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HEAT CAPACITY AND THERMODYNAMIC PROPERTIES OF RAMSDELLITE, $Li_2Ti_3O_7$, AND SPINEL, $Li_{4/3}Ti_{5/3}O_4$

V.I. KOLOTYRKIN, J.A. KESSLER, V.A. SHCHELKOTUNOV, I.V. GORDEYEV, Yu.G. METLIN and Yu.D. TRETYAKOV

Chemistry Department, Moscow State University, 117234 Moscow (U.S.S.R.)

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ABSTRACT

The heat capacity and heat content of $Li_{4/3}Ti_{5/3}O_4$ and $Li_2Ti_3O_7$ have been measured in the temperature range 198—960 K. The lattice and dilation contributions to the heat capacity have been estimated. The standard thermodynamic functions and the high temperature enthalpy and entropy have been derived. The lattice heat capacity of $Li_{4/3}Ti_{5/3}O_4$ spinel appears to be consistent with the phonon model put forward by Grimes.

INTRODUCTION

The high Li-ionic conductivity of compounds in the Li_2O—TiO_2 system has attracted much attention [1,2]. Up to now crystallochemical [3], conducting [4,5], electrolytical [6] and certain thermodynamic properties [6] of these compounds have been studied. In order to further study the thermodynamics of $Li_2Ti_3O_7$ (ramsdellite) and $Li_{4/3}Ti_{5/3}O_4$ (spinel), heat capacity and heat content measurements were carried out and the results are reported here.

SAMPLE PREPARATION

The samples were prepared by sintering high-purity Li_2CO_3 and TiO_2 (at 750 + 1020 + 1080°C for the ramsdellite and at 750 + 900°C for the spinel). From X-ray powder diffraction of fired samples we obtained $a = 0.8345$ nm for $Li_{4/3}Ti_{5/3}O_4$ and $a = 0.4982$ nm, $b = 0.9549$ nm, $c = 0.2950$ nm for $Li_2Ti_3O_7$ (± 0.0002 nm). Details of the preparation and X-ray analysis technique are described elsewhere [7].

EXPERIMENTAL AND RESULTS

The heat capacity of $Li_{4/3}Ti_{5/3}O_4$ and $Li_2Ti_3O_7$ was measured by conventional adiabatic calorimetric techniques [8] from 198 to 673 K with 15-grade steps, reproducibility being better than 1%. Heat content measure-

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TABLE 1

Resolution of the heat capacity of $Li_{4/3}Ti_{5/3}O_4$ and $Li_2Ti_3O_7$ into lattice and dilational components

Compound	T(K)	C_p(J mole^{-1} K^{-1})	C_v(J mole^{-1} K^{-1})	C_d(J mole^{-1} K^{-1})
$Li_{4/3}Ti_{5/3}O_4$ [a]	198	74.82		
	228	98.65	98.65	
	273	115.37	114.53	
	313	125.82	124.65	1.63
	353	135.01	132.88	1.96
	393	142.96	140.45	2.30
	433	148.81	145.67	2.63
	473	152.99	149.64	3.01
	513	156.75	152.70	3.34
	553	160.09	156.16	3.72
	593	163.02	157.80	4.05
	633	164.69	159.04	4.39
	673	165.95	159.92	4.72
$Li_2Ti_3O_7$ [b]	213	174.69		
	228	187.00		
	273	214.30	214.25	
	313	231.27	230.69	
	353	244.40	242.46	5.79
	393	255.19	251.40	6.79
	433	264.45	259.63	7.73
	473	272.68	265.23	8.78
	513	280.19	270.12	9.82
	553	287.18	273.33	10.87
	593	293.78	276.82	12.00
	633	300.09	279.40	13.13
	653	303.16	280.13	14.04

[a] C_v computed by eqn. (3), C_d calculated by eqn. (4).
[b] C_v computed by eqn. (5), C_d estimated by the Nernst—Lindemann formula.

