

## A low-temperature heat-capacity study of synthetic anhydrous Mg-cordierite (Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>)

IGOR E. PAUKOV,<sup>1,\*</sup> YULIA A. KOVALEVSKAYA,<sup>1</sup> NOURI-SAID RAHMOUN,<sup>2</sup> AND CHARLES A. GEIGER<sup>2</sup>

<sup>1</sup>Institute of Inorganic Chemistry, Lavrentiev prosp. 3, Novosibirsk 630090, Russia

<sup>2</sup>Institut für Geowissenschaften, Universität Kiel, Olshausenstrasse 40, 24098 Kiel, Germany

### ABSTRACT

The heat capacity of synthetic anhydrous Mg-cordierite (Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>) was measured using adiabatic calorimetry between 6 and 300 K. Mg-cordierite was synthesized from a glass of stoichiometric cordierite composition at 1250 °C for one week. The refined cell dimensions using powder X-ray diffraction give  $a = 17.0553(2)$  Å,  $b = 9.7167(1)$  Å, and  $c = 9.3375(1)$  Å with  $V = 1547.428(1)$  Å<sup>3</sup> and a distortion index of  $\Delta = 0.25$  indicating complete Al-Si ordering. The absence of channel H<sub>2</sub>O was confirmed by powder IR spectroscopy, which did not show the presence of any bands located around 3600 cm<sup>-1</sup>. The  $C_p$  results values agree with those obtained previously by Weller and Kelley (1963) who measured the  $C_p$  of Mg-cordierite between 50 K and 298 K. The calculated entropy of Mg-cordierite at standard condition is  $S_{298.15}^0 = 404.0 \pm 1.6$  J/(mol·K) using the  $C_p$  data from this study. This value is in agreement with the value presented by Weller and Kelley [407.2 ± 3.77 J/(mol·K)], but appears to be very slightly lower than estimates made from various modeling studies incorporating phase-equilibrium data on Mg-cordierite.

**Keywords:** Calorimetry, cordierite, low-temperature study, crystal synthesis

### INTRODUCTION

Cordierite is a rock-forming mineral typically found in low- to medium-pressure amphibolite- and granulite-facies metamorphic rocks of appropriate composition. Natural cordierites are Fe-Mg solid solutions with the ideal formula (Mg,Fe)<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>·x(H<sub>2</sub>O, CO<sub>2</sub>). Nearly all natural cordierites contain H<sub>2</sub>O and CO<sub>2</sub>, and also sometimes other atomic and/or molecular species (e.g., Ar, N<sub>2</sub>), which are located in the infinite channels that run parallel to the *c*-axis in the crystal structure. The weakly bound molecules (Langer and Schreyer 1976; Goldman et al. 1977; Kolesov and Geiger 2000) can be driven off by heating crystals at elevated temperatures without altering the aluminosilicate framework. Most natural cordierites are Mg-rich and crystals have been found closely approaching the Mg end-member (Pryce 1973). Anhydrous end-member Mg-cordierite (Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>) can be synthesized in the laboratory at 1-atm and high-temperature conditions and its phase relations in the system MgO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> have been determined (Schreyer and Schairer 1961). Mg-rich cordierite is also important in a number of technical applications. For example, because of its low thermal expansion and resistance to thermal shock, it is used as a substrate material for filters and catalytic converters that operate at elevated temperatures.

Thus, several investigations have been made over the years on the thermodynamic and physical properties of “low” Mg-cordierite, whose Al-Si distribution over the tetrahedral sites is ordered. The low-temperature heat capacity of end-member anhydrous Mg-cordierite, whose structural state was not described, was first determined by Weller and Kelley (1963) using adiabatic calorimetry at temperatures between 50 and 298 K. The heat capacity above room temperature was determined using drop

calorimetry (Pankratz and Kelley 1963) and DSC methods (Carey 1993; Geiger and Voigtländer 2000). Because of its importance in petrological and geochemical investigations and also in various technical applications, we have reinvestigated the  $C_p$  behavior of synthetic anhydrous “low” Mg-cordierite having complete Al-Si order at temperatures between 6 and 300 K using high-precision adiabatic calorimetry. From these measurements, including for the first time  $C_p$  data obtained below 50 K, a new revised standard third-law entropy value can be calculated for Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>. This value can be compared to that given by Weller and Kelley (1963) obtained from their calorimetric measurements and also to various values obtained through modeling studies incorporating phase-equilibrium data on Mg-cordierite (Berman and Aranovich 1996; Gottschalk 1997; Chatterjee et al. 1998; Holland and Powell 1998).

