Hexagonal CaAl$_2$SiO$_6$: A new synthetic phase

R. James Kirkpatrick[1]

Department of Geology, University of Illinois, Urbana, Illinois 61801

Ian M. Steele

Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637

Abstract

Crystals of a hexagonal polymorph of CaAl$_2$SiO$_6$ were grown from a stoichiometric, dry melt of the same composition in the temperature range 950°C to 1050°C at ambient atmosphere. This phase is uniaxial positive ($\omega = 1.597 \pm 0.002$, $\epsilon = 1.603 \pm 0.002$, and hexagonal ($a = 9.943 \pm 0.002$Å, $c = 8.228 \pm 0.003$Å) with space group symmetry either $P3c1$ or $P\bar{3}c1$. Prominent X-ray powder diffractions occur at 2.979, 3.033, and 2.874Å.

During an experimental investigation of crystal growth kinetics in the system CaMgSi$_2$O$_6$ — CaAl$_2$SiO$_6$ (Kirkpatrick, 1972), a new phase with the approximate composition CaAl$_2$SiO$_6$ was found. The synthesis conditions and crystal data are described in this note. For convenience this phase is referred to as H-Cats (Hexagonal Ca-Tschermak's molecule) to distinguish it from a monoclinic polymorph (here referred to as M-Cats) first described by Clark *et al* (1962). The phase relations of M-Cats were later described by Hays (1966), who also showed tentatively (based on a comparison of powder data) that M-Cats is isostructural with diopside.

Crystals of H-Cats were grown from a nominally stoichiometric, dry melt with the composition CaAl$_2$SiO$_6$. The melt was produced by melting together the required amounts of reagent grade CaCO$_3$, Al$_2$O$_3$, and G. E. 201 fused quartz in a platinum crucible in a MoSi$_2$ resistance furnace at 1600°C. The melt was then quenched to room temperature. Not all the alumina dissolved, however, and the melt is believed to be slightly aluminum deficient, as found in other studies of this composition (Hays, 1966). The H-Cats crystals were grown by reheating the glass to between 950°C and 1050°C in a nichrome resistance furnace at ambient atmosphere. Nucleation occurred both internally, perhaps on un-

dissolved Al$_2$O$_3$, and externally on the surface of the specimens, but no optical difference was seen between the crystals. At 968°C a few crystals were visible in about 4 hours, and crystallization was complete in about 14 hours. The largest crystals observed were about 1 mm long and 0.3 mm across.

de Neufville and Schairer (1962) investigated the system CaMgSi$_2$O$_6$ — CaAl$_2$SiO$_6$ at atmospheric pressure. At CaAl$_2$SiO$_6$ below 1350°C they found the assemblage gehlenite + anorthite + spinel + "alumina." None of these phases, except undissolved corundum, was found in this work. Nor does H-Cats occur in their work. Although it is possible that H-Cats is a stable phase at the lower temperatures, it seems more likely to be a metastable phase produced at large undercoolings.

The average of three electron-microprobe analyses of H-Cats is (oxide wt percent): CaO = 25.8; SiO$_2$ = 28.4; Al$_2$O$_3$ = 45.6; total = 99.8. The number of cations based on 6 oxygens are: Ca = 1.01; Si = 1.03; Al = 1.95. The slight excess of (Si + Ca) over Al probably results from aluminum deficiency of the melt.

In thin section the crystals appear as hexagonal stars when viewed parallel to c. Optical data are: uniaxial positive; $\omega = 1.597(2)$; $\epsilon = 1.603(2)$. In thin section the crystals appear to be biaxial positive with a $2V$ of about 10°. When separated from the sample and observed in oils, however, the separation of the isogyres disappeared, and the optical symmetry is consistent with the X-ray symmetry. The anoma-

[1] Present Address: Esso Production Research, P. O. Box 2189, Houston, Texas 77001.

TABLE 1. Powder X-Ray Data for Hexagonal $CaAl_2SiO_6$

hkl	d(calc)	d(obs)	I/I_o	hkl	d(calc)	d(obs)	I/I_o
100	8.61	8.60	17	213	2.097	2.097	11
110	4.97	4.98	18	004	2.057	2.065	18
020	4.31	4.31	3	104	2.001	1.999	11
002	4.11	4.12	11	320	1.976	1.974	2
102	3.712	3.720	6	321	1.921	1.921	5
210	3.255	3.258	18	410	1.879	1.880	4
112	3.169	3.173	4	204	1.856	1.856	12
211	3.027	3.033	32	411	1.832	1.831	12
022	2.974	2.979	100	313	1.801	1.801	1
030	2.870	2.874	28	322	1.781	1.781	7
212	2.552	2.552	2	214	1.739	1.738	4
220	2.486	2.487	6	500	1.722	1.721	4
113	2.401	2.402	3	412	1.709	1.710	4
221	2.380	2.382	3	304	1.672	1.671	1
302	2.354	2.350	1	421	1.596	1.596	7
311	2.294	2.292	22	502	1.589	1.590	11
040	2.153	2.151	3	314	1.559	1.559	3

Data collection: Powder diffractometer; monochromatized Cu-radiation ($\lambda = 1.5418$ for $2\theta < 30°$; $\lambda = 1.5405$ for $2\theta < 30°$; 45kV, 15ma; internal silicon metal standard ($a_o = 5.43062Å$ at 21°C); scan speed of 1/2 deg/min.

Intensities are given relative to 022 peak.

Peaks were indexed on a hexagonal cell (a = 9.943 and c = 8.228 Å).

lous $2V$ probably results from strain due to differential contraction of the crystals and the glass on cooling.

X-ray data were obtained using a powder diffractometer with monochromatized Cu-radiation and a silicon metal internal standard (Table 1). The calculated d-spacings were obtained from a least-squares refinement of the observed data. The resulting cell parameters (and, in parentheses, the standard errors in terms of the last decimal place cited) are: $a = 9.943(2)Å$; $c = 8.228(3)Å$; $V = 704.5(3)Å^3$. Pre-

cession photographs of H-Cats showed diffraction symmetry $\overline{3}m$ and the systematic absence of $h0il$ diffractions when $l = $ odd. This is consistent with space groups $P3c1$ and $P\overline{3}c1$. Single crystal structure analysis is in progress.

A value of 6 formula units ($6\ CaAl_2SiO_6$) is consistent with the observed space group symmetry, and the calculated density using $Z = 6$ is 3.08 gm/cm³. A density determination using a Berman balance and a fully crystallized sample gave 2.80 gm/cm³. This value is low relative to the calculated value, perhaps, because of the many cracks, averaging about 0.05 mm apart, observed in a thin section of the specimen used.

Acknowledgments

References

CLARK, S. P., JR., J. F. SCHAIRER, AND J. DE NEUFVILLE (1962) *Carnegie Inst. Washington Year Book,* **61,** 59–68.

DE NEUFVILLE, J., AND J. F. SCHAIRER (1962) *Carnegie Inst. Washington Year Book,* **61,** 56–59.

HAYS, J. F. (1966) *Amer. Mineral.* **51,** 1524–1529.

KIRKPATRICK, R. J. (1972) Ph.D. dissertation, The University of Illinois at Urbana-Champaign, Urbana, Illinois.