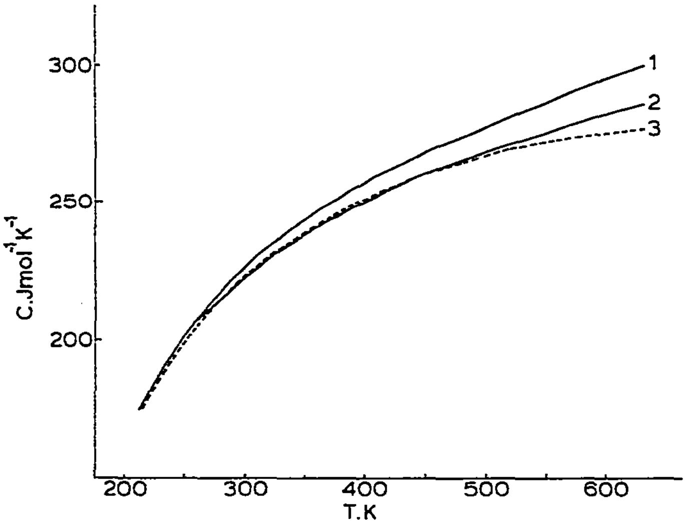

Fig. 1. Heat capacity vs. temperature for $Li_2Ti_3O_7$. 1, C_p; 2, $C_p - C_d$; 3, C_v [from eqn. (5)].

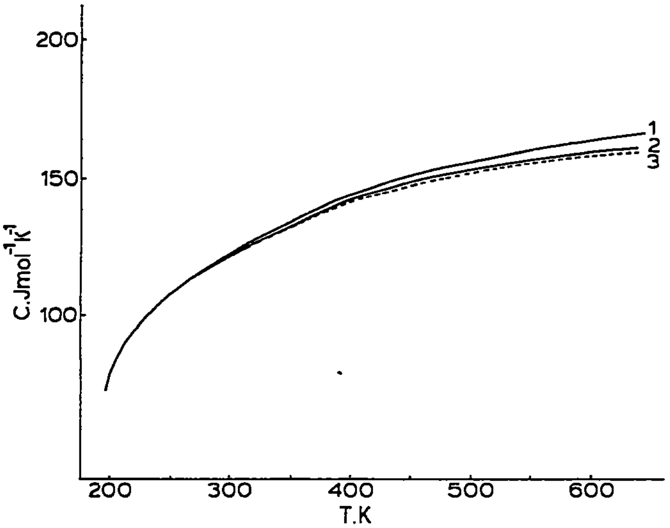

Fig. 2. Heat capacity vs. temperature for $Li_{4/3}Ti_{5/3}O_4$. 1, C_p; 2, $C_p - C_d$; 3, C_v [from eqn. (3)].

ments were carried out by drop-calorimetry with 50-grade steps from 310 to 960 K in the Calvet-type double microcalorimeter previously described [9]. No anomalies were observed in both cases. In the temperature range 410—660 K the two sets of experimental data coincide within 0.5%. The experimental results are presented in Table 1 and Figs. 1 and 2.

The heat capacity values from smoothed curves fit the Meyer—Kelly [10]

TABLE 2

High temperature enthalpy and entropy of $Li_{4/3}Ti_{5/3}O_4$ and $Li_2Ti_3O_7$

Compound	T(K)	$H_T - H_{298}$ (kJ mole^{-1})	$S_T - S_{298}$ (J mole^{-1} K^{-1})
$Li_{4/3}Ti_{5/3}O_4$	300	0.22	0.75
	400	13.64	39.19
	500	28.70	72.75
	600	44.68	101.86
	700	61.27	127.42
	800	78.31	150.17
	900	95.71	170.66
	1000	113.43	189.33
$Li_2Ti_3O_7$	300	1.05	1.53
	400	25.34	72.19
	500	52.12	132.87
	600	80.77	186.07
	700	111.04	233.69
	800	142.78	277.06
	900	175.92	317.08
	1000	210.42	354.41

equations

$$C_{p\,\mathrm{Li_{4/3}Ti_{5/3}O_4}} = 163.64 + 19.33 \times 10^{-3}T - 43.46 \times 10^{5}T^{-2}\ \mathrm{J\ mole^{-1}\ K^{-1}}$$
$$(0.5\%\ \text{within}\ 298\text{–}960\ \mathrm{K}) \tag{1}$$

and

$$C_{p\,\mathrm{Li_2Ti_3O_7}} = 230.00 + 135.40 \times 10^{-3}T - 37.21 \times 10^{5}T^{-2}\ \mathrm{J\ mole^{-1}\ K^{-1}}$$
$$(0.8\%\ \text{within}\ 298\text{–}960\ \mathrm{K}) \tag{2}$$

The high temperature enthalpy and entropy values calculated by eqns. (1) and (2) are given in Table 2.

