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SHORT COMMUNICATIONS

Thermodynamic Properties of Natural Lepidolite

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INTRODUCTION

Lepidolite is a widespread iron-poor lithium–aluminum mica, the composition of which approaches the ideal formula $KLi_{1.5}Al_{1.5}AlSi_3O_{10}F_2$. However, natural lepidolite has a much more complex variable composition owing to isovalent and heterovalent isomorphic substitutions resulting in the formation of isomorphic series with muscovite, biotite, phlogopite, siderophyllite, and various lithium micas. According to the recent mica nomenclature [1], lepidolite is a lithium mica of intermediate composition between trilithionite ($KLi_{1.5}Al_{1.5}AlSi_3O_{10}F_2$) and polylithionite ($KLi_2AlSi_4O_{10}F_2$). Lepidolite is a characteristic mineral of rare-metal granites and pegmatites, occurs in metasomatic rocks and greisens, and is used as a lithium ore and as a source of rubidium and cesium, which can be recovered from it as by-products. During recent years, lepidolite and its solid solutions have been increasingly used in the construction of modern glass ceramic materials, because the incorporation of lithium oxide into the glass matrix imparts a number of unique properties to the synthetic material [2]. The development of new technological schemes for the treatment of lithium raw materials and the creation of new materials requires the knowledge of the thermodynamic properties of minerals used in these processes.

The only available publication on the thermodynamic properties of lepidolite is that of Ogorodova et al. [3], who used the method of high-temperature melt calorimetry to determine the standard enthalpy of formation and to measure enthalpy differences within temperatures of 444–972 K. The low-temperature heat capacity of lepidolite was never measured, and there are no data in the literature on its standard entropy and Gibbs free energy.

This paper presents the results of measurements of the low-temperature heat capacity of natural lepidolite by the method of adiabatic vacuum calorimetry within the temperature range 5–300 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 the lepidolite of the theoretical composition $KLi_{1.5}Al_{1.5}AlSi_3O_{10}F_2$, which can be useful for the investigation of equilibria and the thermodynamic analysis of aluminosilicate systems containing lithium. Some recent handbooks [4] present internally consistent thermodynamic parameters only for mineral endmembers of solid solution series.

SAMPLE CHARACTERISTICS

Thermodynamic investigations were carried out using a sample of natural lepidolite from Na–Li rare-metal pegmatites of the Eastern Sayan, Russia. Transparent lepidolite flakes of pinkish or pinkish lilac color and up to 1–2 cm in diameter were separated under a binocular microscope. The complete chemical analysis of the sample was obtained at the chemical laboratory of the Fedorovskii All-Russia Institute of Mineral Resources, and the contents of Li, Rb, and Cs were determined by flame photometry (Table 1). The following crystal chemical formula was calculated for a cation charge of 22: $(K_{0.80}Na_{0.05}Ca_{0.07}Rb_{0.16}Cs_{0.03})(Li_{1.34}Al_{1.40}Fe^{3+}_{0.01})[Si_{3.25}Al_{0.75}O_{10}]F_{1.80}(OH)_{0.20}$; the molecular weight is 409.637 g/mol. The lepidolite is the $2M_2$ polytype, which was determined by electron diffraction at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences. This polytype is typical of lepidolites whose octahedral lattice is dominated by Li and Al, which is the case for our sample. Its unit-cell parameters ($a = 8.98$ Å, $b = 5.19$ Å, $c = 20.25$ Å, and $\alpha = 99.58°$) were measured by X-ray diffractometry at the Fedorovskii All-Russia Institute of Mineral Resources and are typical of the $2M_2$ polytype [5]. The thermal behavior of the lepidolite sample is similar to that described in [5] and is characterized by the presence of two endothermic effects on the DTA curve. These effects are related to the processes of simultaneous loss of water and fluorine and destruction of the crystal structure: the

Table 1. Chemical composition of the lepidolite studied

Component	Wt %
SiO_2	47.86
TiO_2	0.025
Al_2O_3	26.84
Fe_2O_3	0.18
FeO	–
MnO	–
MgO	–
CaO	0.90
Na_2O	0.40
K_2O	9.20
Rb_2O	3.75
Cs_2O	1.00
Li_2O	4.90
F	8.38
H_2O^+	0.45
H_2O^-	0.19
Total	104.08
$–O=F_2$	3.53
Total	100.55

first effect occurs in the temperature range 675–960°C (T_{max} = 895°C), and the second weaker effect is observed at 1000–1250°C (T_{max} = 1150°C).

