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# Heat capacity and thermodynamic functions of leucite at low temperatures

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## Abstract

The heat capacity $C_p(T)$ of leucite with chemical composition $(K_{0.91}Na_{0.04}Ca_{0.01})[Al_{0.97}Si_{2.03}O_6]\cdot0.084H_2O$ from Orvieto, Italy was measured in a vacuum adiabatic calorimeter in the temperature range 5.9–310 K. No anomalies were detected in the $C_p(T)$ dependence. Calculated values of heat capacity and thermodynamic functions at standard conditions are as follows: $C_p^\circ(298.15) = 166.4 \pm 0.2$ J mol$^{-1}$ K$^{-1}$; $S^\circ(298.15) = 182.4 \pm 0.3$ J mol$^{-1}$ K$^{-1}$; $H^\circ(298.15) - H^\circ(0) = 28120 \pm 40$ J mol$^{-1}$; $\Phi^\circ(298.15) = 88.04 \pm 0.3$ J mol$^{-1}$ K$^{-1}$. These results are in good agreement with previous measurements above 51 K [US Bur. Mines Rep. Invest. 4955 (1992) 22]. Recommended values of heat capacity and absolute entropy at standard conditions for stoichiometric leucite $KAlSi_2O_6$ are: $C_p^\circ(298.15) = 163.8 \pm 1.0$ J mol$^{-1}$ K$^{-1}$; $S^\circ(298.15) = 180.0 \pm 1.0$ J mol$^{-1}$ K$^{-1}$.

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## 1. Introduction

Leucite $KAlSi_2O_6$ is a characteristic mineral of young volcanic rocks, relatively poor in silica and rich in potassium. It is also found in hypabyssal rocks such as nepheline dolerites, but is not typical in abyssal and metamorphic rocks.

The crystal structure of leucite is based on the isometric aluminosilicate framework of the ANA topology (IUPAC Code), which is typical for analcime, pollucite, wairakite and some other natural and synthetic compounds [1]. The main secondary building units (SBU) of this framework are four- and six-membered rings of $[(Al, Si)O_4]$ tetrahedra. Potassium atoms are situated in the W positions with the 6 + 6 co-ordination. The S positions are vacant and blocked by potassium atoms in leucite [2,3]. A system of channels can be recognised in the framework along [0 0 1] direction bounded by strongly distorted eight-membered rings [1]. Natural leucite crystallises at high temperature in a cubic form, space group *Ia*3*d* [4]. Below 938 K it transforms to tetragonal phase [3] and at room temperature leucite has space group $I4_1/a$ [2]. The enthalpy of this transformation as well as the enthalpy of formation of leucite from the elements has been determined by the high-temperature solution calorimetry [5].

The only low-temperature heat capacity measurements for leucite, which are required for the calculation

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of its thermodynamic functions, were done in 1953 [6]. These measurements were conducted with an annealed sample in the limited temperature range from 51 to 296 K, which did not allow thermodynamic functions to be calculated in the most reliable way. We therefore measured heat capacity in the extended temperature range from 5.9 to 310 K.

## 2. Experimental

Leucite-bearing trachyphonolite samples were collected by the authors (IAB and BAF) in the vicinity of Orvieto (Umbria, Italy) under the kind guidance of Dr. Francesco Stoppa from Perugia University. White to light-gray or light-brownish euhedral leucite crystals as large as 10–15 mm with icositetrahedral {2 1 1} habit of various degrees of perfection constituted up to 15–20% of the bulk rock. Monomineralic leucite samples were separated from a single piece of the rock (about 3 kg) under the microscope and single crystal grains of 0.1–0.25 mm were prepared for the calorimetric measurements.

In thin-sections under the polarising microscope, leucite crystals appeared colourless, transparent, inclusion-free, weakly anisotropic, and showed complex repeated fine-scale twinning on {1 1 0}. The mean refractive index was measured to be 1.509 ± 0.001. Unit cell parameters of our sample are: $a = 13.084(3)$ Å, $c = 13.756(5)$ Å, $V = 2355(1)$ Å$^3$ (Cu K$\alpha$ radiation, $Al_2O_3$ as an internal standard). It is in good agreement with the published data [7].