THERMODYNAMIC PROPERTIES OF $Li_{4/3}Ti_{5/3}O_4$

The low-temperature heat capacity of $Li_{4/3}Ti_{5/3}O_4$ was evaluated using the Grimes approximation [11]. According to Grimes [11], the lattice heat capacity of a spinel may be written as

$$C_v = D\left(\frac{\theta_1}{T}\right) + 2E\left(\frac{\theta_2}{T}\right) + 2D\left(\frac{\theta_3}{T}\right) + 2E\left(\frac{\theta_4}{T}\right),$$

where $\theta_i = (h/k)\nu_i$; ν_i = IR-active frequencies; D, E = Debye and Einstein functions, respectively; h, k = the Planck and Boltzmann constants, respectively. From IR absorption spectra of $Li_{4/3}Ti_{5/3}O_4$ shot with a FIS-2 IR spectrophotometer we obtained $\nu_1 = 209$ cm^{-1}, $\nu_2 = 405$ cm^{-1}, $\nu_3 = 505$ cm^{-1} and $\nu_4 = 650$ cm^{-1}. Using these data we derived C_v as

$$C_v = D\left(\frac{300}{T}\right) + 2E\left(\frac{582}{T}\right) + 2D\left(\frac{726}{T}\right) + 2E\left(\frac{934}{T}\right) \tag{3}$$

From low-temperature heat capacity measurements (1—15 K) McCallum et al. [12] found the equivalent Debye temperature $\theta_D = 610 \pm 4$ K. At $T \rightarrow 0$ K one can neglect the Einstein function's contribution in eqn. (3) which can now be rewritten as

$$C_{v_{T\to 0\mathrm{K}}} = D\left(\frac{300}{T}\right) + 2D\left(\frac{720}{T}\right).$$

Following Grime's approach [13], we calculated the mean square equivalent Debye temperature $\theta_D = 617$ K, that is consistent with McCallum's value.

In order to verify the lattice heat capacity estimate, the observed heat capacity C_p is considered to be a sum: $C_p = C_v + C_d + C_m + C_{el}$. Here C_d is the dilation contribution, C_m is the contribution of unpaired electrons, and C_{el} is the conduction electrons' contribution. $Li_{4/3}Ti_{5/3}O_4$ is known to be a dielectric and a diamagnet [12], so $C_m = 0$ and $C_{el} = 0$. In principle, some excess heat capacity contribution can arise from the cation distribution change at elevated temperatures. However, the calculation based on the Poix invariant distance approach [14] appeared to be consistent with random distribution even at room temperature. For this reason the distribution change is not likely to add to the heat capacity.

The dilation contribution C_d was evaluated by use of the Grüneisen relation

$$C_d = 3\alpha\Gamma C_v T \tag{4}$$

where Γ is the Grüneisen constant equal to 1.7 ± 0.1 as found for spinels [15], α is the expansivity estimated to be $\alpha = (8 \pm 2)10^{-6}$ K^{-1} [16].

The lattice heat capacity C_v calculated as $C_v = C_p - C_d$ appeared to be consistent with the previous computation based on eqn. (3) within 1%. The C_v and C_d values at selected temperatures are given in Table 1. The consistency of the two estimates of C_v places confidence in the correctness of the analysis.

The calculated standard vibrational entropy of $Li_{4/3}Ti_{5/3}O_4$ is $S^0_{298} = 95$ J mole^{-1} K^{-1}. Furthermore, the configuration entropy increment must be taken into account. As noted above, the cationic distribution is close to random at room temperature. At $T \rightarrow 0$ K the significant difference in Li and Ti [17] charges should result in an ordering of 1 : 5 type leading to the formula $Li[Li_{1/3}Ti_{5/3}]O_4$. The configuration entropy of this ordering can be evaluated by conventional statistical methods [18]

$$S^0_{\text{conf.}} = -R[(5/9)\ln(5/9) + (4/9)\ln(4/9) + (8/9)\ln(4/9) + (10/9)\ln(5/9)$$
$$+ (1/3)\ln(1/6) + (5/3)\ln(5/6)] = 24.7 \text{ J mole}^{-1} \text{ K}^{-1}$$

Hence, the total standard entropy of $Li_{4/3}Ti_{5/3}O_4$ is $S^0_{298} = S^0_{\text{vibr.}} + S^0_{\text{conf.}} = 120 \pm 6$ J mole^{-1} K^{-1}.

