

Thermodynamics of natural tourmaline–elbaite

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Abstract

The first experimental data on the heat capacities, enthalpies of formation from the oxides and elements of a natural elbaite: $(\text{Na}_{0.48}\text{Ca}_{0.44}\text{K}_{0.02})(\text{Li}_{1.45}\text{Mn}_{0.05}\text{Fe}_{0.03}^{3+}\text{Mg}_{0.09})\text{Al}_{7.01}\text{Si}_{6.00}\text{B}_{3.05}(\text{OH})_{2.57}\text{F}_{0.44}\text{O}_{27.18}$ (Malkhan pegmatite field, east Siberia, Russia) have been obtained. The heat capacities of elbaite were measured by DSC method from $T = 270$ to 540 K. High-temperature enthalpy increments were determined on the Tian–Calvet microcalorimeter at interval of 569 – 1023 K using the drop method. A value of $C_{p,m}^{\circ}(298.15 \text{ K}) = 757.3 \text{ J K}^{-1} \text{ mol}^{-1}$ was obtained and the resultant $C_{p,m}^{\circ}(T)$ equation in the interval $T = 298.15$ – 1023 K was calculated: $C_{p,m}^{\circ} = 919.7 + 366.2 \times 10^{-3}T - 241.4 \times 10^{-5}T^{-2}$ ($\text{K}^{-1} \text{ mol}^{-1}$) ($\pm 1.4\%$). The standard molar enthalpy of formation from the elements was determined by high-temperature solution calorimetry in molten lead borate at $T = 973$ K on the Tian–Calvet microcalorimeter. The value of $\Delta_f H_m^{\circ}(298.15 \text{ K})$ of elbaite was found to be $-15129 \pm 19 \text{ kJ mol}^{-1}$. The value of $\Delta_f G_m^{\circ}(298.15 \text{ K})$ was calculated as $-14213 \text{ kJ mol}^{-1}$.

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1. Introduction

Elbaite–Li-rich varieties of boron minerals tourmalines are widespread in the upper crust, occurring in different geological environments. Colored natural and synthetic varieties of elbaite are used as a gem quality stone, transparent crystals have pyro- and piezoelectric effects. Understanding of geology and mechanisms of tourmaline precipitation requires that the thermodynamic properties of these boron-bearing minerals be known. Unfortunately, such information has been largely unavailable. Today thermodynamic data on Li-tourmaline–elbaite are absent.

The purpose of this study is the experimental determination of the standard molar thermodynamic properties of elbaite using calorimetric methods.

2. Sample description

Crystals of natural pink transparent tourmaline–elbaite were taken from miarole of Mokhovaya vein (Malkhan peg-

matite field, east Siberia, Russia). The chemical composition of mineral given in Table 1 was determined by following methods: photocalorimetry (Si, Al, B, F), atomic adsorption method (Ca, Mg, Fe, Mn), flame photometry (K, Na, Li) and H_2O –Penfild’s method (Table 1). The chemical formula of elbaite calculated on the basis of six Si atoms in the framework is: $(\text{Na}_{0.48}\text{Ca}_{0.44}\text{K}_{0.02})(\text{Li}_{1.45}\text{Mn}_{0.05}\text{Fe}_{0.03}^{3+}\text{Mg}_{0.09})\text{Al}_{7.01}\text{Si}_{6.00}\text{B}_{3.05}(\text{OH})_{2.57}\text{F}_{0.44}\text{O}_{27.18}$.

The thermodynamic properties of elbaite obtained in this work are based on this formula.

3. Experimental techniques

All thermochemical investigations of elbaite were performed using a Tian–Calvet high-temperature (1000°C) heat-flux microcalorimeter (“Setaram”) and a differential scanning calorimeter (DSC) “Mettler TA-2000B”, described in detail in [2,3].

