

Low-temperature heat capacities of CaAl₂SiO₆ glass and pyroxene and thermal expansion of CaAl₂SiO₆ pyroxene

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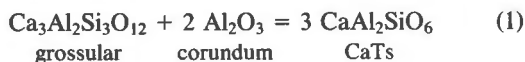
Abstract

Low-temperature heat capacities (5–380 K) have been measured by adiabatic calorimetry for synthetic CaAl₂SiO₆ glass and pyroxene. The values of $S_{298.15}^{\circ} - S_0^{\circ}$ are 155.3 J/mol · K for the glass and 135.3 J/mol · K for the pyroxene. These entropies do not include zero-point contributions arising from configurational disorder. From an analysis of conflicting data bearing on the amount of Al/Si tetrahedral disorder in the pyroxene, we conclude that a small amount of tetrahedral short-range order probably exists.

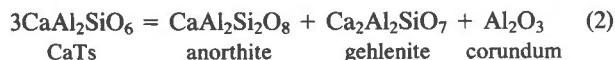
High-temperature unit-cell parameters were measured for CaAl₂SiO₆ pyroxene by means of a Nonius Guinier–Lenne powder camera. The mean coefficient of thermal expansion is $\alpha_v = 2.78 \times 10^{-5}/^{\circ}\text{C}$ in the temperature range 25° to 1200°C.

Introduction

Knowledge of the thermodynamic properties of calcium Tschermaks' pyroxene (CaTs) is desirable for evaluating the thermodynamic properties of other minerals in the CaO–Al₂O₃–SiO₂ system and of aluminous clinopyroxenes in more complicated systems. In the silica-undersaturated part of the CaO–Al₂O₃–SiO₂ system, Hays (1966a) showed that CaTs is stable only at relatively high pressures and temperatures. The stability field is bounded at subsolidus temperatures by the two univariant reactions:



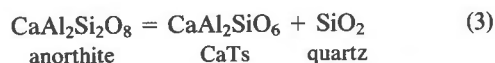
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which intersect, yielding an invariant point at approximately 1160°C and 11.6 kbar, the lowest pressure and temperature at which pure CaTs can exist stably. Hijikata and Yagi (1967), Wood (1978), and Gasparik (1981) have also attempted to fix the position of reaction (1), with conflicting results. Only Hays (1966a) has determined the location of reaction (2), but the slope of the boundary is poorly known.

Stoichiometric CaTs is not stable in the silica-saturated part of the CaO–Al₂O₃–SiO₂ system. Wood and Henson (1978) and Gasparik and Lindsley (1980) have demonstrated quite conclusively that CaTs dissolves excess silica. This solid solution is not only of crystal-chemical importance, but it is of considerable thermodynamic

utility because Wood (1977, 1979) has used the *calculated* metastable position of the reaction



in deducing CaAl₂SiO₆ and CaMgSi₂O₆ activities on the CaAl₂SiO₆–CaMgSi₂O₆ join.

When MgO is added to the CaO–Al₂O₃–SiO₂ system, the characteristic mineralogy of the upper mantle is represented, and several reactions that are diagnostic of pressure and temperature can be studied experimentally. In particular, the alumina content of the clinopyroxene, which can be attributed to a CaTs component, can be used as a geothermometer when the pyroxene coexists with spinel and forsterite. At higher pressures where aluminous clinopyroxene coexists with garnet and forsterite, the alumina content can be used as a geobarometer. Newton (1977), Obata (1976), and Herzberg (1977) have discussed some of the theoretical and practical aspects of these calculations.

The variation of the alumina content of orthoenstatite is quantitatively similar to that of alumina in diopside; however, unlike CaTs, magnesium Tschermaks' pyroxene (MgAl₂SiO₆ or Mg₃Al₂Si₃O₁₂) cannot be synthesized. Hence, the thermodynamic properties of CaTs, which can be synthesized relatively easily at high pressures, may yield insights when aluminous orthopyroxenes are considered.

Until recently, the thermodynamic properties of CaTs, with the exception of the enthalpy of formation (Shearer, 1973), were deduced from Hays's (1966a) phase-equilibrium study. The properties of grossular used in the estimation of the CaTs properties were estimated as well. In the

last several years, Newton et al. (1977) have measured enthalpies of solution of CaTs and six other synthetic compositions on the $\text{CaAl}_2\text{SiO}_6$ - $\text{CaMgSi}_2\text{O}_6$ join. Thompson et al. (1978) have used portions of the same samples to measure heat capacities (350–1000 K) by differential scanning calorimetry. The thermal expansion and compressibility have not been measured. The unit-cell parameters have been measured by powder diffractometry many times (e.g., Hays, 1966b; Newton et al., 1977; Wood, 1978) and are in good agreement.

The crystal structure of CaTs pyroxene was refined by Grove and Burnham (1974) and Okamura et al. (1974). Grove and Burnham concluded from a comparison of refinements in $C2$ versus $C2/c$ that short-range order was probably present for tetrahedral aluminum and silicon. Okamura et al. enumerated several models incorporating Al, Si tetrahedral order that would yield $C2/c$ average symmetry, but they concluded that CaTs was tetrahedrally disordered. Aluminous orthopyroxenes have $Pbca$ symmetry with two crystallographically distinct tetrahedral chains. Ganguly and Ghose (1979) have shown that Al segregates into the B chain; therefore, Al/Si ordering in aluminous enstatite is not strictly analogous to that in aluminous diopside.

In order to quantify the thermophysical properties of CaTs pyroxene and possibly to identify Al/Si short-range order, we have measured low-temperature heat capacities for synthetic CaTs pyroxene. In principle, a comparison of the measured entropy and that calculated from phase-equilibrium work should yield the configurational entropy attributable to Al/Si disorder. To facilitate this comparison we have also measured the thermal expansion by means of a high-temperature Nonius¹ Guinier-Lenne powder camera. Heat capacities were measured for the $\text{CaAl}_2\text{SiO}_6$ glass to characterize the influence of structural state on the low-temperature thermal properties.