### EXPERIMENTAL METHODS

#### Synthesis and sample characterization

Anhydrous Mg-cordierite was synthesized from a glass of stoichiometric cordierite composition. The glass was made from MgO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> having purities of 99.995, 99.99, and 99.999%, respectively. Prior to weighing, all oxides were fired for 12 h at 1200 °C to remove surface water and combustible impurities. An oxide mix of cordierite composition having a total mass of about 30 g was then weighed and thoroughly mixed and homogenized under acetone in an agate mortar. The mix was placed in a Pt crucible for subsequent melting. The crucible was heated stepwise from 800 to 1580 °C and held there for 1 hour. The Pt crucible was then quickly removed from the oven and quenched in a water bath. The resulting glass was removed from the crucible and broken into small pieces and remelted two more times. The final glass was completely clear and transparent and free from any crystals. Its composition was measured by electron microprobe analysis, which showed the glass to be homogeneous. The mean composition calculated from 25 measured points yielded Mg<sub>1.98(0.02)</sub>Al<sub>4.01(0.05)</sub>Si<sub>5.00(0.05)</sub>O<sub>18</sub> and, hence, the glass did not deviate within experimental error from ideal cordierite stoichiometry.

Anhydrous Mg-cordierite was crystallized from glass pellets weighing about 2.5 g held in a ceramic crucible at 1-atm. Several cordierite glass pellets were

\* E-mail: paukov@che.nsk.su

stacked on top of each other within the crucible. The bottom pellet was used as a "buffer" and was not used for further study. It simply ensured that the other pellets did not come into contact with the crucible. Moreover, the pellets were "free standing" and did not have contact with the crucible walls. The pellets were sintered at 950 °C for about 1 hour and then at 1250 °C for one week to ensure a fully ordered Al-Si distribution. The sintered polycrystalline pellets were measured by powder X-ray diffraction (XRD) and they showed only reflections related to Mg-cordierite. The refined cell dimensions gave  $a = 17.0553(2)$  Å,  $b = 9.7167(1)$  Å, and  $c = 9.3375(1)$  Å with  $V = 1547.428(1)$  Å<sup>3</sup>. A determination of the distortion index gave  $\Delta = 0.25$  and, hence, the Mg-cordierite was completely ordered. The absence of channel H<sub>2</sub>O was confirmed by powder IR spectroscopy, which did not show the presence of any bands located around 3600 cm<sup>-1</sup>. A number of different crystallites from different pellets were measured with the electron microprobe and gave an average formula of Mg<sub>1.98(0.01)</sub>Al<sub>3.93(0.03)</sub>Si<sub>5.06(0.02)</sub>O<sub>18</sub>. We use this composition with the cation numbers slightly modified to produce electroneutrality, yielding the final formula of Mg<sub>1.97</sub>Al<sub>3.94</sub>Si<sub>5.06</sub>O<sub>18</sub> used for the heat-capacity determination. X-ray elemental distribution maps were made on several crystallites and they did not show the presence of other phases. The molar mass was taken as 584.290 g. As a further check for the presence of water, 0.178 g of cordierite was heated at 900 °C in an Ar atmosphere, and its weight loss was determined to be 0.06%. This value is considered to be adsorbed surface water.

### Calorimetric calibration and C<sub>p</sub> measurements

A computerized vacuum adiabatic calorimeter was used for the heat-capacity measurements. The device is similar to that described previously (Paukov et al. 2001), but for these measurements on Mg-cordierite, the internal volume (about 6 cm<sup>3</sup>) of the calorimeter was greater. The exact mass of the cordierite sample used for the measurements was 6.5070 g. The weight of the empty calorimeter itself was 20.4 g. The heat capacity of the sample relative to the C<sub>p</sub> of the calorimeter was about 15, 25, 33, and 64% at 10, 50, 100, and 300 K, respectively. The C<sub>p</sub> measurements were carried out automatically in the temperature interval between 6 and 300 K, and to promote rapid temperature equilibration during the measurements, the calorimetric ampoule was filled with gaseous He under a pressure of 30 mm Hg (1.3 × 10<sup>3</sup> Pa).