The heat capacity was measured within 270 – 540 K by DSC method in a nitrogen flow with a scanning rate of 0.17 K s^{-1} . Samples of mass 30 – $50 \pm 2 \times 10^{-3} \text{ mg}$ were sealed in aluminum pans and placed in calorimeter. The metallic indium (99.9999% purity grade), which was provided by the calorimeter manufacturer, with a

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Table 1
The chemical composition and lattice parameters of natural elbaite

	Chemical composition (wt.%)
Oxide	
SiO ₂	38.95
TiO ₂	0.04
Al ₂ O ₃	38.61
Fe ₂ O ₃	0.22
FeO	–
MnO	0.39
MgO	0.38
CaO	2.65
Na ₂ O	1.60
K ₂ O	0.11
Li ₂ O	2.34
B ₂ O ₃	11.48
H ₂ O ⁺	2.50
H ₂ O [–]	0.10
F	0.90
–O=F ₂	0.38
CyMMA	99.89
Cations and anions in formula	
Na	0.48
Ca	0.44
K	0.02
∑(Na, Ca, K)	0.94
Li	1.45
Mn	0.05
Fe ³⁺	0.03
Mg	0.09
Al	7.01
∑(Li, Mn, Fe ³⁺ , Mg, Al)	8.63
Si	6.00
B	3.05
OH	2.57
F	0.44
O	27.18
∑(O, F, OH)	30.19
Lattice parameters ^a	
<i>a</i> (×10 ^{–10} m)	15.840
<i>c</i> (×10 ^{–10} m)	7.100
<i>V</i> (×10 ^{–10} m ³)	1542.7
<i>Z</i>	3

^a Lattice parameters for this sample are given in [1].

melting temperature $T = 429.76$ K and an enthalpy of 3.264 kJ mol^{–1} [4] were used for calibration. Reproducibility of enthalpy and temperature of melting experiments were ± 0.3 and $\pm 0.01\%$, respectively. The errors in the heat capacity measurements, based on earlier runs performed on a standard substance (fine-grained α -Al₂O₃), were ± 2 – 3% at temperatures lower than $T = 300$ K and ± 1.5 – 2% between $T = 300$ and 810 K.

High-temperature heat contents were determined on the Tian–Calvet microcalorimeter at interval of 569 – 1023 K using the drop method. A tourmaline sample weighing 3 – $10 \pm 2 \times 10^{-3}$ mg was dropped directly from room temperature into the calorimeter at experiment temperature and the enthalpy

increment ($\Delta_{298.15}^T H_m^\circ$) was measured. Calibration was performed by dropping standard substance corundum α -Al₂O₃, the required thermochemical data were taken from [4].

The enthalpy of formation of elbaite was determined by high-temperature oxide melt solution calorimetry. To measure the enthalpy of solution ($\Delta_{\text{sol}} H_m^\circ$) 10 – $20 \pm 2 \times 10^{-3}$ mg of sample was placed in a foil cup and then equilibrated thermally in the calorimeter usually 2 – 3 h before being dissolved in about 30 g of molten $2\text{PbO} \cdot \text{B}_2\text{O}_3$. Dissolution of the sample is initiated by dipping the cup with the sample into the melt solvent. Stirring is manual by moving the platinum cup up and down several times. The sample dissolved readily and gave a complete reaction within 30 – 50 min before a steady baseline signal was restored. The same method was used to measure the enthalpy of solution of synthetic single crystal LiF (99.9% purity). Calibration of the calorimeter was performed by dropping pieces of platinum wire and using its known enthalpy increments data [4].

4. Results and discussion

The average results of six scans of heat capacity measurements, by the method of differential scanning calorimetry, for elbaite at temperatures ranging from 270 to 510 K are listed in Table 2. The enthalpy increment data obtained by drop method on Tian–Calvet microcalorimeter at $T = 569$, 712 , 803 , 951 , 973 and 1023 K are presented in Table 3. All these experimental data were combined and fitted by

Table 2
Experimental heat capacities of elbaite (M.m. = 923.49 g mol^{–1})

<i>T</i> (K)	<i>C</i> ^o _{p,m} (JK ^{–1} mol ^{–1})	<i>T</i> (K)	<i>C</i> ^o _{p,m} (JK ^{–1} mol ^{–1})
270	716.6	400	902.2
280	722.2	410	917.0
290	739.7	420	924.4
300	761.0	430	937.3
310	779.4	440	940.1
320	797.9	450	953.0
330	808.1	460	966.0
340	825.6	470	979.8
350	837.6	480	994.6
360	851.5	490	1003.8
370	862.5	500	1010.3
380	876.4	510	1021.4
390	888.4		

Table 3
Experimental data on $\Delta_{298.15}^T H_m^\circ$ for elbaite (M.m. = 923.49 g mol^{–1})