Experimental

Sample preparation

The $\text{CaAl}_2\text{SiO}_6$ glass was prepared from CaCO_3 (Fisher, reagent grade, dried at 130°C for 3 days), SiO_2 (General Electric, fused SiO_2 , dried at 500°C for 4 days), and Al_2O_3 (Baker, reagent grade, dried at 1200°C for 3 days). After drying, the reagents were stored in a desiccator over P_2O_5 . Stoichiometric amounts of the reagents were mixed with an Al_2O_3 mortar and pestle under ethanol; the mix was decarbonated at 800°C and fused at 1625°C. As did previous workers (Hays, 1966b; Newton et al. 1977; and Wood, 1978), we had difficulty dissolving corundum in the melt. After about 1.5 hours, most of the corundum had dissolved, and the pattern of the remaining crystals indicated that the melt had been convecting. The mix was fused for an additional 2 hours and then was air quenched. The glass was crushed and again homogenized in an Al_2O_3 mortar and pestle.

The glass was crystallized with a piston-cylinder apparatus in the laboratory of Julian R. Goldsmith and Robert C. Newton at the University of Chicago. Approximately 2.2 g were crystallized per run in graphite capsules at 20 kbar and 1320–1330°C for 2 hours. The thin layer of graphite adhering to the sample was subsequently removed by oxidation in air at 825°C for about 1/2 hour.

Characterization

No birefringent material was seen in the glass when it was examined microscopically. The density, 2.792(3) g/cm^3 , was measured with a pycnometer. Electron microprobe analyses of 15 randomly chosen fragments did not reveal chemical heterogeneity (Table 1). Kyanite was the standard for Al_2O_3 and SiO_2 ; wollastonite was the standard for CaO.

The crystalline material was in the form of discs, 6 mm in diameter, and chips composed of aggregated crystals, 5–10 μm in size. Microscopic examination of random discs did not show any glass or crystals that could be differentiated from CaTs. Powder X-ray patterns were collected for each of the synthesis runs, and all peaks were attributable to CaTs pyroxene. Analyses of several chips (Table 1) were collected by means of an electron microprobe during the same session in which the analyses of the glass were made. Given the accuracy of the electron microprobe, there is no evidence of nonstoichiometry or a significant difference in the analyses of the glass and pyroxene.

The unit-cell parameters were refined from powder X-ray data collected with $\text{CuK}\alpha$ radiation at a scan speed of $1/8^\circ$ $2\theta/\text{min}$, using Si metal ($a_0 = 0.543054$ nm (Parrish, 1960)) as an internal standard. The parameters (Table 2) are very similar to those of previous refinements by Hays (1966b), Newton et al. (1977), and Wood (1978), who used a similar synthesis method. The parameters differ from those determined in the single-crystal study by Okamura et al. (1974). The a and b dimensions measured by Okamura et al. are significantly smaller than the present values. Notably, Okamura et al.'s specimen was crystallized from anorthite, gehlenite, and corundum via reaction (2) instead of from glass, but under similar conditions of pressure and temperature. They concluded from electron-microprobe analyses that their sample was approximately 6 mole % aluminum deficient. The only cited impurity in their synthesis run was gehlenite which would not explain this compositional deviation.

Calorimetry

The heat-capacity data were collected using an automated adiabatic low-temperature calorimeter which has been described

Table 1. Electron microprobe analyses of $\text{CaAl}_2\text{SiO}_6$ glass and pyroxene

	Analyses, weight %		
	Glass	Pyroxene	Calculated
CaO	25.21	25.10	25.71
Al_2O_3	45.83	45.99	46.74
SiO_2	<u>27.41</u>	<u>27.30</u>	<u>27.55</u>
	98.45	98.39	100.00
	Oxide molar ratios		
CaO	0.99	0.99	
Al_2O_3	1.99	2.00	
SiO_2	1.01	1.01	

¹ Any use of trade names in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 2. High-temperature unit-cell parameters and coefficients of mean thermal expansion for CaAl₂SiO₆ pyroxene (25–1200°C)

T(°C)	a(nm)	b(nm)	c(nm)	α(°)	β(°)	γ(°)	V(cm ³)
25*	0.96176(7)	0.86578(7)	0.52779(4)	90.00	106.085(7)	90.00	63.574(6)
25	0.9617(1)	0.8659(2)	0.5276(1)	90.00	106.11(1)	90.00	63.55(1)
200	0.9634(2)	0.8676(2)	0.5284(1)	90.00	106.15(2)	90.00	63.87(2)
400	0.9644(2)	0.8707(3)	0.5294(1)	90.00	106.22(2)	90.00	64.25(2)
600	0.9658(2)	0.8718(2)	0.5301(1)	90.00	106.32(2)	90.00	64.48(2)
800	0.9677(3)	0.8737(2)	0.5308(1)	90.00	106.39(3)	90.00	64.82(2)
1000	0.9694(2)	0.8760(2)	0.5321(1)	90.00	106.50(2)	90.00	65.23(2)
1200	0.9722(2)	0.8785(2)	0.5333(1)	90.00	106.63(2)	90.00	65.71(2)

α_a = 0.882 × 10⁻⁵/°, α_b = 12.04 × 10⁻⁵/°, α_c = 0.888 × 10⁻⁵/°, α_v = 2.78 × 10⁻⁵/°

*Data for this refinement were taken with a powder diffractometer; the others were taken with a Nonius Guinier-Lenne high-temperature camera. The number in parentheses is 1 std.

in detail with the exception of the acquisition and control system by Robie and Hemingway (1972) and Robie et al. (1976). The masses (*in vacuo*) of the samples were 43.5862 g and 19.8671 g for the CaAl₂SiO₆ glass and for CaTs pyroxene, respectively. For both sets of measurements, approximately 4 × 10⁻⁵ mole of He gas was present in the calorimeter to promote thermal equilibration. The formula weight was assumed to be 218.126 g/mol (Commission on Atomic Weights, 1976). Temperatures refer to the International Practical Temperature Scale of 1968.

