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A low-temperature heat capacity study of natural lithium micas

Heat capacity of zinnwaldite

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Abstract Low-temperature heat capacity of natural zinnwaldite was measured at temperatures from 6 to 303 K in a vacuum adiabatic calorimeter. An anomalous behavior of heat capacity function $C_p(T)$ has been revealed at very low temperatures, where this function does not tend to zero. Thermodynamic functions of zinnwaldite have been calculated from the experimental data. At 298.15 K, heat capacity $C_p(T) = 339.8$ J K^{-1}mol^{-1}, calorimetric entropy $S^o(T) - S^o(6.08) = 329.1$ J K^{-1} mol^{-1}, and enthalpy $H^o(T) - H^o(6.08) = 54{,}000$ J mol^{-1}. Heat capacity and thermodynamic functions at 298.15 K for zinnwaldite having theoretical composition were estimated using additive method of calculation.

Keywords Micas · Adiabatic calorimetry · Heat capacity · Entropy · Enthalpy

Introduction

This work continues a series of experimental investigations of low temperature heat capacity of the natural micas including ferrous micas, annite [1] and biotite [2], and lithium micas, lepidolite [3] and polylithionite [4], which, in turn, is the part of large work on thermodynamic properties of minerals [5, 6]. Zinnwaldite is widespread trioctahedral lithium–ferrous mica of formula $KLi(Fe,Al)_2[AlSi_3O_{10}](F,OH)_2$ with wide variability in the chemical composition because of the tendency for isovalent and heterovalent isomorphism. According to modern classification [7], zinnwaldite is an intermediate member of the join (series of minerals) between siderophyllite $KFe_2^{2+}Al[Al_2Si_2O_{10}](OH)_2$ and polylithionite $KLi_2Al[Si_4O_{10}]F_2$ Zinnwaldite is a typical mineral of rare-metal granites and pegmatites and is used as ore for lithium, rubidium and cesium. The development of new schemes of ore treatment of lithium micas requires thermodynamic data on the minerals involved in these processes.

The low-temperature thermochemical properties of zinnwaldite were previously never investigated, and there are neither experimental, nor calculated thermodynamic data on zinnwaldite in the literature.

The purpose of this study is the experimental determination of the low temperature heat capacity of natural zinnwaldite using adiabatic calorimetry in the temperature range 6–303 K. The obtained results have been used to calculate the thermodynamic functions of zinnwaldite in the same temperature range and its calorimetric entropy at 298.15 K. Furthermore, heat capacity and thermodynamic functions at 298.15 K for zinnwaldite of ideal composition $KLiFeAl_2Si_3O_{10}F_2$ have been estimated.

Experimental

For the present thermochemical study, natural zinnwaldite from tin mine Omchikandja (Yakutija, Russia) was taken. The chemical composition of sample given in Table 1 was determined by traditional "wet" chemical analytical

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Table 1 The chemical composition of natural zinnwaldite

Component	Mass/%
SiO_2	42.79 ± 0.84
TiO_2	0.19 ± 0.05
Al_2O_3	21.75 ± 1.19
Fe_2O_3	0.89 ± 0.21
FeO	10.77 ± 0.59
MnO	3.13 ± 0.17
MgO	0.95 ± 0.24
ZnO	–
CaO	–
Na_2O	0.19 ± 0.07
K_2O	10.14 ± 0.7
Rb_2O	0.45 ± 0.12
Cs_2O	0.029 ± 0.001
Li_2O	3.25 ± 0.34
F	6.11 ± 0.77
H_2O^+	1.24 ± 0.17
Σ	101.88
$-O{=}F_2$	2.57
Σ	99.31

method. The concentrations of Li, Rb, Na, and K were determined by flame photometry method. The chemical formula of zinnwaldite calculated on the basis of 22 charges was: $(K_{0.94}Na_{0.03}Rb_{0.02})(Li_{0.95}Al_{0.96}Fe^{3+}_{0.05}Fe^{2+}_{0.65}Mn_{0.19}Mg_{0.10}Ti_{0.01})$ $[Si_{3.10}Al_{0.90}O_{10}](OH)_{0.60}F_{1.40}$ (molar mass was taken as 432.24 g mol^{-1}). Structural investigations were carried out by electron and X-ray diffraction methods. The obtained lattice parameters were: $a = 5.27$ Å, $b = 9.13$ Å, $c = 10.0$ Å, $\beta = 100.08°$. The octahedral ordering scheme of zinnwaldite was determined as 1 M.