EXPERIMENTAL RESULTS AND DISCUSSION

The heat capacity of lepidolite was measured using an automated adiabatic vacuum calorimeter within the temperature range 5.3–302 K. Measurements were carried out by means of a calorimetric ampoule and a method described in detail in [6]. The mass of the specimen was 1.5125 g. The $C^0_\mathrm{p}(T)$ dependence is smooth and shows no anomalies. The results of measurements are given in Table 2. The smoothed values of C^0_p and main thermodynamic functions calculated from the $C^0_\mathrm{p}(T)$ dependence are shown in Table 3. The reported errors of thermodynamic functions at standard temperature (Table 3) were estimated from the results of control measurements of the heat capacity of a standard substance (benzoic acid) and the chemical analysis of the sample. It should be noted that the entropy values shown in Table 3 are not absolute because the degree of atomic disorder in the lepidolite molecule is

Table 2. Experimental values of the C^0_p of lepidolite, J/K mol

T, K	C^0_p	T, K	C^0_p	T, K	C^0_p	T, K	C^0_p
5.29	0.1341	45.35	32.85	124.77	155.2	224.64	278.1
6.46	0.2141	49.50	38.63	131.68	165.5	226.76	281.3
7.58	0.3093	53.70	44.83	135.02	170.5	234.70	287.9
8.78	0.4181	56.85	49.24	138.60	175.6	235.59	289.3
9.91	0.5448	60.44	54.43	147.05	187.3	245.67	299.0
11.04	0.7072	65.48	62.03	151.19	193.3	255.71	307.2
12.30	0.9806	70.49	69.92	156.97	200.8	265.62	315.0
13.29	1.317	75.49	77.77	161.21	206.5	270.14	318.2
13.59	1.392	80.52	85.88	166.95	213.5	275.52	323.0
15.83	2.396	81.56	87.88	171.18	219.2	277.00	323.2
16.46	2.720	84.56	92.64	174.98	223.8	280.17	326.2
17.08	2.963	84.98	93.06	177.03	226.0	286.96	331.1
17.94	3.500	85.60	94.19	181.11	231.5	290.17	334.1
18.33	3.782	87.57	97.60	187.09	237.6	291.96	334.8
19.42	4.413	90.01	101.1	191.05	242.8	295.52	338.5
21.20	5.626	92.65	105.4	197.03	248.4	296.92	338.3
23.33	7.402	94.95	109.2	201.47	254.2	297.14	337.8
25.46	9.312	99.71	116.9	203.97	257.7	297.26	338.4
27.56	11.39	99.90	117.2	204.88	257.8	299.64	339.4
29.67	13.62	103.56	122.9	206.95	259.6	299.73	339.8
32.31	16.62	104.89	125.0	211.44	265.1	300.07	340.8
35.40	20.17	110.87	134.4	211.56	265.7	301.86	341.4
38.51	23.98	113.51	138.3	214.70	267.7	302.14	341.2
41.67	27.93	117.83	144.8	219.17	272.8	302.19	341.2

unknown. These values correspond to calorimetric entropy. A characteristic feature of the structure of lithium micas [5, 7] is a strongly ordered distribution of cations between the octahedral positions; however, partial disordering of Si and Al between the tetrahedral positions is possible in some polytypes. It can therefore be supposed that the measured values of calorimetric entropy differ only slightly from the absolute entropy. The following values were obtained for the heat capacity, calorimetric entropy, enthalpy difference, and reduced Gibbs potential of the lepidolite at 298.15 K: 339.3 J/K mol, 312.6 J/K mol, 52780 J/mol, and 135.5 J/K mol, respectively.

Since lepidolite is a sheet mineral, it is reasonable to suppose that its $C_p^0(T)$ dependence will be quadratic at the lowest temperatures, which is suggested by theoretical models [8, 9]. This is confirmed by Fig. 1, where our experimental data are presented as the $C_p^0/T(T)$ function. It can be seen that within the temperature range from 5 to 11 K, the $C_p^0/T(T)$ dependence is linear.

Ogorodova et al. [3] reported measurements of enthalpy difference in the temperature range 444–972 K for the same lepidolite sample that was investigated here. It is interesting to compare the results of the two studies and calculate on this basis the thermodynamic functions of lepidolite within the temperature range from 0 to 1000 K. Using the experimental data on the enthalpy difference [3] and the results of the present study, the following equation was derived for the $C_p^0(T)$ dependence between 298.15 and 1000 K: $C_p^0 = 262.34 + 294.1 \times 10^{-3}T - 9.55 \times 10^5T^2$. The temperature dependence of the heat capacity of lepidolite is shown in Fig. 2. It can be seen that the results of the two studies are in adequate agreement with each other. This equation and the thermodynamic properties at 298.15 K obtained here (Table 3) allow us to calculated the $C_p^0(T)$ dependence, change of calorimetric entropy, and enthalpy difference within the temperature range 298.15–1000 K (Table 4).

