

## Thermodynamic properties of uvarovite garnet ( $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ )

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### ABSTRACT

The low-temperature heat capacity of uvarovite ( $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ ) was measured between 2 and 400 K, and thermochemical functions were derived from the results. The measured heat-capacity curve shows a significant lambda-shaped anomaly peaking at around 9 K. The nature of this transition is unknown. From our data, we suggest a standard entropy for uvarovite at 298.15 K of  $320.9 \pm 0.6$  J/(mol·K).

### INTRODUCTION

Uvarovite ( $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ ) garnets are only rarely found in metamorphic rocks, the most prominent locality of which is probably Outokumpu in Finland (Deer et al. 1992). Metamorphic uvarovites are commonly interpreted to have formed from Cr-rich spinels by metasomatic reaction, the exact nature of which is uncertain (Arai et al. 1999; Challis et al. 1995; Frankel 1959; Franklin et al. 1992; Graham et al. 1996; Proenza et al. 1999; Viswanathiah et al. 1979; Wan and Yeh 1984). However, as the Earth's mantle usually contains much more Cr than the Earth's crust (Green and Falloon 1998; O'Neill and Palme 1998), uvarovite is an important mineral end-member component of most mantle garnets.

Given the importance of garnets in both metamorphic and magmatic systems, a large number of studies have investigated thermodynamic properties of garnets (among many others, Anovitz et al. 1993; Hensen et al. 1975; Newton et al. 1977; Wood 1988; Wood and Kleppa 1984). As calculations of phase equilibria in the Earth's mantle require reliable thermodynamic data for Cr-bearing minerals, the thermodynamic properties of Cr-bearing pyroxenes (Klemme and O'Neill 2000), Cr-bearing spinels (Ehrenberg et al. 2002; Klemme and O'Neill 1997; Klemme et al. 2000; Klemme and van Miltenburg 2002), and knorringite garnet ( $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ ) (Klemme 2004) were investigated in a series of previous studies.

Most Cr-garnets such  $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$  (knorringite) or  $\text{Fe}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$  are only stable at very high pressures (Doroshev et al. 1997; Girnis et al. 2003; Klemme 2004; Ringwood 1977; Turkin et al. 2002), and high-precision calorimetric data probably will never be available for these phases. Uvarovite, however, is stable at atmospheric pressure and, therefore, may be synthesized in large quantities relatively easily (Carda et al. 1989; Geller and Miller 1959; Glasser 1959; Hummel 1950; Isaacs 1963; Llusar et al. 1999a; Llusar et al. 1999b; Lowell et al. 1971). Despite this, little is known about the thermodynamics of uvarovite. A number

of studies have investigated the crystal structure, elasticity, and low-pressure stability of uvarovite (Andrut and Wildner 2001; Arnould et al. 1969; Bass 1986; Carda et al. 1994b; Geller and Miller 1959; Glasser 1959; Huckenholz and Knittel 1975, 1976; Isaacs 1963, 1965; Leger et al. 1990; Milman et al. 2001; Wildner and Andrut 2001), but apart from a study that investigated the thermodynamics of mixtures along the join  $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ - $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  (Wood and Kleppa 1984; Mattioli and Bishop 1984) there are, to our knowledge, no previous studies on the thermodynamic properties of end-member uvarovite garnet. To partially address these matters, the present study was initiated to determine the low-temperature heat capacity of uvarovite between 2 and 400 K.

### EXPERIMENTAL TECHNIQUES

#### Sample preparation and characterization

Heat-capacity measurements were performed on synthetic polycrystalline uvarovite samples.  $\text{CaCO}_3$  (purity 99.99%),  $\text{Cr}_2\text{O}_3$  (purity 99.999%), and  $\text{SiO}_2$  (purity 99.999%) were mixed stoichiometrically in an agate mortar under acetone. The mixture was then pressed into pellets (1.27 cm diameter) and sintered in a conventional gas-mixing vertical furnace at atmospheric pressure and 1250 °C for 24 h using  $\text{CO}_2$  gas. The pellets were then quenched in the cold part of the furnace. The samples were subsequently reground, repressed, and reannealed under identical conditions for another 24 h before being quenched rapidly. X-ray diffraction (XRD) indicated mostly  $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ . Only very little ( $\leq 5\%$ ) unreacted  $\text{Cr}_2\text{O}_3$  was detected. Our synthetic uvarovite had a cell parameter of  $a_0 = 12.021 \pm 0.002$  Å, which compares reasonably well with previous results for synthetic uvarovite (Carda et al. 1994a; Hummel 1950; Lowell et al. 1971; Milman et al. 2001).

