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Metastable Solid Solution with Nepheline-type Structure in the CaO–Al_2O_3–SiO_2 System

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The metastable nepheline-type solid solution in the CaO–Al_2O_3–SiO_2 system shows the best crystal development upon devitrification on the $CaAl_2O_4$–$CaAl_2Si_2O_8$ join. The crystallization occurs through the devitrification of glass at relatively low subsolidus temperatures, around 1000°C in the air. The X-ray powder diffraction patterns of the solid solution can be indexed on the basis of a hexagonal unit cell of the nepheline structure without exception. The cell parameter *a* of the solid solution is similar to that of nepheline, while its parameter *c* is smaller than that of nepheline and corresponds to that of high-temperature tridymite. When the cell parameters of the solid solution on the join are plotted against the composition, there is a break in the slope at $Ca_6Al_{12}Si_4O_{32}$, though the cell volume varies continuously. The nepheline-type solid solution on the join may be expressed as $Ca_{8-(1/2)x}\square_{(1/2)x}Al_{16-x}Si_xO_{32}$, where $\square$ means the interstitial vacant site. The relationship between the cell parameter and the composition suggests that there should be two kinds of Ca-sites in the structure of the present solid solution, and that these kinds correspond to the alkali sites of two different sizes in the nepheline structure.

Certain aluminosilicate crystals composed of a three-dimensional network of AlO_4 and SiO_4 tetrahedra are known to have crystallographic structures similar to those of some silica modifications. They have been termed "the stuffed derivatives of the silica structures".[1] A wide range of solid solutions are often formed between the stuffed derivatives and pure silica.[2-6]

Sugiura and Yoshioka[7] reported a new metastable solid solution in the CaO–Al_2O_3–SiO_2 system, a solid solution which was formed as a single phase over a relatively wide range of composition within a triangle having $CaAl_2O_4$, $CaAl_4O_7$, and $CaAl_2Si_2O_8$(anorthite) as the vertices; crystals of the solid solution were developed best on the $CaAl_2O_4$–$CaAl_2Si_2O_8$ join. Since then, it has been made clear by the present author[8] that the solid solution is structurally related to nepheline or one of the stuffed derivatives of high-temperature tridymite. The nepheline-type solid solution may be regarded as a solid solution formed between $CaAl_2O_4$,[9] one of the stuffed derivatives of the tridymite structure, and pure silica.

The present paper will deal mainly with the members formed on the $CaAl_2O_4$–$CaAl_2Si_2O_8$ join.

Experimental

Preparation of Glass. Homogeneous glass of the CaO–Al_2O_3–SiO_2 system was prepared by melting mixtures of chemicals in a platinum crucible at from 1600°C to 1700°C in an electric furnace. Pure quartz powder and guaranteed reagents of $CaCO_3$ and Al_2O_3 obtained from the Kanto Kagaku Co., Ltd., were used as the raw materials. The homogeneity of the glass was tested by the uniformity of its refractive index.

Divitrification of Glass. Crushed glass (2—8 mmϕ) was heated and devitrified under various conditions in an electric furnace equipped with SiC heating elements. The products were identified by a polarizing microscope and by the X-ray powder diffraction.

X-Ray Powder Diffraction. The cell parameter *a* was determined on the basis of the 52.0 reflection, using Si as the standard, and the parameter *c*, from the 00.4 reflection, using quartz as the standard. Diffraction

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[1] M. J. Buerger, *Amer. Min.*, **39**, 600 (1954).

[2] R. Roy and E. F. Osborn, *J. Amer. Chem. Soc.*, **71**, 2086 (1947).

[3] R. Roy, Symposium on Nucleation and Crystallization of Glasses and Melts, Amer. Ceram. Soc., Columbus, Ohio, p. 39 (1962).

[4] W. Shreyer and J. F. Schairer, *Z. Kristallogr.*, **116**, 60 (1961).

