation between the oxide composition and their heat capacity [11], it can be noted that in the system Er_2O_3 – CuO the values of C_p^o (in units of J/(g·K)) increase in the series Er_2O_3 (0.28) – $Er_2Cu_2O_5$ (0.39) – CuO (0.53). The values of C_p^o for Er_2O_3 and CuO were taken from [12]. Such change of C_p^o in the Er_2O_3 – CuO system agrees with the atomic mass effect: the phonon frequencies must be lower in the case of the oxides with the high content of Er_2O_3.

Conclusion

The heat capacity of $Er_2Cu_2O_5$ has been studied first experimentally in the temperature range 359-974 K. It has been established that there is a correlation between the composition of the Er_2O_3 – CuO system and the specific heat capacity of the oxide compounds of this system.

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