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Enthalpy of Formation of $Cu_2ZnSnSe_4$ from Its Constituent Elements

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Abstract—The standard enthalpy of formation of the $Cu_2ZnSnSe_4$ compound has been determined by measuring the heat of its formation from its constituent elements according to the reaction scheme $2Cu + Zn + Sn + 4Se \rightarrow Cu_2ZnSnSe_4$ in a calorimeter: $\Delta_f H^0_{298.15\ K}(Cu_2ZnSnSe_4) = -392.00 \pm 2.56$ kJ/mol.

Keywords: $Cu_2ZnSnSe_4$, enthalpy, thermochemistry, calorimetry, photovoltaics

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INTRODUCTION

The quaternary compound $Cu_2ZnSnSe_4$ is a selenium analog of the natural mineral kesterite, Cu_2ZnSnS_4. According to previous work [1], kesterite and Se-kesterite form a continuous series of solid solutions. In addition, there was research concerned with the Fe–Zn and S–Se distributions between sphalerite and kesterite solid solutions [1]. $Cu_2ZnSnSe_4$ is thought to be a promising direct-gap semiconductor material for producing photon-absorbing layers in thin-film solar cells [2–5]. It has a large absorption coefficient in the visible range ($>10^4$ cm^{-1}), is *p*-type, and offers the ultimate photoelectric conversion efficiency: 32.2%.

Thin-film materials usually contain expensive components: indium, gallium, tellurium, and (toxic) cadmium. $Cu_2ZnSnSe_4$ consists of widespread, less toxic components, which makes the production of this material cheaper and facilitates the disposal of used solar cells based on them.

Compared to expensive and time-consuming vacuum methods, selenizing a precursor produced by electrochemical deposition appears a more attractive method [6]. It allows one to produce thin films or precursors in wide ranges of sulfur and selenium concentrations and utilize various types of substrates, including roll substrates.

The Cu_2ZnSnS_4 compound (kesterite), its structural analog $Cu_2ZnSnSe_4$, and their solid solutions can find practical application in the fabrication of broadband photoconverters, near-IR photodetectors, and other opto- and microelectronic devices. However, there are some difficulties in realizing the potentialities of these materials. The lack of reliable information about the methods for the preparation of these compounds, their physicochemical properties, and the effect of the preparation process on their physical properties is one of the main factors limiting technological applications of these materials [7]. Only theoretical calculations of the standard enthalpy of formation of $Cu_2ZnSnSe_4$ are available in the literature [8].

In this paper, we report a calorimetric determination of the standard enthalpy of formation of $Cu_2ZnSnSe_4$ from its constituent elements.

EXPERIMENTAL

The standard enthalpy of formation of $Cu_2ZnSnSe_4$ was assessed by comparing the heat transferred to a sample in the form of electrical energy to ensure the formation of $Cu_2ZnSnSe_4$ from its constituent elements and the heat obtained by cooling the system, including the heat released (absorbed) during the reaction. As shown in preliminary studies, $Cu_2ZnSnSe_4$ can be synthesized by reacting its constituent elements in evacuated silica ampules at a temperature of ~750°C for 6–7 min:

$$2Cu + Zn + Sn + 4Se \rightarrow Cu_2ZnSnSe_4.$$

The compound was synthesized from high-purity and extrapure elements: extrapure-grade copper (99.999%, electrolytic Cu in the form of a plate), zinc shot (99.9999%, Alfa Aesar), extrapure-grade tin (99.999%, bar, manufactured at the Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Sciences), and selenium shot (99.999%, Alfa Aesar). The starting chemicals

† Deceased.

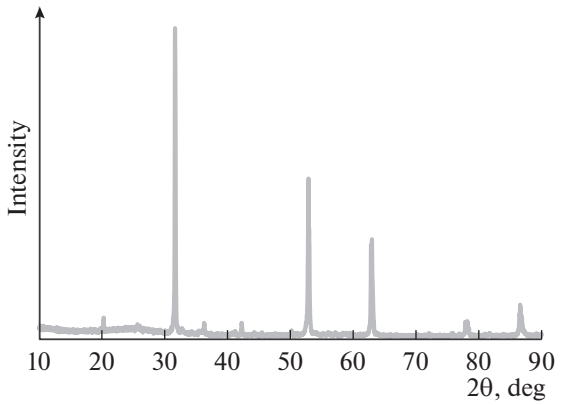

Fig. 1. X-ray diffraction pattern of selenium kesterite ($Cu_2ZnSnSe_4$) after the experiment (run 3 in Table 1).

were weighed out on a Sartorius ED224-RCE analytical balance (0.1 mg divisions). The atomic masses of the elements were borrowed from Wieser [9].

