ISSN 0016-7029, Geochemistry International, 2007, Vol. 45, No. 9, pp. 926–930. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © I.E. Paukov, Yu.A. Kovalevskaya, I.A. Kiseleva, T.N. Shuriga, V.N. Ikorskii, 2007, published in Geokhimiya, 2007, No. 9, pp. 1008–1014.

SHORT
COMMUNICATIONS

Low-Temperature Heat Capacity and Thermodynamic Properties of Natural Polylithionite

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Received July 31, 2006

DOI: 10.1134/S0016702907090066

INTRODUCTION

Polylithionite is a trioctahedral lithium mica with the general formula $XY_3Z_4O_{10}(F, OH)_2$. The sum of cations in the interlayer X positions is close to one. In addition to potassium, sodium and rubidium always occur as interlayer cations. The octahedral positions (Y) of natural polylithionite are mainly occupied by lithium and aluminum. Divalent cations (Fe, Mg, and Mn) are present in significant amounts only in iron-rich polylithionite varieties. Tetrahedral cations (Z positions) are mainly represented by silicon and minor aluminum (usually in a proportion of approximately 3.8 : 0.2), which allows polylithionite classification as a silica-rich mica. Among lithium micas, polylithionite shows the highest Li_2O content of 5.5–8.0%, which corresponds to 1.5–2.0 formula units. Another characteristic feature of polylithionite composition is higher fluorine content compared with other lithium micas. Polylithionite is a typomorphic mineral of peralkaline pegmatites and rare-metal metasomatic rocks and is common in alkaline metasomatic zones. Together with other lithium micas, polylithionite can be used as a lithium ore and for the manufacturing of modern glass-ceramic materials.

Currently, there is no information in the literature, both experimental and theoretical, on the thermodynamic properties of polylithionite.

This paper presents the results of measurements of the low-temperature heat capacity of natural polylithionite by the method of vacuum adiabatic calorimetry within the temperature range 5.5–303 K. Calorimetric entropy, enthalpy difference, and Gibbs free energy were calculated for this temperature range and for a standard temperature of 298.15 K. Thermodynamic parameters were estimated for polylithionite of the theoretical composition $KLi_2Al[Si_4O_{10}]F_2$.

SAMPLE CHARACTERISTICS

Calorimetric measurements were performed on a natural polylithionite sample from the rare-earth peralkaline pegmatites of Madagascar. The complete chemical analysis of the sample (Table 1) was obtained at the chemical laboratory of the Fedorovskii All-Russia Institute of Mineral Resources (analyst S.P. Purusova); the contents of Li, Na, and K were determined by flame photometry at the spectral laboratory of the same institute. The crystal chemical for-

Table 1. Chemical composition of the polylithionite sample

Component	Wt %
SiO_2	53.54
TiO_2	0.19
Al_2O_3	19.97
Fe_2O_3	0.33
FeO	0.15
MnO	2.71
MgO	0.01
ZnO	n.d.
CaO	0.06
Na_2O	0.19
K_2O	9.74
Li_2O	6.26
F	7.96
H_2O^+	0.72
H_2O^-	1.12
Σ	102.95
$-O{=}F_2$	3.35
Σ	99.60

Table 2. Experimental values of C_p for polylithionite, J(K mol)

T, K	C_p	T, K	C_p	T, K	C_p	T, K	C_p
5.49	0.5141	17.38	3.088	70.97	70.31	200.16	250.48
6.38	0.4478	17.68	3.328	77.98	81.67	210.04	261.36
6.50	0.5013	18.62	3.992	82.82	90.13	220.03	269.35
7.43	0.5626	19.23	4.255	85.00	93.09	230.02	280.26
7.67	0.5787	19.86	4.537	85.86	94.91	240.02	289.21
8.49	0.5836	20.80	5.120	89.93	101.36	250.00	297.74
8.89	0.6282	21.60	5.761	94.91	109.65	259.96	305.55
9.50	0.7066	23.69	7.531	99.86	117.76	269.90	313.12
10.01	0.7832	25.76	9.346	104.75	125.50	279.84	321.08
10.56	0.7925	27.84	11.40	109.71	133.23	280.18	321.51
11.10	0.8949	29.95	13.63	114.68	140.78	288.09	328.02
11.71	0.9948	32.03	15.95	120.64	149.78	289.78	328.79
12.30	1.122	34.73	19.15	127.70	160.39	293.11	331.09
12.77	1.189	37.32	22.17	134.82	170.98	294.95	330.96
13.58	1.507	41.14	26.91	141.87	181.15	296.03	333.38
13.81	1.540	44.73	31.53	150.35	192.82	297.97	332.66
14.85	1.837	48.29	36.38	160.33	205.51	299.71	334.69
14.86	1.901	52.54	42.52	170.29	217.78	299.84	334.34
16.13	2.658	57.59	49.62	180.26	229.88	302.84	336.05
16.14	2.649	62.63	56.85	190.27	240.73		