THERMODYNAMIC PROPERTIES OF $Li_2Ti_3O_7$

To analyse the heat capacity of the $Li_2Ti_3O_7$ ramsdellite we set $C_v = C_p - C_d$ ($C_m = 0$, $C_{el} = 0$ as in the case of $Li_{4/3}Ti_{5/3}O_4$). The dilation contribution was estimated by the Nernst—Lindemann formula $C_d = 0.0214\ (T/T_m)C_p^2$, where the melting point of the ramsdellite T_m was known to be $T_m = 1653$ K [19,20]. The expansivity of $Li_2Ti_3O_7$, measured with a DKV 5A quartz dilatometer in the range 298—1173 K, remains roughly constant ($\alpha = 1.35 \pm 0.02 \times 10^{-5}$ K^{-1}). The Grüneisen parameter Γ calculated by use of eqn. (4) is the same as that of $Li_{4/3}Ti_{5/3}O_4$ (~1.7).

Low-temperature heat capacity was estimated from IR absorption data. Five modes were observed with the FIS 2 spectrophotometer: at $\nu_1 = 208$ cm^{-1}, $\nu_2 = 340$ cm^{-1}, $\nu_3 = 403$ cm^{-1}, $\nu_4 = 500$ cm^{-1} and $\nu_5 = 720$ cm^{-1}. In the range 200—350 K, C_v, evaluated by subtracting C_d from the experimental C_p curve, can be described adequately by the following Debye-Einstein functions combination

$$C_v = D\left(\frac{299}{T}\right) + 2E\left(\frac{489}{T}\right) + 6E\left(\frac{580}{T}\right) + 2D\left(\frac{719}{T}\right) + E\left(\frac{1035}{T}\right) \tag{5}$$

Assuming eqn. (5) valid at low temperatures, we computed the vibrational entropy $S^0_{\text{vibr.}}(298) = 174$ J mole^{-1} K^{-1}. At $T > 500$ K, C_v values derived from C_p exceed those calculated by eqn. (5). The discrepancy may be dealt

TABLE 3

The standard thermodynamic functions of $Li_{4/3}Ti_{5/3}O_4$ and $Li_2Ti_3O_7$

Compound	S^0_{298} (J mole^{-1} K^{-1})	$\Delta H^0_{f,298}$ (I) (kJ mole^{-1})	$\Delta H^0_{f,298}$ (II) (kJ mole^{-1})
$Li_{4/3}Ti_{5/3}O_4$	120 ± 6	—74.6 ± 0.7	—2050 ± 10
$Li_2Ti_3O_7$	193 ± 20 200 [23]	—97.0 ± 2.3	—3530 ± 130 —3580 [23]

with the superionic nature of $Li_2Ti_3O_7$. The mobile Li-ions positioned in the channels can contribute to the heat capacity considerably at elevated temperatures.

The elementary cell of the ramsdellite is known to contain eight oxygen atoms and four metal atoms [21]. The framework forms channels partly filled with lithium. From this viewpoint the ramsdellite formula can be written as $Li_{\sim 1.72}[Li_{\sim 0.57}Ti_{\sim 3.43}]O_8$, i.e. part of the available lithium and all the titanium atoms fill in the oxygen octahedra providing tetrahedral positions partly vacant. At low temperatures an ordering may take place, which is considered formally as 1 : 6 in the octahedra. The configurational entropy of such an ordering is $S^0_{conf.} = 17.9$ J mole^{-1} K^{-1}, then the resulting total standard entropy of $Li_2Ti_3O_7$ is S^0 (298 K) $= S^0_{vibr.} + S^0_{conf.} = 192$ J mole^{-1} K^{-1}, with an accuracy supposed to be about 10%.

Using enthalpy-of-formation data for $Li_{4/3}Ti_{5/3}O_4$ and $Li_2Ti_3O_7$ obtained previously at 900 K [7], heat content data for TiO_2 (rutile) and Li_2O [22] and those from Table 2, we calculated the standard enthalpy of formation ΔH^0_f (I) from binary oxides and ΔH^0_f (II) from elements for the two ternary Li—Ti-oxides. For $Li_2Ti_3O_7$ our values S^0 (298 K) and ΔH^0_f (298 K) are consistent with the semi-empirical estimate of S^0 (298 K) = 200 J mole^{-1} K^{-1} and ΔH^0_f (298 K) = —3580 kJ mole^{-1} as seen from Table 3.

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