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Thermodynamic properties of lithium mica: Lepidolite

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Abstract

Calorimetric measurements were made on natural sample of lepidolite having the composition $(K_{0.80}Na_{0.05}Ca_{0.07}Rb_{0.16}Cs_{0.03})$-$(Li_{1.34}Al_{1.40}Fe^{3+}_{0.01})[Si_{3.25}Al_{0.75}O_{10}]F_{1.80}(OH)_{0.20}$ from Na–Li-type rare-element-rich pegmatites of East Sayany, Russia. High-temperature enthalpy increments were measured with a Tian–Calvet calorimeter at 444–972 K using the drop method. The resultant $C^{o}_{p,m}(T)$ equation in the interval $T = 298.15$–972 K was calculated: $C^{o}_{p,m} = 316.10 + 228.12 \times 10^{-3}\,T - 50.10 \times 10^{5}\,T^{-2}$ (J K^{-1} mol^{-1}) [± 0.4%] and the value of $C^{o}_{p,m}$ (298.15 K) = 327.8 J K^{-1} mol^{-1} was obtained. The standard molar enthalpy of formation from the elements was determined by high-temperature drop solution calorimetry in molten lead borate at $T = 973$ K. The value of $\Delta_f H^{o}_{m}(298.15\,K)$ for lepidolite was found to be -6201 ± 18 kJ mol^{-1}. The thermodynamic properties of lepidolite of idealized composition $KLi_{1.5}Al_{1.5}[Si_3AlO_{10}]F_2$ were estimated based on the experimental data obtained.

Keywords: Thermochemistry; Lepidolite; Heat capacity; Enthalpy of formation

1. Introduction

Lepidolite is widespread in the upper crust 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. The development of new schemes of ore treatment of lithium micas requires thermodynamic data on the minerals involved in these processes. Such information on lepidolite has been largely unavailable.

The purpose of this study is the experimental determination of the heat capacity and the enthalpy of formation of lepidolite with calorimetric methods.

2. Sample description

Natural samples of lepidolite from Na–Li-type rare-element-rich pegmatites of East Sayany, Russia, were chosen for study. Transparent and semitransparent pink and lilac-pink, large lepidolite crystals (some as large as 1–2 cm in diameter) were found as nests in light gray quartz of pegmatites. Very pure transparent cleavage flakes with no inclusions (muscovite and other ones) were hand-picked from quartz under a binocular microscope. The chemical composition of 500 mg of homogeneous samples was determined by traditional “wet” chemical methods (Table 1). The chemical formula of lepidolite calculated on the basis of 22 charges is: $(K_{0.80}Na_{0.05}Ca_{0.07}Rb_{0.16}Cs_{0.03})(Li_{1.34}Al_{1.40}Fe^{3+}_{0.01})$-$[Si_{3.25}Al_{0.75}O_{10}]F_{1.80}(OH)_{0.20}$ (409.637 g mol^{-1}). The lepidolite studied contains 2.75 octahedral cations per formula unit. According to the nomenclature of micas [1], micas with ≥2.5 octahedral cations are trioctahedral. Structural investigations were performed by Professors Zvyagin and Zhukhlistov (Institute of Geology of Ore Deposits,

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Table 1
The chemical composition of natural lepidolite[a]

Component	wt.%
SiO_2	47.86
TiO_2	0.025
Al_2O_3	26.84
Fe_2O_3	0.18
ZnO	н.о.
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[b]
H_2O^-	0.19[c]
Σ	104.08
$-O{=}F_2$	3.53
Σ	100.55

[a] The chemical analysis was made in chemical laboratory (N.M. Fedorovsky Russian Institute of Mineral Materials), S. Purusova, analyst.
[b] High temperature water.
[c] Low temperature (hygroscopic) water.

Petrology, Mineralogy and Geochemistry RAN, Moscow) using X-ray and electron diffraction methods, to whom we express our thanks. The lattice parameters were obtained: $a = 8.98$ Å, $b = 5.19$Å, $c = 20.25$Å, $\alpha = 99.58°$. 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 [2].

3. Experimental techniques

All thermochemical investigations were performed with a Tian–Calvet high-temperature (1000 °C) heat-flux calorimeter (“Setaram”), described in detail in [3]. The enthalpy of formation was determined by “transposed temperature drop solution calorimetry”. In each run, 2.5–4.5 ($\pm 2 \times 10^{-3}$) mg of lepidolite was dropped into molten $2PbO{\cdot}B_2O_3$ in the calorimeter at $T = 973$ K from room temperature ($T = 298.15$ K). The heat measured contained two contributions, the heat content of the sample and the enthalpy of solution at $T = 973$ K ($\Delta_{298.15}^{973}H_m^o + \Delta_{sol.973}H_m^o) = \Delta_{dropsol}H_m^o$. High-temperature heat contents were determined at interval of 444–972 K using the “drop” method. A lepidolite sample weighing 8–17 ($\pm 2 \times 10^{-3}$) mg was dropped directly from room temperature into the calorimeter at the experiment temperature and the enthalpy increment was measured ($\Delta_{298.15}^{T}H_m^o) = \Delta_{drop}H_m^o$. Before experiments, all samples were heated at 150 °C to remove low-temperature water. Calibration of the calorimeter was performed by dropping pieces of platinum wire (in the solution experiments) and standard corundum α-Al_2O_3 (in the heat-content measurements), with known enthalpy increments [4].

