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PHYSICS

High-Temperature Specific Heat of $Cu_5Bi_2B_4O_{14}$

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Abstract—$Cu_5Bi_2B_4O_{14}$ single crystals are grown by spontaneous crystallization from a melt of a CuO, Bi_2O_3, and B_2O_3 mixture. The specific heat of the crystals in the temperature range 396–633 K is measured by differential scanning calorimetry. Using the experimental data, the thermodynamic properties of the $Cu_5Bi_2B_4O_{14}$ solid compound are calculated.

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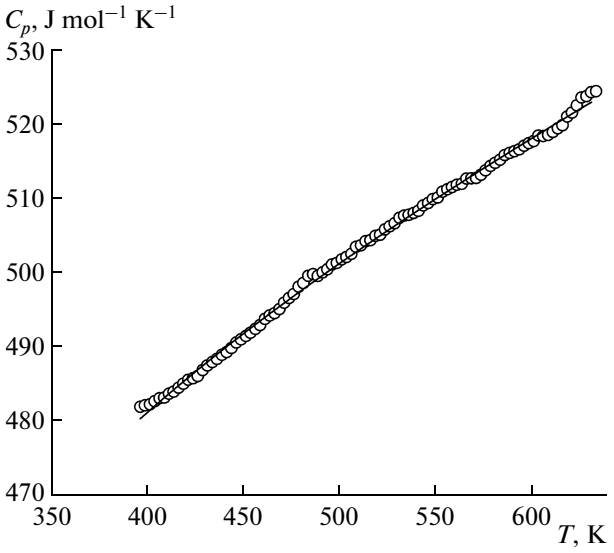
Oxocuprates have been intensively investigated since the discovery of high-temperature superconductivity. In the study of the ternary system $CuO–Bi_2O_3–B_2O_3$, two oxide compounds, $2Bi_2O_3 \cdot CuO \cdot B_2O_3$ and $Bi_2O_3 \cdot 2CuO \cdot B_2O_3$ crystallizing in rhombic syngony were found [1]. The authors of study [2] obtained the new compound $Cu_5Bi_2B_4O_{14}$. The crystal of this compound is characterized by triclinic symmetry with the $P\bar{1}$ space group. Its structural, magnetic, and resonance properties were studied in [2, 3]. Nevertheless, there are no literature data on the thermodynamic properties of $Cu_5Bi_2B_4O_{14}$, although these characteristics allow optimizing the synthesis conditions and providing recommendations on the use of the materials. One should take into account that the thermodynamic study of the synthesis of complex oxide compounds can be carried out only with the thermodynamic data available.

The aim of this study was to investigate experimentally the high-temperature specific heat of $Cu_5Bi_2B_4O_{14}$ and to determine the thermodynamic functions of this compound from the obtained data.

To measure specific heat C_p, we used single crystals grown by spontaneous crystallization from the melt of the CuO, Bi_2O_3, and B_2O_3 mixture. The melt composition and crystal growth technique were described in detail in [2]. The obtained samples were controlled on an X'Pert Pro X-ray analyzer (Panalytical, Netherlands). The unit cell parameters of $Cu_5Bi_2B_4O_{14}$ are $a = 10.1497(3)$ Å, $b = 9.3986(3)$ Å, and $c = 3.4652(1)$ Å, $\alpha = 105.442(2)°$, $\beta = 97.439(2)°$, and $\gamma = 107.776(2)°$. These values are sufficiently close to the values reported in [2]: $a = 10.132$, $b = 9.385$, and $c = 3.458$ Å and $\alpha = 105.443°$, $\beta = 97.405°$, and $\gamma = 107.784°$. It should be noted, however, that the small discrepancies may be related to the following phenomenon. The copper contents in $Cu_5Bi_2B_4O_{14}$ single crystals grown in one crucible can vary within 4.89–5.0. For experiments, we selected the crystals with the copper content close to stoichiometric.



Temperature dependence of specific heat of $Cu_5Bi_2B_4O_{14}$.

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Smoothed values of molar specific heat and thermodynamic functions for $Cu_5Bi_2B_4O_{14}$

T, K	C_p, J mol^{-1} K^{-1}	$H_T^0 - H_{396}^0$, kJ mol^{-1}	$S_T^0 - S_{396}^0$, J mol^{-1} K^{-1}
396	480.2	–	–
400	481.1	1.923	4.831
450	491.7	26.25	62.13
500	501.2	51.08	114.4
550	509.8	76.35	162.6
600	518.0	102.1	207.3
630	522.7	117.7	232.7

The specific heat was measured in platinum crucibles on an STA 449 C Jupiter (NETZCSH) device. The measuring technique was described in detail in [4].

The temperature dependence of C_p of the $Cu_5Bi_2B_4O_{14}$ compound is shown in the figure. It was established that in the temperature range 396–633 K, C_p regularly grows and there are no extrema on the dependence $C_p = f(T)$. The investigated temperature range was chosen in accordance with the differential thermal analysis made. The obtained values of $C_p = f(T)$ can be presented in the form

$$C_p = 448.72 + 129.9 \times 10^{-3} T - 31.7 \times 10^5 T^{-2}. \quad (1)$$

This equation allows us to calculate the enthalpy and entropy variation $H_T^0 - H_{396}^0$ and $S_T^0 - S_{396}^0$ by the known thermodynamic equations. The obtained data are given in the table.

The obtained values of C_p for $Cu_5Bi_2B_4O_{14}$ cannot be compared with other data because of the lack of the latter. For this compound, the normalized molar specific heat at room temperature determined from the relation $C_p^* = \frac{C_p}{s}$, where s is the number of atoms in the $Cu_5Bi_2B_4O_{14}$ formula unit ($s = 25$), is $C_p^* = 18.09$ J mol^{-1} K^{-1}. This is close to the values for other complex compounds: $C_p^* = 17.61$ J mol^{-1} K^{-1} for $Li_2Ge_7O_{15}$ and $C_p^* = 17.91$ J mol^{-1} K^{-1} for $NaLiGe_4O_9$ [5]. Thus, we may conclude that the obtained values of C_p for $Cu_5Bi_2B_4O_{14}$ are reliable.

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