

THERMODYNAMICS OF INORGANIC COMPOUNDS

Standard Enthalpy of Cu_2SnS_3 (Mohite) Formation from Sulfides

T. A. Stolyarova^{a, †}, E. A. Brichkina^a, and E. G. Osadchii^{a, *}

^aInstitute of Experimental Mineralogy, Russian Academy of Sciences,
Chernogolovka, Moscow oblast, 142432 Russia

*e-mail: euo@iem.ac.ru

Received November 15, 2019; revised November 26, 2019; accepted December 27, 2019

Abstract—Copper tin sulfide Cu_2SnS_3 (mohite) is the endmember of the binary system $\text{Cu}_2\text{SnS}_3\text{—Me}^{\text{II}}\text{S}$, in which a number of four-component compounds (known as stannic minerals) are formed; it is also a representative of a large number of solid solutions, some occurring in nature and used in metallurgy and as promising materials for the production of solar cells. The standard enthalpy of mohite formation from covellite (CuS) and herzenbergite (SnS) has been determined: $2\text{CuS} + \text{SnS} \rightarrow \text{Cu}_2\text{SnS}_3$, $\Delta_f H_{298.15\text{ K}}^\circ(\text{Cu}_2\text{SnS}_3) = -(51.01 \pm 1.26)$ kJ/mol. The standard enthalpy of Cu_2SnS_3 formation from elements kJ/mol has been calculated using reference data: $\Delta_f H_{298.15\text{ K}}^\circ(\text{Cu}_2\text{SnS}_3) = -(263.79 \pm 2.28)$.

Keywords: Cu_2SnS_3 , mohite, enthalpy, thermochemistry, calorimetry, photovoltaics

DOI: 10.1134/S003602362005023X

INTRODUCTION

Mohite is a copper tin sulfide mineral with the chemical formula Cu_2SnS_3 (space group $P1(1)$), which is rare in hydrothermal veins of tin ore deposits. Despite the fact that the mineral is rare, the compound is the endmember of a number of stannic solid solutions, the semiconductor properties of which are now being actively studied in connection with their possible use, specifically as a promising material for solar cells. The compound has a wide variety of compositions with complete or partial isomorphic substitution of cations and anions of monovalent (Cu and Ag), bivalent (Fe , Zn , Cd , Hg , Mg), tetravalent (Sn and Ge) metals, and partially divalent non-metals (S and Se) [1–4], possessing the properties of semiconductor materials (see [5] and the references cited therein). The fundamental thermodynamic properties of stannic solid solutions and their endmembers are relevant from the point of view of the practical application of materials based on them and partially obtained numerically by measurements and theoretical modeling [6–14].

Theoretical methods for calculating the thermodynamic properties of compounds are currently being developed. Thus, works are known in which the enthalpy of formation of Cu_2SnS_3 is calculated. The calculation of the thermodynamics of absorbing layers where the values of the standard enthalpy of formation of Cu_2SnS_3 (ΔH_f^{DFT} and $\Delta H_f^{\text{DFT-D2}}$, respectively) were

calculated using the density functional and van der Waals forces was reported in 2018 [11]. However, the values obtained in the two approximations differ significantly from each other (by 1.4 times); their values are given in Results and Discussion. The equations of the Gibbs energy versus temperature for equilibria in the Cu—Sn—S three-component system were also theoretically calculated using the CALPHAD system [12]. Experimental data on the thermodynamics of Cu_2SnS_3 are also available; in 2011, [13] a table of thermodynamic data for the $(\text{Cu,Ag})\text{SnS}_3$ compounds was published obtained by measuring the emf using Cu^+ - and Ag^+ -conducting solid electrolytes, where the standard enthalpies of Cu_2SnS_3 formation were also reported. Using the electrochemical method, one can determine the Gibbs energy of the reaction and, having reference data on entropy, calculate the enthalpy of formation. Unfortunately, it was not possible to find the primary source of these data [14] published only in the conference proceedings. In 2019, our preliminary results on the calculation of the standard enthalpy of formation of mohite [6] from elements were published.

In this work, we studied the formation of mohite from binary covellite sulfides (CuS) and herzenbergite (SnS).