High temperature X-ray

The high-temperature X-ray diffraction data were obtained using a Nonius Guinier-Lenne camera. Temperatures were calibrated at the melting points of aluminum and gold. No internal standard was used. The high-temperature data were corrected by means of a comparison of the 25°C data set obtained here and the 2θ values predicted from the parameters obtained above. The high-temperature cell parameters were refined by using the least-squares program of Appleman and Evans (1973). At a heating rate of 10°/hr, CaTs remains stable in air to 1200°C, at which temperature it breaks down rapidly to anorthite, gehlenite, and corundum.

Results

Heat-capacity measurements for the CaAl₂SiO₆ glass and pyroxene, corrected for curvature, are listed chronologically in Tables 3 and 4. These values subsequently were smoothed by using cubic splines and extrapolated to zero kelvin by using a C_p/T vs. T² plot. The resulting heat capacities and derived functions for glass and pyroxene are listed at selected temperatures in Tables 5 and 6, respectively. Note that the configurational disorder contribution has not been included in the entropy and Gibbs energy function. The pyroxene properties given in Table

Table 3. Experimental heat capacities for CaAl₂SiO₆ glass

Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)
Series 1		Series 2		Series 5	
51.83	21.18	209.11	128.5	5.47	0.0420
55.70	24.15	214.51	131.3	9.77	0.2074
60.54	28.10	219.65	133.7	11.18	0.3189
65.74	32.41	224.84	136.1	12.20	0.4387
71.80	37.48	230.27	138.5	13.54	0.6283
77.90	42.55	235.70	141.3	15.04	0.8904
84.02	47.56	241.15	143.8	16.67	1.244
90.14	52.40	246.59	146.1	18.52	1.735
96.23	57.09	252.02	148.3	20.57	2.382
102.28	61.80	257.44	150.4	22.86	3.192
108.28	66.22	262.84	152.7	25.42	4.248
114.24	70.67	268.24	154.9	28.29	5.593
120.17	74.93	273.61	157.2	31.48	7.347
126.05	79.24	278.97	159.3	35.06	9.496
131.91	83.22	284.33	161.1	39.06	12.25
137.75	87.15	289.66	163.0	43.51	15.31
143.56	91.11	294.99	164.7	48.52	18.79
149.35	94.92	300.31	166.7	54.10	22.92
155.13	98.46	305.63	168.3	60.19	27.79
160.88	101.9	310.93	170.1	66.26	32.82
166.61	105.5	316.23	171.7		
172.32	108.9	326.57	175.4	Series 4	
178.02	112.3				
183.71	115.6	Series 3		311.09	170.2
189.38	118.4	336.69	178.2	316.31	172.0
195.04	121.5	341.91	179.5	326.39	175.3
200.69	124.5	347.13	180.8	331.60	176.6
		352.32	182.4	336.80	178.1
		357.51	183.7	341.99	179.5
		362.69	185.3	347.16	181.0
		367.87	186.5	352.33	182.8
		373.02	187.6	357.49	184.2
		378.15	189.4	362.64	185.0
				367.78	186.3
				372.90	187.9
				378.01	189.6

Table 4. Experimental heat capacities for CaAl₂SiO₆ pyroxene

Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)	Temp. K	Heat capacity J/(mol·K)
Series 1		Series 2		Series 3	
306.23	168.7	47.82	8.760	227.00	135.3
311.28	170.6	53.33	11.44	232.36	137.8
316.33	172.3	59.39	15.43	237.48	140.2
321.54	174.3	65.74	20.28	242.65	142.5
326.75	175.5	72.11	25.41	248.02	144.9
331.94	176.9	78.42	30.71	253.37	147.5
337.13	178.6	84.64	35.81	258.71	150.2
342.30	179.9	90.78	40.77	264.05	152.5
347.47	181.7	96.86	45.74	269.40	154.8
352.62	183.0	102.87	50.59	274.73	157.1
357.77	184.5	108.82	55.38	280.05	159.2
362.89	186.0	114.71	60.29	285.35	161.0
368.01	188.0	120.57	64.90	290.64	163.1
373.12	189.5	126.38	69.44	295.91	165.1
		132.16	73.82	301.16	167.0
		137.90	78.76	306.41	168.6
		143.64	83.06	311.65	170.7
9.05	0.0267	149.34	87.36	316.87	172.3
10.00	0.0395	155.01	91.56	322.08	173.9
11.11	0.0371	160.67	95.31		
12.28	0.0431	166.30	99.29	Series 4	
13.59	0.0731	171.91	103.6		
15.04	0.1175	177.52	107.1	323.42	174.0
16.66	0.1795	183.13	110.3	328.57	176.3
18.46	0.2778	188.72	113.9	333.53	178.0
20.46	0.4204	194.30	117.1	338.49	179.4
22.68	0.5999	199.86	120.4	343.64	180.3
25.17	0.8776	205.42	123.5	348.79	182.4
27.96	1.315	210.97	126.4	353.92	183.6
31.09	2.031	216.52	129.5	359.05	184.8
34.60	3.124	222.07	132.3	364.17	186.6
38.52	4.766			369.28	188.1
42.89	6.654			374.37	189.4
				379.46	190.8

capacity as expected from a density consideration. As temperature increases the relative difference diminishes, the pyroxene having a slightly greater heat capacity from 300 to 380 K. At present, the only other silicates for which heat capacities of both the crystals and their respective glasses have been measured at low temperatures are CaAl₂Si₂O₈, KAlSi₃O₈, NaAlSi₃O₈ (Openshaw et al., 1976; Robie et al., 1978), and SiO₂ (E. F. Westrum, Jr., unpublished data). For each of these compositions, a maximum occurs below 100 K in the difference between the heat capacities of the glasses and crystals. The overall pattern is slightly more complicated for the feldspar samples than for CaTs. The new measurements for analbite and sanidine by Haselton et al. (1983) do not significantly alter the pattern given in Figure 6 of Robie et al. (1978). The maximum at T < 100 K is also present in

Table 5. Smoothed thermodynamic values for CaAl₂SiO₆ glass. Formula weight = 218.126 g/mol.