4. Results and discussion

The calorimetry results are given in Tables 2 and 3. Table 2 also contains the necessary thermochemical data for the constituent oxides and fluorides. With the calorimetric data from Table 2 and reference data on $\Delta_f H_m^o$(298.15 K) from [12] for Rb_2O and Cs_2O and from [4] for other components, the standard enthalpy of formation of natural lepidolite from the elements was calculated on the basis of reaction (1):

$$\begin{aligned}&0.40K_2O + 0.025Na_2O + 0.07CaO + 0.08Rb_2O\\&\quad + 0.015Cs_2O + 1.00Al_2O_3 + 0.005Fe_2O_3 + 3.25SiO_2\\&\quad + 1.34LiF + 0.153AlF_3 + 0.1H_2O\\&\qquad = (K_{0.80}Na_{0.05}Ca_{0.07}Rb_{0.16}Cs_{0.03})(Li_{1.34}Al_{1.40}Fe^{3+})\\&\qquad\ [Si_{3.25}Al_{0.75}O_{10}]F_{1.80}(OH)_{0.20}.\end{aligned} \tag{1}$$

This reaction combines Li with F and partially with Al because the value of the enthalpy of solution of Li_2O cannot be obtained experimentally because it tends to absorb moisture to form $LiOH{\cdot}H_2O$. Previous experimental data on the enthalpy of solution of LiF [10] was used.

Table 2
The calorimetric data used for calculation of enthalpy of formation of lepidolite

Substance	$\Delta_{298.15}^{973}H_m^o + \Delta_{sol.973}H_m^o$(kJ mol^{-1})	Reference
Lepidolite	516.9 ± 17.0 (6)[a]	This work
Na_2O (s)	−111.8 ± 0.9	[5]
K_2O (s)	−193.7 ± 1.1	[5]
Rb_2O (s)	−223.2 ± 1.2	[6]
Cs_2O (s)	−230.0 ± 4.1	[7]
CaO (s)	−21.78 ± 0.29[b]	[3]
Al_2O_3 (s) corundum	107.38 ± 0.59[b]	[7]
Fe_2O_3 (s)	171.6 ± 1.9[b]	[8]
SiO_2 (s) quartz	39.43 ± 0.21[b]	[3]
H_2O (l)	40.9 ± 2.5[b]	[9]
LiF (s)	92.8 ± 1.2	[10]
AlF_3 (s)	92.72 ± 0.79[b]	[11]

[a] Experimental errors are expressed at the 95% confidence level, number of determinations is given in parentheses.
[b] Calculated using experimental data on $\Delta_{sol.973}H_m^o$ [3,7–9,11] and reference data on $\Delta_{298.15}^{973}H_m^o$ from [4], respectively.

Table 3
Experimental data on the enthalpy increments for studied lepidolite

T (K)	$\Delta_{298.15}^{T}H_m^o$(kJ mol^{-1})
444	53.1 ± 1.2 (7)[a]
508	77.3 ± 3.0 (6)
565	103.1 ± 3.5 (7)
733	179.3 ± 4.3 (5)
833	227.3 ± 1.8 (5)
920	270.8 ± 7.8 (4)
972	299.6 ± 13.6 (5)

[a] Experimental errors are expressed at the 95% confidence level, number of determinations is given in parentheses.

For the calculation the Eq. (2) we used:

$$\begin{aligned}
&\Delta_{\mathrm{f}} H^{0}_{\mathrm{m}}\,(298.15\,\mathrm{K})\ \text{lepidolite}\\
&\quad = \sum_i \nu_i (\Delta^{973}_{298.15} H^{\mathrm{o}}_{\mathrm{m}} + \Delta_{\mathrm{sol}} H^{\mathrm{o}}_{\mathrm{m}})\mathrm{ox}_i\\
&\qquad + 1.34(\Delta^{973}_{298.15} H^{\mathrm{o}}_{\mathrm{m}} + \Delta_{\mathrm{sol}} H^{\mathrm{o}}_{\mathrm{m}})\mathrm{LiF}\\
&\qquad + 0.153(\Delta^{973}_{298.15} H^{\mathrm{o}}_{\mathrm{m}} + \Delta_{\mathrm{sol}} H^{\mathrm{o}}_{\mathrm{m}})\mathrm{AlF_3}\\
&\qquad - (\Delta^{973}_{298.15} H^{\mathrm{o}}_{\mathrm{m}} + \Delta_{\mathrm{sol}} H^{\mathrm{o}}_{\mathrm{m}})\text{lepidolite}\\
&\qquad + \sum_i \nu_i \Delta_{\mathrm{f}} H^{\mathrm{o}}_{\mathrm{m}}(298.15\,\mathrm{K})\mathrm{ox}_i\\
&\qquad + 1.34\Delta_{\mathrm{f}} H^{\mathrm{o}}_{\mathrm{m}}(298.15\,\mathrm{K})\mathrm{LiF}\\
&\qquad + 0.153\Delta_{\mathrm{f}} H^{\mathrm{o}}_{\mathrm{m}}(298.15\,\mathrm{K})\mathrm{AlF_3}, \qquad (2)
\end{aligned}$$