EXPERIMENTAL

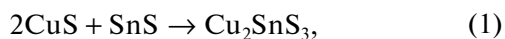
Measurement Procedure

Calorimetric studies were carried out in a high-temperature vacuum-block calorimeter manufactured

[†] Deceased.

and improved at the Mineral Thermodynamics Laboratory of the Institute of Experimental Mineralogy (Laboratory number VBC-3) and described early [15, 16]. The calorimeter allows one to determine the standard (298.15 K, 10⁵ Pa) enthalpy of a solid-state reaction by comparing the value of the heat transferred to the initial mixture of reactants in the form of electrical energy for the reaction to the value of heat measured during cooling of the system, which includes the heat released (absorbed) during the reaction.

A direct measurement of the enthalpy of formation of sulfides from elements is impossible due to the high sulfur vapor pressure arising at the reaction temperature (the temperature is set in the calorimeter furnace at which the expected reaction must complete in 7–10 min). The vapor pressure of sulfur will lead to rupture of the quartz glass ampoule. As a rule, multicomponent compounds can be obtained in the reactions of binary or more complex compounds, the thermodynamics of which are well studied. For example, there can be several reactions of Cu₂SnS₃ formation from compounds:



The enthalpies of reactions from different starting materials will be different. In the case of measuring the enthalpy of formation of a compound from complex substances rather than from elements in a calorimeter, it is necessary to calculate the final value of the standard enthalpy of formation from elements, which is easy to perform from the measured value of the enthalpy of reaction:

$$\Delta H(\text{reaction}) = \sum \Delta H(\text{reaction products}) - \sum \Delta H(\text{reagents}),$$

where $\sum \Delta H(\text{reaction products})$ is the desired quantity.

Thus, it is possible to calculate and compare the values of the standard enthalpy of formation by measuring the standard enthalpies of reactions for its preparation from various starting materials.

Reagent Synthesis and Calorimeter Preparation

To determine the enthalpy of reaction (1) by solid-phase synthesis in silica glass ampoules, sulfides were prepared. To obtain them, copper powder (99.96%), chopped tin foil (99.99%), and crystalline sulfur (99.99%, AlfaAesar) were used.

Copper sulfide CuS. Synthesis at 600°C with excess sulfur was performed followed by grinding, annealing at 600°C, and annealing at 300°C with distillation of sulfur into the cold zone.

Tin sulfide SnS. Synthesis at 600°C with excess sulfur was performed followed by grinding, annealing at 600°C, and annealing at 300°C with metal tin (separated by a gas permeable partition (kaolin wool)).

The obtained compounds were tested for single-phase by X-ray powder diffraction using a Bruker D2 PHASER diffractometer (CoK_{α1} radiation, $\lambda = 1.78897 \text{ \AA}$).

To carry out calorimetric experiments, stoichiometric mixtures of the initial sulfides, according to the reaction of mohite formation, in an amount of 1.8–2.0 g were poured into a quartz glass ampoule. After evacuation to a residual pressure of 0.13 Pa, the ampoule was sealed in an oxygen burner flame. During sealing, the ampoule was wrapped with a moist asbestos thread to prevent overheating and a possible start of the reaction.

To determine the operating mode, an ampoule with Al₂O₃ and a thermocouple were installed in the calorimeter furnace. The heating temperature of the initial mechanical mixture of substances was selected by preliminary experiments and determined by the kinetics of the reaction (the reaction should complete at a given temperature in the range 298–1273 K in 7–10 min). The thermocouple readings were consistent with the voltage readings on the stabilized source of direct current, and in the following, the thermocouple was not used to exclude heat transfer through it. In our case, the reaction was carried out at a temperature of $1093 \pm 5 \text{ K}$.

Measurement Technique

The ampoule was heated in a resistance furnace inside a massive copper block. The block was filled with argon under a pressure of 10⁶ Pa. The vacuum block (isothermal shell) into which the massive block was placed was pumped out to a residual pressure of 10⁻³ Pa, which was maintained during the entire experiment. The temperature of the isothermal shell (298.15 ± 0.02) K was maintained automatically by a water thermostat with a volume of 300 L. The temperature change during the experiment was measured with a resistance thermometer (total resistance 988 Ω at 298.15 K), consisting of nine miniature platinum film temperature sensors located uniformly along the generatrix of the massive block on the outside.