mula was calculated for a total cation charge of 22: $(K_{0.83}Na_{0.02})(Li_{1.68}Al_{1.15}Fe^{3+}_{0.03}Mn_{0.15}Ti_{0.01})[Si_{3.58}Al_{0.42}O_{10}]$ $F_{1.68}(OH)_{0.32}$ (molecular mass of 395.231).

The mineral was assigned to the 1M polytype on the basis of electron diffraction data (B.B. Zvyagin and A.P. Zhukhlistov, Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences). The unit-cell parameters of the mica were determined by X-ray diffractometry (Fedorovskii Institute of Mineral Resources): a = 5.18 Å, b = 8.97 Å, c = 10.20 Å, and β = 100.33°. They are typical of polylithionite-1M.

EXPERIMENT AND DISCUSSION

The heat capacity of the polylithionite sample was measured in a vacuum adiabatic calorimeter using a small-volume ampoule within the temperature interval 5.5–303 K. The measurements were performed in an automatic mode. The procedure of measurements was described in detail elsewhere [1]. The temperature increment in calorimetric experiments was 1.0–1.5 K at 5–20 K, 10% of absolute temperature at 20–100 K, and 10 K above 100 K. The mass of the sample was 0.9090 g. The results of measurements are given in Table 2. Figure 1 shows the $C_p(T)$ dependence within 5–20 K. For comparison, also shown is the $C_p(T)$ dependence for a closely related mica, lepidolite, which was studied by us previously [2]. A comparison of the $C_p(T)$ curves for the two micas showed that they behave similarly within 15–303 K, when the difference between them is no higher than 1–2%. The two curves diverge below 15 K, and the difference reaches ~400% at 5–6 K. The $C_p(T)$

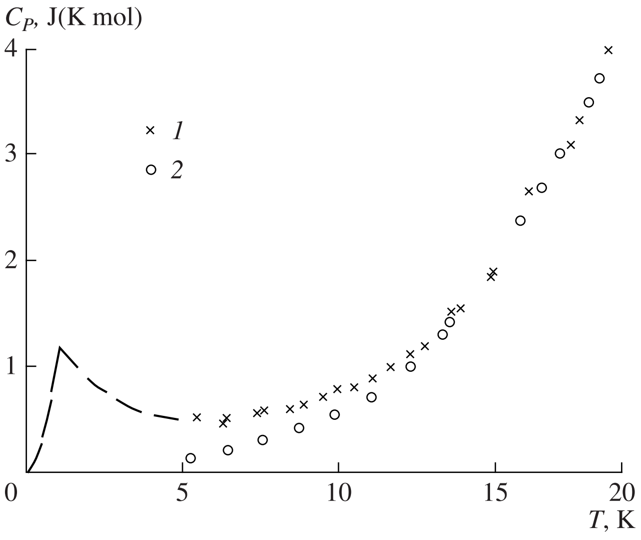

Fig. 1. Low-temperature $C_p(T)$ versus T for (1) polylithionite and (2) lepidolite.

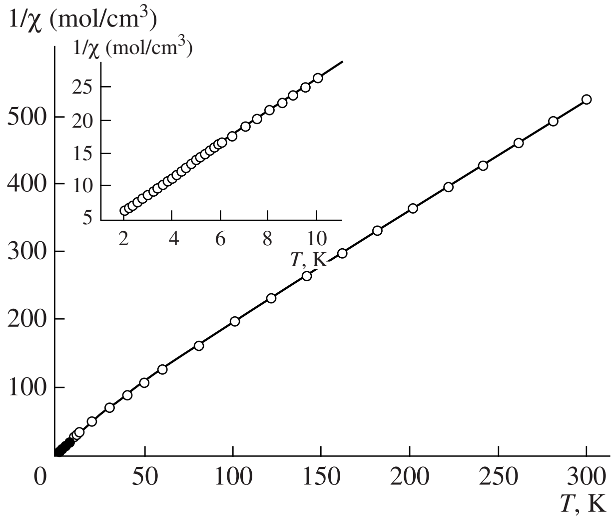

Fig. 2. Reciprocal magnetic susceptibility of polylithionite as a function of temperature, $1/\chi(T)$.