#### Low-temperature calorimetry

The heat capacity of uvarovite was measured between 20 and 400 K using adiabatic calorimetry. We used home-built adiabatic calorimeter (laboratory-designation CAL V), which has been described before (van Miltenburg et al. 1987, 1998). Temperature was measured with a calibrated 27 ohm Rh/Fe thermometer (calibration by Oxford Instruments), using an automated AC bridge (Tinsley). The thermometer scale used was the ITS-90 scale (Preston-Thomas 1990). The sample (altogether 10.07 g) was broken into several grains of about 2 mm. A helium pressure of 1000 Pa was established in the sample chamber to promote heat exchange. Measurements were made in the intermittent mode, and stabilization periods of about 500 s were used in between the heating periods. Below 30 K, the periods were on the order of 150 s. Every temperature interval was measured at least twice.

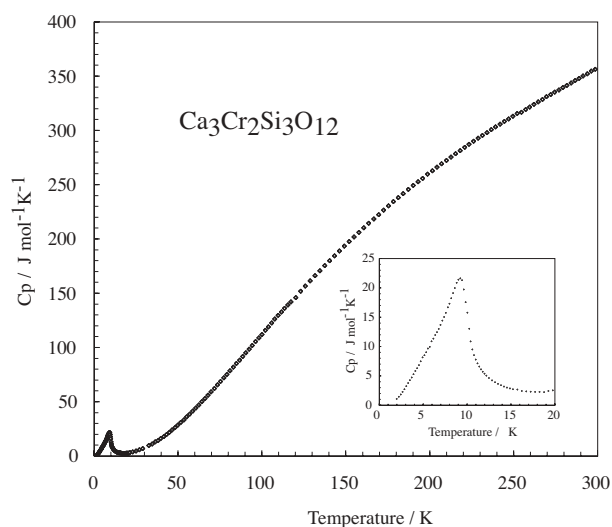
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Below 30 K, the reproducibility of the adiabatic calorimeter is about one percent, between 30 and 100 K 0.05–0.1%, and above 100 K 0.03%. Checking the adiabatic calorimeter with standard materials (n-heptane and synthetic sapphire) showed no deviations larger than 0.2% from the recommended values.

Additional heat-capacity measurements at very low temperatures ( $2 < T < 40$  K) were done at ITU Karlsruhe using a commercial PPMS-9 instrument (Quantum Design). The measurements were done on a 2.3 mg sample thermally connected by grease (apiezon N). The two-tau relaxation method was used to determine the heat capacity with the PPMS software. General reliability of the heat-capacity measurements using the PPMS instrument is reported by Lashley et al. (2003). The accuracy of the apparatus installed at ITU Karlsruhe was verified, e.g., with gold samples (NBS/NIST purity) (Javorsky et al. 2005). The uncertainty of the measurements reported in this paper (with respect to actual sample mass) is estimated to be below 1%.

## RESULTS AND DISCUSSION

The experimental values for the low-temperature heat capacity of uvarovite are compiled in Table 1 and results are depicted in Figure 1. The data fit a smooth and continuous curve at temperatures above 20 K, whereas below 20 K, the data indicate a lambda transition that peaks at around 9 K. To our knowledge, this transition has not been reported before. The standard entropy at 298.15 K was calculated from the  $C_p$  data (using a  $T^3$  extrapolation to 0 K) and resulted in  $S_{298.15}^0 = 320.9 \pm 0.6$  J/(mol·K). Table 2 compiles selected thermodynamic properties for  $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ . The latter were calculated from the experimental results using interpolations of the data for every degree. The interpolation procedure is such that interpolated data always pass through the experimental data. Then  $S(T)$  and  $H(T)$  are calculated by numerical integration. This procedure was compared to a direct integration of a fitted  $C_p$ -curve and gives the same result within the expected uncertainties. Further work is clearly needed to investigate magnetic properties of uvarovite at low temperatures, which may help to shed some light on the aforementioned heat-capacity anomaly.



**FIGURE 1.** The heat capacity of polycrystalline  $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$  (Uvarovite) measured between 2 and 300 K. A sharp heat-capacity anomaly occurs at around 9 K, the nature of which is unknown. The insert shows an enlarged view of the low temperature part of the experimental data and the heat-capacity anomaly.

