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Enthalpy of formation of natural hydrous copper sulfate: Chalcanthite

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ABSTRACT

This paper presents the results of the thermochemical study of hydrous copper sulfate $CuSO_4{\cdot}5H_2O$ performed on a high-temperature heat-flux Tian–Calvet microcalorimeter. The samples of two natural chalcanthite (Kosmurun ore deposit, Kazakhstan, and Lavrion deposit, Greece) and synthetic hydrous copper sulfate (blue vitriol) were characterized by X-ray microprobe analysis, X-ray powder diffraction, thermal analysis, FTIR and Raman spectroscopy. The enthalpy of dehydration at $T = 298.15$ K was measured, and the standard molar enthalpies of formation from the elements were determined by the melt solution calorimetry in accordance with Hess's law. The values of $\Delta_f H_m^0$ ($T = 298.15$ K) were found to be $-(2267.2 \pm 4.1)\ \text{kJ}\cdot\text{mol}^{-1}$ for natural chalcanthite and $-(2272.6 \pm 6.0)\ \text{kJ}\cdot\text{mol}^{-1}$ for synthetic hydrous copper sulfate (blue vitriol).

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1. Introduction

Natural hydrous copper sulfate $CuSO_4{\cdot}5H_2O$, chalcanthite is a secondary mineral, which is formed in the oxidation zone of copper sulfide deposits by sedimentation from waters saturated with dissolved copper sulfate, as well as in the areas of volcanic activity. Under industrial conditions, a synthetic analog of chalcanthite (blue vitriol) is obtained by slow evaporation of an aqueous solution of copper sulfate or by dissolution of copper in sulfuric acid. The product is used in chemical and tinctorial industry, and in agriculture as a fertilizer and for pest control.

For physicochemical modeling of stability of hydrous sulfates of bivalent metals and the sequence of their sedimentation in the hypergenesis zone of sulfide ores, on the evaporation barrier of water-salt basins and in hydrothermal solutions containing acidic sulfate waters near the craters of volcanoes – fumaroles, it is necessary to have reliable thermodynamic data for both hydrous and anhydrous participants of processes [1]. The data on thermodynamic properties of hydrous and anhydrous copper sulfate available in the literature are limited. In a previously reported study [2] the enthalpy of formation of anhydrous copper sulfate $CuSO_4$ has been determined from the obtained experimental data on dissolution of copper oxide in sulfuric acid. Based on the data [3,4] on the enthalpy of dissolution of synthetic copper sulfate in water, Bergman [5] calculated the values of $\Delta_f H_m^0$ ($T = 298.15$ K) for $CuSO_4$. The available reference books [7–9] also used the results of the only experimental work [2]. Only one experimental value of the enthalpy of dissolution of a synthetic crystalline hydrous copper sulfate in water has been reported in the literature [4]. Based on the results of this work, the value of the enthalpy of formation of synthetic $CuSO_4{\cdot}5H_2O$ was calculated in [6], and subsequently this value was included in the reference books [7,9].

In this work, we carried out the first thermochemical study of natural chalcanthite and its synthetic analog (blue vitriol) using a Calvet microcalorimeter and obtained new data on the enthalpies of dehydration and formation of hydrous copper sulfate from its constituent elements.

2. Experimental

2.1. Materials, equipment and diagnostic methods

A thermochemical study of natural chalcanthite from the oxidation zone of the Kosmurun ore deposit (the mountain ridge Genghis, Eastern Kazakhstan) (sample I) has been carried out; and for comparison we studied a sample from the Lavrion deposit (Greece) (sample II), as well as a sample of synthetic hydrous copper sulfate (blue vitriol) (sample III) (table 1).

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TABLE 1
Provenance and mass fraction purity of substances used in this study.

Substance name	Source	State	Mass fraction purity	Further treatments
Chalcanthite	Natural (Kosmurun, Kazakhstan)	Crystal	>0.99[a]	Calcination at $T = 630$ K
Chalcanthite	Natural (Lavrion, Greece)	Crystal	>0.99[a]	Calcination at $T = 630$ K
Blue vitriol	Synthetic (Mosreactiv Co., Russia)	Crystal	>0.99[b]	Calcination at $T = 630$ K
Corundum	Mosreactiv Co., Russia	Crystal	0.999[b]	None
Platinum	Myprom Co., Russia	Solid	0.999[b]	None
Lead oxide	Mosreactiv Co., Russia	Powder	0.99[b]	Melting of the mixture of lead oxide and boric acid in a ratio 2PbO: B_2O_3 at $T = 1073$ K
Boric acide	Mosreactiv Co., Russia	Crystal	0.99[b]	

[a] Purity was estimated according X-ray data.
[b] Purity grade as given by the supplier.

Before study the samples of natural chalcanthite were carefully selected by hand picking under a binocular microscope. Detailed diagnostics of substances was done with use of modern physicochemical methods.