[5] M. D. Karkhanavala and F. A. Hummel, *J. Amer. Ceram. Soc.*, **36**, 393 (1953).

[6] T. I. Prokopowicz and F. A. Hummel, *ibid.*, **39**, 266 (1956).

[7] K. Sugiura and T. Yoshioka, Proc. 5th Internl. Symposium on Cement Chemistry, Tokyo, **1**, p. 370 (1968).

[8] T. Yoshioka, *J. Mineral Soc. Japan*, Vol. 9, No. 6 (1970), to be published.

[9] M. W. Dougill, *Nature*, **180**, 292 (1957). Also in the "Chemistry of Cements", Tailor, edited, Academic Press, London, **1**, p. 153 (1964).

conditions of the Geigerflex (Rigaku Denki Co., Ltd.) were as follows: Ni filtered Cu*K*α radiation, 40 KV-20 mA or 35KV-15 mA; slits, 1°-1°-0.1 mm; scanning speed, 0.25°(2θ)/min; chart speed, 10 mm/min; time constant, 4 sec; full scale, 200 counts/sec.

Measurement of Refractive Index. The refractive index of the phases encountered in the study was measured by the oil-immersion method with the sodium light at 20°C. The measurements were made within an accuracy of ±0.002.

Results

Mode of Formation. The subsolidus crystallization products of the glasses on the $CaAl_2O_4$-$CaAl_2Si_2O_8$ join in the CaO-Al_2O_3-SiO_2 system are given in Table 1; they are also shown in Fig. 1. As may be seen in Table 1 the single phase of the nepheline-type solid solution was obtained in the compositions between No. 4 and No. 7.

TABLE 1. SUBSOLIDUS CRYSTALLIZATION PRODUCTS OF THE GLASSES ON THE $CaAl_2O_4$-$CaAl_2Si_2O_8$ 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			
1	33.37	60.67	5.96	1000	5 min	Much Ks-type, little Gl.
	(6)	(6)	(1)	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	59.95	7.07	950	40 min	Much Ks-type, little Ne-type, (little Gl).
	(5)	(5)	(1)	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	58.91	8.68	950	21 hr	Much Ks-type, much Ne-type, little Gl.
	(4)	(4)	(1)	1000	5 min	Little Ks-type, little Ne-type in Gl.
				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 $CaAl_2O_4$.
4	31.49	57.26	11.25	900	19 hr	Little Ne-type in glass.
	(3)	(3)	(1)	1000	4 hr	All Ne-type.
			powdered glass	1000	14 hr	Much Ne-type, little Gehl.
				1000	2 days	
				1000	2 weeks	Much Ne-type, little Gehl, little $CaAl_4O_7$.
				1100	6 hr	
				1100	2.5 days	Much Gehl, much $CaAl_4O_7$.
				1200	6.5 hr	
5	30.80	56.00	13.20	1000	2 days	All Ne-type.
	(5)	(5)	(2)			
6	28.31	51.47	20.22	900	20 hr	All glass.
	(3)	(3)	(2)	950	21 hr	Much Ne-type, little Gl.
				1000	4 hr	All Ne-type
				1000	1 month	
				1100	12 hr	
		powdered Ne-type crystal		1000	12 days	Much Ne-type, litle Geh.
		powdered Ne-type crystal		1100	2.5 days	Much Ne-type, moderate amount Gehl, little An.
				1200	10 hr	Much Ne-type, moderate amount Gehl, little $CaAl_{12}O_{19}$, little An.
				1300	5 hr	Much Gehl, moderate amounts $CaAl_{12}O_{19}$ and An.
7	25.71	46.74	27.55	950	21 hr	Much Ne-type, little Gl.
	(1)	(1)	(1)	1000	2 days	All Ne-type.
				1100	2 hr	
				1100	12 hr	Much Ne-type, little An.
			powdered glass	1100	2.5 days	Much Ne-type, moderate amounts Gehl and An.
				1200	10 hr	Moderate amounts Ne-type, Gehl and An, little $CaAl_{12}O_{19}$.
				1300	5 hr	Much Gehl, much An, little $CaAl_{12}O_{19}$.