**TABLE 1.** Experimental data

$T$ K	$C_p$ J/(mol·K)	$T$ K	$C_p$ J/(mol·K)	$T$ K	$C_p$ J/(mol·K)	$T$ K	$C_p$ J/(mol·K)
1.99	1.07	12.20	5.03	75.44	68.61	198.79	259.45
2.23	1.44	12.49	4.63	77.32	71.77	201.61	262.75
2.45	1.83	12.84	4.23	79.2	75.11	204.42	265.99
2.66	2.26	13.19	3.91	81.09	78.43	207.21	269.13
2.86	2.72	13.53	3.64	82.99	81.71	209.98	272.30
3.08	3.24	13.87	3.40	84.88	85.01	212.73	275.30
3.28	3.78	14.21	3.18	86.78	88.31	215.46	278.40
3.49	4.26	14.55	3.01	88.67	91.64	218.18	281.31
3.69	4.73	14.89	2.86	90.58	95.08	220.88	284.19
3.90	5.28	15.23	2.72	92.48	98.43	223.56	286.95
4.11	5.83	15.73	2.68	94.39	101.76	226.23	289.79
4.31	6.30	16.24	2.43	96.3	105.23	228.89	292.63
4.52	6.84	16.75	2.36	98.22	108.58	231.53	295.23
4.72	7.48	17.25	2.30	100.14	111.90	234.15	297.81
4.93	8.15	17.76	2.27	102.06	115.86	236.76	300.50
5.15	8.52	18.26	2.26	103.98	118.96	239.36	303.14
5.35	9.03	18.77	2.24	105.91	122.42	241.95	305.50
5.55	9.65	19.28	2.42	107.84	126.14	244.52	308.06
5.76	9.94	19.78	2.53	109.77	129.37	247.09	310.52
5.96	10.89	20.30	2.61	111.70	132.65	249.64	313.00
6.16	11.35	20.82	2.64	113.64	135.89	252.18	315.42
6.38	11.95	21.5	3.13	115.58	139.09	254.71	316.69
6.57	12.44	23.14	3.69	117.36	141.97	257.23	319.22
6.77	12.98	25.04	4.58	120.23	145.83	259.75	321.46
6.98	13.68	27.02	5.61	123.11	151.74	262.25	323.86
7.18	14.42	29.04	6.62	125.99	156.59	264.74	326.14
7.39	15.03	32.63	9.51	128.88	161.34	267.23	328.41
7.59	15.72	34.73	11.04	131.77	165.98	269.7	330.79
7.82	16.68	36.55	12.86	134.67	170.64	272.16	332.88
8.00	17.29	38.22	14.06	137.56	175.28	274.61	335.04
8.20	18.23	39.86	15.99	140.47	179.8	277.05	337.16
8.41	19.10	41.53	17.65	143.37	184.31	279.49	339.34
8.61	19.96	43.2	19.65	146.28	188.73	281.92	341.4
8.82	20.86	44.88	21.58	149.19	193.2	284.34	343.43
9.02	21.39	46.58	23.8	152.11	197.49	286.75	345.65
9.23	21.61	48.29	26.03	155.03	201.79	289.15	347.81
9.43	21.30	50.02	28.37	157.95	205.95	291.54	349.94
9.64	19.71	51.77	30.79	160.88	210.16	293.93	352.05
9.84	17.56	53.52	33.25	163.8	214.19	296.31	354.4
10.04	15.76	55.29	35.86	166.73	218.23	298.68	356.29
10.25	13.03	57.08	38.56	169.66	222.32	301.04	358.4
10.41	10.86	58.87	41.22	172.59	226.42	303.4	360.93
10.60	9.49	60.68	44.11	175.52	230.28	305.75	362.91
10.80	8.54	62.49	47.04	178.45	234.16	308.1	361.68
10.99	7.78	64.32	49.92	181.39	237.99	310.45	360.91
11.19	7.13	66.15	52.92	184.32	241.67	312.79	361.42
11.39	6.58	67.99	55.96	187.26	245.39	315.14	362.41
11.59	6.11	69.85	59.07	190.17	249.09	317.48	363.26
11.79	5.71	71.71	62.15	193.07	252.58	319.82	364.26
11.99	5.37	73.57	65.35	195.94	255.54		

Note:  $C_p$  data were collected using a PPMS (Quantum Design) from 2–20.8 K. All  $C_p$  data at higher temperatures were collected with an adiabatic calorimeter (see text for details). Uncertainties at 2 K  $< T < 21$  K are about 2%, whereas uncertainties at higher temperatures are about 0.2%.

