High-Temperature Heat Capacity of Erbium Cuprate

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Data on the molar heat capacity of Er$_2$Cu$_2$O$_5$ (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.
Introduction

For a long time interest in metal oxide compounds including Er$_2$Cu$_2$O$_5$ 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$_2$Cu$_2$O$_5$ 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$_2$Cu$_2$O$_5$ using the data obtained.

Experimental

The Er$_2$Cu$_2$O$_5$ samples were prepared by a solid-phase synthesis technique. Taking into account peculiarities of CuO behavior at high temperatures, the weighed Er$_2$O$_3$ 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, CuK$_\alpha$ 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$_2$Cu$_2$O$_5$ at 298 K
Results and discussion

The results of experiments on the measurements of the heat capacity of $\text{Er}_2\text{Cu}_2\text{O}_5$ 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:

$$C_p = a + b \cdot 10^{-3} - c \cdot 10^5 T^2 = 200.50 + 34.50 \cdot 10^{-3} T - 7.38 \cdot 10^5 T^{-2}. \quad (1)$$

This makes it possible to determine the enthalpy increment ($H^o_T - H^o_{359}$) and entropy change ($S^o_T - S^o_{359}$) 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 $\text{Er}_2\text{Cu}_2\text{O}_5$ formula unit ($s = 9$). Using the experimental data on $C_p$ for $\text{Er}_2\text{Cu}_2\text{O}_5$ at low temperatures, we determined the Debye temperature. It was found to be 400 K.

Fig. 2. Temperature dependences of the heat capacity of $\text{Er}_2\text{Cu}_2\text{O}_5$

Table 1. Thermodynamic properties of $\text{Er}_2\text{Cu}_2\text{O}_5$

<table>
<thead>
<tr>
<th>$T$, K</th>
<th>$C_p$, J/(mole K)</th>
<th>($H^o_T - H^o_{359}$), kJ/mole</th>
<th>($S^o_T - S^o_{359}$), J/(mole K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>359</td>
<td>212.9</td>
<td>8.757</td>
<td>23.10</td>
</tr>
<tr>
<td>400</td>
<td>214.3</td>
<td>19.52</td>
<td>48.43</td>
</tr>
<tr>
<td>450</td>
<td>216.0</td>
<td>30.36</td>
<td>71.29</td>
</tr>
<tr>
<td>500</td>
<td>217.7</td>
<td>41.29</td>
<td>92.12</td>
</tr>
<tr>
<td>550</td>
<td>219.5</td>
<td>52.31</td>
<td>111.3</td>
</tr>
<tr>
<td>600</td>
<td>221.2</td>
<td>63.41</td>
<td>129.1</td>
</tr>
<tr>
<td>650</td>
<td>222.9</td>
<td>74.60</td>
<td>145.6</td>
</tr>
<tr>
<td>700</td>
<td>224.6</td>
<td>85.87</td>
<td>161.2</td>
</tr>
<tr>
<td>750</td>
<td>226.4</td>
<td>97.24</td>
<td>175.9</td>
</tr>
<tr>
<td>800</td>
<td>228.1</td>
<td>108.7</td>
<td>189.7</td>
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<tr>
<td>850</td>
<td>229.8</td>
<td>120.2</td>
<td>202.9</td>
</tr>
<tr>
<td>900</td>
<td>231.5</td>
<td>131.8</td>
<td>215.5</td>
</tr>
</tbody>
</table>
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$_2$O$_3$ – CuO the values of $C_p^o$ (in units of J/(g·K)) increase in the series Er$_2$O$_3$ (0.28) – Er$_2$Cu$_2$O$_5$ (0.39) – CuO (0.53). The values of $C_p^o$ for Er$_2$O$_3$ and CuO were taken from [12]. Such change of $C_p^o$ in the Er$_2$O$_3$ – 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$_2$O$_3$.

**Conclusion**

The heat capacity of Er$_2$Cu$_2$O$_5$ 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$_2$O$_3$ – CuO system and the specific heat capacity of the oxide compounds of this system.

**References**

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