Chemical analysis of leucite was done directly on the material recovered from the calorimeter after heat capacity measurements using X-ray fluorescence analysis (VRA-20R, Carl Zeiss, Jena). The $H_2O$ content 0.69 mass%, was determined as the weight loss after heating the sample at 900 °C for 1 h (average of three independent measurements on ≈1 g samples giving: 0.66, 0.69 and 0.73 mass%). The chemical composition of our sample is presented in Table 1, together

Table 1
Chemical composition of leucite samples

| | Present paper | Kelley et al. [6] | Deer et al. [8] | Kiseleva et al. [5] | Theoretical composition of $KAlSi_2O_6$ |
|---|---|---|---|---|---|
| Oxides | Mass percent | | | | |
| $SiO_2$ | 55.75 | 54.67 | 53.69 | 56.40 | 55.06 |
| $TiO_2$ | 0.05 | 0.03 | 0.15 | – | |
| $Al_2O_3$ | 22.69 | 22.00 | 22.72 | 22.94 | 23.26 |
| $Fe_2O_3$ | 0.22 | 0.89 | 1.01 | – | |
| FeO | – | 0.14 | 0.14 | 0.44 | |
| MnO | 0.11 | 0.00 | 0.00 | – | |
| MgO | 0.00 | 0.00 | 0.21 | – | |
| CaO | 0.12 | 0.10 | 0.46 | – | |
| $Na_2O$ | 0.57 | 0.23 | 0.30 | 0.48 | |
| $K_2O$ | 19.56 | 21.48 | 20.69 | 20.67 | 21.58 |
| $P_2O_5$ | 0.01 | – | – | – | |
| $H_2O$ | 0.69 | – | 0.19 | – | |
| Σ | 99.78 | 99.54 | 99.56 | 100.93 | 100 |
| Atom | Atomic ratios | | | | |
| Si | 2.025 | 2.007 | 1.972 | 2.02 | 2.00 |
| Al | 0.972 | 0.952 | 0.984 | 0.97 | 1.00 |
| Ti | 0.001 | 0.001 | 0.004 | – | |
| $Fe^{3+}$ | 0.006 | 0.024 | 0.028 | – | |
| $Fe^{2+}$ | | 0.004 | 0.004 | 0.01 | |
| Mn | 0.003 | | 0.00 | – | |
| Mg | | | 0.011 | – | |
| Ca | 0.005 | 0.004 | 0.018 | N/a | |
| Na | 0.040 | 0.016 | 0.021 | 0.03 | |
| K | 0.906 | 1.01 | 0.970 | 0.95 | 1.00 |
| $H_2O$ | 0.084 | | – | | |

Table 2
Experimental heat capacities $C_p^\circ$ (J mol$^{-1}$ K$^{-1}$) of leucite from Orvieto (molar mass: 217.58 g)

| $T$ (K) | $C_p^\circ$ | $T$ (K) | $C_p^\circ$ | $T$ (K) | $C_p^\circ$ | $T$ (K) | $C_p^\circ$ |
|---|---|---|---|---|---|---|---|
| 5.95 | 0.1141 | 20.64 | 7.097 | 71.84 | 52.20 | 187.98 | 122.5 |
| 5.99 | 0.1077 | 22.54 | 8.687 | 76.70 | 55.90 | 198.45 | 127.3 |
| 6.97 | 0.1932 | 24.42 | 10.42 | 81.39 | 59.43 | 209.55 | 132.5 |
| 7.32 | 0.2232 | 26.77 | 12.60 | 82.83 | 60.38 | 219.70 | 136.6 |
| 7.78 | 0.2963 | 28.55 | 14.30 | 86.06 | 62.77 | 230.00 | 141.1 |
| 8.39 | 0.3804 | 30.98 | 16.68 | 86.79 | 63.24 | 240.27 | 145.3 |
| 9.17 | 0.5813 | 33.88 | 19.49 | 93.16 | 67.77 | 250.60 | 149.5 |
| 9.56 | 0.6636 | 36.75 | 22.25 | 100.81 | 72.93 | 260.91 | 153.2 |
| 9.78 | 0.7498 | 39.64 | 25.02 | 108.34 | 77.97 | 271.22 | 157.4 |
| 10.94 | 1.085 | 43.17 | 28.31 | 117.67 | 83.83 | 281.52 | 160.8 |
| 11.22 | 1.172 | 46.92 | 31.71 | 127.78 | 90.07 | 291.81 | 164.2 |
| 11.29 | 1.218 | 50.40 | 34.81 | 137.70 | 95.96 | 302.19 | 167.7 |
| 12.86 | 1.898 | 53.81 | 37.75 | 147.53 | 101.5 | 303.45 | 168.2 |
| 14.75 | 2.954 | 57.27 | 40.63 | 157.45 | 106.9 | 310.03 | 170.4 |
| 16.77 | 4.200 | 61.89 | 44.41 | 167.45 | 112.3 | | |
| 18.72 | 5.584 | 66.91 | 48.38 | 177.66 | 117.5 | | |