TEMP. T KELVIN	HEAT CAPACITY C _p ^o	ENTROPY (S _T ^o -S ₀ ^o) J/(mol·K)	ENTHALPY FUNCTION (H _T ^o -H ₀ ^o)/T	GIBBS ENERGY FUNCTION -(G _T ^o -H ₀ ^o)/T
5	0.026	0.008	0.006	0.002
10	0.224	0.069	0.052	0.017
15	0.872	0.261	0.200	0.062
20	2.190	0.678	0.520	0.158
25	4.063	1.358	1.032	0.326
30	6.504	2.305	1.732	0.573
35	9.482	3.525	2.621	0.905
40	12.87	5.010	3.688	1.323
45	16.32	6.726	4.900	1.826
50	19.84	8.626	6.217	2.409
60	27.64	12.92	9.123	3.794
70	35.97	17.80	12.36	5.440
80	44.28	23.15	15.83	7.316
90	52.29	28.83	19.44	9.388
100	60.02	34.74	23.11	11.63
110	67.53	40.82	26.81	14.00
120	74.85	47.01	30.51	16.49
130	81.93	53.28	34.20	19.08
140	88.72	59.60	37.85	21.75
150	95.25	65.95	41.46	24.49
160	101.4	72.29	45.02	27.27
170	107.5	78.63	48.52	30.11
180	113.4	84.94	51.96	32.98
190	118.8	91.22	55.34	35.88
200	124.1	97.45	58.64	38.80
210	129.1	103.6	61.88	41.74
220	133.9	109.7	65.04	44.69
230	138.6	115.8	68.14	47.65
240	143.2	121.8	71.17	50.62
250	147.5	127.7	74.13	53.58
260	151.6	133.6	77.04	56.55
270	155.7	139.4	79.87	59.51
280	159.5	145.1	82.65	62.46
290	163.1	150.8	85.36	65.41
300	166.5	156.4	88.01	68.35
310	169.8	161.9	90.60	71.28
320	173.1	167.3	93.13	74.20
330	176.2	172.7	95.60	77.10
340	179.1	178.0	98.01	79.99
350	181.8	183.2	100.4	82.86
360	184.5	188.4	102.7	85.72
370	187.1	193.5	104.9	88.57
380	189.9	198.5	107.1	91.39
273.15	157.2	141.2	80.73	60.44
298.15	166.1	153.3	87.53	67.81

6 may be calculated at higher temperatures by means of the following heat-capacity equation:

$$C_p^o \text{ (J/mol} \cdot \text{K)} = 4.6518 \times 10^2 - 7.8375 \times 10^{-2}T + 6.7294 \times 10^5 T^{-2} - 4.9211 \times 10^3 T^{-0.5} + 1.9341 \times 10^{-5} T^2 \quad (4)$$

This equation is consistent with our low-temperature heat-capacity measurements and the differential scanning calorimetric measurements (350–1000 K) of Thompson et al. (1978). Although no statement of the accuracy was given by Thompson et al. in their report, measurements of this type are generally accurate to ±1% (Krupka et al. 1979). At temperatures greater than 1000 K, we constrained the heat-capacity equation by the heat capacities of diopside and an oxide sum.

The difference in the heat capacities, C_p(glass) – C_p(crystals), at low temperatures has been plotted in Figure 1 to show the influence of structural state on the heat capacity. In addition to the noncrystalline-versus-crystalline state, Virgo et al. (1979) have interpreted the Raman spectra of the glass, suggesting that all the Al is in tetrahedral coordination in contrast to the coordination of the Al in the pyroxene. The difference in C_p is quite large at very low temperatures, the glass having the higher heat

Table 6. Smoothed thermodynamic values for $\text{CaAl}_2\text{SiO}_6$ pyroxene. Configurational disorder has not been included in the entries for the entropy and Gibbs energy function. Formula weight = 218.126 g/mol.

TEMP.	HEAT CAPACITY	ENTROPY	ENTHALPY FUNCTION	GIBBS ENERGY FUNCTION
T	C_p°	$(S_T^\circ - S_0^\circ)$	$(H_T^\circ - H_0^\circ)/T$	$-(G_T^\circ - H_0^\circ)/T$
KELVIN		$J/(\text{mol}\cdot\text{K})$		
5	0.0008	0.0003	0.0002	0.0001
10	0.030	0.004	0.003	0.001
15	0.302	0.025	0.020	0.004
20	0.385	0.089	0.073	0.016
25	0.855	0.220	0.178	0.043
30	1.754	0.447	0.357	0.090
35	3.292	0.824	0.658	0.166
40	5.389	1.398	1.116	0.282
45	7.533	2.157	1.710	0.446
50	9.770	3.064	2.402	0.662
60	15.87	5.345	4.102	1.243
70	23.69	8.366	6.331	2.036
80	31.99	12.07	9.019	3.052
90	40.16	16.31	12.03	4.286
100	48.27	20.96	15.25	5.718
110	56.40	25.94	18.62	7.328
120	64.43	31.20	22.10	9.096
130	72.12	36.66	25.65	11.01
140	80.19	42.30	29.26	13.04
150	87.85	48.10	32.91	15.18
160	94.98	54.00	36.57	17.42
170	102.0	59.96	40.22	19.75
180	108.5	65.98	43.83	22.15
190	114.6	72.02	47.40	24.62
200	120.4	78.04	50.91	27.14
210	125.9	84.05	54.35	29.70
220	131.4	90.04	57.73	32.31
230	136.6	95.99	61.04	34.95
240	141.4	101.9	64.29	37.62
250	146.0	107.8	67.47	40.31
260	150.7	113.6	70.58	43.01
270	155.1	119.4	73.63	45.73
280	159.1	125.1	76.61	48.47
290	162.9	130.7	79.52	51.21
300	166.5	136.3	82.36	53.95
310	170.0	141.8	85.13	56.70
320	173.4	147.3	87.84	59.44
330	176.6	152.7	90.48	62.18
340	179.5	158.0	93.06	64.92
350	182.4	163.2	95.57	67.66
360	185.3	168.4	98.02	70.38
370	188.3	173.5	100.4	73.10
380	191.1	178.6	102.8	75.81
273.15	156.7	121.2	74.58	46.59
298.15	166.1	135.3	81.84	53.44

measurements of excess heat capacity in pyrope-grossular and analbite-sanidine solid solutions (Haselton and Westrum, 1980; Haselton et al., 1983). Clearly, the thermochemical functions are most sensitive to the structural state of the material at very low temperatures. The higher heat capacity of the glasses with respect to the crystalline phases could be explained by low-frequency vibrational modes (Kieffer, 1979).