At the start of the study, the heat capacity of the empty calorimeter was first measured at 69 different temperatures between 5.7 and 304.3 K. Then, to check the precision and accuracy of the calorimeter, we measured the heat capacity of standard reference benzoic acid. The mass of benzoic acid in the calorimeter was 4.063 g and its heat capacity was measured in 53 experiments from 5.8 to 308 K. We compared the measured experimental C<sub>p</sub> data with those obtained in a very thorough and accurate study (Rybkin et al. 1974) and with results obtained using more-recent vacuum adiabatic calorimetric systems (Moriya et al. 1982; Sorai et al. 1992). Figure 1 shows the deviations of our experimental heat capacities from the smoothed C<sub>p</sub> values obtained from the cited studies. The average deviation between 5 and 15 K is about 0.6%, and the maximum deviation at a single temperature is 1.5%. The corresponding values in the temperature interval between 15 and 40 K are 0.3 and 1.8%, and between 40 and 300 K they are 0.1 and 0.3%, respectively. Taking into consideration that we used a mass of benzoic acid that was considerably less than the amounts used in the above-cited studies, we conclude that our standard

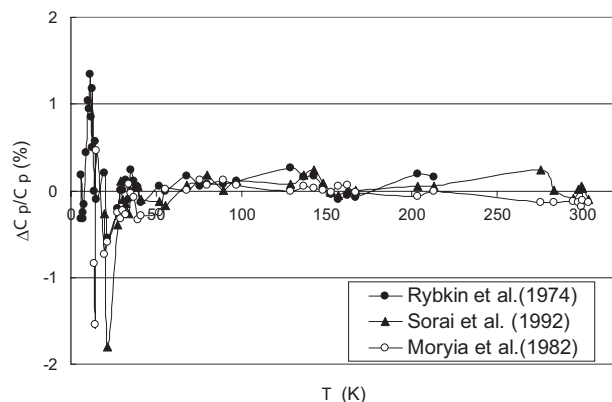


FIGURE 1. Plot of the deviations of our C<sub>p</sub> data on benzoic acid from previous investigations: (filled circle) Rybkin et al. (1974), (open circle) Moriya et al. (1982), and (triangle) Sorai et al. (1992).

measurements agree very well with the published values and that our calorimetric system yields good C<sub>p</sub> data at temperatures up to at least 300 K.

## RESULTS AND DISCUSSION

The experimental heat-capacity data of synthetic anhydrous Mg-cordierite are given in Table 1 and shown in Figure 2. The experimental C<sub>p</sub> values were smoothed using spline functions and extrapolated from 6 K down to 0 K using the Debye function. The final smoothed heat-capacity values and values for the derived thermodynamic functions are listed in Table 2. The average deviation of the experimental heat-capacity values from the smoothed curve is 1.4% in the temperature interval of 6 to 10 K, 0.5% from 10 to 30 K, and 0.02% from 30 to 300 K.

The accuracy of the heat-capacity values was estimated considering the scatter in the experimental data and considering the

TABLE 1. Experimental molar heat capacities of anhydrous Mg-cordierite

T (K)	C <sub>p,m</sub> <sup>o</sup> (T) [J/(mol·K)]	T (K)	C <sub>p,m</sub> <sup>o</sup> (T) [J/(mol·K)]
6.27	0.0587	132.26	219.53
6.43	0.0679	134.43	223.70
6.72	0.0798	137.14	228.77
6.82	0.0829	139.31	232.86
7.35	0.1033	142.02	237.92
7.67	0.1126	144.23	241.97
8.02	0.1352	146.92	246.93
8.05	0.1355	149.32	251.30
8.43	0.1611	151.86	255.83
8.53	0.1651	154.25	260.08
8.77	0.1846	156.77	264.56
9.14	0.2169	159.09	268.61
9.35	0.2356	161.66	273.03
9.93	0.2880	163.90	276.81
10.28	0.3261	166.53	281.20
10.87	0.3898	168.71	284.86
10.99	0.3972	171.38	289.33
11.35	0.4312	173.51	292.87
12.01	0.5212	176.23	297.31
12.65	0.6130	178.36	300.77
12.90	0.6523	181.08	305.01
13.04	0.6812	183.28	308.50
13.70	0.7869	185.93	312.64
14.08	0.8413	188.20	316.15
14.14	0.8678	190.78	320.11
14.75	0.9948	193.05	323.53
15.38	1.1310	195.70	327.50
16.09	1.3343	197.89	330.64
16.63	1.4885	200.55	334.61
17.63	1.8511	202.75	337.88
17.89	1.9397	205.35	341.65
19.18	2.5400	207.54	344.91
19.70	2.8222	210.14	348.62
20.76	3.3803	212.34	351.69
21.28	3.7197	214.95	355.17
22.34	4.4083	217.21	358.24
23.91	5.5996	219.81	361.80
25.45	6.9289	222.08	365.09
27.51	9.0741	224.65	368.58
30.06	12.019	226.89	371.60
32.33	14.978	229.51	374.98
32.64	15.432	231.72	377.82
34.44	18.003	234.40	381.20
37.08	21.967	236.58	383.98
40.18	27.047	239.30	387.36
43.33	32.617	241.46	390.12
46.48	38.486	244.22	393.48
50.38	46.032	246.37	396.11
54.48	54.362	249.10	399.48
58.53	62.821	251.23	402.09
62.53	71.500	253.93	405.31
66.54	80.299	256.05	407.87
70.56	89.150	258.80	411.03