with the data for the samples studied in [5,6] (sample of L.I. Panina in [5] also was from Orvieto, Italy). Data from [8] and the theoretical leucite composition are presented for comparison. The crystal chemical formula of our sample may be written as follows:

$(K_{0.91}Na_{0.04}Ca_{0.01})[Al_{0.97}Si_{2.03}O_6]\cdot 0.084H_2O$ and is close to typical leucite analyses known from literature. Following the usual practice minor quantities of Ti, Fe and Mn (see Table 1) were combined with Si, Al and Ca, respectively. This formula was used for the calculation of heat capacity and thermodynamic functions. The molar mass is 217.58 g.

Experimental technique used for heat capacity measurement have been described elsewhere [9]. A leucite

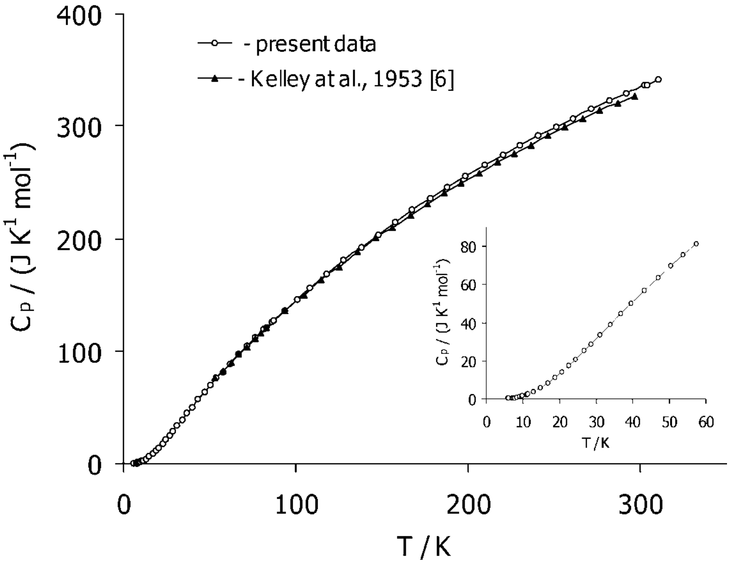

Fig. 1. Low-temperature heat capacity of leucite: present data in the range 5.9–310 K, data from [6] in the range 51–296 K. Present data below 60 K are shown on insertion.

sample with total mass 6.1604 g was placed in calorimetric capsule with the volume 5.7 cm$^3$.

## 3. Results

The experimental results are summarised in Table 2 and Fig. 1. No anomalies were detected in the $C_p(T)$ dependence. The experimental curve was smoothed by the spline-function method. Thermodynamic parameters were calculated on the basis of these smoothed $C_p(T)$ values at selected temperatures and are given in Table 3 together with the smoothed $C_p$ values. Average deviations of the experimental points from the smoothed $C_p(T)$ curve are 1.9, 0.17, and 0.05% in the temperature ranges 6–12, 12–30, and 30–310 K, respectively.