We have calculated an approximate value for the Debye temperature, θ_D , of CaTs from our heat capacity data using the relation

$$\theta_D = (1943.7qT^3/C_V)^{1/3}$$

where q is the number of atoms in the formula and C_V is the measured heat capacity at constant volume. For the

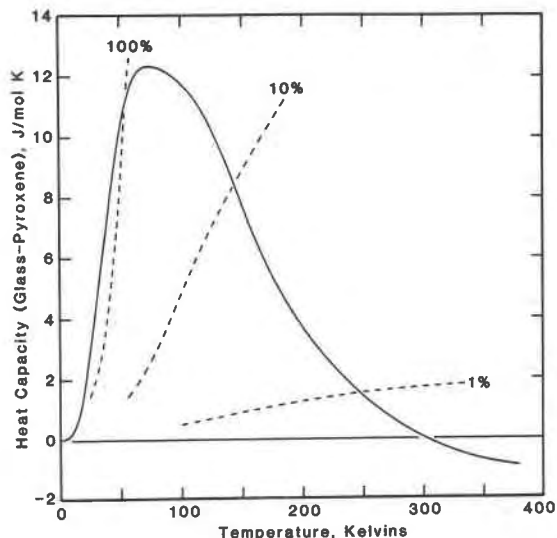


Fig. 1. The difference in heat capacities of $\text{CaAl}_2\text{SiO}_6$ glass and pyroxene as a function of temperature. Differences relative to the heat capacity of the pyroxene are indicated by the dashed curves.

temperatures considered here $C_V \approx C_p^\circ$. The calculated value of θ_D is 820 ± 50 K. The Debye model is generally believed to be accurate for temperatures less than $\theta_D/50$.

The high-temperature cell parameters and coefficient of mean thermal expansions (25–1200°C) are listed in Table 2. The slopes for the coefficients were obtained by linear regression. The curvature in the variation of all cell parameters would be better fit with quadratic expres-

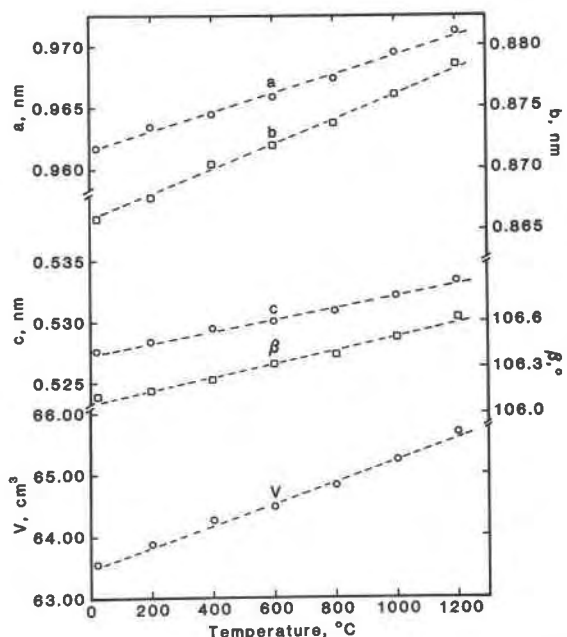


Fig. 2. The variation of unit-cell parameters of $\text{CaAl}_2\text{SiO}_6$ pyroxene with temperature. Lines were fit by linear regression.

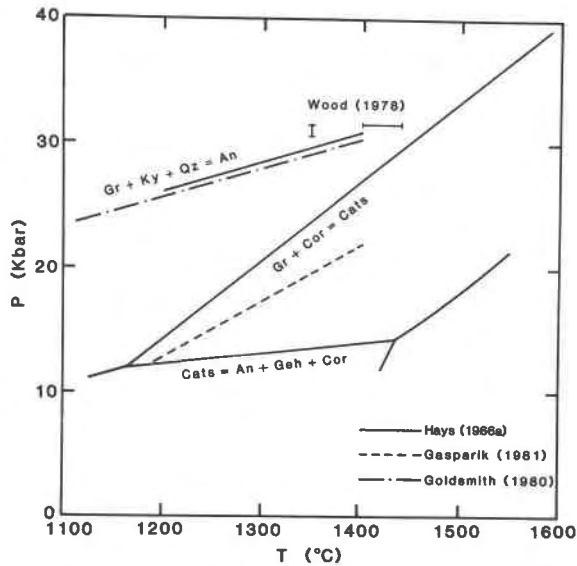


Fig. 3. Plot of the stability boundaries of $\text{CaAl}_2\text{SiO}_6$ pyroxene. The determinations of the Grossular + Corundum = CaTs reaction include studies by Hays (1966a), Gasparik (1981), and the horizontal bracket by Wood (1978). Studies of the reaction Anorthite = Grossular + Kyanite + Quartz which has been used for calibrating pressure are by Hays (1966a) and Goldsmith (1980). Also plotted for this reaction is the single vertical bracket by Wood (1978).

sions. We question whether the accuracy of the data warrants the higher order term. The variation of cell parameters with temperature (Fig. 2) is broadly comparable with the data on six $C2/c$ pyroxenes studied by Cameron et al. (1973).

Discussion

Evaluation of the zero-point entropy in CaTs requires a comparison of the entropy of CaTs deduced from phase-equilibrium studies and the values measured by calorimetry. Quartz-present reactions are unsuitable for this purpose because of nonstoichiometry toward possible fictive endmembers that have M1 and/or M2 vacancies (Wood and Henderson, 1978; Gasparik and Lindsley, 1980).

