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Low temperature measurements of the heat capacity and thermodynamic functions of pseudo-malachite $Cu_5(PO_4)_2(OH)_4$

M.R. Bissengaliyeva[a,*], D.B. Gogol[a], N.S. Bekturganov[b]

[a] Institute of Complex Development of Mineral Resources, Ippodromnaya Str. 5, Karaganda 100019, Kazakhstan
[b] SC 'National Scientific-Technological Holding "Parasat"' Republic Ave. 18, Astana 010000, Kazakhstan

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ABSTRACT

The investigation of the heat capacity of a natural specimen of copper phosphate—pseudo-malachite $Cu_5(PO_4)_2(OH)_4$ in the temperature range between 4.2 K and 320 K has been carried out by the method of low-temperature adiabatic calorimetry. Tabulated values of the heat capacity and thermodynamic functions of the mineral including the changes of entropy and enthalpy and the Gibbs function of free energy have been calculated. The standard values of thermodynamic functions of pseudo-malachite at $T = 298.15$ K are $C^{\circ}_{p,m} = (385.43 \pm 0.41)$ J mole^{-1} K^{-1}, $\Delta^{T}_{0}S^{\circ}_{m} = (412.16 \pm 0.61)$ J mole^{-1} K^{-1}, $\Delta^{T}_{0}H^{\circ}_{m} = (63681.5 \pm 57.0)$ J mole^{-1}, $F^{\circ}_{m} = (198.57 \pm 0.47)$ J mole^{-1} K^{-1}. In the low-temperature area $0 < (T/K) < 22.69$ an anomaly has been registered in the variation of the heat capacity of the mineral, for which the lattice constituent has been determined. The contribution of anomalous component into entropy and enthalpy of the mineral is $\Delta S_{tr} = (5.772 \pm 0.081)$ J mole^{-1} K^{-1}, $\Delta H_{tr} = (29.94 \pm 0.42)$ J mole^{-1}.

1. Introduction

The matter about structure and properties of natural copper phosphates has been discussed in the literature for a long time. Since minerals of this group are similar in appearance and crystalline structure, and due to the presence of polymorphism and variable content of water there was some uncertainty in the description of minerals and their crystal-chemical formulae. As a rule, it resulted in lack of reliable data about their physical–chemical characteristics, in particular, thermo-chemical and thermodynamic properties. The present study describes the results of calorimetric investigations of thermodynamic functions of one of copper phosphates—pseudo-malachite $Cu_5(PO_4)_2(OH)_4$.

2. Experiment

2.1. Specimen description

A specimen of natural copper phosphate presented in this study at first was identified as elite [1]. Further investigations of the specimen specifically the roentgenophase and X-ray structure analyses established the correspondence of crystallographic parameters of its elementary cell to the known structural data on pseudo-malachite [ASTM, 13–28] (Fig. 1). A chemical analysis of the copper phosphate specimen has been carried out by the Central Chemical Laboratory of the Institute of geology of ore deposits of RAS; analysis # 3910 (Table 1). In addition, the content of new primary elements (mass fraction): 0.514 Cu and 0.100 P has been determined by the method of X-ray spectrum analysis (ASIC FGUP "All-Russian Scientific-Research Institute of Mineral Resources named after N.M. Fedorovsky", analysis # 6nh13-1) and a semi-quantity roentgen fluorescent analysis of the specimen has been carried out using Axios Advanced spectrometer (The Institute of Geochemistry and Analytical Chemistry named after Vernadsky).

The infrared spectrum of the specimen has been registered at PerkinElmer Spectrum One FT-IR Spectrometer, class Universal ATR, resolution 4 cm^{-1}, the number of scans 4 (The Institute of Chemical Sciences named after Bekturov of the MES RK). Positions of the absorption bands maxima of the specimen demonstrate high correspondence with the positions of pseudo-malachite absorption bands given in [2]. The IR-spectrum of pseudo-malachite is shown in Fig. 2.

The absorption bands in infrared spectrum of pseudo-malachite at frequencies 3438 and 3389 cm^{-1} belong to stretching vibrations of OH-group; the absorption bands at frequencies 886, 808 and 757 cm^{-1} correspond to deformation vibrations of hydroxyl groups.

Three intensive absorption bands in the infrared spectrum of pseudo-malachite in area 1100–900 cm^{-1} belong to stretching vibrations of bonds P–O in phosphate-ion PO_4. Absorption bands in spectral range 600–400 cm^{-1} refer to deformation vibrations of phosphate-ion.

The absorption bands at frequencies 1507, 1374 and 1320 cm^{-1} taking into account the performed roentgenographic investigations

* Corresponding author. Tel.: +7 7212 414814; fax: +7 7212 414520.
E-mail addresses: mirabis@ipkon.kz, 160655@mail.ru (M.R. Bissengaliyeva).

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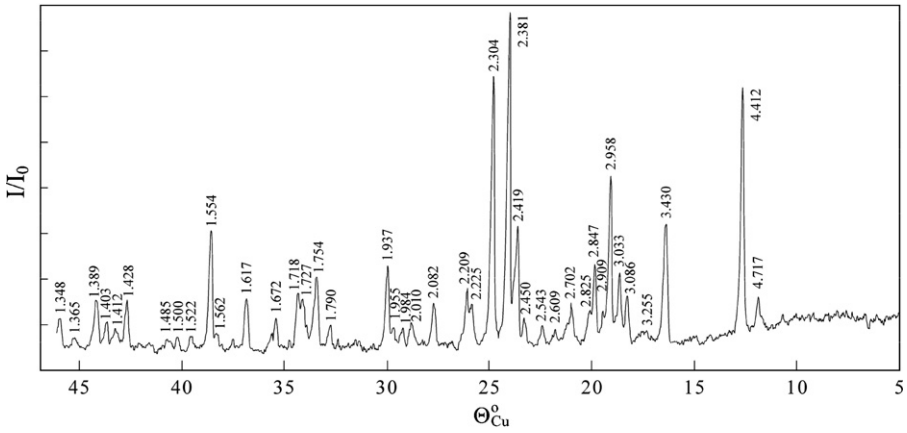

Fig. 1. Diffractogram of monomineral fraction of pseudo-malachite.

