ISSN 0016-7029, Geochemistry International, 2006, Vol. 44, No. 11, pp. 1151–1153. © Pleiades Publishing, Inc., 2006.
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SHORT COMMUNICATIONS

Thermodynamic Properties of the Lithium Mica Polylithionite

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Received April 7, 2005

DOI: 10.1134/S0016702906110061

INTRODUCTION

Polylithionite is a characteristic lithium mica of alkaline pegmatites, metasomatized peralkaline granites, and zones of alkaline metasomatism [1]. Among lithium-bearing micas, polylithionite shows the highest lithium oxide content of 5.5–8.0%, which corresponds to 1.5–2.0 Li atoms per formula unit. The theoretical composition of polylithionite can be expressed as $KLi_2Al[Si_4O_{10}]F_2$. The octahedral positions of natural polylithionite are occupied mainly by Li and Al, with a minor admixture of divalent cations, Fe, Mg, and Mn. A characteristic feature of polylithionite composition is the absence or minor amounts of tetrahedrally coordinated aluminum and higher fluorine content than in other lithium micas. There are no thermodynamic data for polylithionite, either experimental or calculated.

This paper reports the first experimental determination of the enthalpy of formation of natural polylithionite by the method of high-temperature melt solution calorimetry; high-temperature components of enthalpy were measured, and the equation of the temperature dependency of heat capacity was calculated.

SAMPLE CHARACTERISTICS

Calorimetric investigations were conducted using a sample of natural polylithionite from the alkaline rare earth pegmatites of Madagascar. The 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 concentrations of Li, Na, and K were determined by flame photometry at the spectral laboratory of the Fedorovskii All-Russia Institute of Mineral Resources. The following crystal chemical formula was calculated for a 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 g/mol.

Structural investigations were carried out by electron diffraction (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 are a = 5.18 Å, b = 8.97 Å, c = 10.20 Å, and β = 100.33° (1 M polytype).

EXPERIMENTS

Thermochemical measurements were carried out using a Tian–Calvet high-temperature (1000°C) microcalorimeter (Setaram, France), which was described by Kiseleva et al. [2]. The enthalpy of formation was determined by the method of high-temperature melt solution calorimetry. A sample with a weight of 2–4 ($\pm 2 \times 10^{-3}$) mg was thermostated at room temperature and dropped into $2PbO \cdot B_2O_3$ melt-solvent occurring in the calorimeter at T = 973 K. The sum of the heat content and enthalpy of dissolution, [$H°$(973 K) – $H°$ (298.15 K) +

Table 1. Chemical composition of the polylithionite studied

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

$\Delta_{soln}H°(973\ K)$], was measured. The enthalpy increment of polylithionite, [$H°(T)$–$H°(298.15\ K)$], was determined at T = 444, 508, 565, 670, 733, 833, and 920 K by dropping samples weighing 5–17 ($\pm 2 \times 10^{-3}$) mg into the calorimeter without melt. In order to eliminate a small amount of adsorbed water, all samples were annealed before the experiments at 150°C. The instrument was calibrated by dropping reference substances: platinum (in dissolution experiments) and corundum α-Al_2O_3 (for measurement of heat contents), and the necessary thermochemical data for them were adopted from [3].

Table 2. Experimental data on the enthalpy increment of the natural polylithionite, kJ/mol

T, K	$H°(T) - H°(298.15)$
444	48.8 ± 2.0 (10)*
508	72.1 ± 1.6 (6)
565	95.4 ± 2.5 (6)
733	165.3 ± 3.6 (6)
833	214.3 ± 3.4 (6)
920	243.6 ± 8.3 (5)

* Errors are given for the 95% confidence level. The number of measurements is given in parentheses.

Table 3. Calorimetric data obtained in this study for the natural polylithionite

Sample weight, mg	[$H°(973\ K) - H°(298.15) + \Delta_{soln}H°(973\ K)$, kJ/mol]
2.067	468.15
3.349	470.01
3.172	456.54
2.969	460.43
2.588	462.74
3.582	474.54
Average 465.4 ± 7.1 (6)*	

* The error is given for the 95% confidence level; the number of measurements is shown in parentheses.

Table 4. Thermochemical data used for the calculation of the enthalpy of formation of polylithionite, kJ/mol

Substance	[$H°(973\ K) - H°(298.15) + \Delta_{soln}H°(973\ K)$	$-\Delta_fH°_{el}(298.15\ K)$
Na_2O(cr)	–111.8 ± 0.8[a]	414.8 ± 0.3[b]
K_2O(cr)	–193.7 ± 1.1[a]	363.2 ± 2.1[b]
MnO(cr)	43.1 ± 0.8[c]	385.2 ± 0.5[b]
Fe_2O_3(cr)	171.6 ± 1.9[d]	826.2 ± 1.3[b]
Al_2O_3(cr)	107.38 ± 0.59[e]	1675.7 ± 1.3[b]
SiO_2(quartz)	39.43 ± 0.21[f]	910.7 ± 1.0[b]
TiO_2(rutile)	54.4 ± 1.5[g]	944.0 ± 0.8[b]
LiF(cr)	92.8 ± 1.2[h]	616.9 ± 0.8[i]
H_2O(liq)	40.9 ± 2.5[j]	285.8 ± 0.1[b]

Note: [a] After [4]; [b] data from handbook [3]; [c] after [5]; [d–f] calculated using tabulated [$H°(973\ K) - H°(298.15\ K)$] [3] and experimental data on $\Delta_{soln}H°(973\ K)$ from [d] [6], [e] [7], [f] [2]; [g] [8]; [h] [9]; [i] data tabulated in [10]; and [j] estimated by [11].