Table 1. (Continued)

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$_2$O$_3$	SiO$_2$			
8	24.84	45.16	30.00	1000	2 days	Much Ne-type, moderate amount Un.
9	24.37 (5)	44.30 (5)	31.33 (6)	950	2 days	Little Ne-type, little Un in Gl.
				1000	2 days	Much Ne-type, much Un.
				1100	2.5 days	Much Un, little An, little Gehl.
				1200	12 hr	Much Un, moderate amounts An and Gehl.
				1300	5 hr	Much An, much Gehl, litile CaAl$_{12}$O$_{19}$.
10	23.42	42.58	34.00	950	2 days	Little Ne-type, little Un in Gl.
				1000	2 days	All Un.
				1100	2.5 days	Much Un, little An.
				1200	10 hr	Moderate amounts Un, An and Gehl.
				1300	5 hr	Much An, moderate amount Gehl, little CaAl$_{12}$O$_{19}$.
11	22.35	40.65	37.00	950	2 days	Little Ne-type, little Un, little An in Gl.
				1000	2 days	Much Un, little An, little Gl.
				1100	2.5 days	Much An, much Un.
				1200	12 hr	Much An, moderate amount Gehl, little CaAl$_{12}$O$_{19}$.

An anorthite, Gehl gehlenite, Gl residual glass, Ks-type kalsilite-type phase, Ne-type nepheline-type solid solution, Un unknown phase.

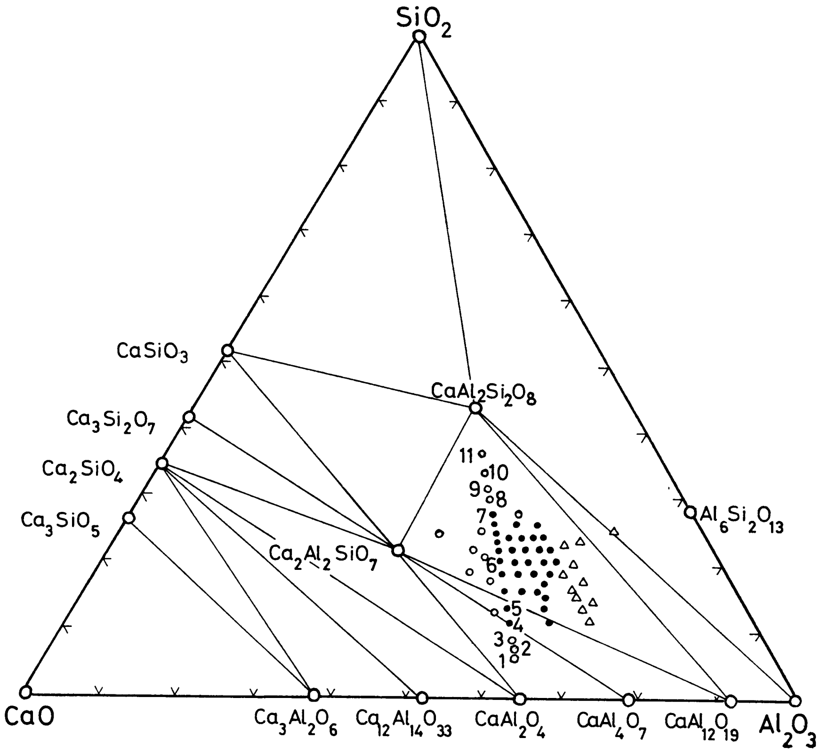

Fig. 1. Mode of formation of the nepheline-type solid solution in the CaO–Al$_2$O$_3$–SiO system.
● All nepheline-type solid solution.
○ Nepheline-type solid solution is accompanied by other crystalline phases.
△ Complete glass is not obtained, but nepheline-type solid solution is crystallized from the glassy part.
Numbers correspond to those in Table 1.

