Journal of Thermal Analysis and Calorimetry, Vol. 94 (2008) 2, 493–497

LOW-TEMPERATURE HEAT CAPACITY OF MONOCLINIC ENSTATITE

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Synthetic enstatite $MgSiO_3$ was crystallized from a melt, quenched into water, and then annealed at 873 K. The product is the monoclinic polymorph with the unit cell parameters of a=0.9619(7), b=0.8832(3), c=0.5177(4) nm, β=108.27(5)°. Heat capacity was measured from 6 to 305 K using an adiabatic vacuum calorimeter. Thermodynamic functions for clinoenstatite differ by about 5% from those predicted after a thermodynamic model in the literature, but are very close to those measured for orthorhombic enstatite.

Keywords: *enstatite, heat capacity, $MgSiO_3$, polymorphs*

Introduction

$MgSiO_3$ crystallizes in several polymorphs with pyroxene, garnet, ilmenite and perovskite structures. Pyroxene structure undergoes phase transitions under variable pressure and temperature, forming a subset of polymorphs. *P–T* diagram for enstatites was investigated about 40 years ago [1]. Structure of polymorphs was investigated in a wide range of thermodynamic variables. Orthorhombic enstatite (space group *Pbca*) is an abundant mineral, metastable under ambient conditions. Monoclinic enstatite ($P2_1/c$) is considered stable under ambient conditions, but is rather rare polymorph, because the natural samples are crystallized from a melt, starting with the orthorhombic polymorph. Protoensttatite (*Pbcn*) is a high-temperature phase [2, 3], together with the high-temperature clinoenstatite (*C*2/*c*) [4]. Natural orthoenstatite was reported to transform reversibly into a novel phase (*Cmca*) at heating up to 1150°C [3].

Thermodynamic functions of enstatite polymorphs were investigated intensively because they are very important for geoscience. Heat capacity of unspecified polymorph of enstatite was measured in a temperature range of 52 to 296 K [5]. Heat capacity of orthorhombic enstatite was measured from 5 to 1000 K [6, 7]. Thermodynamic data for the rest enstatite polymorphs are known only from the estimates, not from experimental data [8]. For clinoenstatite, calculated thermodynamic functions were reported in [9].

The main reason for the lack of reliable thermodynamic data is the difficulties with the sample preparation. There are no homogeneous natural polymorphs of enstatite in an amount large enough for the heat capacity measurements. The synthesis of the polymorphs is very arduous because of very high melting point of $MgSiO_3$ [10]. Industrial production of refractories yields inhomogeneous and non-stoichiometric phases [11, 12]. There are three ways for the formation of synthetic enstatite for the investigations. First way is the crystallization of protoenstatite from a melt (1563±2°C) [13] with the subsequent transformation of this unquenchable phase into clinoenstatite after rapid cooling. The product is very strained crystals, not appropriate for the structural investigations. Second way is the crystallization with a flux [14]. It was used for the preparation of orthorhombic enstatite for calorimetric measurements [6].

The objectives of this work were (1) to synthesize the pure polymorph of clinoenstatite in an amount large enough for the calorimetric experiments, and (2) to obtain the thermodynamic properties of clinoenstatite. As the structural defects in the monocrystals affect the heat capacity much less as compared to the impurities and nonstoichiometry, we chose the first way of the synthesis, i.e., direct crystallization from a melt and subsequent quenching.

Experimental

Synthesis of clinoenstatite

The starting materials for the synthesis were oxides MgO and SiO_2 of the highest purity grade. Prior to the weighing, the reagents were calcinated in Pt crucible at 1100°C and then cooled down to ambient