The behavior of studied zinnwaldite at heating is similar to that described in the literature [8] and is characterized by endothermic effect with a maximum at 1,000 °C connected with removal of constitutional water and fluorine and destruction of the lattice.

The heat capacity measurements were carried out using a computerized vacuum adiabatic calorimeter [9]. The sample mass was 2.2253 g. After loading the sample, the calorimetric ampoule was evacuated and filled with helium at a pressure of 30 mm Hg to improve the heat exchange at the measurements.

Results and discussion

The low temperature heat capacity of zinnwaldite was measured by pulse heating method at 64 points in the temperature interval from 6 to 300 K. The experimental heat capacity data are given in Table 2.

Table 2 Experimental molar heat capacities of zinnwaldite in J K^{-1} mol^{-1}

T/K	C^o_p	T/K	C^o_p
Series 1		8.20	3.555
299.97	340.8	9.37	3.904
302.96	342.9	10.53	4.113
Series 2		11.71	4.526
83.02	95.85	12.99	4.896
88.07	104.2	14.32	5.426
93.11	112.4	15.61	5.962
98.17	120.8	16.91	6.691
104.77	131.2	18.22	7.450
111.81	142.1	19.53	8.257
118.81	153.0	20.83	9.014
125.80	163.5	22.82	10.96
132.88	173.8	25.38	13.24
140.00	183.6	27.96	15.59
148.49	195.3	30.55	18.37
158.41	208.3	33.64	22.25
168.34	220.7	37.23	26.87
178.20	232.5	40.82	31.17
188.12	243.8	44.42	35.91
198.20	254.6	48.74	41.93
208.36	265.4	53.82	49.38
218.52	274.9	58.92	57.08
228.69	285.1	64.00	65.17
238.81	294.3	69.06	73.44
248.85	302.7	74.10	81.37
258.95	311.0	79.12	89.66
269.01	318.8	84.18	97.94
279.04	326.2	*Series 5*	
289.13	333.5	6.08	3.077
299.20	340.8	7.16	3.312
Series 3		8.69	3.693
296.97	339.0	10.63	4.169
299.99	340.7	*Series 6*	
Series 4		20.74	9.228
7.13	3.288	22.35	10.54

The average deviation of experimental points from smoothed curve are about 0.7% at temperatures from 6 to 20 K, 0.5% between 20 and 50 K, and 0.06% from 50 to 300 K. The obtained function $C_p(T)$ is a smooth curve without any obvious anomalies in the studied temperature interval. However, at very low temperatures, the function $C_p(T)$ behaves unusually, it does not tend to zero. It is shown in Fig. 1 where the $C_p(T)$ curves of other micas at temperatures below 15 K are also presented.

It is seen that the curves $C_p(T)$ for annite, biotite, and lepidolite tend to the origin of the coordinates, but those for polylithionite and zinnwaldite don't go to zero point. It

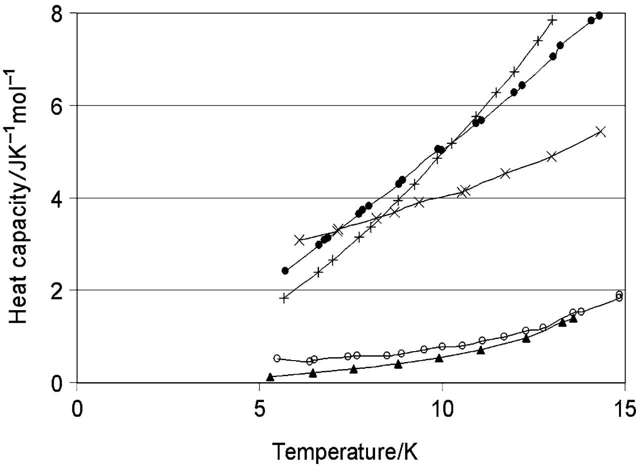

Fig. 1 Heat capacity of studied natural micas at very low temperatures: +—annite, •—biotite, ×—zinnwaldite, o—polylithionite, ▲—lepidolite