The nepheline-type solid solution appears as the first crystalline phase during the devitrification of glasses of these compositions at low subsolidus temperatures (around 1000°C).

The nepheline-type solid solution crystallized at a certain temperature decomposes when it is treated at higher subsolidus temperatures, or it decomposes when treated at the same temperature after a longer time of heating; in either case, this leads to a different assembly of crystalline products, as is shown in Table 1. This tendency was promoted when the solid solution was pulverized and reheated. In addition, the solid solution was shown by differential thermal analysis,7) to undergo an exothermic reaction and to decompose into just the same assembly of the crystalline products described above. These results clearly suggest that the nepheline-type solid solution is of a metastable nature. The nepheline-type solid solution persists at higher temperatures or persists for much longer periods of heating at a given temperature when the solid solution increases in its SiO_2 content along the $CaAl_2O_4$–$CaAl_2Si_2O_8$ join (Table 1). A similar quality of persistence is shown by the metastable quartz-type solid solution on the SiO_2–$MgAl_2O_4$ join.4)

X-Ray Observations. The X-ray powder patterns of the nepheline-type solid solution in the CaO–Al_2O_3–SiO_2 system are similar to those of nepheline, and all the reflections can be indexed on the basis of a hexagonal unit cell which is similar to that of nepheline. The cell parameters of the solid solution on the $CaAl_2O_4$–$CaAl_2Si_2O_8$ join are shown in Table 3. However, there are some differences between synthetic nepheline10) and the present solid solution; they are compared in Table 2 for the sake of convenience. The cell volume of the nepheline-type solid solution on the $CaAl_2O_4$–$CaAl_2Si_2O_8$ join decreases continuously with an increase in the SiO_2 content over all the compositions. The variations in the two cell-parameters, *a* and *c*, are not thoroughly continuous against the composition; rather, they show a break in the cell parameters at the composition of No. 6 (Fig. 2).

Optical Properties. The nepheline-type solid solution on the $CaAl_2O_4$–$CaAl_2Si_2O_8$ join showed the best crystal development, while all those which were crystallized not on the join but in the lime-poor side of the CaO–Al_2O_3–SiO_2 system showed poor crystal development (Fig. 3), though they were formed as a single phase. The solid solution showed a granular or lathlike shape with an irregular outline, and those which were crystallized from the high SiO_2 compositions often showed a hexagonal skeletal development. Neither a characteristic twin nor a cleavage was ob-