The calorimeter was calibrated using electric energy with an ampoule in a resistance furnace, in which the test reaction had already occurred under conditions (heating time at a fixed power and the initial temperature) identical to the experimental conditions. Subsequently, a series of experiments was accompanied by intermediate test measurements of the thermal value of the calorimeter. Each experiment consisted of at least two measurements: the first to determine the enthalpy of the reaction, the second to make sure that the reaction passed to the end during the first measurement and there would be no additional thermal effect. The X-ray powder diffraction studies of the products of calorimetric experiments

confirmed the presence of Cu_2SnS_3 as the only phase (Fig. 1).

RESULTS AND DISCUSSION

The results obtained in a series of experiments are shown in Table 1. In the literature [11] there are data on the enthalpy of mohite formation calculated using density functional theory (DFT) and the van der Waals forces of molecular (atomic) interaction (DFT D2):

$$\Delta H_f^{\text{DFT}} = -241.4 \text{ kJ/mol,}$$

$$\Delta H_f^{\text{DFT-D2}} = -338.8 \text{ kJ/mol.}$$

There is also a standard formation enthalpy calculated from electrochemical data: $\Delta H_f^\circ(\text{Cu}_2\text{SnS}_3) = -242.6 \pm 12.0 \text{ kJ/mol}$ [14].

The reference data for binary sulfides and measured reaction enthalpy (1),

$$\Delta_f H_{298.15}^\circ(\text{CuS, cr}) = -(53.14 \pm 2.28) \text{ J/mol} [19],$$

$$\Delta_f H_{298.15}^\circ(\text{SnS, cr}) = -(106.5 \pm 1.5) \text{ J/mol} [20],$$

$$\Delta_r H_{298.15}^\circ(1) = -(51.01 \pm 1.26) \text{ kJ/mol,}$$

were used to calculate the standard enthalpy of Cu_2SnS_3 formation from elements:

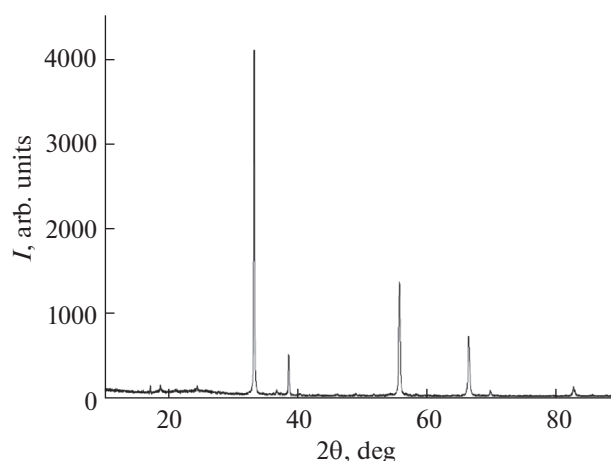


Fig. 1. X-ray powder diffraction pattern of reaction products.

$$\Delta_f H_{298.15}^\circ(\text{Cu}_2\text{SnS}_3) = -(263.79 \pm 2.28) \text{ kJ/mol.}$$

ACKNOWLEDGMENTS

The authors thank engineers M.V. Fokeev and N.N. Zhdanov for conducting calorimetric experiments and T.N. Dokina for the implementation of the X-ray powder diffraction studies.

Table 1. Standard enthalpy of reaction (1) of the Cu_2SnS_3 formation from sulfides. FW = 342.03 g/mol [17]

Experiment no.	Weight, g	$\Delta R + \sigma, \Omega$	Heat released in experiment, J			$-\Delta_r H_{298.15}^\circ(1),$ kJ/mol
			total	on heater	in reaction	
1	1.7977	28.3292	82154.7	81888.5	266.2	50.64
2	1.7975	28.3229	82136.4	81863.0	273.4	52.02
3	1.7994	28.3651	82258.8	81997.2	261.6	49.72
4	1.8031	28.436	82464.4	82192.2	272.2	51.63
5	1.7993	28.4376	82469.0	82202.6	266.4	50.64
6	1.8009	28.3179	82121.9	81851.0	270.9	51.45
7	1.8011	28.3329	82165.4	81904.6	260.8	49.52
8	1.8041	28.3289	82153.8	81880.9	272.9	51.73
9	1.8005	28.2948	82176.8	81905.6	271.2	51.51
10	1.8008	28.2916	82167.3	81906.9	260.4	49.45
11	1.8035	28.3168	82189.5	81920.3	269.2	51.05
12	1.8013	28.3026	82148.3	81886.0	262.3	49.80
13	1.7984	28.3086	82165.7	81892.8	272.9	51.90
14	1.7992	28.312	82175.6	81896.5	279.1	53.05
Av.						51.01 ± 1.26