Calorimetric data were obtained using a high-temperature vacuum calorimeter made and modified at the Laboratory of Thermodynamics of Minerals, Institute of Experimental Mineralogy, Russian Academy of Sciences (laboratory identification number VBC-3) and described previously [10, 11]. To control the operation of the calorimeter and visualize and analyze data, we used a specially designed interface and application software.

An ampule containing an appropriate elemental mixture was pumped down to a residual pressure of 10^{-2} Pa, sealed off using an oxygen torch flame, and placed in a resistance furnace inside a massive copper block, which was then filled with argon to a pressure of 10^6 Pa. The vacuum unit (isothermal shell) in which the massive block was placed was pumped down to a residual pressure of 10^3 Pa, which was then maintained constant throughout the experiment. The temperature of the isothermal shell was maintained constant at 298.15 ± 0.02 K by a 300-L water thermostat equipped with a propeller stirrer. The preset temperature in the thermostat was maintained by a purpose-designed temperature controller.

Electrical energy was measured with an accuracy of 0.02%. During heating in our experiments, the temperature was monitored with a resistance thermometer consisting of nine miniature platinum temperature sensors evenly distributed over the surface of the copper block. The total resistance of the thermometer was 988 Ω at 298.15 K. The calorimeter was calibrated using electrical energy with the ampule in the resistance furnace, in which the reaction under investigation had already reached completion under conditions (heating time, electrical energy, and initial temperature) identical to the experimental conditions.

In all of our experiments, the heating time was set automatically (360 s), as was the total time of each experiment (50 min). The heat value was determined with an accuracy of 0.05%. Second heating yielded no additional heat effect, indicating that the reaction reached completion in the first heating cycle.

X-ray diffraction characterization (Bruker D2 PHASER diffractometer, $CoK_{\alpha 1}$ radiation, λ = 1.78897 Å) showed that, after the calorimetric experiments, the only phase present was $Cu_2ZnSnSe_4$ (sp. gr. $I\bar{4}2m$). Its lattice parameters were a = 5.682 Å, c = 11.342 Å, c/a = 1.996, and V = 366.1761 Å^3. Its X-ray diffraction pattern obtained in this study (Fig. 1) is essentially identical to that reported by Matsushita et al. [12] (JCPDS card no. 52-0868, a = 5.693 Å, c = 11.333 Å). The Miller indices of observed reflections for calculating lattice parameters were taken from that report.

Table 1. Enthalpy of formation of $Cu_2ZnSnSe_4$ from its constituent elements (molecular mass, 627.0647 g/mol [9])

Run	Sample weight, g	$\Delta R + \sigma$, Ω	Heat released in the experiment, J			$-\Delta_f H^0_{298.15\ K}$, kJ/mol
			total	on the heater	in the reaction	
1	2.0000	11.8503	68910.7	67650.1	1260.6	395.24
2	1.9896	11.8413	68858.6	67622.1	1236.5	389.71
3	1.9967	11.8264	68992.8	67737.5	1256.3	394.23
4	2.0014	11.8157	68931.6	67699.2	1232.4	386.13
5	2.0000	11.8139	68921.1	67671.1	1250.0	391.92
6	1.8023	11.7934	68801.5	67668.4	1133.1	394.23
7	2.0007	11.8385	68958.1	67711.1	1247.0	390.84
8	1.8017	11.8055	68765.8	67636.6	1129.2	393.01
Average						391.91 ± 2.34

$\Delta R + \sigma$ is the change in the reading of the resistance thermometer with correction for heat exchange. The heat value of the calorimeter was W = 5815.1 ± 2.0 J/Ω in runs 1 and 2, W = 5833.9 ± 2.0 J/Ω in runs 3–6, and W = 5824.9 ± 2.0 J/Ω in runs 7–9.

RESULTS AND DISCUSSION

Tsuyoshi et al. [8] presented theoretical calculation of the enthalpy of $Cu_2ZnSnSe_4$ with the use of experimentally determined enthalpies of Cu_2Se, ZnSe, and $SnSe_2$ (they did not specify the source of the data for the binary selenides). As a result, they obtained $\Delta_f H^0(Cu_2ZnSnSe_4) = -312.2$ kJ/mol.

In this study, the enthalpy of formation of this compound from its constituent elements was determined experimentally. The experimental calorimetry data for $Cu_2ZnSnSe_4$ are summarized in Table 1. The root mean square deviation in our measurements was evaluated for a 95% confidence interval [13].

As a result, the standard enthalpy (p = 105 Pa) of selenium kesterite (CZTSe) was determined to be

$$\Delta_f H^0_{298.15K}(Cu_2ZnSnSe_4) = -(391.91 \pm 2.34)\ \text{kJ/mol}.$$

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