The obtained values of the heat capacity and entropy of natural lepidolite provide an opportunity to estimate these parameters for the lepidolite of the theoretical composition $KLi_{1.5}Al_{1.5}AlSi_3O_{10}F_2$. To this end, we used the well-known empirical rule of additivity [10]. According to this rule, the heat capacity and thermodynamic functions of any complex compound can be presented as a sum of the corresponding thermodynamic parameters of simple substances composing it (oxides and salts). The thermodynamic properties of the lepidolite studied here can be derived using the following equation (for the calculation of C_p^0 as an example): $0.40C_p^0(K_2O) + 0.025C_p^0(Na_2O) + 0.07C_p^0(CaO) + 0.08C_p^0(Rb_2O) + 0.015C_p^0(Cs_2O) + C_p^0(Al_2O_3) + 0.005C_p^0(Fe_2O_3) + 3.25C_p^0(SiO_2) + 1.34C_p^0(LiF) + 0.153C_p^0(AlF_3) + 0.1C_p^0(H_2O) = C_p^0\ (K_{0.80}Na_{0.05}Ca_{0.07}Rb_{0.16}Cs_{0.03})(Li_{1.34}Al_{1.40}Fe^{3+}_{0.01})[Si_{3.25}Al_{0.75}O_{10}]F_{1.80}(OH)_{0.20}.$

The thermodynamic parameters necessary for these calculations were taken from the handbook [11]. The calculation of thermodynamic parameters for 298.15 K showed that the use of the additivity rule [10] gives satisfactory results for our sample. The following values were obtained for the heat capacity, enthalpy difference

Table 3. Heat capacity and thermodynamic functions of lepidolite; $C_p^0(T)$, $S^0(T) - S^0(0)$, and $\Phi_0(T)$ are in J/K mol, and $H^0(T) - H^0(0)$ is in J/mol

T, K	$C_p^0(T)$	$S^0(T) - S^0(0)$	$H^0(T) - H^0(0)$	$\Phi^0(T)$
5.29	0.1338	0.0446	0.177	0.0112
10	0.5536	0.2364	1.697	0.0667
15	1.986	0.6731	7.320	0.1851
20	4.814	1.604	23.83	0.4122
25	8.880	3.092	57.56	0.7897
30	13.95	5.147	114.3	1.337
35	19.66	7.719	198.1	2.059
40	25.83	10.74	311.6	2.951
45	32.40	14.16	457.0	4.003
50	39.30	17.93	636.1	5.204
60	53.87	26.37	1101	8.013
70	69.21	35.81	1716	11.30
80	85.11	46.09	2487	15.00
90	101.2	57.04	3419	19.06
100	117.2	68.54	4511	23.43
120	148.2	92.66	7167	32.94
140	177.5	117.7	10430	43.25
160	204.7	143.2	14250	54.15
180	229.7	168.8	18600	65.47
200	252.7	194.2	23430	77.08
220	273.8	219.3	28700	88.87
240	292.9	244.0	34370	100.8
260	310.2	268.1	40400	112.7
280	325.9	291.7	46760	124.7
300	340.6	314.7	53430	136.6
302.19	342.2	317.1	54170	137.9
298.15	339.3 ± 0.6	312.6 ± 0.6	52780 ± 100	135.5 ± 0.5

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

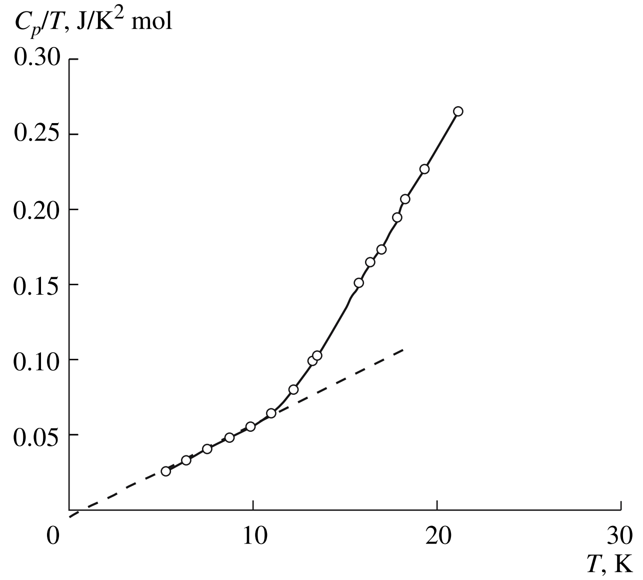

Fig. 1. Dependence of C_P/T on temperature.