The accuracy of the heat capacity values and the deduced thermodynamic parameters 298.15 K (Table 4) is from the experimental scatter estimated to be around

Table 3
Molar thermodynamic properties of leucite from Orvieto (molar mass: 217.58 g)

| $T$ (K) | $C_p^\circ(T)$ (J mol$^{-1}$ K$^{-1}$) | $S^\circ(T) - S^\circ(0)$ (J mol$^{-1}$ K$^{-1}$) | $H^\circ(T) - H^\circ(0)$ (J mol$^{-1}$) | $\Phi^\circ(T)$[a] (J mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|---|
| 5 | (0.125) | (0.041) | (0.155) | (0.010) |
| 10 | 0.7983 | 0.2120 | 1.646 | 0.04740 |
| 15 | 3.082 | 0.9095 | 10.64 | 0.2006 |
| 20 | 6.581 | 2.252 | 34.38 | 0.5328 |
| 25 | 10.93 | 4.175 | 77.88 | 1.060 |
| 30 | 15.69 | 6.585 | 144.3 | 1.774 |
| 35 | 20.55 | 9.370 | 235.0 | 2.656 |
| 40 | 25.33 | 12.43 | 349.7 | 3.684 |
| 45 | 29.97 | 15.68 | 488.0 | 4.835 |
| 50 | 34.44 | 19.07 | 649.1 | 6.088 |
| 60 | 42.89 | 26.11 | 1036 | 8.835 |
| 70 | 50.81 | 33.32 | 1505 | 11.82 |
| 80 | 58.36 | 40.60 | 2051 | 14.96 |
| 90 | 65.55 | 47.89 | 2671 | 18.21 |
| 100 | 72.42 | 55.16 | 3361 | 21.54 |
| 120 | 85.33 | 69.52 | 4940 | 28.35 |
| 140 | 97.25 | 83.58 | 6768 | 35.24 |
| 160 | 108.3 | 97.29 | 8825 | 42.14 |
| 180 | 118.6 | 110.7 | 11100 | 49.01 |
| 200 | 128.1 | 123.7 | 13560 | 55.83 |
| 220 | 136.9 | 136.3 | 16220 | 62.57 |
| 240 | 145.2 | 148.6 | 19040 | 69.23 |
| 260 | 153.0 | 160.5 | 22020 | 75.79 |
| 280 | 160.2 | 172.1 | 25150 | 82.26 |
| 300 | 167.0 | 183.4 | 28430 | 88.62 |
| 310 | 170.4 | 188.9 | 30120 | 91.80 |
| 298.15 | 166.4 ± 0.2 | 182.4 ± 0.3 | 28120 ± 40 | 88.04 ± 0.3 |

[a] $\Phi^\circ(T) = S^\circ(T) - S^\circ(0) - \{H^\circ(T) - H^\circ(0)\}/T$.

Table 4
Heat capacity $C_p^\circ$ and entropy $S^\circ$ of leucite at 51 and 298.15 K in J mol$^{-1}$ K$^{-1}$

| $C_p^\circ(298.15)$ | $C_p^\circ(51)$ | $S^\circ(298.15)$ | $S^\circ(51)$ | $S^\circ(298.15) - S^\circ(51)$ | Reference |
|---|---|---|---|---|---|
| 166.4 | 35.29 | 182.4 | 19.8 | 162.6 | Present work |
| 163.4 | 34.8 | 179.3 | 19.6 | 160.9 | Present work with corrections |
| 164.1 | 35.81 | 184.1 | 23.14 | 161.2 | [6] |

0.2%. This level of accuracy is confirmed by comparison with our previous data on the heat capacity of benzoic acid [9].

## 4. Discussion

Comparison of the present results with those of [6] is complicated by the fact that the leucite samples studied have slightly different chemical compositions, which deviate from the ideal leucite formula (cf. Table 1). To calculate heat capacity and thermodynamic functions for stoichiometric "ideal" leucite, $KAlSi_2O_6$, from their experimental data, the authors of [6] described the chemical composition of their sample as the sum of 98.4% $KAlSi_2O_6$ and 1.6% $NaAlSi_2O_6$. Though the latter compound corresponds in its chemical composition to dehydrated analcime, the correction was made not on the basis of analcime, but using the difference between the heat capacities of albite, $NaAlSi_3O_9$, and adularia, $KAlSi_3O_9$, which were studied in the same work [6]. The validity of this correction is debatable, but because of the small absolute value involved (<0.1%) it is not very significant.