should be noted that polylithionite and zinnwaldite differ from other mentioned micas by their composition. They contain a quantity of manganese. In this connection, in the paper [4] on the thermodynamic data of polylithionite, it was supposed that a magnetic phase transition could take place at temperatures below 5 K. Such an assumption could be also expressed about zinnwaldite. Low temperature heat capacity of various compounds containing Mn(II) ions was studied many times (see for example [10, 11]) and magnetic phase transitions in these compounds were observed on numerous occasions. Therefore, the thermodynamic functions– the calorimetric entropy and the difference of enthalpies of zinnwaldite were calculated only for the temperature interval from 6.08 to 303 K. They are presented in Table 3.

Table 3 Heat capacity and thermodynamic functions of zinnwaldite. $C_p^o(T)$, $S^o(T) - S^o(6.08)$ in J K^{-1} mol^{-1}; $H^o(T) - H^o(6.08)$ in J mol^{-1}

T, K	$C_p^o(T)$	$S^o(T) - S^o(6.08)$	$H^o(T) - H^o(6.08)$
6.08	3.077	0	0
10	4.012	1.750	13.92
15	5.712	3.667	37.84
20	8.608	5.675	73.09
25	12.81	8.029	126.2
30	17.88	10.80	202.6
35	23.82	13.99	306.6
40	30.16	17.58	441.4
45	36.78	21.52	608.6
50	43.79	25.75	809.9
60	58.82	35.04	1,322
70	74.76	45.30	1,989
80	91.03	56.35	2,818
90	107.4	68.01	3,810
100	123.5	80.16	4,965
120	154.7	105.5	7,751
140	183.7	131.5	11,140
160	210.3	157.8	15,080
180	234.6	184.0	19,540
200	256.6	209.9	24,450
220	276.7	235.3	29,790
240	295.1	260.2	35,510
260	311.7	284.5	41,580
280	326.8	308.1	47,970
298.15	339.8 ± 0.6	329.1 ± 0.6	54,000 ± 100
300	341.2	331.2	54,650
303.06	343.2	334.5	55,660

To calculate the standard values of entropy and difference of enthalpies of zinnwaldite at 298.15 K, the values of $S^o(6.08)$ and $H^o(6.08) - H^o(0)$ are necessary. When experimental curve $C_p(T)$ follows the normal path to zero point, its extrapolation below the lowest experimental temperature is usually executed according to cubic Debay law. Following this extrapolated curve, one can calculate the values of thermodynamic functions at the lowest experimental temperature. For zinnwaldite, as it was mentioned above, the curve of $C_p(T)$ doesn't tend to zero point. Therefore, to estimate roughly entropy and enthalpy at 6.08 K, the experimental curve $C_p(T)$ has been arbitrary extrapolated to zero point by a straight line between the first experimental point at 6.08 K and the origin of the coordinates. Evaluation of calorimetric parts of $S^o(6.08) - S^o(0)$ and $H^o(6.08) - H^o(0)$ gives 3.1 J K^{-1} mol^{-1} and 9.4 J mol^{-1}, respectively. On the assumption of antiferromagnetic phase transition below 6 K, one can also estimate the magnetic parts of $S^o(6.08) – S^o(0)$ and $H^o(6.08) – H^o(0)$. The spin of manganese ion is equal to 5/2 and the magnetic part of entropy connected with an assumed phase transition will be Rln6 = 14.9 J K^{-1} mol^{-1}. One mole of studied sample of zinnwaldite contains only 0.19 Mn, therefore, magnetic entropy will be equal to 2.8 J K^{-1} mol^{-1}. So, the value of $S^o(6.08) - S^o(0) =$ 5.9 J K^{-1} mol^{-1}. The accuracy of this value was estimated to be about ±2 J K^{-1} mol^{-1}. The magnitude of $H^o(6.08) - H^o(0)$ is much less than the error in the value of $H^o(298.15)$. Finally, the values of entropy and of the difference of enthalpies for studied zinnwaldite at 298.15 K can be considered to be equal to 335 ± 2 J K^{-1} mol^{-1} and 54,000 ± 100 J mol^{-1}. The obtained value of $S^o(298.15) - S^o(0)$ is not absolute, it is only calorimetric entropy, because there is no information on the degree of atomic disorder in the zinnwaldite crystal structure.