$\Delta R + \sigma$ is the change in the readings of the resistance thermometer adjusted for heat transfer. In experiments 1–8, the thermal value of the calorimeter is $2900.0 \pm 1.0 \text{ J}/\Omega$; in experiments 9–10, it is $2904.3 \pm 1.0 \text{ J}/\Omega$; in experiments 11–14, it is $2902.5 \pm 1.0 \text{ J}/\Omega$. The standard measurement error was calculated for a confidence interval of 95% [18].

FUNDING

This work was supported by the Russian Foundation for Basic Research, grant no. 16-05-00700.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. MinDat <https://www.mindat.org/chemsearch.php>
2. MinCryst <http://database.iem.ac.ru/mincryst/rus/index.php>
3. Thermal Constants of Substances. <http://www.chem.msu.ru/cgi-bin/tkv.pl>
4. E. G. Osadchii and V. I. Sorokin, Stannine-Containing Sulfide Systems (Nauka, Moscow, 1989) [in Russian].
5. V. A. Milichko, A. S. Shalin, I. S. Mukhin, et al., *Usp. Fiz. Nauk* **186**, 801 (2016).
<https://doi.org/10.3367/UFNr.2016.02.037703>
6. T. A. Stolyarova, E. A. Brichkina, E. G. Osadchii, et al., *Exp. GeoSci.* **25** (1), 89 (2019).
7. A. V. Baranov, T. A. Stolyarova, E. A. Brichkina, et al., *Geochem. Int.* **57**, 1120 (2019).
<https://doi.org/10.1134/S0016702919100033>
8. T. A. Stolyarova, E. A. Brichkina, A. V. Baranov, et al., *Inorg. Mater.* **55**, 755 (2019).
<https://doi.org/10.1134/S0020168519080168>
9. T. A. Stolyarova, E. G. Osadchii, and A. V. Baranov, *Geochem. Int.* **57**, 109 (2019).
<https://doi.org/10.1134/S0016702919010117>
10. T. A. Stolyarova, A. V. Baranov, and E. G. Osadchii, *Geochem. Int.* **56**, 75 (2018).
<https://doi.org/10.1134/s001670291801007>
11. A. Shigemi and T. Wada, *Jpn. J. Appl. Phys.* **57**, 3 (2018).
<https://doi.org/10.7567/JJAP.57.08RC17>
12. C. Guo, X. Zhang, Ch. Li, and Zh. Du, *Int. J. Mater. Res.* **109**, 201 (2018).
<https://doi.org/10.3139/146.111592>
13. M. Babanly, Y. Yusibov, and N. Babanly, *The EMF Method with Solid-State Electrolyte in the Thermodynamic Investigation of Ternary Copper and Silver Chalcogenides*, Ed. by Kara Sadik (2013).
<https://doi.org/10.5772/2109>
14. M. B. Babanly, N. B. Babanly, and L. F. Mashadiyeva, Proceedings of VI International School-Conference "Phase Diagrams in Material Science", Kiev, 2001 (Kiev, 2011), p. 5.
15. Ya. V. Vasil'ev and M. S. Soboleva, *Zh. Fiz. Khim.* **36**, 907 (1962).
16. L. L. Fleisher and T. A. Stolyarova, *Izm. Tekh.*, No. 2, 60 (1978).
17. J. Meija, T. B. Coplen, M. Berglund, et al., *Pure Appl. Chem.* **88**, 265 (2016).
<https://doi.org/10.1515/pac-2015-0305>
18. V. V. Nalimov, *Mathematical Statistics in Materials Analysis* (Nauka, Moscow, 1960) [in Russian].
19. L. Cemic and O. J. Kleppa, *Phys. Chem. Miner.* **16** (2), 172 (1988).
20. R. A. Robie and B. S. Hemingway, U.S. Government Print. Office, 461 (1995).

Translated by V. Avdeeva

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