Continued on next page

TABLE 1.—Continued

$\bar{T}$ (K)	$C_{p,m}^0(T)$ [J/(mol·K)]	$T$ (K)	$C_{p,m}^0(T)$ [J/(mol·K)]
74.59	97.868	260.90	413.48
78.57	106.84	263.68	416.62
82.22	114.83	265.78	419.01
82.52	115.62	268.53	422.16
84.28	119.38	270.63	424.50
86.23	123.77	273.47	427.61
88.31	128.33	275.43	429.78
90.19	132.41	278.43	433.01
92.31	137.14	280.27	434.98
94.13	141.10	283.29	438.27
96.31	145.89	285.14	440.10
98.12	149.75	288.12	443.29
100.28	154.47	289.97	445.12
102.11	158.28	292.98	448.50
104.26	162.86	294.77	450.22
106.08	166.78	295.16	450.56
108.23	171.26	295.37	450.63
110.07	174.96	295.74	451.15
112.32	179.72	297.86	453.37
114.59	184.35	298.28	453.56
117.35	190.01	298.59	453.82
119.56	194.52	298.67	454.05
122.30	199.99	299.54	454.96
124.52	204.52	301.00	456.18
127.31	209.88	301.18	456.49
129.50	214.20		

TABLE 2. Molar thermodynamic properties of anhydrous Mg-cordierite

$\bar{T}$ (K)	$C_{p,m}^0(T)$ [J/(mol·K)]	$S_m^0(T) - S_m^0(0)$ [J/(mol·K)]	$H_m^0(T) - H_m^0(0)$ (J/mol)	$\Phi_m^0(T)$ [J/(mol·K)]
6.27	0.0617	0.0206	0.0967	0.00514
10	0.2968	0.0889	0.6752	0.02134
15	1.046	0.3290	3.760	0.07837
20	2.958	0.8536	13.10	0.1984
25	6.543	1.865	36.10	0.4211
30	11.95	3.511	81.64	0.7894
35	18.80	5.851	158.0	1.337
40	26.77	8.870	271.5	2.083
45	35.68	12.53	427.3	3.035
50	45.28	16.78	629.4	4.192
60	66.02	26.84	1184	7.102
70	87.87	38.66	1954	10.75
80	110.0	51.83	2942	15.05
90	132.0	66.06	4153	19.92
100	153.8	81.10	5582	25.28
120	195.4	112.9	9079	37.20
140	234.2	145.9	13380	50.36
160	270.1	179.6	18430	64.41
180	303.3	213.3	24170	79.08
200	333.9	246.9	30540	94.19
220	362.2	280.1	37510	109.6
240	388.3	312.7	45020	125.2
260	412.4	344.8	53030	140.8
280	434.7	376.1	61500	156.5
298.15	453.5 ± 1.8	404.0 ± 1.6	69560 ± 280	170.7 ± 0.7
300	455.4	406.9	70400	172.2
301.18	456.6	408.6	70940	173.1

Note:  $\Phi_m^0(T) = S_m^0(T) - S_m^0(0) - [H_m^0(T) - H_m^0(0)]/T$ .

$C_p$  values measured on the benzoic acid standard. One additional source of error derives from the uncertainty in the chemical composition of the sample. We calculate an uncertainty of 0.3% to the molar heat capacity related to composition in the temperature interval of 6 to 300 K. To conclude, the overall accuracy in the  $C_p$  data is estimated to be around 3% at 6 K, 1% at 20 K, and 0.4% at temperatures from 40 to 300 K.

