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Thermodynamic properties of uvarovite garnet (Ca₃Cr₂Si₃O₁₂)

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ABSTRACT

The low-temperature heat capacity of uvarovite (Ca₃Cr₂Si₃O₁₂) was measured between 2 and 400 K, and thermocchemical 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 ± 0.6 J/(mol·K).

INTRODUCTION

Uvarovite (Ca₃Cr₂Si₃O₁₂) 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 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 (Mg₃Cr₂Si₃O₁₂) (Klemme 2004) were investigated in a series of previous studies.

Most Cr-garnets such Mg₃Cr₂Si₃O₁₂ (knorringite) or Fe₃Cr₂Si₃O₁₂ are only stable at very high pressures (Doroshev et al. 1997; Girmis 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 (Andrút 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 Andrút 2001), but apart from a study that investigated the thermodynamics of mixtures along the join Ca₃Cr₂Si₃O₁₂-Ca₃Al₂Si₃O₁₂ (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. CaCO₃ (purity 99.99%), Cr₂O₃ (purity 99.999%), and SiO₂ (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 CO₂ 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 Ca₃Cr₂Si₃O₁₂. Only very little (<5%) unreacted Cr₂O₃ was detected. Our synthetic uvarovite had a cell parameter of a₀ = 12.021 ± 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.