

Standard Enthalpy of the Formation of Selenium Stannite $\text{Cu}_2\text{FeSnSe}_4$

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Abstract—The standard enthalpy of formation of selenium stannite $\text{Cu}_2\text{FeSnSe}_4$ (CFTSe) was determined calorimetrically for the first time. This compound does not occur in nature, but is a promising functional material (direct-band semiconductor) and utilized in photovoltaics for fabricating the solar cells alternatively to silicon ones. The standard enthalpy of formation of $\text{Cu}_2\text{FeSnSe}_4$ was obtained by the measurement of heat of its formation from elements in calorimeter according to reaction $2\text{Cu} + \text{Fe} + \text{Sn} + 4\text{Se} \rightarrow \text{Cu}_2\text{FeSnSe}_4$. As a result, the standard enthalpy of formation of $\text{Cu}_2\text{FeSnSe}_4$ was $\Delta_f H^0(298.15 \text{ K})_{\text{cr}} = -(253.94 \pm 3.91) \text{ kJ/mol}$.

Keywords: $\text{Cu}_2\text{FeSnSe}_4$, CFTSe, enthalpy, calorimetric measurements, photovoltaics

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INTRODUCTION

Four-component compound $\text{Cu}_2\text{FeSnSe}_4$ is a structural analogue of stannite ($\text{Cu}_2\text{FeSnS}_4$). Stannite occurs in minor amounts at all tin deposits, usually in intergrowths with Fe-sphalerite. This steady assemblage represents two coexisting solid solutions: stannite–kesterite $\text{Cu}_2(\text{Fe,Zn})\text{SnS}_4$ and sphalerite $(\text{Fe,Zn})\text{S}$ (Osadchii and Sorokin, 1983, 1989). In nature, practically all stannite-group minerals contain Se admixture.

In recent years, stannite-group minerals are intensely studied by physicists and chemists (Agawane et al., 2014; Hall et al., 1978; Khadka et al., 2014; Matsushita et al., 2000) as promising material for photovoltaic converters. In spite of the lower efficiency, they have some advantages relative to silicon photovoltaics, that is, the opportunity of fabricating the flexible (roll) solar panels by sputtering, painting (nanopaints), electrolytic precipitating, and other methods. In photovoltaics, this compound is commonly abbreviated by the first English letters of constituent elements. For instance, kesterite is designated as CZTS (Copper, Zinc, Tin, Sulfur).

Selenium stannite, as selenium kesterite $\text{Cu}_2\text{ZnSnSe}_4$, is regarded to be a promising direct-band semiconductor material for application as photon-absorbing layers in thin-film photovoltaic devices (Infante et al., 1997; Meng et al., 2015). Similarly to $\text{Cu}_2\text{ZnSnSe}_4$, $\text{Cu}_2\text{FeSnSe}_4$ is characterized by the high absorption

coefficient within a visible range ($>10^4 \text{ cm}^{-1}$), *p*-type conductivity, as well as maximum conversion efficiency of 32.2%. A method of electrochemical precipitation of precursors and their subsequent selenization was developed (Meng et al., 2014; Stanchik et al., 2018), which provides obtaining thin films or precursors with different combination of metals. However, few thermodynamic data on stannite-group minerals complicates obtaining end product.

This work is a continuation of a series of studies aimed at determining the standard enthalpy of formation of synthetic stannite-group minerals. Data on the standard enthalpy of formation were recently published for stannite (Stolyarova et al., 2018; Stolyarova et al., 2018), kesterite (Stolyarova et al., 2019a, 2019b), as well as selenium analogue of kesterite $\text{Cu}_2\text{ZnSnSe}_4$ (Stolyarova et al., 2019).

EXPERIMENTAL

Reagents

$\text{Cu}_2\text{FeSnSe}_4$ was synthesized in the calorimeter from analytical grade pure elements: electrolytic copper (99.999%) as chips cut from a plate; carbonyl iron (99.99%); tin (99.999%) cut as chips from a rod; and selenium (99.999%) as a shot. The elements were weighed on a Sartorius ED224-RCE analytical balance with an error of 10^{-1} mg . Atomic masses of the elements were taken from (Wieser, 2006). The elements are devoid of dust-like particles and did not

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leave residuals on funnel during loading in capsule. Control weighing of loaded capsules showed similar results.

