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A New Crystal with Kalsilite-type Structure on the $CaAl_2O_4$-SiO_2 Join

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A new crystal phase with a kalsilite-type structure has been found in devitrified glass with compositions close to $CaAl_2O_4$ on the $CaAl_2O_4$-SiO_2 join. The crystal can be synthesized as a nearly pure phase by heating the glass for 5 to 20 min at 1000°C. After prolonged heating, the crystal easily decomposes into an assemblage of the stable compounds, $CaAl_2O_4$, $CaAl_4O_7$, and $Ca_2Al_2SiO_7$(gehlenite). Most of the X-ray powder diffraction lines of the kalsilite-type phase can be indexed on the basis of a hexagonal unit cell with $a=5.0$ Å and $c=8.1$ Å. In addition to these reflections, some weak ones which cannot be indexed on the basis of this unit cell are also present. The kalsilite-type phase reacts with water, resulting in heat liberation and hardening.

In the course of an experimental investigation of a nepheline-type solid solution,[1] two kinds of new crystals were found along the $CaAl_2O_4$-SiO_2 join. One was a kalsilite-type phase formed in compositions closer to $CaAl_2O_4$ than the nepheline-type solid solution, while the other was formed closer to $CaAl_2Si_2O_8$(anorthite). The latter has not yet been investigated in detail. These phases are crystallized from glass at relatively low subsolidus temperatures around 1000°C in the air and gradually disappear at the same temperatures.

In the present report, the mode of formation and some of the physical properties of the kalsilite-type phase will be described.

TABLE 1. SUBSOLIDUS CRYSTALLIZATION PRODUCTS OF GLASSES ON THE $CaAl_2O_4$-SiO_2 JOIN

No.	Composition of glass in weight per cent ( ) mol ratio			Heat treatment of glass °C		Phases as determined optically and by X-ray
	CaO	Al_2O_3	SiO_2			
	35.48 (1)	64.52 (1)	0 (0)			$CaAl_2O_4$
1	33.37 (6)	60.67 (6)	5.96 (1)	1000	5 min	Much Ks-type, little Gl.
				1000	10 min	Much Ks-type, little Ne-type, (little Gl).
				1000	30 min	Much Ks-type, little Ne-type
				1000	2 days	Much $CaAl_2O_4$, moderate amounts Gehl and $CaAl_4O_7$.
2	32.97 (5)	59.95 (5)	7.07 (1)	950	40 min	} Much Ks-type, little Ne-type, (little Gl).
				1000	5 min	
				1000	10 min	
				1000	30 min	Much Ks-type, little Ne-type.
				1000	2 days	} Much $CaAl_2O_4$, moderate amounts Gehl and $CaAl_4O_7$.
				1100	12 hr	
3	32.40 (4)	58.91 (4)	8.68 (1)	950	21 hr	Mcuh Ks-type, much Ne-type, little Gl.
				1000	5 min	Little Ks-type, little Ne-type in glass.
				1000	20 min	Moderate amounts Ks-type, Ne-type and Gl.
				1000	13 hr	Much Ne-type, little Ks-type.
				1000	2 days	Much Ne-type, little Gehl.
				1100	12 hr	Moderate amounts Gehl, Ne-type and $CaAl_4O_7$.
				1200	3 hr	Much Gehl, moderate amounts $CaAl_4O_7$ and $CaAl_2O_4$.

Gehl; gehlenite, Gl; residual glass, Ks-type; kalsilite-type phase, Ne-type; nepheline-type solid solution.

1) T. Yoshioka, This Bulletin, **43**, 1981 (1970).

Experimental

Homogeneous glass with compositions close to $CaAl_2O_4$ on the $CaAl_2O_4$-SiO_2 join was prepared by melting mixtures of chemicals above 1700°C in an electric furnace. Crushed glass was heated and devitrified under various conditions. The products were identified by means of a polarizing microscope and X-ray powder diffraction. The powder patterns of the kalsilite-type phase were indexed.

The rate of the heat liberation of the kalsilite-type phase in a hydration reaction was observed with a conduction calorimeter,[2] CM-502 type, of the Oyo Denki Kenkyusho Co., Ltd. Two kinds of kalsilite-type phases were synthesized by heating glass No. 1 and glass No. 2 (Table 1) for 20 min at 1000°C. They were then pulverized, and grains 4 to 16 microns in

