ENTHALPY OF FORMATION OF NATURAL Li-MUSCOVITE

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The melt solution calorimetry was used to determine the enthalpy of formation of natural Li-muscovite on a high-temperature heat flux Tian-Calvet microcalorimeter. The natural sample having high lithium content (Li_2O 2.75 %) from rare metal pegmatites (Toporok deposit, East Sajany, Russia) was choused for investigations. The chemical formula was calculated on the basis of 22 charges: $(K_{0.85}Na_{0.02}Rb_{0.11}Cs_{0.01})_{0.99}(Li_{0.74}Al_{1.62}Fe^{2+}_{0.01}Fe^{3+}_{0.02}Mn_{0.05})_{2.44}(Si_{3.22}Al_{0.78})_{4.00}O_{10}[F_{0.39}(OH)_{1.02}O_{0.29}]_{1.70}$.

The lattice parameters (a=5.19 Å, b=8.99 Å, c=20.10 Å, β=95.33°) are determined; the polytype of the mica studied is $2M_1$. The calorimetric experiments were performed by "drop" method: the sample of Li-muscovite of mass between 3 mg and 10 mg ($\pm 2 \cdot 10^{-3}$) was dropped from room temperature into calorimeter at T=973 K with molten $2PbO \cdot B_2O_3$, the heat effect measured was the sum of the heat content and the heat of solution of the muscovite, $[H^o(973\ K) - H^o(298.15\ K) + \Delta_{sol}H^o(973\ K)]$. The value obtained (473.1± 12.2 J/g) is in a good agreement with our calorimetric solution results for natural muscovite having composition which is close to the theoretical one, $(K_{0.89}Na_{0.11})_{1.00}(Al_{1.84}Mg_{0.09}Fe^{2+}_{0.07}Fe^{3+}_{0.05})_{2.05}(Si_{3.01}Al_{0.99})_{4.00}O_{10}[(OH)_{1.96}O_{0.02}]_{1.98}$ (465.9±10.0 J/g); it shows minor energetic influence of substitution of Al for Li. Using obtained experimental and reference data [1] for mineral, constituent oxides and LiF the standard enthalpy of formation of Li-muscovite from the elements was calculated, $\Delta_f H^o(298.15\ K) = -5899.8 \pm 12.9$ kJ/mol. Obtained molar value of the enthalpy of formation of Li-muscovite from the elements agrees also within experimental uncertainties with our data for muscovite with close to idealized stoichiometry composition (-5914.6±11.1 kJ/mol).

Table. Thermochemical data used in calculation of the enthalpy of formation of Li-muscovite (kJ/mol)

Substance	$[H^o(973\ K) - H^o(298.15\ K) + \Delta_{sol}H^o(973\ K)]$	$-\Delta_f H^o_{el}(298.15\ K)$
Na_2O(s)	-111.8±0.8	414.8±0.3
K_2O(s)	-193.7±1.1	363.2±2.1
Li_2O(s)	-15.3±4.2	597.9±2.1
Rb_2O(s)	-223.2±1.2	338.0±8.0
Cs_2O(s)	-230.0±4.1	346.0±1.2
MnO(s)	43.1±0.8	385.2±0.5
Fe_2O_3(s)	171.6±1.9	826.2±1.3
Al_2O_3(corund)	107.38±0.59	1675.7±1.3
SiO_2(quartz)	39.43±0.21	910.7±1.0
LiF(s)	92.8±1.2	616.9±0.8
H_2O(l)	40.9±2.5	285.8±0.1

Reference

1. *Robie R.A. Hemingway B.S.* Thermodynamic properties of Minerals and Related Substances at 298.15 K and 1 Bar (105 Pascal) Pressure and at Higher Temperatures // U.S. Geol. Surv. Bull. 1995. N. 2131. 462 p.

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