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Short communication

Low temperature heat capacity and thermodynamic standard values at 298.15 of β-eucryptite ($LiAlSiO_4$)

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Abstract

We report measurements of the heat capacity of the one-dimensional ionic conductor β-eucryptite ($Li_xAl_xSi_{1-2x}O_4$) over the temperature range 1.5–320 K. The entropy and enthalpy at 298.15 K were found to be $S^\circ(298.15) = (105.34 \pm 0.7)$ J/mol K and $H^\circ(298.15) = (21406.5 \pm 8)$ J/mol. The data are compared with specific heat results, reported in the literature for different temperature ranges.

Keywords: Specific heat capacity; β-Eucryptite ($LiAlSiO_4$); Adiabatic calorimetry

1. Introduction

Internally consistent thermodynamic data are an important basis for the calculation of phase diagrams and heats of formation in chemistry and geology. Thermodynamic calculations involving minerals, in particular those with lithium, are still hampered through lack of adequate data or inconsistent data. Eucryptite is of special interest because it is one of the commercial sources of lithium. It is also a so-called super-ionic conductor which attracted attention due to potential for technical application and new microscopic transport mechanisms involved [1].

For β-eucryptite, some earlier heat capacity measurements exist: Pankratz and Weller [2] reported data for synthetic β-eucryptite (sample mass ca. 138 g) by adiabatic calorimetry in the temperature range 51–298 K. Böhmer et al. [3] performed adiabatic measurements between 5 and 50 K with a polycrystalline sample with 94% of ideal density, and Fasshauer et al. [4] executed DSC experiments (on coarse-grained, natural material; sample mass 20–40 mg) in the temperature range 133–823 K. Other specific heat results refer only to the low temperature range ($T < 2.5$ K) in the context of studying specifically low-energy configurational excitations arising from quantum mechanical tunnelling [5,6].

The present paper reports the results of heat capacity measurements of sample of β-eucryptite ($Li_xAl_xSi_{1-2x}O_4$, with $x \approx 1$) in the temperature range from 1.5 K to room temperature.

2. Experimental

The synthetic β-eucryptite sample used in this study is *identical* to the samples used in earlier investigations [5–10]. The colourless, inclusion-free crystals (of several millimetres size) were grown by the flux method [7,9]. The polycrystalline samples had a density of nearly 100%. The phase purity was checked by

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X-ray analysis, i.e. the stoichiometry is nearly perfect ($x \geq 0.98$).

The heat capacities were determined with a previously described calorimeter [11–13] using the adiabatic (Nernst type) heat step technique and a sapphire plate as sample holder [14]. The sample consisted of two pieces, weighing together 1.7561 g; the molar weight was taken as 126.006 g/mol.

3. Results and discussion

The measured molar heat capacities $C_p(T)$ are plotted in Fig. 1, together with the three sets of data, taken from the literature [2–4]. The low temperature range, $6\,K \leq T \leq 22\,K$, for which we could find only one reference [3], is displayed in more detail in the insert of Fig. 1 in a diagram C_p/T vs. T^2.

The present results agree well, within 1%, with the adiabatic measurements of Pankratz and Weller [2] above 100 K but, with decreasing temperature, the deviations increase: at 50 K, the data of Ref. [2] are lower by ca. 12% compared to our data, whereas the values of Böhmer et al. [3] exceed our data by ca. 7% at 50 K. However, the data by Böhmer et al. [3] agree with our results within <1% in the range 25–35 K and within 3% near 10 K (Fig. 2). Finally, the present data join smoothly our earlier published low temperature measurements [5]. The results from DSC experiments [4] are systematically lower than the adiabatic measurements, by ca. 12% at 130 K, ca. 4% at 200 K and ca. 1.6% near 300 K.