Table 2. Indexed powder patterns of the kalsilite-type phase

Crystallized from No. 1 glass. Indexed based on Hexagonal, a 5.0268 Å, c 8.1223 Å. (Da .0003, Dc .0007)			Crystallized from No. 2 glass. Indexed based on Hexagonal, a 5.0204 Å, c 8.1673 Å (Da .0004, Dc .0009)			Kalsilite, $Ks_{100}Ne_0$. J. V. Smith and O. F. Tuttle[3]		
I_{obs}	d_{obs}	$hk.l$	I_{obs}	d_{obs}	$hk.l$	I	d_{obs}	Indices
* 3b	4.676	—						
17	4.059	00.2	23	4.085	00.2	12	4.3512	00.2
6b	3.841	10.1	55	3.840	10.1	45	3.9733	10.1
100	2.969	10.2	100	2.977	10.2	100	3.1184	10.2
* 8b	2.850	—	* 7	2.847	—			
		tri 41.0			tri 41.0			
		tetr 32.2			— —			
		ord 21.0			ord 21.0			
60	2.513	11.0	61	2.509	11.0	50	2.5789	11.0
			* 6	2.487	—			
					tri 50.1			
					tetr 53.0, 70.0			
			* 8	2.477	—			
					tetr 51.2			
36	2.401	11.1	6	2.400	11.1	15	2.4724	11.1
* 5	2.307	—						
		tetr 71.0						
6	2.299	10.3	18	2.307	10.3	10	2.4319	10.3
* 4b	2.199	—	* 4	2.205	—			
		tri 22.3			tri 22.3			
		ord 20.3			ord 20.3			
6	2.177	20.0	5	2.173	20.0	3	2.236	20.0
5	2.137	11.2	4	2.138	11.2	10	2.2183	11.2
			4	2.100	20.1	17	2.1753	00.4
8b	2.030	00.4	8	2.042	00.4	5	2.164	20.1
20	1.919	20.2	23	1.919	20.2	5	1.9868	20.2
						3	1.9546	10.4
4b	1.842	11.3	3	1.846	11.3	4	1.9270	11.3
			9	1.699	20.3	3	1.7703	20.3
			3	1.584	11.4	4	1.6621	11.4
						4	1.6580	21.1
16	1.525	21.2	13	1.529	10.5	6	1.6220	10.5
14	1.522	10.5	24	1.525	21.2	9	1.5742	21.2
* 5	1.458	—				3	1.5588	20.4
		tri 71.3						
		ord 32.3						
16	1.451	30.0	23	1.449	30.0	10	1.4895	30.0
			19	1.407	21.3	3	1.4598	21.3
			3	1.369	11.5			

tri a×3, tetr a×4, ord a×$\sqrt{3}$. CuKα radiation. Da, Dc, standard deviation.

2) U. Danielson, Chemistry of Cement, Proc. 4th Internl. Symp., Washington, **1**, 519 (1960).

diameter were used for the hydration examination. Ten milliliters of water were added to 10g of the specimen. The measurement of the rate of heat liberation was performed at 20°C.

Results

Mode of Formation. The kalsilite-type phase was produced when the glass was heated for a short time at approximately 1000°C (Table 1). The crystallized products of glass No. 1 and glass No. 2 after 10 mins' heating at 1000°C were composed mostly of this phase, plus a trace of the nepheline-type solid solution or residual glass. After prolonged heating, this phase easily decomposed into an assemblage of compounds, $CaAl_2O_4$, $CaAl_4O_7$, and $Ca_2Al_2SiO_7$, as shown in the table. The crystallized product of glass No. 3, obtained by 20 mins' heating at 1000°C, was composed of both the kalsilite-type phase and the nepheline-type solid solution with residual glass. Further heating at 1000°C resulted in the formation of the nepheline-type solid solution with a concomitant disappearance of the kalsilite-type phase.