Temperature and pressure coordinates for reaction (1) have been determined in several independent studies (Fig. 3). Reaction (1) was initially studied over a wide range of pressures and temperatures using synthetic materials and a piston-cylinder apparatus by Hays (1966a). The experimental dP/dT slope of 63.8 bar/K is well defined by reversed experiments. Hijikata and Yagi (1967) also attempted to locate this reaction. Their experiments were conducted with a girdle-type apparatus which was calibrated with regard to pressure at the transition points of Bi(I-II), Bi(II-III), and Tl(II-III). Though not explicitly stated, these calibrations are usually done near 25°C. Hijikata and Yagi claim a pressure accuracy of 1 kbar; however, if the transition points were observed at

25°C, the pressure correction at high temperatures may be significantly smaller. The reaction boundaries were not reversed; hence, equilibrium was not demonstrated. Wood (1978), in a study principally directed at the incorporation of excess SiO_2 into CaTs and CaTs-diopside solid solutions, also reversed reaction (1), yielding a bracket centered at 31.5 kbar and 1420°C. Wood also used a piston-cylinder apparatus and synthetic starting materials. Gasparik (1981) has presented a preliminary report of reversals on reaction (1) in the temperature range 1200–1400°C, yielding a dP/dT slope of 46 bar/K. The reaction boundaries for reaction (1) determined by Hays (1966a) and Gasparik (1981) are plotted in Figure 3. Wood's (1978) single reversal bracket for this reaction is also shown. Wood's (1978) bracket lies slightly above the boundary of Hays (1966a); the results of Gasparik are considerably different.

An appeal to a pressure correction error to explain the disparate results is not reasonable here. All three authors, including Gasparik (oral communication, 1981), have reversed the reaction



The boundaries for this reaction determined by Hays (1966a) and Goldsmith (1980) are shown in Figure 3. Hays's determination was part of the same study as that for reaction (1). Gasparik (oral communication, 1981) used Goldsmith's study as his pressure calibration. The reversal bracket determined by Wood as a part of his study is also shown. Because the agreement on the anorthite breakdown reaction is within 1 kbar and this reaction boundary is relatively close to the reaction boundary of interest, it is very unlikely that individual pressure corrections are at fault. Wood (oral communication, 1982) has suggested that a partial explanation may involve the use of Pt-PtRh thermocouples by Hays and Wood and W-WRe thermocouples by Gasparik. Contamination of Pt-PtRh thermocouples, which is well documented at high pressures and temperatures (e.g., Presnall et al., 1973), and the pressure correction to the emf could lead to a significant error. An argument against this explanation is, again, the agreement on reaction (4). Hays's reaction boundary requires a higher entropy for CaTs, but the boundary lies at relatively lower temperature with respect to Gasparik's determination. This thermodynamically inconsistent relationship prevents variable disorder in CaTs from being an explanation.

If Gasparik's (1981) determination is correct, the CaTs sample synthesized in the present study and the samples synthesized by Newton (1977) were made metastably in the grossular + corundum stability field. We note that the metastable synthesis of pyroxene from glass in a garnet stability field has been commonly observed.

The CaTs zero-point entropy, S_0^{CaTs} , can be readily calculated from reaction (1). A summary of the needed thermo-physical properties of the participating phases appears in Table 7.

Table 7. Thermodynamic parameters for grossular, corundum, and CaTs pyroxene used in calculations

Parameter	Grossular	Corundum	CaTs Pyroxene
a	5.1633x10 ^{2a}	1.5736x10 ^{2f}	4.6518x10 ²ⁱ
b	3.2184x10 ⁻²	7.1899x10 ⁻⁴	-7.8375x10 ⁻²
c			1.9341x10 ⁻⁵
d	-1.4031x10 ³	-9.8804x10 ²	-4.9211x10 ³
e	-9.9419x10 ⁶	-1.8969x10 ⁶	6.7294x10 ⁵
α (K ⁻¹)	2.78x10 ^{-5b}	2.66x10 ^{-5g}	2.47x10 ^{-5h}
β (bar ⁻¹)	7.41x10 ^{-7c}	3.63x10 ^{-7h}	7.5 x10 ⁻⁷ⁱ
V _{1,298} ⁱ (J/bar)	12.529 ^d	2.558 ^f	6.357 ⁱ
S ₂₉₈ ^g - S ₀ ^g (J/mol·K)	260.12 ^d	50.92 ^f	135.30 ⁱ
H _{970,oxide} ^g (kJ/mol)	-325.98 ^e	0	-76.27 ^e

The parameters (a-e) refer to the coefficients of the heat capacity polynomial C_p (J/mol·K) = $a + bT + cT^2 + dT^{-0.5} + eT^{-2}$. The sources of data are (a) Haselton and Newton (1980), (b) Meagher (1975), (c) Hazen and Finger (1978), (d) Haselton and Westrum (1980), (e) Newton et al. (1977), (f) Robie et al. (1979), (g) Skinner (1966), (h) Birch (1966), Coefficient of compressibility of CaTs pyroxene assumed equal to that of jadeite, (i) present work.

By using the expression below and the data from Table 7,

$$S_0^g = 1/3 ((dP/dT)\Delta V_{P,T} + S_{P,T}^{Gr} + 2S_{P,T}^{Cof}) - S_{P,T}^{CaTs} \quad (5)$$

we can calculate the zero-point entropy, S_0^g , attributable to frozen-in disorder in CaTs. At 1300°C on the basis of Hays' (1966a) experimental slope of 63.8 bar/K, $S_0^g = 11.5$ J/mol · K, and, similarly, from Gasparik's (1981) experimental slope of 46 bars/K, $S_0^g = 3.8$ J/mol · K.