where ν_i are the stoichiometric coefficients in reaction (1). The resulting value of $\Delta_{\mathrm{f}} H^{\mathrm{o}}_{\mathrm{m}}(298.15\mathrm{K})$ is $-6201 \pm 18\,\mathrm{kJ\,mol^{-1}}$.

The enthalpy increment data obtained by the drop method at $T = 444$, 508, 565, 733, 833, 920 and 972 K are presented in Table 3. These results were fitted by least-squares yielding, with the respective average deviation presented in brackets:

$$\begin{aligned}
C^{\mathrm{o}}_{\mathrm{p,m}} &= 316.10 + 228.12 \times 10^{-3} T - 50.10\\
&\quad \times 10^{5} T^{-2} (\mathrm{J\,K^{-1}\,mol^{-1}})\ [\pm 0.4\%]\ \text{at}\ 298.15\text{–}972\,\mathrm{K};
\end{aligned} \qquad (3)$$

$$C^{\mathrm{o}}_{\mathrm{p,m}}(298.15\,\mathrm{K}) = 327.8\,\mathrm{J\,K^{-1}\,mol^{-1}};$$

$$\begin{aligned}
\Delta^{\mathrm{T}}_{298.15} H^{\mathrm{o}}_{\mathrm{m}} &= 316.10T + 114.06 \times 10^{-3} T^{2} + 50.10\\
&\quad \times 10^{5} T^{-1} - 121188\ (\mathrm{J\,mol^{-1}}).
\end{aligned} \qquad (4)$$

With the experimental data for natural mica, the thermodynamic characteristics of lepidolite of idealized composition $\mathrm{KLi_{1.5}Al_{1.5}[Si_3AlO_{10}]F_2}$ can be estimated. The correction for the difference in the composition of these minerals was made with the thermochemical data for the corresponding constituent components; $\Delta_{\mathrm{dropsol}} H^{\mathrm{o}}_{\mathrm{m}}$ from Table 3 and $\Delta_{\mathrm{drop}} H^{\mathrm{o}}_{\mathrm{m}}$ from [12] for $\mathrm{Rb_2O}$ and $\mathrm{Cs_2O}$ and from [4] for other substances. Thus, for lepidolite $\mathrm{KLi_{1.5}Al_{1.5}[Si_3AlO_{10}]F_2}$, the following thermodynamic propertieswere obtained: $\Delta_{\mathrm{f}} H^{\mathrm{o}}_{\mathrm{m}}(298.15\mathrm{K}) = -6284\,\mathrm{kJ\,mol^{-1}}$ and

$$\begin{aligned}
C^{\mathrm{o}}_{\mathrm{p,m}} &= 336.25 + 190.42 \times 10^{-3} T - 55.18\\
&\quad \times 10^{5} T^{-2} (\mathrm{J\,K^{-1}\,mol^{-1}})\ [\pm 0.4\%]\ \text{at}\ 298.15\text{–}972\,\mathrm{K};
\end{aligned} \qquad (5)$$

$$C^{\mathrm{o}}_{\mathrm{p,m}}(298.15\,\mathrm{K}) = 331.0\,\mathrm{J\,K^{-1}\,mol^{-1}};$$

$$\begin{aligned}
\Delta^{\mathrm{T}}_{298.15} H^{\mathrm{o}}_{\mathrm{m}} &= 336.25T + 95.21 \times 10^{-3} T^{2} + 55.18\\
&\quad \times 10^{5} T^{-1} - 127225\ (\mathrm{J\,mol^{-1}}).
\end{aligned} \qquad (6)$$

The calculated enthalpy of formation of an ideal lepidolite $\mathrm{KLi_{1.5}Al_{1.5}[Si_3AlO_{10}]F_2}$ is about 100 kJ more exothermic, than for natural lepidolite. Similarly, the enthalpy of formation of natural fluorphlogopite as recently determined in our work [13] differs by about the same magnitude from the enthalpy of formation of ideal synthetic fluorphlogopite [11] and known reference data [4].

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