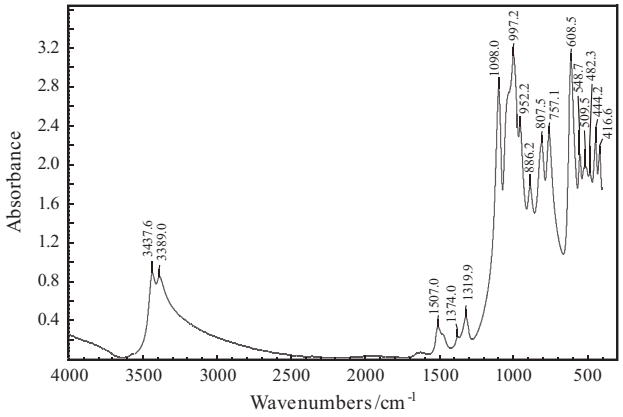

Fig. 2. The infrared spectrum of pseudo-malachite.

can be referred to deformation vibrations of water molecules being in interplanar channels of pseudo-malachite crystalline structure.

Thus, the investigations carried out allowed to determine the specimen as mineral pseudo-malachite having crystal-chemical formula $Cu_5(PO_4)_2(OH)_4$.

Table 1
The results of chemical analysis of natural copper phosphate.

Oxides	Mass fraction	
	Experimental	Theoretical
SiO_2	0.0015	0.001498
Al_2O_3	0.00056	0.000559
Fe_2O_3	0.00026	0.000260
MnO	0.000008	0.000008
MgO	0.000065	0.000065
CaO	0.0015	0.001498
Na_2O	0.00011	0.000110
K_2O	0.00004	0.000040
H_2O^+	0.0743	0.074210
Zn	0.000206	0.000206
CuO	0.6543	0.653510
P_2O_5	0.2652	0.264880
BaO	0.00012	0.000120
As_2O_3	0.0029	0.002896
V_2O_5	0.00014	0.000140
Total	1.00121	1.0000

2.2. Calorimetric measurements

The temperature dependence of the heat capacity of natural copper phosphate specimen has been investigated by the method of adiabatic vacuum calorimetry in the temperature range of 2 K and 320 K and its thermodynamic functions have been calculated. Measurements of the specimen heat capacity from $T = 2$ K while evacuating liquid helium were carried out at an installation belonging to the Physical-Technical Institute of Low Temperatures of AS UkSSR in 1991; in doing so the measurements made at temperature higher than $T = 20$ K were characterized by instability and a wide spacing of points. The main experimental part of the investigation in the temperature range between 4.2 K and 320 K has been carried out at a low-temperature thermophysical installation BKT-10.04 produced by firm "Termax" [3]. The installation error when measuring a reference copper specimen did not exceed $\pm 0.0143 \cdot C_p$ at $T = 5$ K, $\pm 0.0023 \cdot C_p$ at $T = 40$ K, and $\pm 0.0011 \cdot C_p$ for $80 \leq (T/\mathrm{K}) \leq 300$.

A specimen of pseudo-malachite was placed into a titanium container of 1 cm^3 in volume, which was filled with heat-exchange helium at pressure of 1 mmHg. The specimen mass was 1.5191 g at measuring in helium area and 1.5178 g for measuring at nitrogen temperatures. Temperature was measured with an iron–rhodium resistance thermometer calibrated according to the international temperature scale ITS-90 ($R_0 = 50\ \Omega$). Pitches of heating were 0.2 K for $4 < (T/\mathrm{K}) \leq 6$, 0.5 K for $6 < (T/\mathrm{K}) \leq 10$, 1 K for $10 < (T/\mathrm{K}) \leq 20$, 2 K for $20 < (T/\mathrm{K}) \leq 70$ and 3 K for $T > 70$ K. The heat capacity was measured in some series – $4 < (T/\mathrm{K}) \leq 25$, $4 < (T/\mathrm{K}) \leq 40$, $35 < (T/\mathrm{K}) \leq 85$, and $80 < (T/\mathrm{K}) \leq 320$, in doing this the temperature ranges were passed at the least twice, and the repeated measurements in the series were performed as a rule at the reduced pitches of heating (Fig. 3).

3. Results and discussion

3.1. The results obtained

The results of calorimetric measurements of the heat capacity of pseudo-malachite are characterized by a good stability and reproducibility. A heat capacity anomaly has been found in the temperature range below 10 K, which is possibly associated with the presence of the Jahn–Teller effect or the Ising phenomenon. The anomaly has been confirmed by the recent measurements [4]. Deviations at higher temperatures, which hypothetically were connected with the specimen devitrification and its dehydration, have not been confirmed. Thus, the data of the year 1991 in the temperature range of 2 K and 4.5 K and the data of recent measurements in the area of $4.2 < (T/\mathrm{K}) < 320$ (Table 2) have been taken into the initial set of points.