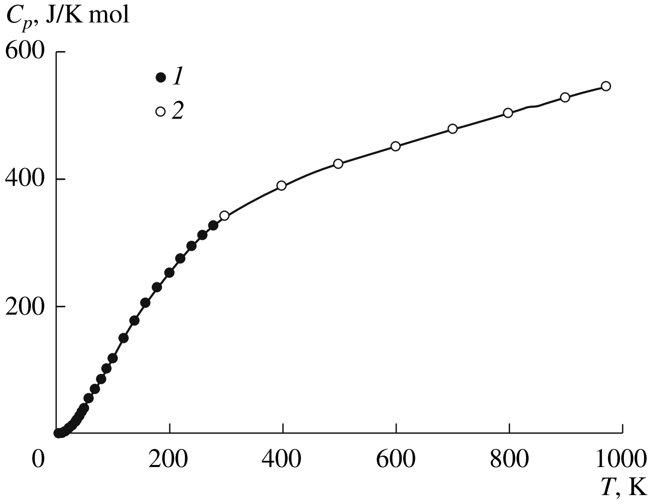

Fig. 2. Heat capacity of lepidolite according to the results of this study (curve *1*) and after [3] (curve *2*).

$H^0(298.15) - H^0(0)$, and calorimetric entropy $S^0(298.15) - S^0(0)$: 339.6 J/K mol, 52050 J/mol, and 305.8 J/K mol, respectively. The calculated values differ from the experimental results by 0.1% for C_p^0, 1.5% for $H^0(298.15) - H^0(0)$, and 2% for $S^0(298.15) - S^0(0)$. These results allowed us to use the additivity rule [10] for the estimation of the $C_p^0(298.15)$, $H^0(298.15) - H^0(0)$, $S^0(298.15) - S^0(0)$, and reduced Gibbs potential at 298.15 K for the lepidolite of the theoretical composition $KLi_{1.5}Al_{1.5}[Si_3AlO_{10}]F_2$. The following equation was used for this purpose (C_p^0 is given as an example): $0.5C_p^0(K_2O) + 1.5C_p^0(LiF) + 0.167C_p^0(AlF_3) + 0.167C_p^0(Al_2O_3) + 3C_p^0(SiO_2) = C_p^0(KLi_{1.5}Al_{1.5}Si_3AlO_{10}F_2)$. The following parameters were obtained for 298.15 K: C_p^0 = 337.3 J/K mol, $H^0(298.15) - H^0(0)$ = 50940 J/mol, $S^0(298.15) - S^0(0)$ = 296.3 J/K mol, and Φ^0 = 125.4 J/K mol. The accuracy of these thermodynamic parameters can be estimated as 1.5–2.0% on the basis of the above-described comparison of experimental data for the lepidolite sample and corresponding thermodynamic parameters calculated on the basis of the additivity rule [10].

Table 4. Heat capacity and thermodynamic functions of lepidolite within the temperature range 298.15–1000 K; $C_p^0(T)$ and $S^0(T) - S^0(0)$ are in J/K mol, and $H^0(T) - H^0(0)$ is in J/mol

T, K	$C_p^0(T)$	$S^0(T) - S^0(0)$	$H^0(T) - H^0(0)$
298.15	339.3	312.6	52780
300	340.0	314.7	53410
400	374.0	417.3	89140
500	405.6	504.1	128100
600	436.2	580.8	170200
700	466.3	650.3	215400
800	496.2	714.5	263500
900	526.0	774.7	314600
1000	554.4	831.6	368600

The Gibbs free energy of natural lepidolite can be calculated from the entropy obtained here and the enthalpy of formation of lepidolite of the same composition determined previously [3] by the calorimetric method, $\Delta_f H_{el}^0(298.15\ K) = -6201 \pm 18$ kJ/mol. For this purpose, the entropy of formation of lepidolite from elements at 298.15 K was calculated as $\Delta_f S_{el}^0$ = -1162.6 ± 0.8 J/K mol, and the necessary data on the entropy of elements were taken from the handbooks [11, 12]. The Gibbs free energy at 298.15 K of the lepidolite appeared to be $\Delta_f G_{el}^0 = -5854 \pm 18$ kJ/mol.

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