For a calculation of the thermodynamic values, it seems therefore reasonable to take the present data in the full temperature range, because they are intermediate between those given in Refs. [2,3] in the critical range around 50 K and agree with Ref. [2] above 100 K very well. The temperature dependence of the specific heat, allowing to calculate thermodynamic functions, has been least square fitted in two temperature ranges, $4\,K < T < 50\,K$ and $50\,K < T < 320\,K$, using the formula

$$C_p(T) = \sum A_i T^i$$

The polynomial coefficients are given in Table 1. The fit yields values for the standard entropy and enthalpy, respectively, $S^\circ(298.15) = (105.34 \pm 0.7)$ J/mol K and $H^\circ(298.15) = (21406.5 \pm 8)$ J/mol. These values are compared in Table 2 with those given in the literature [2,4,15,16]. We note, however, that the reported values [2,4,16] are *not independent* since the calculation of

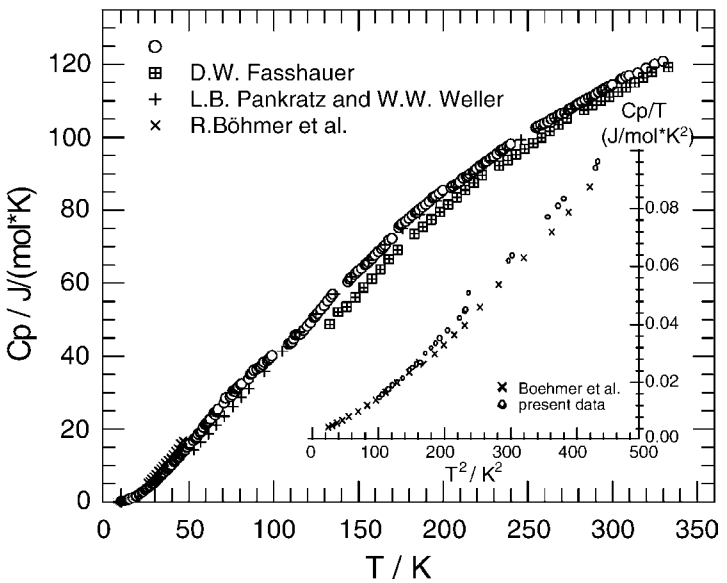

Fig. 1. Measured specific heat capacity of β-eucryptite in J/mol K. Earlier data, reported in Refs. [2–4] are shown for comparison. The insert shows the present data (○) and those from Ref. [3] (×) in the low temperature range, for $T < 23$ K, in a diagram C_p/T vs. T^2.

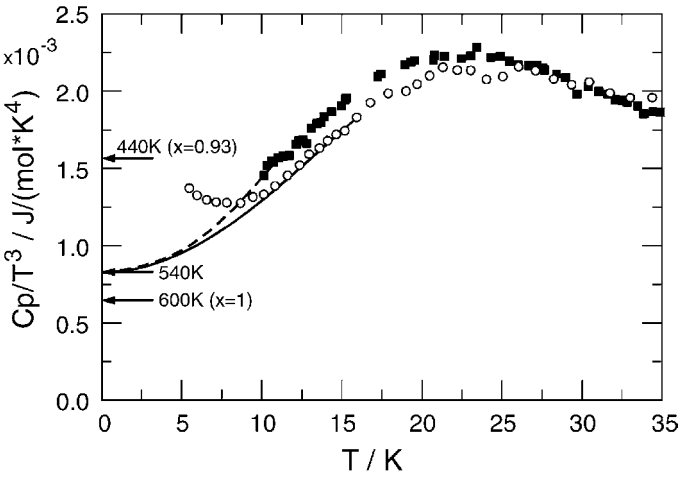

Fig. 2. Low temperature range of the specific heat of β-eucryptite for the present data (○), data from Ref. [3] (●) and Ref. [6] (arrows), shown in a plot C_p/T^3 vs. T. The arrows at 0 K indicate the corresponding Debye temperatures $\theta_0(T = 0\,\mathrm{K})$ for the present sample and that of Ref. [6] (540 K) and two samples with the different stoichiometry, $x = 1$ and 0.93, respectively [6].