RESULTS

The results of calorimetric measurements are given in Tables 2 and 3. Table 4 presents the necessary thermochemical data for the calculation of the enthalpy of formation of polylithionite: the enthalpies of solution, heat contents, and enthalpies of formation of its constituent oxides and lithium fluoride.

Using the data of Tables 3 and 4, the standard enthalpy of formation of the polylithionite from elements was calculated on the basis of the following reaction:

$$\begin{aligned} &0.415\ K_2O + 0.01\ Na_2O + 1.68\ LiF \\ &+ 0.785\ Al_2O_3 + 0.015\ Fe_2O_3 + 0.01\ TiO_2 \\ &+ 0.15\ MnO + 3.58\ SiO_2 + 0.16\ H_2O \qquad (1) \\ &= (K_{0.83}Na_{0.02})(Li_{1.68}Al_{1.15}Fe^{3+}_{0.03}Mn_{0.15}Ti_{0.01}) \\ &\cdot [Si_{3.58}Al_{0.42}O_{10}]F_{1.68}(OH)_{0.32}. \end{aligned}$$

The calculations were carried out by the formula

$$\begin{aligned} &\Delta_fH°_{el}(298.15\ K)\text{polylithionite} \\ &= \Sigma\nu_i[H°(973\ K) - H°(298.15\ K) \\ &+ \Delta_{soln}H°(973\ K)]\text{"component} \\ &- [H°(973\ K) - H°(298.15\ K) \\ &+ \Delta_{soln}H°(973\ K)]\text{polylithionite} \\ &+ \Delta\nu_i\Delta_fH°_{el}(298.15\ K)\text{component}_i, \end{aligned} \qquad (2)$$

where ν_i is the stoichiometric coefficient in Eq. (1). The following value was obtained for the polylithionite: $\Delta_fH°_{el}(298.15\ K) = -6041.8 \pm 8.5$ kJ/mol.

Using the experimental data on the enthalpy increment (Table 2), the temperature dependencies of the heat capacity and heat content of the natural polylithionite at 298.15–920 K were approximated by the following equations:

$$\begin{aligned} &C°_p(T) = 343.79 + 161.24 \times 10^{-3}T \\ &- 95.69 \times 10^5T^{-2}\ \text{J/K mol} \\ &\text{maximum error of approximation } \pm 1.2\% \end{aligned} \qquad (3)$$

$$C°_p(298.15\ K) = 284.2\ \text{J/K mol};$$

$$\begin{aligned} &H°(T) - H°(298.15\ K) \\ &= 343.79T + 80.62 \times 10^{-3}T^2 \\ &+ 95.69 \times 10^5T^{-1} - 141762\ \text{J/mol}. \end{aligned} \qquad (4)$$

THERMODYNAMIC PROPERTIES OF POLYLITHIONITE OF THE THEORETICAL COMPOSITION

Based on the obtained calorimetric data for the natural polylithionite, thermodynamic parameters were calculated for polylithionite of the theoretical composition $KLi_2Al[Si_4O_{10}]F_2$. To this end, the experimental data for the natural mineral were adjusted to account for the deviation of its composition from the theoretical one. The corrections were estimated from the appropriate thermochemical data for the constituents of polylithionite (Table 4 and [3]). The $\Delta_f H^\circ_{el}$ (298.15 K) of polylithionite of the composition $KLi_2Al[Si_4O_{10}]F_2$ was calculated as 6045 kJ/mol using Eq. (2) and the corrected calorimetric data.

In the experimental data on the enthalpy increment of natural polylithionite (Table 2), the correction for the deviation of the composition of the mineral from the ideal formula is 0.2%. Using the parameters recalculated to the theoretical composition, we determined the coefficients of equations describing the temperature dependencies of the heat capacity and heat content of polylithionite of the composition $KLi_2Al[Si_4O_{10}]F_2$ for the temperature range 298.15–920 K:

$$C_p^\circ(T) = 343.11 + 160.90 \times 10^{-3}T - 95.50 \times 10^5 T^{-2}\ \text{J/K mol} \quad \text{(maximum error of approximation } \pm 1.4\%\text{)}; \tag{5}$$

$$C_p^\circ(298.15\ \text{K}) = 283.7\ \text{J/K mol};$$

$$H^\circ(T) - H^\circ(298.15\ \text{K}) = 343.11T + 80.45 \times 10^{-3}T^2 + 95.59 \times 10^5 T^{-1} - 141481\ \text{J/mol}. \tag{6}$$

The first thermodynamic data for polylithionite obtained in this study can be used for the thermodynamic modeling of processes of mineral formation with the participation of lithium micas.

ACKNOWLEDGMENTS

This study was financially supported by the Russian Foundation for Basic Research, project no. 03-05-64283.

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