TABLE 2. INDEXED POWDER PATTERN OF THE NEPHELINE-TYPE SOLID SOLUTION

Nepheline-type solid solution No. 6 member Indexed based on hexagonal *a* 9.9961Å, *c* 8.2195Å (Da 0.0006, Dc 0.0007)			Synthetic Nepheline $Ne_{62.5}Ks_{37.5}$ J. V. Smith and O. F. Tuttle (1957)10)		
I_{obs}	d_{obs}	Indices	I	d_{obs}	Indices
31	8.68	10.0			
36	5.00	11.0	3	5.030	11.0
2	4.31	20.0	10	4.354	20.0
—	—	—	10	4.319	11.1
22	4.11	00.2	35	4.211	00.2
—	—	—	60	3.870	20.1
9	3.71	10.2	5	3.789	10.2
28	3.280	21.0	40	3.294	21.0
11	3.175	11.2			
55	3.041	21.1	10	3.065	21.1
100	2.980	20.2	100	3.027	20.2
39	2.886	30.0	35	2.905	30.0
—	—	—	1	2.670	10.3
5	2.560	21.2	20	2.593	21.2
6	2.499	22.0	15	2.515	22.0
8	2.402	11.3 31.0	10	2.415	31.0
3	2.362	30.2	3	2.390	30.2
—	—	—	30	2.359	20.3
35	2.306	31.1	20	2.322	31.1
4	2.165	40.0	5	2.1773	40.0
3	2.135	22.2	1	2.1582	22.2
15	2.101	21.3	7	2.1350	21.3
26	2.074	31.2	15	2.1046	00.4
12	2.055	00.4	5	2.092	31.2
11	2.000	10.4			
3	1.986	32.0	2	1.9990	32.0
4	1.931	32.1	7	1.945	32.1
—	—	—	5	1.939	11.4
—	—	—	5	1.900	41.0
3	1.916	40.2			
18	1.856	20.4	5	1.895	20.4
11	1.841	41.1	1	1.8527	41.1
3	1.806	31.3			
10	1.788	32.2	5	1.8047	32.2
4	1.740	21.4	1	1.7200	40.3
3	1.731	50.0			
6 2	1.716 1.674	41.2 30.4	5	1.7051	50.1 30.4
— 2	— 1.633	— 33.1	3	1.6458	42.0 33.1
—	—	—	7	1.6276	32.3
8	1.604	42.1			
13	1.595	50.2	4	1.6094	50.2
6	1.561	11.5 31.4			
15	1.555	41.3 51.0	5	1.574	41.3
—	—	—	15	1.5705	20.5

Cu*Kα* radiation. Da, Dc standard deviation.

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

TABLE 3. CHEMICAL COMPOSITIONS AND PHYSICAL CONSTANTS OF THE NEPHELINE-TYPE SOLID SOLUTION ON THE $CaAl_2O_4$-$CaAl_2Si_2O_8$ JOIN

No.	Chemical composition						
	Weight per cent			Atomic ratio, 0=32			
	CaO	Al_2O_3	SiO_2	Ca	Interstitial vacant site	Al	Si
3*	32.40	58.91	8.68	7.11	0.89	14.23	1.77
4	31.49	57.26	11.25	6.86	1.14	13.72	2.28
5	30.80	56.00	13.20	6.66	1.34	13.33	2.67
	29.82	54.21	15.97	6.40	1.60	12.80	3.20
	28.90	52.53	18.57	6.15	1.85	12.31	3.69
6	28.31	51.47	20.22	6.00	2.00	12.00	4.00
	27.21	49.47	23.32	5.71	2.29	11.43	4.57
	26.61	48.38	25.00	5.56	2.44	11.13	4.87
7	25.71	46.74	27.55	5.33	2.67	10.66	5.34

No.	Cell dimentions, density				Refractive index, sign		
	(Å), a	(Å), c	($Å^3$), V	ρ_{calcd}	ε	ω	Sign
3*	10.023	8.240	717.0	2.850	n≒1.632		–
4	10.016	8.236	715.6	2.833	n≒1.626		(+)
5	10.016	8.232	715.2	2.817	n≒1.622		+
	10.009	8.224	713.5	2.801	1.617	1.614	+
	10.002	8.218	711.9	2.785			+
6	9.995	8.216	710.8	2.776	1.611	1.606	+
	9.980	8.228	709.7	2.756	1.608	1.601	+
	9.965	8.234	708.1	2.748			+
7	9.946	8.240	705.9	2.736	1.604	1.597	+

* Little gehlenite and little kalsilite-type phase coexisted.