Setup and Operation of Calorimeter

Calorimetric measurements were carried out using a high-temperature vacuum-blocking calorimeter manufactured at the Laboratory of Thermodynamics of Minerals of the Institute of Experimental Mineralogy of the Russian Academy of Sciences and described in (Vasil'ev and Soboleva, 1962; Fleisher and Stolyarova, 1978). The calorimeter was essentially modified at the Laboratory of Electrochemistry, Thermodynamics, and Physics of Minerals. The measurements were conducted using an automated on-line device consisting of a specially developed measurement block and software module.

Capsule with a mixture of precursors was degassed up to a residual pressure of 10^{-2} Pa, welded in a flame of oxygen burner, and loaded in the resistance furnace within a massive copper block (bomb, 64 kg in weight) of cylindrical shape, which then was welded, evacuated, and filled with argon up to a pressure of 10^6 Pa. Filling with argon is required to improve heat transfer and to provide even temperature distribution over the entire volume of the massive copper block. The vacuum block (isothermal shell) into which the massive block was placed was evacuated to 1.3 Pa, and this pressure was maintained throughout the whole experiment. The temperature of the isothermal shell (298.15 ± 0.02) K was maintained in a water thermostat 300 L in volume. Temperature on a massive block during experiment was measured by the resistance temperature detector consisting of nine miniature Pt temperature detectors distributed evenly over the massive block. The total resistance was 988 Ohm at 298.15 K. The measurements were carried out using a four-wire scheme.

The heating time or the main period (power supply on the resistance heater) in all experimental runs was recorded automatically (600 s). The device was switched on and off with an electron key, and the whole experiment lasted 60 min. Preliminary studies established that $\text{Cu}_2\text{FeSnSe}_4$ is synthesized from elements ($2\text{Cu} + \text{Fe} + \text{Sn} + 4\text{Se} \rightarrow \text{Cu}_2\text{FeSnSe}_4$) in evacuated capsules made up of quartz glass at ~ 1023 K for 10 minutes.

Determination of the Correction for Heat Exchange

Voltage and current on the heater were determined with a frequency of 1 kHz. The measurements of voltage ($U(t)$) and current ($I(t)$) were accompanied by the calculation of heat energy (Q_h) released by heater:

$Q_h(\text{J}) = \int_0^{t_n} I(t)U(t) dt$, where the upper integration limit (t_n) is the time of heating, and the lower integra-

tion limit is the beginning of counting ($t_0 = 0$). The rate of the change of resistance temperature detector is caused by the heat exchange and proportional to the temperature difference between thermostat and calorimetric block

$$V_t = k(R_t - R_k), \quad (1)$$

where V_t is the change in the resistance temperature detector; R_t is the temperature detector resistance uninterruptedly measured with a frequency of 1 Hz; k is the proportionality coefficient between value of temperature trend and R_k ; R_k is the detector resistance at which heat exchange equals zero; R_t and V_t are instant values of resistance and the rate of resistance change at the time moment t , while k and R_k are unknown.

The rate (V_t) is determined only at the beginning and end of the experiment; in other cases, the rate is determined from equation (1). Then, the system of two linear equations is solved: $V_0 = k(R_0 - R_k)$ and $V_f = k(R_f - R_k)$, where R_0 and V_0 are the resistance and rate at the beginning of the experiment, while R_f and V_f are the resistance and rate at the end of experiment, respectively. As a result, we obtain: $k = (V_f - V_0)/(R_f - R_0)$ and $R_k = R_0 - V_0/k$. The heater-cased change in the resistance is determined from the measured total difference in resistances ($\Delta R = R_f - R_0$) and correction for heat exchange (δ , Ohm). The value of V_t is determined from equation (1) using measured R_t . Correction for heat exchange for dt is $dR(t) = -V(t)dt$. During experiment ($t_f - t_0$), the correction for heat exchange is determined as follows:

$$\begin{aligned} \delta &= -\int_{t_0}^{t_f} V(t) dt = -\int_{t_0}^{t_f} k[R_t - R_k] dt \\ &= -k \left[\int_{t_0}^{t_f} R_t dt - \int_{t_0}^{t_f} R_k dt \right], \\ \delta &= -k \left[\int_{t_0}^{t_f} R_t dt - R_k(t_f - t_0) \right]. \end{aligned}$$