The value deduced from Hays's study is virtually identical with $2R \ln 2$ (11.53 J/mol · K) which would be predicted for total tetrahedral disorder. Wood's (1978) work supports this value, as did the X-ray structural refinement by Okamura et al. (1974). The zero-point entropy calculated from Gasparik's experiments is much smaller and requires a considerable amount of short-range order in the tetrahedral sites. All tetrahedral sites are crystallographically identical in $C2/c$ symmetry, and the short-range ordering may simply relieve local charge imbalance.

Supporting evidence for short-range order comes from other experimental methods. The structural refinements of Grove and Burnham (1974) showed no significant difference for refinements of X-ray data in $C2/c$ and $C2$ symmetries, suggesting that some short-range order was present.

A slope for reaction (1) can also be calculated from heat of solution measurements provided by Newton et al.

(1977). This calculation benefits from the inclusion of disorder effects in the heat of solution measurements; hence, no assumptions are required about the configurational entropy. Newton et al. made measurements on material synthesized at 1250° and 1500°C. Because these samples gave the same result, the data suggest that the order state was independent of temperature in this range.

The ΔH_{rxn} at 970K is 92.05 ± 3.75 kJ and increases to 96.34 ± 3.75 kJ at 1300°C. Through the relation

$$\frac{dP}{dT} = \frac{\Delta H_{1,T} + \int_1^P \Delta V dP}{T \Delta V_{P,T}} \quad (6)$$

the slope calculated for Hays' determination is 56.6 bar/K and that for Gasparik is 54.5 bar/K. The approximate uncertainty is 4 bar/K. The heat of solution data, thus, predict an intermediate value and do not provide a means of distinguishing between the phase equilibrium studies; but they do yield a calculated slope that is significantly less than that required for total disorder.

The results of Newton et al.'s (1977) measurements for diopside-CaTs solid solutions, coupled with solution models, indicated that the total disorder model was adequate for diopside-rich samples but failed for CaTs-rich samples. Newton et al. argued from a charge-balance consideration that the CaTs-rich solutions were partially ordered. Without low-temperature C_p measurements for CaTs-diopside solid solutions, an additional uncertainty is present because the excess entropy of mixing arising from vibrational contributions must be assumed to be negligible. For this reason, Newton et al. were hesitant to state vigorously the structural implications of their measurements.

Ganguly and Ghose (1979) stated that tetrahedral disorder in CaTs does not necessarily imply Al-O-Al linkages in the chains. Although one can enumerate a large number of complexions for a mole of CaTs without requiring Al-O-Al linkages, this number $(N_0/2 + 1)^2$, where N_0 is Avogadro's number, does not contribute significantly to the configurational entropy. The number of complexions is larger than initially expected because a Si-O-Si group is permitted on each chain.

Summary

We have presented low-temperature heat capacity measurements for CaAl₂SiO₆ glass and pyroxene. In addition, thermal expansion data are provided for the pyroxene.

The evaluation of the zero-point entropy of CaTs is precluded by a lack of agreement in the phase equilibrium studies. Both disordered and short-range order models are supported by experimental data, but the data for short-range order are more recent and extensive. We suggest, therefore, that a small amount of short-range order is present in CaTs pyroxene.

