THERMODYNAMIC PROPERTIES OF LITHIUM TOURMALINE – ELBAITE

L.P.Ogorodova, L.V.Melchakova, I.A.Kiseleva, I.S.Peretyazhko*, V.E.Zagorsky*
Lomonosov Moscow State University, Geological department, Moscow, Russia
*Institute of Geochemistry, SB RAS, Irkutsk, Russia

Herald DGGGMS RAS № 5 (15)'2000 v.2
URL: *http://www.scgis.ru/russian/cp1251/h_dgggms/5-2000/term11.eng*

The thermodynamic modelling of boron mineralization in different natural processes needs the reliable thermochemical data on tourmalines. The previous experimental determination of thermodynamic properties has been made only for alumodravite [1]. The study of thermodynamic parameters of tourmalines of other composition was began by us with thermochemical investigation of natural lithium tourmaline – liddicoatite-elbaite.

We chose to investigate a sample of natural elbaite from pegmatites East Siberia [2]. The chemical composition and structural characteristics were determined. The tourmaline studied has high contents of Li_2O (2.34 %) and CaO (2.65 %) and can be considered as calcium elbaite - liddicoatite. The formula of tourmaline investigated was calculated for 31 anions: $(Na_{0.49}Ca_{0.45}K_{0.02})_{0.96}(Li_{1.49}Mn_{0.05}Fe^{+3}_{0.03}Mg_{0.09}Al_{7.20})_{8.86}Si_{6.16}B_{3.13}O_{27.91}(OH)_{2.64}F_{0.45}$.

The thermochemical investigations were performed in differential scanning calorimeter DSC «Mettler TA-2000B» and high-temperature heat-flux Calvet microcalorimeter «Setaram».

The heat capacity of lithium tourmaline was measured by DSC method in the interval of 110 – 800 K in flowing nitrogen with a heating rate of 10 K/min and a cooling rate of 5 K/min. Details of instrument operation are described in [3]. The molar enthalpy and melting temperature of indium reference substance (99.9999 % purity) were used to calibrate the DSC.

The values of enthalpy increments H^o_T-$H^o_{298.15}$ of mineral studied were measured in Calvet microcalorimeter by the «drop» method at the temperatures T=712, 803, 973 K. The calibration of the calorimeter was achieved by dropping pieces of corundum α-Al_2O_3.

The DSC measurements results in the interval of 290-650 K and Calvet microcalorimeter experimental data were fitted by least-squares yielding with respective average deviation of approximation presented in brackets:

$$C°p = 982.88 + 313.69\cdot10^{-3}T - 274.70\cdot10^{5}T^{-2}\ \text{J/mol·K}\ (\pm\ 1.3\%)\ \text{at}\ 298.15–800\ \text{K},$$
$$C°p(298.15) = 767.4\ \text{J/mol·K};$$

$$H°_T - H°_{298.15} = 982.88\ T + 156.84\cdot10^{-3}T^2 + 274.70\cdot10^{5}T^{-1} - 399119.24\ \text{J/mol}.$$

The enthalpy of formation of liddicoatite-elbaite was determined in Calvet microcalorimeter by high-temperature melt solution calorimetry. The solution in solvent $2PbO\cdot B_2O_3$ at T=973 K was made using special designed equipment which was described in [4]. To calibrate calorimeter the «drop» method of Pt wire was used. A precision of the weighing the samples was $\pm\ 2\cdot10^{-3}$ mg.

The enthalpy of formation of liddicoatite-elbaite from the elements was calculated from experimental values of heat of solution of mineral studied and constituent oxides and fluorides, the experimental and reference data on enthalpy increments $H°_{973}–H°_{298.15}$ and enthalpies of formation $\Delta H^o_f(298.15)$ of oxides and fluorides.

The standard entropy at T=298.15 K was estimated by us from exchange reaction between elbaite and alumodravite investigated in [1] by low-temperature adiabatic calorimetry method.

On the basis of obtained in this work values of $\Delta H^o_f(298.15)$ and $S^o(298.15)$ the free Gibbs energy of formation from the elements $\Delta G^o_f(298.15)$ of liddicoatite-elbaite $(Na_{0.49}Ca_{0.45}K_{0.02})_{0.96}(Li_{1.49}Mn_{0.05}Fe^{+3}_{0.03}Mg_{0.09}Al_{7.20})_{8.86}Si_{6.16}B_{3.13}O_{27.91}(OH)_{2.64}F_{0.45}$ was calculated.

Table

Thermodynamic properties of natural liddicoatite-elbaite
$(Na_{0.49}Ca_{0.45}K_{0.02})_{0.96}(Li_{1.49}Mn_{0.05}Fe^{+3}_{0.03}Mg_{0.09}Al_{7.20})_{8.86}Si_{6.16}B_{3.13}O_{27.91}(OH)_{2.64}F_{0.45}$
at T=298.15 K (M.м.=948.13g/mol)

C^o_p, J/mol·K	S^o, J/mol·K	ΔH^o_f, kJ/mol	ΔG^o_f, kJ/mol
767.4	624.1*	-15555.7±2.1	-14613.5

*-estimated from exchange reaction

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