dependence of lepidolite tends toward zero at 0 K, whereas polylithionite shows an anomalous behavior. Its $C_p(T)$ does not tend toward zero with decreasing temperature (Fig. 1). Such a character of $C_p(T)$ dependence is indicative of a heat capacity anomaly at temperatures of less than 5 K. Since the polylithionite molecule contains the magnetic ion Mn(II), we measured its magnetic susceptibility as a function of temperature [$\chi(T)$] from 2 to 300 K in an external magnetic field of 5 kOe. The magnetic susceptibility appeared to be independent of the magnetic field. The paramagnetic component of sample susceptibility (χ) was calculated accounting for a diamagnetic contribution of 178×10^6 cm^3/mol. Figure 2 shows the results of measurements of reciprocal magnetic susceptibility versus temperature. As can be seen in the diagram, the $1/\chi(T)$ dependence is linear at both low and high temperatures (inset), which is characteristic of paramagnetic behavior and corresponds to the Curie–Weiss law $\chi = C/(T - \theta)$. Within the whole temperature range, the magnetic susceptibility can be described by the sum $\chi = C_1/(T - \theta_1) + C_2/(T - \theta_2)$ (solid line) with the optimized parameters $C_1 = 0.354$ cm^3 K/mol, $\theta_1 = -0.21$ K, $C_2 = 0.272$ cm^3 K/mol, and $\theta_2 = -74$ K. The negative values of the Weiss constants (θ), which characterize the magnitudes and signs of exchange interactions between paramagnetic centers, unequivocally indicate antiferromagnetic interactions, mainly between the magnetic moments of Mn(II) ions with the spin $S = 5/2$. The resolution of magnetic susceptibility into two components suggests a statistically disordered distribution of two types of Mn(II) ions in the sample structure. The first of them includes quasi-isolated Mn(II) ions weakly interacting with other ions (first term of the equation). The second type involves aggregation with the formation of a set of exchange clusters of various compositions and configurations, within which interaction between magnetic moments is much stronger. The latter suggestion is based on a comparison of θ_1 and θ_2 values. The fractions of the supposed ion groups are about 56 and 44%. Cooperative ordering effects were not observed during cooling to a temperature of 2 K. This can be attributed to the fact that the above small-sized clusters are separated and weakly interact with each other. The magnetic ordering of such clusters is not accompanied by a phase transition and occurs gradually. A Schottky anomaly may be observed on the heat capacity curve. The departure from linearity below 60 K corresponds to the process of magnetic ordering at decreasing temperature within small-sized clusters with various ion numbers and energy parameters of exchange between them. The linear trend in the region below 10 K is related to the group of widely spaced quasi-isolated ions, which weakly interact with each other and with clusters. The effects of magnetic ordering can be observed for this ion group below 2 K. It should be noted that the low-temperature heat capacity of various Mn(II)-bearing compounds was repeatedly studied (e.g., [2, 3]), and magnetic phase transitions were detected in all cases.

The entropy and other integral thermodynamic functions of polylithionite corresponding to the temperature interval from 5.5 K to T were calculated from experimental data and are shown in Table 3.

In order to estimate the entropy of the sample corresponding to the temperature interval from 0 K to T, it was supposed that the antiferromagnetic transition in polylithionite occurs below 1 K. The proposed $C_p(T)$ dependence below 5 K is shown in Fig. 1 by the dashed line. Since the spin of Mn(II) ion is 5/2, the magnetic component of the entropy related to the supposed phase transition is $R\ln 6 = 14.9$ J/(K mol). Taking into account that one mole of polylithionite contains only 0.15 Mn, the magnetic entropy can be estimated as 2.23 J/(K mol). This value was added to the calculated calorimetric entropy, $S^0(298.15) - S^0(5.5)$, to obtain $S^0(298.15) - S^0(0) = 313$ J/(K mol). The accuracy of this value was estimated as ±2 J/(K mol). Correspondingly, the value of $\Phi^0(298.15)$ was estimated as 137.3 ± 2 J/(K mol), and the value $H^0(298.15) - H^0(0)$ is equal to $H^\circ(298.15) - H^\circ(5.5)$ within the uncertainty of computations. The smoothed values of C_p and main thermodynamic functions calculated on the basis of the $C_p(T)$ dependence within the temperature range 5.5–300 K are shown in Table 3. The errors of thermodynamic functions at standard temperature reported in Table 3 were estimated taking into account the results of control measurements of the heat capacity of a standard substance (benzoic acid) and the chemical composition of the sample. It should be noted that the entropy values reported in Table 3 are not absolute because of the unknown degree of disorder of atoms in the polylithionite molecule. These values correspond therefore to the calorimetric entropy.