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References

- Appleman, D. E. and Evans, H. T., Jr. (1973) Job 9214: indexing and least-squares refinement of powder diffraction data. U.S. Department of Commerce National Technical Information Service, PB2-16188.
- Birch, Francis (1966) Compressibility; elastic constants. In S. P. Clark, Jr., Ed., *Handbook of Physical Constants*, p. 97-173, Geological Society of America Memoir 97.
- Cameron, Maryellen, Sueno, S. S., Prewitt, C. T., and Papike, J. J. (1973) High temperature crystal chemistry of acmite, diopside, hedenbergite, jadeite, spodumene, and ureyite. *American Mineralogist*, 58, 594-618.
- Commission on Atomic Weights (1976) Atomic weights of the elements. *Pure and Applied Chemistry*, 47, 75-95.
- Ganguly, Jibamitra and Ghose, Subrata (1979) Aluminous orthopyroxene: order-disorder, thermodynamic properties, and petrologic implications. *Contributions to Mineralogy and Petrology*, 69, 375-385.
- Gasparik, Tibor (1981) Mixing properties of the binary Jd-CaTs. *EOS (Transactions, American Geophysical Union)*, 62, 412.
- Gasparik, Tibor and Lindsley, D. H. (1980) Experimental study of pyroxenes in the system $\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{SiO}_6$ - $\text{Ca}_{0.5}\text{AlSi}_2\text{O}_6$. *EOS (Transactions, American Geophysical Union)*, 61, 402-403.
- Goldsmith, J. R. (1980) The melting and breakdown reactions of anorthite at high pressures and temperatures. *American Mineralogist*, 65, 272-284.
- Grove, T. L. and Burnham, C. W. (1974) Al-Si disorder in calcium Tschermak's pyroxene, $\text{CaAl}_2\text{SiO}_6$ (abstr.). *EOS (Transactions, American Geophysical Union)*, 55, 1202.
- Haselton, H. T., Jr., Hovis, G. L., Hemingway, B. S., and Robie, R. A. (1983) Calorimetric investigation of the excess entropy of mixing in analbite-sanidine solid solutions: lack of evidence for Na,K short-range order and implications for two-feldspar thermometry. *American Mineralogist*, 68, 398-413.
- Haselton, H. T. and Newton, R. C. (1980) Thermodynamics of pyrope-grossular garnets and their stabilities at high temperatures and high pressures. *Journal of Geophysical Research*, 85, 6973-6982.
- Haselton, H. T., Jr. and Westrum, E. F., Jr. (1980) Low-temperature heat capacities of synthetic pyrope, grossular, and pyrope₆₀-grossular₄₀. *Geochimica et Cosmochimica Acta*, 44, 701-709.
- Hays, J. F. (1966a) Lime-alumina-silica. *Carnegie Institution of Washington Year Book*, 65, 234-241.
- Hays, J. F. (1966b) Stability and properties of the synthetic pyroxene $\text{CaAl}_2\text{SiO}_6$. *American Mineralogist*, 51, 1524-1529.
- Hazen, R. M. and Finger, L. W. (1978) Crystal structures and compressibilities of pyrope and grossularite to 60 kbar. *American Mineralogist*, 63, 297-303.
- Herzberg, C. T. (1977) Pyroxene geothermometry and geobarometry: experimental and thermodynamic evaluation of some subsolidus phase relations involving pyroxenes in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$. *Geochimica et Cosmochimica Acta*, 42, 945-957.
- Hijikata, Ken-ichi and Yagi, Kenzo (1967) Phase relations of Ca-Tschermak's molecule at high pressures and temperatures. *Hokkaido University, Faculty of Science, Journal, Series IV, Geology and Mineralogy*, 13, 407-417.
- Kieffer, S. W. (1979) Thermodynamics and lattice vibrations of minerals: 3. Lattice dynamics and an approximation for minerals with application to simple substances and framework silicates. *Reviews of Geophysics and Space Physics*, 17, 35-59.
- Krupka, K. M., Robie, R. A., and Hemingway, B. S. (1979) High-temperature heat capacities of corundum, periclase, anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass, muscovite, pyrophyllite, KAlSi_3O_8 glass, grossular, and $\text{NaAlSi}_3\text{O}_8$ glass. *American Mineralogist*, 64, 86-101.
- Meagher, E. P. (1975) The crystal structures of pyrope and grossularite at elevated temperatures. *American Mineralogist*, 60, 218-228.
- Newton, R. C. (1977) Thermochemistry of garnets and aluminous pyroxenes in the CMAS system. In D. G. Fraser, Ed., *Thermodynamics in Geology*, p. 29-55. Reidel, Dordrecht, The Netherlands.
- Newton, R. C., Charlu, T. V., and Kleppa, O. J. (1977) Thermochemistry of high pressure garnets and clinopyroxenes in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$. *Geochimica et Cosmochimica Acta*, 41, 369-377.
- Obata, M. T. (1976) The solubility of Al_2O_3 in orthopyroxenes in spinel and plagioclase peridotites and spinel pyroxenite. *American Mineralogist*, 61, 840-816.
- Okamura, F. P., Ghose, Subrata, and Ohashi, Haruo (1974) Structure and crystal chemistry of calcium Tschermak's pyroxene, $\text{CaAl}_2\text{SiO}_6$. *American Mineralogist*, 59, 549-557.
- Openshaw, R. E., Hemingway, B. S., Robie, R. A., Waldbaum, D. R., and Krupka, K. M. (1976) The heat capacities at low temperatures and entropies at 298.15 K of low albite, analbite, microcline, and high sanidine. *U.S. Geological Survey Journal of Research*, 4, 195-204.
- Parrish, William (1960) Results of the I.U.Cr. precision lattice project. *Acta Crystallographica*, 13, 838-850.
- Presnall, D. C., Brenner, N. L., and O'Donnell, T. H. (1973) Drift of Pt/Pt10Rh and W3Re/W25Re thermocouples in single stage piston-cylinder apparatus. *American Mineralogist*, 58, 771-777.
- Robie, R. A. and Hemingway, B. S. (1972) Calorimeters for heat of solution and low-temperature heat capacity measurements. *U.S. Geological Survey Professional Paper* 755.
- Robie, R. A., Hemingway, B. S., and Fisher, J. R. (1979) Thermodynamic properties of the minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. *U.S. Geological Survey Bulletin* 1452.
- Robie, R. A., Hemingway, B. S., and Wilson, W. H. (1976) The heat capacities of Calorimetry Conference copper and of muscovite $\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$, pyrophyllite $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, and illite $\text{K}_2(\text{Al}_7\text{Mg})(\text{Si}_{14}\text{Al}_2)\text{O}_{40}(\text{OH})_8$ between 15 and 375 K and their standard entropies at 298.15 K. *U.S. Geological Survey Journal of Research*, 4, 631-644.
- Robie, R. A., Hemingway, B. S., and Wilson, W. H. (1978) Low-temperature heat capacities and entropies of feldspar glasses and of anorthite. *American Mineralogist*, 63, 109-123.

- Shearer, J. A. (1973) Thermochemistry of the garnets and some related compounds. Unpublished Ph.D. thesis. Department of Chemistry, University of Chicago.
- Skinner, B. J. (1966) Thermal expansion. In S. P. Clark, Jr., Ed., Handbook of Physical Constants, p. 75-96, Geological Society of America Memoir 97.
- Thompson, A. B., Perkins, D., III, Sonderegger, U., and R. C. Newton (1978) Heat capacities of synthetic $\text{CaAl}_2\text{SiO}_6$ - $\text{CaMgSi}_2\text{O}_6$ - $\text{Mg}_2\text{Si}_2\text{O}_6$ pyroxenes. EOS, (Transactions, American Geophysical Union), 59, 395.
- Virgo, David, Seifert, F. A., and Mysen, B. O. (1979) Three-dimensional network structures of glasses in the systems CaAl_2O_4 - SiO_2 , NaAlO_2 - SiO_2 , $\text{NaFe}_2\text{SiO}_2$, and NaGaO_2 - SiO_2 at 1 atm. Carnegie Institution of Washington Year Book, 78, 506-511.
- Wood, B. J. (1977) Experimental determination of the mixing properties of solid solutions with particular reference to garnet and clinopyroxene solutions. In D. G. Fraser, Ed., Thermodynamics in Geology, p. 11-27. Reidel, Dordrecht, The Netherlands.
- Wood, B. J. (1978) Reactions involving anorthite and $\text{CaAl}_2\text{SiO}_6$ pyroxene at high pressures and temperatures. American Journal of Science, 278, 930-942.
- Wood, B. J. (1979) Activity-composition relationships in $\text{Ca}(\text{Mg}, \text{Fe})\text{Si}_2\text{O}_6$ - $\text{CaAl}_2\text{SiO}_6$ solid solutions. American Journal of Science, 279, 854-975.
- Wood, B. J. and C. M. B. Henderson (1978). Compositions and unit-cell parameters of synthetic non-stoichiometric tschermakitic clinopyroxenes. American Mineralogist, 63, 66-72.

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