The obtained heat capacity and entropy of studied sample at 298.15 K were compared with the values of $C_p^o(298.15)$ and $S^o(298.15)$ calculated on the basis of the well-known principle of additivity [12]. It implies that thermodynamic parameter of a complex compound can be approximated by the sum of the corresponding thermodynamic functions of simple substances (oxides or salts) composing it. The validity of this rule was checked using the obtained thermodynamic parameters of natural zinnwaldite sample. The calculation of the heat capacity at 298.15 K (as an example) was made by the following equation: $0.47C_p(K_2O) + 0.015C_p(Na_2O) + 0.01C_p(Rb_2O) + 0.95C_p(LiF) + 0.15C_p(AlF_3) + 0.855C_p(Al_2O_3) + .025C_p(Fe_2O_3) + 0.65C_p(FeO) + 0.01C_p(TiO_2) + 0.19C_p(MnO) + 0.10C_p(MgO) + 0.10C_p(SiO_2) + 0.3C_p(H_2O) = C_p(K_{0.94}Na_{0.03}Rb_{0.02})(Li_{0.95}Al_{0.96}Fe^{3+}_{0.05} + Fe^{2+}_{0.65} + Mn_{0.19}Mg_{0.10}Ti_{0.01})[Si_{3.10}Al_{0.90}O_{10}](OH)_{0.60}F_{1.40}$

The necessary thermodynamic parameters of oxides and salts were taken from handbook [13]. The calculation showed that the additivity rule yields satisfactory results. The calculated heat capacity at 298.15 K and calorimetric entropy $S^o(298.15) - S^o(0)$ were obtained as 355.2 and 331.3 J K^{-1} mol^{-1}, respectively. The associated experimental values with regard to the assumed value of $S^o(6.08)$ are 339.8 and 335 ± 2 J K^{-1} mol^{-1} and differ from calculated quantities by 4.5% for C^o_p and 1.2% for $S^o(298.15) - S^o(0)$. Such satisfactory agreement allowed applying the additivity rule to estimate the thermodynamic parameters at 298.15 K of zinnwaldite of the theoretical composition $KLiFeAl_2Si_3O_{10}F_2$. For ideal zinnwaldite, the following values at 298.15 K have been obtained: $C^o_p = 351$ J K^{-1} mol^{-1}; $S^o(298.15) - S^o(0) = 332$ J K^{-1} mol^{-1}; $H^o(298.15) - H^o(0) = 56{,}000$ J mol^{-1}.

Conclusions

This study is a sequential part of investigations of lithium micas. Earlier, thermodynamic properties of two widespread micas containing large amount of Li cations—lepidolite [3] and polylithionite [4] were studied. Measurements of low temperature heat capacity of the lithium micas show that an increase in the lithium content in a mica lowers the heat capacity. The most lithium-rich polylithionite (6.26% Li_2O) has at 298.15 K the lowest standard heat capacity $C^o_p = 334.4$ J mol^{-1} K^{-1}. The heat capacity of lepidolite containing 4.90% Li_2O is greater: $C^o_p = 339.3$ J mol^{-1} K^{-1}. However, the standard heat capacity of zinnwaldite, $C^o_p = 339.8$ J mol^{-1} K^{-1} is close to that of lepidolite in spite of lower Li content (3.25% Li_2O). The reason may be connected with the difference in the composition of micas in question. Zinnwaldite differs from lepidolite and polylithionite, first of all, in high content of bivalent iron (10.77% of FeO). Study of lithium–ferrous micas (Li-annite and Li-biotite [1, 2]) shows that the content of Fe^{+2} affects the heat capacity and thermodynamic functions more than Li. The appearance of manganese cations in the octahedral layer can disturb the regular course of heat capacity at very low temperatures and result in anomalies in heat capacity. Polylithionite (2.7% MnO) [4] and zinnwaldite (3.13 MnO) are examples.

The experimental data obtained in present work are the first determination of low temperature thermodynamic properties of zinnwaldite. Together with earlier data on thermodynamic properties of annite, biotite, lepidolite, and polylithionite [1–4], they enlarge the present base of data on the most naturally widespread lithium micas and can be used at thermodynamic modeling of mineral-forming processes involving lithium micas.

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