<i>T</i> (K)	Enthalpy increment (kJ mol ^{–1})
569	252.6 ± 8.1
712	409.3 ± 5.4
803	517.1 ± 1.7
951	694.6 ± 6.1
973	739.2 ± 10.2
1023	766.4 ± 11.5

Table 4
Results of drop and solution calorimetry on elbaite and lithium fluoride

Substance	$\Delta_{298.15}^{973}H_m^\circ$ (kJ mol ⁻¹)	$\Delta_{\text{sol},973}H_m^\circ$ (kJ mol ⁻¹)
Elbaite	739.2 ± 10.2 (6) ^a	428.3 ± 13.8 (6) ^a
LiF (s)	35.17 ± 0.37 (6) ^a	57.59 ± 1.16 (6) ^a

^a Errors are expressed by interval for $P = 95\%$, in parentheses the number of determinations is given.

least-squares method yielding, with respective average deviation of approximation presented in parentheses:

$$C_{p,m}^\circ = 919.7 + 366.2 \times 10^{-3}T - 241.4 \times 10^5 T^{-2} \quad (\text{J K}^{-1} \text{ mol}^{-1}) (\pm 1.4\%) \text{ at } 298.15\text{--}1023 \text{ K},$$

$$C_{p,m}^\circ(298.15 \text{ K}) = 757.3 \text{ J K}^{-1} \text{ mol}^{-1} \quad (1)$$

$$\Delta_{298.15}^T H_m^\circ = 919.7 + 183.1 \times 10^{-3}T^2 + 241.4 \times 10^5 T^{-1} - 371438.4 \text{ (J K}^{-1} \text{ mol}^{-1}) \quad (2)$$

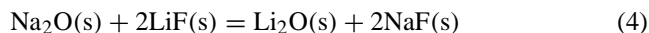
The calorimetric solution data for natural elbaite and lithium fluoride obtained in this work are listed in Table 4. The standard molar enthalpy of formation of studied natural elbaite from the elements at $T = 298.15 \text{ K}$ was calculated from thermochemical data of Table 4, using the necessary thermochemical parameters of constituent oxides, sodium fluoride and synthetic eucryptite LiAlSiO₄ (Table 5) and the reference thermodynamic characteristics for needed compounds [4] according to the following equation:

$$\begin{aligned} \Delta_f H_m^\circ(298.15 \text{ K})_{\text{elbaite}} &= \sum v_i (\Delta_{298.15}^{973} H_m^\circ + \Delta_{\text{sol}} H_m^\circ)_{\text{ox}_i} + 0.44 (\Delta_{298.15}^{973} H_m^\circ + \Delta_{\text{sol}} H_m^\circ)_{\text{LiF}} - (\Delta_{298.15}^{973} H_m^\circ + \Delta_{\text{sol}} H_m^\circ)_{\text{elbaite}} \\ &+ \sum v_i \Delta_f H_m^\circ(298.15 \text{ K})_{\text{ox}_i} + 0.44 \Delta_f H_m^\circ(298.15 \text{ K})_{\text{LiF}}, \end{aligned} \quad (3)$$

where v_i is the stoichiometric coefficients in the reaction of elbaite formation from the oxides and lithium fluoride, the

values $\Delta_{298.15}^{973} H_m^\circ$, $\Delta_{\text{sol}} H_m^\circ$, $(\Delta_{298.15}^{973} H_m^\circ + \Delta_{\text{sol}} H_m^\circ)$ the heat contents, heats of solution and drop solution of all constituent compounds and elbaite under the same calorimetric conditions (Tables 4 and 5).

The required value of the enthalpy of solution of Li₂O cannot be obtained experimentally, because it tends to absorb moisture to form LiOH·H₂O, therefore this value was estimated from the exchange reaction:



using experimental data (Tables 4 and 5) and reference enthalpies increments and enthalpies of formation of all substances from [4], LiF from [15]. The enthalpy of drop solution of lithium oxide ($-15.3 \pm 4.2 \text{ kJ mol}^{-1}$) estimated in this work is in an agreement with value calculated on a basis of experimental data on $(\Delta_{298.15}^{973} H_m^\circ + \Delta_{\text{sol}} H_m^\circ)$ of Li₂CO₃ ($-18.28 \pm 2.17 \text{ kJ mol}^{-1}$) [14].