Chemical analysis was carried out on a microanalyzer «CAMEBAX SX-50» (Cameca, France). To determine elemental composition, we used the analytical line Kα and the following standards: Cu – cuprite (natural); Mg – hornblende (natural); Ca – tremolite (natural); Co – CoSi (synthetic); Zn – ZnO (synthetic); Fe – spinel (natural); Pb – nodorite (natural); S – celestine (natural). All synthetic oxides were provided by company Cameca. The natural minerals were provided by A.E. Fersman Mineralogical Museum and were tested using standards provided by company Cameca using the "Camebax SX-50" and a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength dispersive spectrometer (Jeol, Japan). The mode of operation was as follows: accelerating voltage 15 kV; probe current 30 nA.

X-ray analysis was performed using a powder diffractometer «STOE-STADI MP» (Germany) equipped with a curved Ge(1 1 1) monochromator which gives strictly monochromatic $CoK_{\alpha 1}$ radiation ($\lambda = 0.178897$ nm). Data were collected in a regime of sequential overlapping of scanned regions using a linear position-sensitive detector with an angle of coverage of 5° at 2θ with a channel width of 0.02°.

IR-spectroscopic investigation was done on a Fourier spectrometer «FSM-1201» (Russia) at room temperature in the air over the range of wave numbers from (400 to 4000) cm^{-1} with a spectral resolution of 4.0 cm^{-1}. The accuracy of the determination of the absorption bands frequencies was ±1 cm^{-1}. Specimens for the studies were prepared in the form of tablets pressed from 3 mg of mineral substance and 250 mg of KBr, as well as in the form of suspensions of mineral powder in petrolatum oil.

Raman spectroscopic study was carried out on a Raman microscope «EnSpectr R532» (Russia) with a diffraction grating (1800 lines per mm) and a spectral resolution of about 6 cm^{-1}. The laser radiation wavelength was equal to 532 nm, the laser radiation power on the sample was approximately 15 mW, a single exposure time was 1 s, signal averaging was done using 50 measurements. The spectrum was obtained on a non-oriented single crystal of about 100 μm in size; a diameter of the focal laser spot was approximately 15 μm.

Thermal behavior of the samples was investigated over the temperature range from room temperature to 773 K on a Derivatograph Q-1500 D (MOM, Hungary) with a heating rate of 10 $K{\cdot}min^{-1}$, weight of the samples was about 90 mg).

2.1.1. Chemical analysis

X-ray microprobe analysis data for the composition of the samples studied are shown in table 2. The chemical formulas calculated for 2 charges coincide with the theoretical formula of $CuSO_4{\cdot}5H_2O$.

2.1.2. X-ray diffraction

The obtained X-ray diffraction patterns of natural minerals and synthetic blue vitriol are identical; in accordance with the database of the powder diffraction patterns ICDD No. 01-070-2158 [10] the studied samples are mono-mineral phases with the structure of chalcanthite (figure 1). No impurity phases were detected.

2.1.3. FTIR spectroscopy

The IR-absorption spectra of all the samples studied were similar to each other, the maximum difference in the values of the wave numbers of the absorption bands did not exceed 4 cm^{-1}; the samples did not contain impurities in the noticeable amounts, and they were monomineral phases. Figure 2 shows the IR absorption spectra for the sample I (Kosmurun, Kazakhstan).

The spectrum of chalcanthite prepared in a tablet with KBr (figure 2a) agrees with the spectra presented in [11,12]. It must be pointed out that this spectrum differs markedly from the spectrum of sample prepared as a suspension in petrolatum oil (figure 2b). The latter one coincides with the data [13,14] obtained by the same method. In opinion of [13], this fact may be explained by the interaction between chalcanthite and KBr, when the specimen was prepared for research. The range of wave numbers (400–4000) cm^{-1} registered in the experiment can be divided into four non-overlapping spectral areas.

The first region (3800–2600) cm^{-1} contains a broad absorption band with a few maxima over the range of (3480–3160) cm^{-1}, corresponding to valence vibrations of water molecules present in the structure in different crystallographic positions.

TABLE 2
Chemical composition of the substances studied.

Oxides	Sample I (Kosmurun, Kazakhstan)		Sample II (Lavrion, Greece)		Sample III (Synthetic)	
	Mass fraction	U[a]	Mass fraction	U[a]	Mass fraction	U[a]
CuO	0.3207	0.0081	0.3220	0.0076	0.3186	0.0074
MgO	0.0001	0.000002	0.0003	0.000006		
CoO			0.0001	0.000002	0.0002	0.000004
ZnO	0.0005	0.00001	0.0001	0.000002	0.0004	0.000008
FeO	0.0049	0.0001	0.0001	0.000002	0.0001	0.000002
CaO	0.0004	0.000008				
PbO	0.0005	0.00001				
SO_3	0.3039	0.0077	0.3128	0.0087	0.3189	0.0060
H_2O[b]	0.369	0.0045[c]	0.364	0.0045[c]	0.361	0.0045[c]

[a] U is the uncertainty of experimental values calculated with 0.95 level of confidence, the uncertainties are calculated on the basis of 10 determinations for each sample.
[b] The water content was determined by the thermogravimetry method.
[c] The uncertainty is an instrumental error (MOM recorder).

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