Thus, the heat value of calorimeter (W) is determined by the heater-induced resistance change equal $\Delta R + \delta$. The heat value of calorimeter is calculated from equation:

$$W (\text{J Ohm}^{-1}) = \left[\int_{t_0}^{t_n} I(t)U(t) dt \right] / (\Delta R + \delta).$$

RESULTS AND DISCUSSION

The primary results of calorimetric measurements are given in Table 1. The total amount of released heat was calculated from formula: $Q_{\text{tot}} = W(\Delta R + \delta)$. The amount of heat released during reaction is determined as $Q_{\text{react}} = Q_{\text{tot}} - Q_{\text{heat}}$. Mean square error cal-

Table 1. Enthalpy of formation of $\text{Cu}_2\text{FeSnSe}_4$ from elements (molecular mass 617.487 g/mol)

Run no.	Amount of material, g	$\Delta R + \delta$, Ohm*	Heat released in experiment, J			$-\Delta_f H_{298.15}^0$, kJ/mol
			total	on heater	in reaction	
1	1.7000	11.6502	68039.5	67352.8	689.0	249.43
2	1.5000	11.6438	68002.1	67384.9	617.2	254.08
3	1.5009	11.6557	68071.6	67436.2	635.4	261.42
4	1.7000	11.7260	68389.3	67683.9	705.4	256.23
5	1.8000	11.7297	68410.0	67684.4	725.6	248.92
6	2.1000	11.7612	68545.4	67681.1	864.3	254.15
7	2.0000	11.7463	68458.6	67636.8	821.8	253.73
Average						253.94 ± 3.88

(*) $\Delta R + \delta$ is the change of the measurement by the resistance thermometer corrected for heat exchange. The heat value of the calorimeter was $W = (5840.2 \pm 2.0)$ J/Ohm in experimental runs 1–3; $W = (5832.2 \pm 2.0)$ J/Ohm in runs 4 and 5; and $W = (5828.1 \pm 2.0)$ J/Ohm in runs 6–7.

culated for 95% confidence interval (Nalimov, 1960) is ± 3.88 kJ/mol.

X-ray phase analysis (Bruker D2 PHASER diffractometer, $\text{CoK}\alpha_1$ radiation, $\lambda = 1.78897$ Å) of products of calorimetric runs confirmed that they contain only given compound $\text{Cu}_2\text{FeSnSe}_4$ (space group I-42m). Obtained X-ray pattern practically completely coincides with that obtained in (Quintero et al., 1999), card 00-052-0998. The unit cell parameters are $a = 5.73$ Å, $c = 11.24$ Å, $c/a = 1.962$; the unit cell volume is 369.042 Å³. These parameters were calculated using reflection indices from (Quintero et al., 1999).

Additional errors arise from the deviation of experimental parameters from accepted standard conditions. In particular, it was established that the final temperature of sample exceeds standard temperature of 298.15 K by approximately 1 K. This deviation leads to error exceeding no 30 J/mol.

The pressure difference between the evacuated capsule and standard pressure is 10^4 Pa. For solid-state reactions, the correction for pressure is negligible and can be neglected.

With allowance for the above mentioned corrections incorporated in the error of final result, the standard enthalpy of formation of selenium stannite $\text{Cu}_2\text{FeSnSe}_4$ is:

