LOW-TEMPERATURE THERMODYNAMIC PROPERTIES OF NATURAL LEPIDOLITE

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Key words: calorimetry, heat capacity, mica, lepidolite

Lepidolite is widespread lithium mica of ideal formula $KLi_{1.5}Al_{1.5}AlSi_3O_{10}F_2$. However, lepidolite is characterized by wide variability in the chemical composition because of the tendency for isovalent and heterovalent isomorphism and formation of solid solution with muscovite, phlogopite and other lithium micas. Lepidolite is a typical mineral of rare-metal granites and pegmatites and used as ore for lithium, rubidium and cesium. Natural sample of lepidolite from Na-Li type rare-element-rich pegmatites of East Sayany, Russia, was chosen for study. The chemical composition was determined by traditional "wet" chemical methods. The chemical formula of lepidolite calculated on the basis of 22 charges is: $(K_{0.80}Na_{0.05}Ca_{0.07}Rb_{0.16}Cs_{0.03})(Li_{1.34}Al_{1.40}Fe^{3+}_{0.01})[Si_{3.25}Al_{0.75}O_{10}]F_{1.80}(OH)_{0.20}$ (M.m. =409.637 g mol^{-1}). The lattice parameters were obtained: a=8.98Å, b=5.19Å, c=20.25Å, α=99.58^{o}. The octahedral ordering scheme of lepidolite has been determined to be $2M_2$. The special features of $2M_2$ polytype of lepidolite mica are the small degree of Si-Al substitution in tetrahedral and large replacement of OH-groups by F. The heat capacity of lepidilite sample with total mass 1.5125 g was measured in a vacuum adiabatic calorimeter in the temperature range 5.3-302 K. No anomalies were detected in the $C_p(T)$ dependence. The experimental curve was smoothed by the spline-function method. Thermodynamic parameters calculated on the basis of these smoothed $C_p(T)$ values are given in Table.

Table. Molar thermodynamic properties of natural lepidolite

T, K	$C^o_p(T)$, J K^{-1} mol^{-1}	$S^o(T)$- $S^o(0)$, J K^{-1} mol^{-1}	$H^o(T)$-$H^o(0)$, J mol^{-1}	$\Phi^o(T)$*, J K^{-1} mol^{-1}
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

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

The thermodynamic characteristics of lepidolite of idealized composition $Li_{1.5}Al_{1.5}[Si_3AlO_{10}]F_2$ can be estimated by additive method using reference data for corresponding constituent components: C_p^o(298.15 K)=337.3 J K^{-1} mol^{-1}; H^o(298.15 K)-H^o(0)=50940 J mol^{-1}; S^o(298.15 K)- S^o(0)=296.3 J K^{-1} mol^{-1} and Φ^o(298.15 K)=125.4 J K^{-1} mol^{-1}.

This work was supported by RFFI (№ 06-05-64305)

Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(24)'2006
ISSN 1819 – 6586
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2006
URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2006/informbul-1_2006/mineral-7e.pdf

Published on July, 1, 2006
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