Our  $C_p$  results on anhydrous Mg-cordierite agree with those obtained previously by Weller and Kelley (1963). Their investigated sample was thought to contain 99.09% cordierite, 0.85% alumina, and 0.07% magnesium oxide. There was no discussion

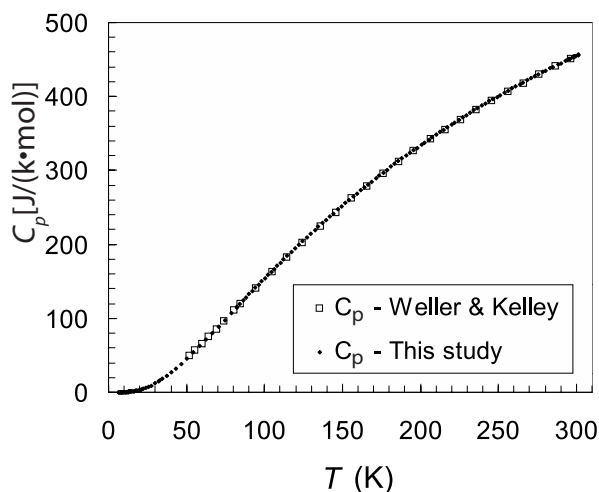


FIGURE 2. Plot of experimental  $C_p$  values of anhydrous synthetic Mg-cordierite between 6 and 302 K.

in their work regarding any corrections to the measured  $C_p$  values resulting from possible deviations from cordierite stoichiometry, nor of the accuracy of their chemical analysis. The structural state of their sample is unknown. The heat-capacity measurements of Weller and Kelley were carried out in the temperature interval from 51 to 296 K. Their  $C_p$  values are about 1% lower than ours at  $T < 150$  K, but the difference around 300 K is less being 0.2–0.3%.

The heat capacity of Mg-cordierite at  $T > 300$  K using DSC methods is presented in Carey (1993) and Geiger and Voigtländer (2000). The difference between the present  $C_p$  data and those determined by Carey (1993) between 295 and 425 K is 0.2% at 300 K. Geiger and Voigtländer (2000) measured the heat capacity of Mg-cordierite between 330 and 920 K. The extrapolated  $C_p$  value derived using the model equation given in their work lies about 0.5% higher than our  $C_p$  data at 300 K. From this, we conclude that the agreement between results obtained from different calorimetric methods (i.e., DSC and adiabatic calorimetry) is very good.

The entropy of Mg-cordierite at standard conditions,  $S_{298.15}^0$ , given by Weller and Kelley (1963) is  $407.2 \pm 3.77$  J/(mol·K). Considering the given experimental uncertainty, the agreement with our determination (Table 2), where  $S_{298.15}^0 = 404.0 \pm 1.6$  J/(mol·K), is excellent. The small difference in the calculated mean values is related to the different temperature intervals measured in the two studies. Weller and Kelley (1963) undertook heat-capacity measurements only at  $T > 51$  K, and the entropy increment between 0 and 51 K was obtained by extrapolation using the comparison method of Kelley et al. (1929). Weller and Kelley (1963) gave an extrapolated value of  $S_{51}^0 = 23.3$  J/(mol·K), whereas our experimental  $C_p$  data yield a value of  $S_{51}^0 = 17.7$  J/(mol·K), which is 6% lower than theirs. The agreement between the standard entropy values at 298.15 K turns out to be very good because of a small “trade-off” effect, whereby their larger value of  $S_{51}^0 = 23.3$  J/(mol·K) offsets their slightly lower experimental  $C_p$  values compared to those obtained in this study. The entropy values in Table 2 are considered the best to date,

**TABLE 3.** Standard third-law entropy values for anhydrous Mg-cordierite

Study	$S_{298.15}^0$ [J/(mol·K)]
This work	404.0 ± 1.6
Weller and Kelley (1963)	407.2 ± 3.77
Holland and Powell (1998)	407.50
Berman and Aranovich (1996)*	416.23
Chatterjee et al. (1998)	408.807 ± 1.466
Gottschalk (1997)	407.753 ± 0.402 (2σ)

\* Citing Weller and Kelley (1963).

because they are based on direct experimentally determined  $C_p$  values down to 6 K.

There also have been several estimates of the standard entropy of cordierite obtained by analyzing phase-equilibrium data often together with calorimetric measurements (Berman and Aranovich 1996; Gottschalk 1997; Chatterjee et al. 1998; Holland and Powell 1998). Several of the more-recent estimates are listed in Table 3. The values are not far removed from the result obtained from this study, but they all tend to be very slightly greater than  $S_{298.15}^0 = 404.0 \pm 1.6$  J/(mol·K).