Table 1
Polynomial coefficients for equation $C_p(T) = \sum A_i T^i$ in text representing the specific heat capacity of β-eucryptite in J/mol K (the units of the coefficients A_i are (J/mol K^{i+1}))

Temperature range coefficients, A_i	$4\,\mathrm{K} < T < 50\,\mathrm{K}$	$50\,\mathrm{K} < T < 320\,\mathrm{K}$
A_1	1.9585500	−4.8193400
A_2	−0.3857700	0.3098100
A_3	0.0229100	0.0026600
A_4	-2.02465×10^{-4}	-1.5859×10^{-5}
A_5		3.56495×10^{-8}
A_6		3.09914×10^{-11}

the standard values are always based on the C_p-results of Pankratz and Weller [2].

The reason for the discrepancies between the various $C_p(T)$ is most likely due to non-stoichiometry. It is well known that the material is often not stoichiometric that may lead to unoccupied lattice sites and lattice defects which, in consequence, may modify the heat capacity, in particular at low temperature. Above 50 K, such effects should not change $C_p(T)$ by more than several percent. Below 10–20 K, however, drastic changes occur for C_p [5,6] due to configurational entropy contributions, resulting from the distribution, respectively disorder, of Li-atoms. The statistically distributed free lattice sites in β-eucryptite and the non-stoichiometry (x) originate ionic conductivity at higher temperature and leads to quantum mechanical tunnelling of atoms at low temperatures [5,6]. The effect on $C_p(T)$ is displayed in Fig. 2 where the equivalent Debye temperature $\theta(T)$, calculated from the specific heat, is plotted. The Debye temperature $\theta_0(T = 0\,\mathrm{K})$ varies between 440 K (for $x = 0.93$) and 600 K (for $x = 1.0$) according to the stoichiometric composition (x) of $Li_xAl_xSi_{1-2x}O_4$ [6]. As a consequence, the heat capacity—and thus the related

Table 2
Comparison of thermodynamic standard values at 298.15 K

	C_p (J/mol K)	S° (J/mol K)	$^\circ H$ (J/mol)
Present data	113.82 ± 1	105.34 ± 1	21406.5 ± 2.5
Pankratz and Weller [2]	103.76 ± 0.8	103.76 ± 0.8	
Robie and Hemmingway [15]		103.8 ± 0.8	21233 ± 2
Fasshauer et al. [4]	111.149	103.814 ± 0.8	21233.99 ± 1.94

entropy and enthalpy—may vary by a factor of 10 below 0.5 K, depending on x.

Applying Debye's T^3-law at 10 K, $\theta_0 = 459$ K (this data), $\theta_0 = 470$ K (Ref. [4]). A more proper extrapolation of the present data together with those from Ref. [5] yield $\theta_0 = 540 \pm 10$ K (Ref. [5]) (dotted line in Fig. 2). The discussion of θ_0 shows that (i) $C_p(T)$ is not identical for the different samples in the low temperature range, and (ii) the stoichiometry plays an important role for the determination of $S^\circ(298)$ and $H^\circ(298)$. Although the influence of strong variation of C_p (below 1 K) on the standard values of enthalpy at 298.15 K presumably remains small (Table 2), the effect of disorder is preferentially reflected in the entropy value. Disorder may also modify $C_p(T)$ over the entire temperature range, from low to high temperatures, and thus influences S° but less H°.

Referring again to Table 2, we note that up-to-date none of the experiments have covered the full range from 4 to 300 K. The most precise measurements by Pankratz and Weller [2] do not extend below 50 K from where essential entropy contribution come. As the data from Ref. [3] and the present ones agree moderately in the range 10–50 K, we believe that the higher entropy, calculated from the present data, is reasonable.

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