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1388–6150/$20.00

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temperature in a desiccator with $MgClO_4$. Dry reagents were mixed in equal molar ratio, total about 5 g. The mixture was ground in a hard-alloy mortar under alcohol until the grains became less than 0.05 mm in size. The sample was heated again in Pt crucible at 1000°C for 8 h. After the cooling down to room temperature, the crucible with the sample was placed in another furnace, heated up to 1550°C, and kept for 8 h. Taken out from the furnace, the crucible was immediately cooled down to room temperature by putting its bottom water. The sample itself was not brought in contact with water. The product was a dense white cake. Investigated by means of microscopy and X-ray powder diffraction, it was found to be homogeneous clinoenstatite, but the crystals were deformed after the phase transformation of protoenstatite into clinoenstatite. To relieve the stress, the sample was ground in the hard-alloy mortar under alcohol again and then heated at 600°C for 48 h. X-ray powder diffraction showed that the deformations disappeared and the reflections became narrow. XRPD pattern contains only reflections of clinoenstatite with the unit cell parameters of a=0.9619(7), b=0.8832(3), c=0.5177(4) nm, β=108.27(5)°.

Calorimetric measurements

Heat capacity was measured in a temperature range of 5 to 305 K by using the calorimetric system described elsewhere [15, 16]. The calorimeter with the internal volume of 5.7 cm^3 was filled with clinoenstatite (4.4467 g) and evacuated. Then it was filled with helium up to the pressure of 80 mm of Hg to provide heat conductivity in the powder sample at low temperatures. As the heat capacity of empty calorimeter was measured with helium of 10 mm Hg, the correction for extra helium was made. It was about 13% at 6 K and 0.5% at 30 K. The excess amount of helium was introduced in the calorimeter because we found out recently that the heat relaxation at temperatures below 15 K becomes incomplete, corrupting the results for a fine-powdered sample [17].

Results and discussion

Heat capacity of clinoenstatite was measured at 66 points with mean temperatures from 6.2 to 302.5 K. Experimental C_P values are listed in Table 1. Heat capacity is a smooth function of temperature, indicating that clinoenstatite has no phase transitions at low temperatures. Nevertheless, there is an anomaly in the heat capacity at very low temperatures. This part of heat capacity is shown in Fig. 1 as C_P/T *vs.* T^2. Instead of a straight line intersecting the point of origin according to the relationship $C\sim aT^3$ of the Debye model, as it is for orthoenstatite, the heat capacity of clinoenstatite deflects upward. As true function $C_P(T)$ of clinoenstatite is not known, there is an uncertainty in the extrapolation of the heat capacity to zero temperature. We used two ways of the fitting. In the first way, the heat capacity was extrapolated below 10 K by the straight line $C_P=aT^3+bT$, with coefficients a and b calculated by the least squares over nine first experimental points (<13 K). In the second way, the heat capacity was fitted to a cubic function starting from the first experimental point at 6.2 K: $C_P=C(6.2)(T/6.2)^3$. The difference between these two ways of calculation is 0.05 J mol^{-1} in enthalpy and 0.02 J mol^{-1} K^{-1} in entropy. Such a difference yields minor uncertainty in the values of thermodynamic functions at high temperatures, for the relative uncertainty is 0.035% for $S(298.15)$ and less than 0.001% for $H(298.15)–H(0)$. The standard deviation of experimental points from the smoothed curve is 1.65% for T<25 K, 1% for 25<T<50 K, and 0.06% for T>50 K. Smoothed values of the heat capacity of clinoenstatite and derived thermodynamic properties are in Table 2.

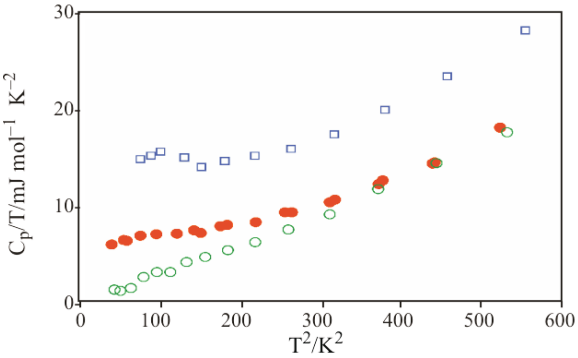

Fig. 1 Low-temperature heat capacity of ○ – orthorhombic and ● – monoclinic polymorphs of enstatite. □ – diopside [6] with non-Debye behavior similar to clinoenstatite