#### REFERENCES CITED

- Berman, R.G. and Aranovich L.Y. (1996) Optimized standard state and solution properties of minerals I. Model calibration for olivine, orthopyroxene, cordierite, garnet, and ilmenite in the system FeO-MgO-CaO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SiO<sub>2</sub>. *Contributions to Mineralogy and Petrology*, 126, 1–24.
- Carey, J.W. (1993) The heat capacity of hydrous cordierite above 295 K. *Physics and Chemistry of Minerals*, 19, 578–583.
- Chatterjee, N.D., Krüger, R., Haller, G., and Olbricht, W. (1998) The Bayesian approach to an internally consistent thermodynamic database: theory, database, and generation of phase diagrams. *Contributions to Mineralogy and Petrology*, 133, 149–168.
- Geiger, C.A. and Voigtländer, H. (2000) The heat capacity of synthetic anhydrous Mg and Fe cordierite. *Contributions to Mineralogy and Petrology*, 138, 46–50.
- Goldman D.S., Rossman, G.R., and Dollase, W.A. (1977) Channel constituents in cordierite. *American Mineralogist*, 62, 1144–1157.
- Gottschalk, M. (1997) Internally consistent thermodynamic data for rock-forming minerals in the system SiO<sub>2</sub>-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-CaO-MgO-FeO-K<sub>2</sub>O-Na<sub>2</sub>O-H<sub>2</sub>O-CO<sub>2</sub>. *European Journal of Mineralogy*, 9, 175–223.
- Holland, T.J.B. and Powell, R. (1998) An internally consistent thermodynamic data set for phases of petrological interest. *Journal of Metamorphic Geology*, 16, 309–343.
- Kelley, K.K., Parks, G.S., and Huffman, H.M. (1929) A new method for extrapolating specific heat curves below the temperatures of liquid air. *Journal of Physical Chemistry*, 33, 1802–1805.
- Kolesov, B.A. and Geiger, C.A. (2000) Cordierite II: The role of H<sub>2</sub>O and CO<sub>2</sub>. *American Mineralogist*, 85, 1265–1274.
- Langer, K. and Schreyer, W. (1976) Apparent effects of molecular water on the lattice geometry of cordierite: a discussion. *American Mineralogist*, 61, 1036–1040.
- Moriya, K., Matsuo, T., and Suga, H. (1982) Low-temperature adiabatic calorimeter with a built-in cryo-refrigerator. *Journal of Chemical Thermodynamics*, 14, 1143–1148.
- Pankratz, L.B. and Kelley, K.K. (1963) High-temperature heat contents and entropies of akermanite, cordierite, gehlenite, and merwinite. U.S. Bureau of Mines, Report of Investigations, 6555.
- Paukov, I.E., Belitsky, I.A., and Kovalevskaya, Y.A. (2001) Thermodynamic properties of the natural zeolite gmelinite at low temperatures. *Journal of Chemical Thermodynamics*, 33, 1687–1696.
- Pryce, M.W. (1973) Low-iron cordierite in phlogopite schist from White Well, Western Australia. *Mineralogical Magazine*, 39, 241–243.
- Rybkin, N.P., Orlova, M.P., Baraniuk, A.K., Nurullaiev, N.G., and Rojnovskaya, L.N. (1974) Exact calorimetry at low temperatures. *Izmeritel'naya Tekhnika*, 7, 29–32.
- Schreyer, W. and Schairer, J.F. (1961) Compositions and structural states of anhydrous Mg-cordierites: a reinvestigation of the central part of the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. *Journal of Petrology*, 2, 324–406.
- Sorai, M., Kaji, K., and Kaneko, Y. (1992) An automated adiabatic calorimeter for the temperature range 13 K to 530 K. *Journal of Chemical Thermodynamics*, 24, 167–180.
- Weller, W.W. and Kelley, K.K. (1963) Low-temperatures heat capacities and entropies at 298.15 K of akermanite, cordierite, gehlenite, and merwinite. U.S. Bureau of Mines Report of Investigations, 6343, 1–8.

MANUSCRIPT RECEIVED NOVEMBER 5, 2004

MANUSCRIPT ACCEPTED JUNE 8, 2005

MANUSCRIPT HANDLED BY MICHAEL TOPLIS