Table 3 compares thermodynamic data for some Ca and Mg garnet end-members that are common components of garnets in the Earth's mantle. It is obvious that Cr-rich garnets have substantially higher entropy values when compared to their Al counterparts as the standard entropy depends on molar mass (Gopal 1966; Hemminger and Höhne 1979). Furthermore, as shown previously also for spinels (Klemme et al. 2000), magnetic transitions at low temperature can also contribute significantly to the standard entropy. Figure 2 compares the low-temperature heat capacity of grossular (Haselton and Westrum 1980) to our new data for uvarovite.

Although we have constrained the standard entropy of  $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$  using low-temperature calorimetry, there is still a

**TABLE 2.** Thermodynamic properties at selected temperatures for  $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ , Molar Mass = 500.47 g/mol

T K	$C_p$ J/(mol·K)	S(T) J/(mol·K)	H(T)-H(0) J/mol
5	8.3	4.0	14.4
10	16.8	13.7	91
15	2.8	16.4	120
20	2.9	17.2	132
30	7.8	19.5	180
40	16.5	22.8	294
50	27.7	26.1	513
60	42.8	33.2	869
70	59.9	42.7	1380
80	76.6	50.6	2058
90	93.8	59.6	2910
100	111.2	69.4	3939
120	145.4	91.8	6528
140	178.8	117.2	9786
160	208.8	144.1	13671
180	236.2	171.6	18125
200	260.8	198.5	23098
220	283.4	222.7	28543
240	303.5	251.1	34415
260	321.4	277.0	40674
280	339.5	300.7	47291
298.15	356.1	320.9	53604
300	357.5	322.7	54263

**TABLE 3.** Thermodynamic data for some Ca and Mg garnet end-member

	$\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	$\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
	Uvarovite	Grossular*	Knorringite	Pyrope
$S_{298}^\circ$	320.9 ± 0.6	260.1 ± 0.5	376.7	266.3 ± 0.8
Reference	this study	HW80	K04	HW80

Notes: HW80 = Haselton and Westrum (1980), K04 = Klemme (2004). Note that knorringite is stable only at pressure of more than 8 GPa so that  $S_{298}^\circ$  ( $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ ) was calculated from high pressure experiments.

\* Kolesnik et al. (1979) presented virtually identical  $C_p$  data for grossular ( $S_{298}^\circ = 259.8 \text{ J/(mol·K)}$ ).

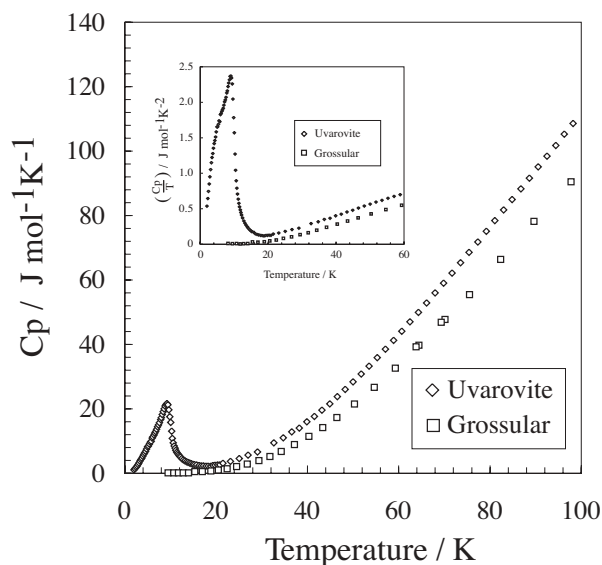
lack of complementary thermodynamic data for  $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$  as there are, to our knowledge, neither high-temperature heat-capacity data nor high-temperature heat content data published in the literature. The determination of the latter remains an important task for experimentalists because uvarovite is an ubiquitous component in garnets of the Earth's mantle. Ca- and Cr-rich rocks (and minerals) are common in the deep Earth, as indicated by xenoliths in kimberlites and inclusions in diamonds (e.g., Nixon 1995; Stachel and Harris 1997; Stachel et al. 1998; Bulanova et al. 2004). To date, meaningful phase-equilibria calculations in realistic mantle compositions cannot be performed, as thermodynamic data for many Cr- and Fe-rich minerals (such as garnets and spinels) are not as well understood as one would wish (e.g., Asimov et al. 1995; Klemme 2004).

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**FIGURE 2.** The heat capacity of grossular ( $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ) compared with our new data for uvarovite ( $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ ). The heat capacity of uvarovite is considerably higher at low temperatures, due to the broad anomaly at 9 K, and to higher molar mass. The insert depicts  $C_p/T$  of uvarovite compared to  $C_p/T$  of grossular. The entropy contributions of the low-temperature  $C_p$  anomaly are significant, as  $S(T) = \int C_p/T dT$ .

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