Comparison with orthoenstatite

It is interesting to compare the heat capacity for two polymorphs, monoclinic and orthorhombic enstatites. Thermodynamics of polymorphs is very important in pharmacy, because molecular crystals are identical in the intramolecular but differ in intermolecular interactions. The latter are very weak as compared with the former, and the polymorphs transform from one to another quickly and often spontaneously, with very small enthalpy of transformation [18, 19]. In geoscience, polymorphism is usually accompanied with the changes in chemical bonding, e.g., diamond–graphite, quartz–crystoballite–trydimite–coesite. Enthalpy of polymorph transformations in minerals is very high, and the transformations themselves are

Table 1 Experimental heat capacity of clinoenstatite $MgSiO_3$ (formula mass=100.39)

T/K	C_P/J mol^{-1} K^{-1}	T/K	C_P/J mol^{-1} K^{-1}	T/K	C_P/J mol^{-1} K^{-1}
6.202	0.0321	27.013	0.6821	119.458	30.87
6.208	0.0317	29.076	0.8738	127.004	33.87
7.323	0.0418	31.740	1.195	134.520	36.78
7.561	0.0428	34.828	1.623	142.167	39.63
8.587	0.0544	37.927	2.122	150.948	42.81
9.679	0.0634	41.006	2.664	160.987	46.40
10.968	0.0727	44.051	3.298	170.978	49.74
11.896	0.0832	47.856	4.178	180.855	52.92
12.231	0.0825	52.431	5.379	190.747	55.95
13.195	0.0984	56.993	6.708	200.674	58.82
13.506	0.1033	61.507	8.146	210.553	61.61
14.765	0.1177	66.041	9.697	220.405	64.16
15.942	0.1438	70.582	11.33	230.242	66.72
16.227	0.1463	75.137	12.98	240.074	69.10
17.616	0.1781	79.684	14.77	249.914	71.34
17.807	0.1851	82.779	15.96	259.770	73.51
19.274	0.2311	84.194	16.54	269.650	75.61
19.402	0.2402	87.822	17.99	279.558	77.60
20.943	0.2967	92.883	20.04	289.500	79.53
20.997	0.3004	97.979	22.13	299.471	81.32
22.873	0.4106	104.273	24.71	299.476	81.40
24.954	0.5401	111.838	27.78	302.449	81.88

very slow even at high temperatures. Usually, mineral polymorphs differ significantly in thermodynamic properties. For example, ilmenite and orthorhombic enstatite, both $MgSiO_3$, differ significantly from one another: $C_P(298)=75.1$ and 82.2 J mol^{-1} K^{-1} [6, 20].

Thermodynamic functions for monoclinic and orthorhombic enstatites are surprisingly close. Difference in heat capacity between two polymorphs is shown in Fig. 2. It is nearly constant with the value of about 1.1% at temperatures starting from 80 K. Below this point, the difference increases with decreasing temperature as if the monoclinic polymorph has a contribution in the heat capacity. This contribution is very significant at extremely low temperatures. We did not show the data below 20 K in Fig. 2, because the whole scale becomes too reduced. Fortunately, the low-temperature part of thermodynamic functions is only a small fraction of the total enthalpy and entropy at 298.15 K, where the values for orthoenstatite and clinoenstatite are very close. For comparison, the data for monoclinic and orthorhombic polymorphs of enstatite are shown in Table 2.

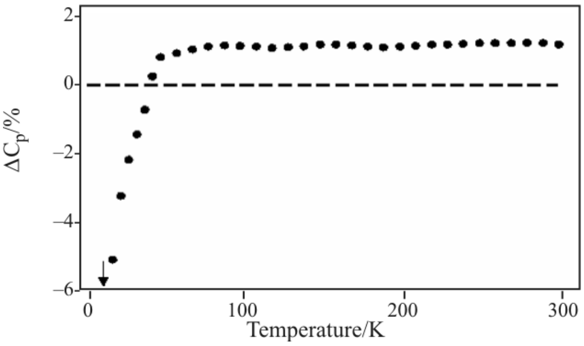

Fig. 2 Difference in heat capacity between monoclinic and orthorhombic enstatites. Points are shown starting from 20 K