$$\Delta_f H^0(298.15 \text{ K}) = -(253.94 \pm 3.91) \text{ kJ/mol.}$$

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REFERENCES

- G. L. Agawane, S. W. Shin, S. A. Vanalakar, A. V. Moholkar, and J. H. Kim, "Next generation promising $\text{Cu}_2(\text{Zn}_x\text{Fe}_{1-x})\text{SnS}_4$ photovoltaic absorber material prepared by pulsed laser deposition technique," *Mater. Lett.*, **137**, 147–149 (2014).
- L. L. Fleisher and T. A. Stolyarova, Automation of measurement of electric energy of high-temperature calorimetric apparatus, *Izmerit. Tekhn.*, No. 2, 60–61 (1978).
- S. R. Hall, J. T. Szymanski, and J. M. Stewart, "Kesterite, $\text{Cu}_2(\text{Zn,Fe})\text{SnS}_{<4}$, and stannite, $\text{Cu}_2(\text{Fe,Zn})\text{SnS}_{<4}$, structurally similar but distinct minerals," *Can. Mineral.* **16**, 131–137 (1978).
- E. R. Infante, J. M. Delgado, and S. A. Lopez Rivera, "Synthesis and crystal structure of $\text{Cu}_2\text{FeSnSe}_4$, a 12 II IV VI4 semiconductor," *Mater. Lett.* **33** (1–2), 67–70 (1997).
- D. B. Khadka and J. H. Kim, "Structural transition and band gap tuning of $\text{Cu}_2(\text{Zn,Fe})\text{SnS}_4$ chalcogenide for photovoltaic application," *J. Phys. Chem.* **118** (26), 14227–14237 (2014).
- H. Matsushita, T. Maeda, A. Katsui, and T. Takizawa, "Thermal analysis and synthesis from the melts of Cu-based quaternary compounds Cu–III–IV–VI₄ and Cu_2 –II–IV–VI₄ (II = Zn, Cd; III = Ga, In; IV = Ge, Sn; VI = Se)," *J. Cryst. Growth* **208**, 416–422 (2000).
- X. Meng, H. Cao, H. Deng, W. Zhou, J. Tao, L. Sun, F. Yue, P. Yang, and J. Chu, "Synthesis and characterization of Cu-based selenide photovoltaic materials: $\text{Cu}_2\text{FeSnSe}_4$ and $\text{Cu}(\text{In,Al})\text{Se}_2$," *J. Alloys Compd.* **644**, 354–362 (2015).
- X. Meng, H. Deng, J. He, L. Zhu, L. Sun, P. Yang, and J. Chu, "Synthesis of $\text{Cu}_2\text{FeSnSe}_4$ thin film by selenization of RF magnetron sputtered precursor," *Mater. Lett.* **117**, 1–3 (2014).
- V. V. Nalimov, *Application of Mathematical Statistics for Analysis of Substance* (Nauka, Moscow, 1960) [in Russian].
- E. G. Osadchii and V. I. Sorokin, *Stannite-Bearing Sulfide Systems* (Nauka, Moscow, 1989) [in Russian].

- M. Quintero, A. Baretto, P. Grime, R. Tovar, E. Quintero, G. Sanchez Porras, J. Ruiz, J. C. Wooley, G. Lamarche, and A.-M. Lamarche, "Crystallographic properties of $\text{I}_2\text{-Fe-IV-Vi}_4$ magnetic semiconductor compounds," *Matter. Res. Bull.*, **34** (14–15), 2263–2270 (1999).
- V. I. Sorokin and E. G. Osadchii, *Thermodynamics of sphalerite and stannite solid solutions, Experimental Studies of Endogenous Ore Formation* (Moscow, 1983), pp. 167–180 [in Russian].
- A. V. Stanchik, V. F. Gremenok, S. A. Bashkirov, M. S. Tivanov, R. L. Yushkenas, G. F. Novikov, R. Geraitis, and A. M. Saad, "Microtexture and Raman spectroscopy of thin films of $\text{Cu}_2\text{ZnSnSe}_4$ precipitated on elastic metallic base," *Phys. Tekhn. Poluprovodn.*, **52** (2), 229–234 (2018).
- T. A. Stolyarova, A. V. Baranov, and E. G. Osadchii, "Calorimetric determination of the standard enthalpy of formation of stannite, $\text{Cu}_2\text{FeSnSe}_4$," *Geochem. Int.* **56** (1), 75–77 (2018).
- T. A. Stolyarova, E. G. Osadchii, and A. V. Baranov, "Standard enthalpy of kesterite ($\text{Cu}_2\text{ZnSnSe}_4$) formation," *Geochem. Int.* **57** (1), pp. 109–112 (2019).
- T. A. Stolyarova, E. A. Brichkina, A. V. Baranov, and E. G. Osadchii, "Enthalpy of $\text{Cu}_2\text{ZnSnSe}_4$ formation from elements," *Inorg. Mater.* (in press).
- Ya. V. Vasil'ev and M. S. Soboleva, "Calorimeter for determination of heats of high-temperature processes," *Zh. Fiz. Khim.* **36**, 907–909 (1962).
- M. E. Wieser, "Atomic weights of the elements 2005 (IUPAC Technical Report)," *Pure App. Chem.* **78**, 2051–2066 (2006).

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