The standard molar enthalpy of formation of elbaite from the elements was calculated using the reference thermodynamic data for constituent compounds [4] to be: $\Delta_f H_m^\circ(298.15 \text{ K}) = -15\,129 \pm 19 \text{ kJ mol}^{-1}$. This value can be calculated also from the reaction of elbaite formation from oxides, sodium fluoride and eucryptite LiAlSiO₄. The necessary thermodynamic constants were taken from Table 5 and from [4]. The resulting value $\Delta_f H_m^\circ(298.15 \text{ K})$ for elbaite is $-15\,140 \pm 19 \text{ kJ mol}^{-1}$. A good agreement of both calculation results confirms a reliability of our data obtained. We prefer the following value of $\Delta_f H_m^\circ(298.15 \text{ K}) = -15\,129 \pm 19 \text{ kJ mol}^{-1}$ for natural elbaite (Table 6).

The value of $S_m^\circ(298.15 \text{ K})$ of elbaite studied was calculated using the known data on the entropy of natural aluminodravite obtained from low-temperature measurements [16]. The entropy contribution arising from the difference between the composition of elbaite and aluminodravite was estimated additively from the entropies of the constituent oxides [4]. The contribution of the entropy of 1 mol of water in tourmaline was estimated

Table 5
The calorimetric data used for calculation of enthalpies of formation of elbaite

Substance	$\Delta_{298.15}^{973} H_m^\circ + \Delta_{\text{sol},973} H_m^\circ$ (kJ mol ⁻¹)	$\Delta_{298.15}^{973} H_m^\circ$ (kJ mol ⁻¹)	$\Delta_{\text{sol},973} H_m^\circ$ (kJ mol ⁻¹)	Reference
Na ₂ O (s)	-111.8 ± 0.9			[5]
K ₂ O (s)	-193.7 ± 1.1			[6]
Li ₂ O (s)	-15.3 ± 4.2			This work
CaO (s)		33.87	-55.65 ± 0.29	[2]
MgO (s)		29.31	4.81 ± 0.59	[7]
MnO (s)	43.1 ± 0.8			[8]
Al ₂ O ₃ (s) corundum		74.67	32.71 ± 0.59	[9]
Fe ₂ O ₃ (s)		96.11	75.48 ± 1.88	[10]
SiO ₂ (s) quartz		43.66	-4.23 ± 0.21	[2]
B ₂ O ₃ (s)		94.08	-55.31 ± 0.84	[11]
H ₂ O (l)		68.94	-28.0 ± 2.5	[12]
NaF (s)	92.72 ± 0.79			[13]
LiAlSiO ₄ (s)	153.69 ± 0.62			[14]

^a From [4].

Table 6

The thermodynamic properties of elbaite ($\text{Na}_{0.48}\text{Ca}_{0.44}\text{K}_{0.02}\text{(Li}_{1.45}\text{Mn}_{0.05}\text{Fe}_{0.03}^{3+}\text{Mg}_{0.09})\text{Al}_{7.01}\text{Si}_{6.00}\text{B}_{3.05}\text{(OH)}_{2.57}\text{F}_{0.44}\text{O}_{27.18}$, obtained in this study

$-\Delta_f H_m^\circ$ (298.15 K) (kJ mol^{-1})	15 129 \pm 19
$-\Delta_f G_m^\circ$ (298.15 K) (kJ mol^{-1})	14 213
S_m° (298.15 K) ($\text{J mol}^{-1} \text{K}^{-1}$)	613
$C_{p,m}^\circ = a + bT \times 10^{-3} - cT^{-2} \times 10^5$ ($\text{J mol}^{-1} \text{K}^{-1}$)	
a	919.7
b	366.2
c	241.4
$C_{p,m}^\circ$ (298.15 K) ($\text{J mol}^{-1} \text{K}^{-1}$)	757.3

using aluminodravite entropy data [16] and was to be $20.3 \pm 1.0 \text{ J K}^{-1} \text{ mol}^{-1}$.

Taking into account the obtained value $S_m^\circ(298.15 \text{ K})$ for elbaite ($613 \text{ J K}^{-1} \text{ mol}^{-1}$) we calculated the Gibbs free energy of its formation from the elements as $\Delta_f G_m^\circ(298.15 \text{ K}) = -14 213 \text{ kJ mol}^{-1}$ (Table 6).

Thermodynamic parameters for elbaite, obtained in this study will assist in the interpretation of physical and chemical conditions of boron mineralization.

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