Low-temperature anomaly

Large difference in low-temperature heat capacity between polymorphs does not seem unusual. For glycine (three polymorphs) [18] and paracetamol (two ones) [19], the difference was the largest also at low temperatures. But the difference in the heat capacity between orthorhombic and monoclinic enstatites is extremely large. Figure 1 shows C/T *vs.* T^2. Heat capacity of orthorhombic enstatite fits the Debye function $C_P=aT^3$ well, but that of monoclinic

Table 2 Thermodynamic functions of clinoenstatite $MgSiO_3$ (formula mass=100.39)

T/K	C_P/ J mol^{-1} K^{-1}	$H(T)$–$H(0)$/ J mol^{-1}	$S(T)$/ J mol^{-1} K^{-1}
5	0.0259	0.06	0.02
10	0.0632	0.28	0.05
15	0.1242	0.73	0.09
20	0.2605	1.64	0.14
25	0.5386	3.57	0.23
30	0.9848	7.30	0.36
35	1.636	13.76	0.56
40	2.485	23.99	0.83
45	3.512	38.90	1.18
50	4.723	59.41	1.61
60	7.656	120.8	2.72
70	11.10	214.2	4.16
80	14.88	343.9	5.88
90	18.87	512.5	7.86
100	22.95	721.5	10.06
110	27.05	971.5	12.44
120	31.09	1262	14.97
130	35.03	1593	17.61
140	38.84	1962	20.35
150	42.51	2369	23.15
160	46.04	2812	26.01
170	49.42	3289	28.90
180	52.65	3800	31.82
190	55.72	4342	34.75
200	58.65	4914	37.68
210	61.43	5514	40.61
220	64.10	6142	43.53
230	66.64	6796	46.44
240	69.06	7474	49.33
250	71.37	8177	52.19
260	73.57	8901	55.03
270	75.68	9648	57.85
280	77.70	10415	60.64
290	79.62	11201	63.40
298.15	81.12	11856	65.63
300	81.45	12007	66.13
orthoenstatite [6]			
298.15	82.06	11989	66.27
clinoenstatite (calculated) [8]			
298.15	81.8		63.2

one deflects upward from the Debye model. This is due to the contribution nearly linear with temperature, $C_P=bT$. Similar relationships were found for other crystalline phases [6]. Of five minerals, three have got the low-temperature anomaly. These are bronzite ($Mg_{0.85}Fe_{0.15}SiO_3$), magnesio-anthophyllite ($Mg_{6.3}Fe_{0.7}Si_8O_{22}(OH)_2$), and diopside ($Mg_{0.5}Ca_{0.5}SiO_3$). Orthorhombic enstatite and wollastonite ($CaSiO_3$) does not have the anomaly. Bronzite and magnesio-anthophyllite contain iron atoms, capable of magnetic interaction and, hence, of magnetic contribution to the heat capacity. It is common for magnetic phases to possess a low-temperature anomaly in the heat capacity [21], but not for diopside. The unusual relationship $C_P(T)$ was explained by the Schottky anomaly [6]. We follow that explanation, for the anomaly in the heat capacity of clinoenstatite in Fig. 1 looks very similar to that of diopside. The boson peak in glasses and its application for the crystalline phases is the subject of the work under preparation.

Conclusions

Stoichiometric and homogeneous monoclinic enstatite was received after especially developed synthesis in an amount large enough for the adiabatic low-temperature calorimetry. Heat capacity was measured from 5 to 300 K, and thermodynamic functions were derived. They were found to be surprisingly close to those of orthorhombic polymorph. Such a result is quite unusual for minerals.

Acknowledgements

The work was supported by RFBR grant 05-05-64556. We thank Dr. Tatiana Drebushchak for X-ray characterization of the sample.

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Received: October 14, 2007
Accepted: May 15, 2008
OnlineFirst: September 20, 2008

DOI: 10.1007/s10973-007-8443-7