Table 3. Heat capacity and thermodynamic functions of polylithionite. $C_p^0(T)$, $S^0(T) - S^0(5.5)$, and $\Phi^0(T)$ are in J/(K mol); and $H^0(T) - H^0(5.5)$ is in J/mol

T, K	$C_p^0(T)$	$S^0(T) - S^0(5.5)$	$H^0(T) - H^0(5.5)$	$\Phi^\circ(T)$
5.5	0.500	0.000	0.000	0.000
10	0.753	0.333	2.560	0.077
15	1.996	0.816	8.726	0.235
20	4.708	1.740	25.10	0.485
25	8.631	3.187	57.89	0.871
30	13.63	5.189	113.2	1.416
35	19.30	7.710	195.3	2.130
40	25.42	10.68	306.9	3.009
45	31.92	14.05	450.2	4.045
50	38.75	17.76	626.7	5.228
60	53.28	26.10	1086	7.996
70	68.81	35.46	1696	11.24
80	84.98	45.70	2464	14.90
90	101.3	56.66	3396	18.92
100	117.6	68.18	4491	23.27
120	148.9	92.41	7158	32.76
140	178.1	117.6	10430	43.07
160	204.9	143.1	14270	53.98
180	229.0	168.7	18610	65.31
200	250.8	194.0	23410	76.91
220	270.6	218.8	28630	88.69
240	288.7	243.2	34230	100.5
260	305.4	266.9	40170	112.4
280	320.9	290.1	46430	124.3
300	335.7	312.8	53000	136.1
302.84	337.8	316.0	54000	137.8
298.15	334.4 ± 0.6	310.7 ± 0.6	52380 ± 100	135.0 ± 0.5

$\Phi^0(T) = S^0(T) - S^0(5.5) - [H^0(T) - H^0(5.5)]/T$.

The obtained values of heat capacity and entropy at 298.15 K for our sample were used to estimate the respective properties of polylithionite of ideal composition on the basis of the well-known principle of additivity [5]. It implies that the heat capacity and thermodynamic functions of a complex compound can be approximated by the sum of the corresponding thermodynamic parameters of simple substances (oxides or salts) composing it. We checked the validity of this rule using the obtained thermodynamic parameters of the natural polylithionite sample. Thermodynamic parameters were calculated by the following expression (using C_p as an example): $0.415C_p(K_2O) + 0.01C_p(Na_2O) + 1.68C_p(LiF) + 0.785C_p(Al_2O_3) + 0.015C_p(Fe_2O_3) + 0.01C_p(TiO_2) + 0.15C_p(MnO) + 3.58C_p(SiO_2) + 0.16C_p(H_2O) = C_p(K_{0.83}Na_{0.02})(Li_{1.68}Al_{1.15}Fe^{3+}_{0.03}Mn_{0.15}Ti_{0.01})[Si_{3.58}Al_{0.42}O_{10}]F_{1.68}(OH)_{0.32}$.

The thermodynamic parameters necessary to compute heat capacity values were taken from handbooks [6]. The calculations of thermodynamic parameters at 298.15 K showed that the additivity rule [5] yields satisfactory results for our sample. The heat capacity at 298.15 K and calorimetric entropy $S^0(298.15) - S^0(0)$ were estimated as 336.1 and 302.3 J/(K mol), respectively. The corresponding values obtained from experiments are 334.4 and 310.7 J/(K mol), respectively. It can be seen that the calculated values differ from the experimental estimates by 0.5% for C_p and ~2.7% for $S^0(298.15) - S^0(0)$. Given the success of these calculations, we applied the additivity rule [5] to estimate the $C_p(298.15)$, $H^0(298.15) - H^0(0)$, $S^0(298.15) - S^0(0)$, and reduced Gibbs potential at 298.15 K of polylithionite of the theoretical composition $KLi_2Al[Si_4O_{10}]F_2$. The following values were obtained for 298.15 K: C_p = 337.5 J/(K mol), $H^0(298.15) - H^0(0)$ = 52500 J/mol, $S^0(298.15) - S^0(0)$ = 310.6 J/(K mol), and Φ^0 = 134.6 J/(K mol). The accuracy of these thermodynamic parameters can be estimated as 2–3% on the basis of the comparison of experimental data for the polylithionite sample with the respective values calculated using the additivity rule [5].

ACKNOWLEDGMENTS

This study was financially supported by the Russian Foundation for Basic Research, project no. 06-05-64305, and Interdisciplinary Integration Project no. 81 of the Siberian Division, Russian Academy of Sciences.

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