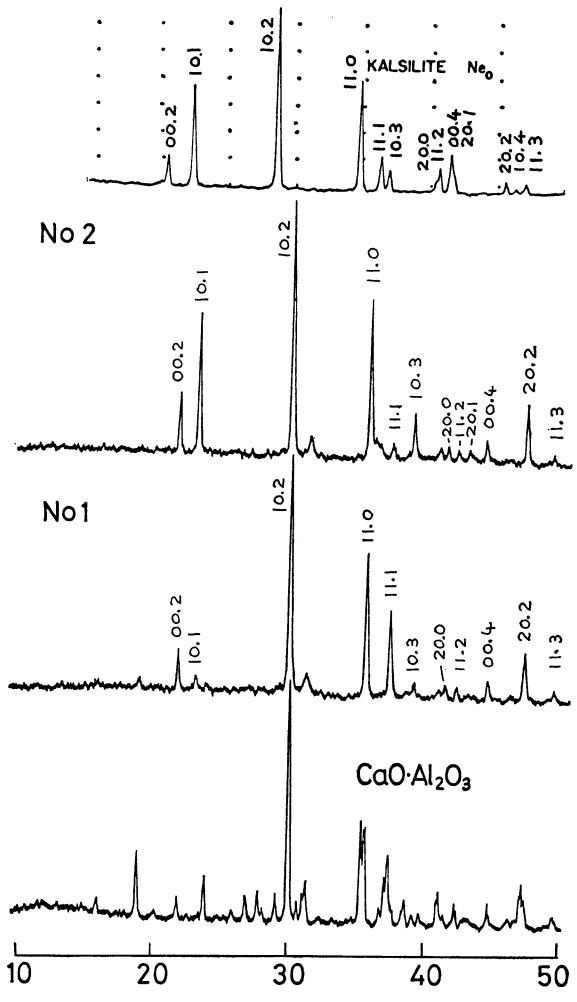

Fig. 1. X-ray powder patterns of the kalsilite-type phase.
Numbers correspond to those in Table 1. The pattern of kalsilite according to J. V. Smith and O. F. Tuttle is reproduced from Fig. 1 in p. 284 of Amer. Journ. Sci., Vol. 255 (1957). Indices are added for convenience by the present writer.

X-Ray Diffraction Pattern. In Fig. 1 powder diffraction patterns of the kalsilite-type phase obtained as a nearly pure phase (no trace of the nepheline-type solid solution was observed in the powder patterns) from glass No. 1 and glass No. 2 by 10 mins' heating at 980°C are shown, along with those of synthetic kalsilite[3] and $CaAl_2O_4$. Indexed powder data are also given in Table 2.

A close resemblance is observed between the kalsilite-type phase from glass No. 2 and the synthetic kalsilite. The diffraction pattern of the phase from glass No. 1 differs from that of the kalsilite. However, it resembles $CaAl_2O_4$ as a whole (Fig. 1). Almost all the diffraction lines of the kalsilite-type phases can be indexed on the basis of a hexagonal unit cell with $a=5.0$ Å and $c=8.1$ Å (ordinary kalsilite $KAlSiO_4$ has a hexagonal unit cell with $a=5.2$ Å and $c=8.7$ Å[3]). In addition to these reflections, some weak ones are also present, although these also are believed to be due to this phase. However, these lines cannot be indexed on the basis of the ordinary kalsilite unit cell;

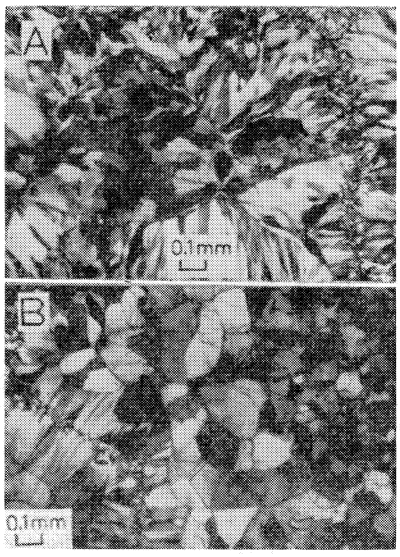

Fig. 2. Photomicrographs of the kalsilite-type phase crystallized from glass No. 2. Crossed nicols.
A) Feather-like form.
B) Granular form. Class was prepared by oxygen-acetylene flames.

3) J. V. Smith and O. F. Tuttle, *Amer. J. Sci.*, **255**, 282 (1957).

some of them can, however, be indexed by making the a parameter three or four times larger than that of the ordinary kalsilite, like that of tri-kalsilite[4] or tetra-kalsilite.[3] Also, some of them can be accounted for by the unit cell in which the a parameter is made $\sqrt{3}$ times larger than that of the ordinary cell, as in the case of ordered kalsilite.[5] However, none of these three unit cells can explain the weak reflections completely. One diffraction line remained unindexed in the pattern of the kalsilite-type phase from glass No. 1. It appears at the angle, about 19°(2θ) Cu$K\alpha$, which coincides with one of the reflections of $CaAl_2O_4$.

Optical Properties. After having been heated at 1000°C for 5 to 30 min, the glass appeared to be translucent; however, under a microscope it was observed as almost fully crystallized with a polycrystalline feature. Most of the crystals of the kalsilite-type phase appeared in a featherlike form, but they varied in their crystal habit according to the way the original glass had been prepared. They appeared in granular form when they were crystallized form the glass prepared by an oxygen-acetylene flame (Fig. 2). No difference was observed between the two forms in chemical composition, X-ray powder pattern, or refractive index. The kalsilite-type phase are uniaxially negative. The refractive indices of the one crystallized from No. 2 glass are ω 1.640 and ε 1.629, and those of the one crystallized from No. 1 glass are ω 1.646 and ε 1.636.