The leucite sample studied in the present work may be represented conventionally as containing 94% of "ideal" leucite $KAlSi_2O_6 + 0.024\ H_2O$ and 6% of analcime $NaAlSi_2O_6 \cdot H_2O$. This assumption is based on the chemical data (Table 1), in particular on the K, Na, and $H_2O$ contents. The presence of Ca shows that the "analcime" is in fact an analcime–wairakite solid solution $Na_{0.67}Ca_{033}AlSi_2O_6 \cdot H_2O$. Still, we used the heat capacity of analcime for our calculations because no data are known for wairakite $C_p$. The isostructural nature of leucite and analcime–wairakite frameworks was taken into account as well as the usual occurrence of substitution: $\square + K^+ \leftrightarrow Na^+ + H_2O$.[1] Heat capacity and absolute entropy values of analcime from [10] were used to correct the present data for the analcime admixture.

The correction for 0.024 extra moles of $H_2O$ was made under the assumption that this water is not a mechanical admixture in the sample but is situated in the channels of the aluminosilicate framework. This assumption was based first on the fact that no fluid inclusions were detected in our sample under the microscope and second on the slight deviation from ideal leucite stoichiometry: $Si/Al > 2$ and sum of cations $< 1$. The latter results in the presence of some vacant potassium positions, where $H_2O$ molecules can be situated. Taking into consideration the structural similarity between leucite and analcime, and the slight structural deformation of analcime upon its dehydration [11], we suggest that the thermodynamic properties of this excess water are comparable to those of "normal" analcime water. The thermodynamic properties of the latter were determined in [10] as the difference between analcime and dehydrated analcime. The introduction of this correction for 6% of analcime and 0.24 mol of water results in 2–3% decrease in the heat capacity and entropy of leucite, depending on the temperature range. The accuracy of this correction is somewhat uncertain, because it is based on several controversial assumptions. In any case, the uncertainty introduced by this correction does not exceed $\pm$ 0.5% of the corresponding values of heat capacity and entropy.

Another approximation, which could be used to estimate heat capacity and thermodynamic parameters of the "ideal" leucite is to represent our sample as containing 96% leucite + 0.44 mol of "analcime" water and 4% analcime (that is neglecting Ca and Mn admixture). The correction obtained differed by about 0.1–0.2% from the previous one. This confirms that the choice of admixture representation is not critical in this particular case of leucite and analcime, both having almost the same framework.

In Table 4 thermodynamic functions calculated for stoichiometric leucite at 51 and 298 K are compared with those obtained in [6], 51 K was chosen because it was the lowest temperature in [6]. It is seen from Table 4 that the values of $C_p^\circ(298.15)$ and $S^\circ(298.15) - S^\circ(51)$ from the two studies are very close, especially after corrections are made for the present data. The remaining differences of 0.3–0.4% may be regarded as acceptable, taking into account the uncertainties in corrections for the excess water and analcime mentioned above. The difference of about 3% in $C_p^\circ(51\ K)$ can again be explained by the uncertainty in the corrections made in both studies and also by the different experimental procedures employed. The high temperature annealing (15 h at 350 °C) of the sample before the $C_p$ measurements in [6] can also introduce some discrepancy.

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[1] $\square$ denotes a cationic vacancy in S position.

The large difference in $S^\circ(51\ \mathrm{K})$ values of about 20% and also in $S^\circ(298.15\ \mathrm{K})$ of 2.5% is apparently due to an error introduced in [6] when extrapolating $C_p(T)$ data from 51 to 0 K. This extrapolation was made using the method elaborated earlier for organic compounds [12]. In any case the value of $S^\circ(51)$ determined in the present work experimentally seems to be more reliable. If this value were used for calculation of $S^\circ(298.15)$ in [6], the resulting value of 180.2 $\mathrm{J\ mol^{-1}\ K^{-1}}$ would be deviate only by 0.4% from our value.

Based on the above analysis of the previous results [6] and our own data on the heat capacity of leucite the following values of heat capacity and absolute entropy at standard conditions may be recommended for stoichiometric leucite $KAlSi_2O_6$: $C_p^\circ(298.15) = 163.8 \pm 1.0\ \mathrm{J\ mol^{-1}\ K^{-1}}$ and $S^\circ(298.15) = 180.0 \pm 1.0\ \mathrm{J\ mol^{-1}\ K^{-1}}$.

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