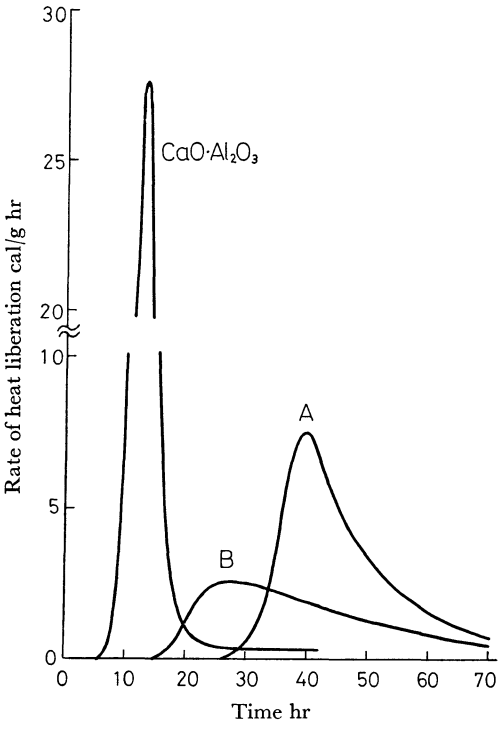

Fig. 3. Rate of heat liberation of the kalsilite-type phase.
A kalsilite-type phase cristallized from glass No. 1.
B kalsilite-type phase cristallized from glass No. 2.

Hydraulic Properties. Since the kalsilite-type phase appears in the compositions close to $CaAl_2O_4$ and has structural similarity to $CaAl_2O_4$, this phase was expected to have a hydraulic property. Generally, the cement-clinker compounds show features characteristic of heat liberation when they react with water. In the present study, therefore, the rates of the heat libetraion of the specimens of the kalsilite-type phase were examined, and they were compared with that of $CaAl_2O_4$, the grain size of which was 10—16 microns in diameter, as is illustrated in Fig. 3. Two kinds of kalsilite-type phases reacted with water, resulting in heat liberation and hardening. The rate of the heat liberation of these specimens was much smaller than that of $CaAl_2O_4$. The hydration products of the phases three days after the addition of water were composed mostly of $CaAl_2O_4 \cdot 10H_2O$, plus a small amount of $Ca_2Al_2O_5 \cdot 8H_2O$. Also, a small amount of the kalsilite-type phase remained unreacted in the No. 1 product, and much, in the No. 2 product.

Consideration

In the previous report[1] the nepheline-type solid solution on the $CaAl_2O_4$–$CaAl_2Si_2O_8$ join was expressed as:
$Ca_{8-(1/2)x}\square_{(1/2)x}Al_{16-x}Si_xO_{32}$. It takes an x value of about from 2 to 5.3. When x became less than 2, the kalsilite-type phase appeared. Kalsilite is the stable form of $KAlSiO_4$ below 850°C,[6] and its structure is based on that of the ideal, high-temperature tridymite. The kalsilite-type phases of this study can be expressed ss follows:
$Ca_{1.82}\square_{0.18}(Al_{3.64}Si_{0.36})O_8$ for the compound crystallized from glass No. 2, and $Ca_{1.85}\square_{0.15}(Al_{3.69}Si_{0.31})O_8$ for the compound crystallized from glass No. 1.

It is interesting to note that some of the weak reflections of the phases can be indexed on the basis of a unit cell similar to those of trikalsilite or tetra-kalsilite; these latter phases are regarded as metastable phases and appear only in compositions near the boundary between the stability ranges for nepheline and for kalsilite.[4,6] That the X-ray powder pattern of the No. 1 phase resembles, in general, that of $CaAl_2O_4$ more closely than that of kalsilite suggests that it is in a transitional stage

4) Th. G. Sahama and J. V. Smith, *Amer. Mineral.*, **42**, 286 (1957).
5) J. V. Smith and Th. G. Sahama, *ibid.*, **42**, 287 (1957).
6) O. F. Tuttle and J. V. Smith, *Amer. J. Sci.*, **256** 571 (1958).

to the monoclinic $CaAl_2O_4$ structure.

Rankin and Merwin[7] and Carstens[8] have reported the existence of uniaxial $CaAl_2O_4$. Recently Nurse *et al.*[9] described, in their study of the CaO–Al_2O_3 system, that the uniaxial $CaAl_2O_4$ was a spherulitic quench-growth of a melt of the composition close to $CaAl_2O_4$. It can be expected that the uniaxial $CaAl_2O_4$ in high aluminous cements will correspond to the kalsilite-type phase because high aluminous cements have compositions close to $CaAl_2O_4$ and usually contain a certain percentage of SiO_2; in addition, they are usually produced by melting.

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7) G. A. Rankin and H. E. Merwin, *J. Amer. Chem. Soc.*, **38**, 568 (1916).
8) C. W. Carstens, *Z. Kristallogr.*, **63**, 473 (1926).
9) R. W. Nurse, J. H. Welch and A. J. Majumdar, *Trans. Brit. Ceram. Soc.*, **64**, 409 (1965).