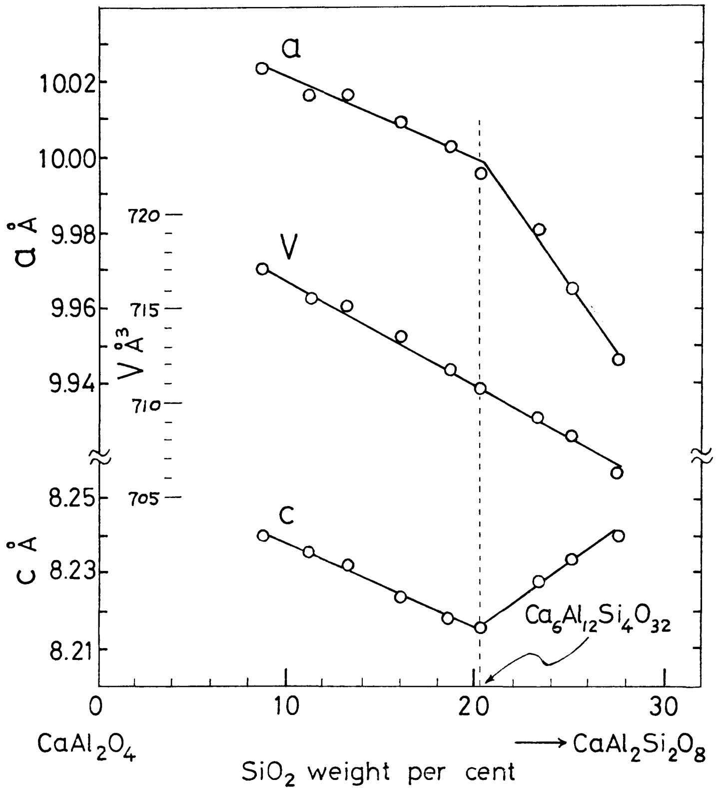

Fig. 2. Cell dimensions of nepheline-type solid solution on the $CaAl_2O_4$-$CaAl_2Si_2O_8$ join.

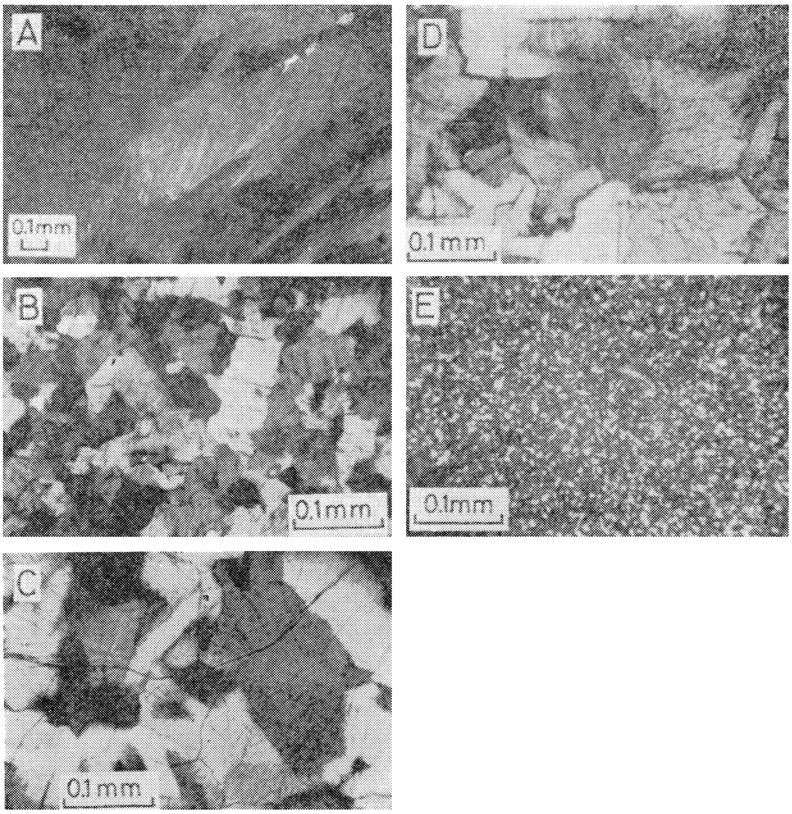

Fig. 3. Photomicrographs of the nepheline-type solid solution.

A) Crystallized from No. 3 glass, small light grains are gehlenite.
B) Member No. 6.
C) Member No. 7.
D) Crystallized from No. 8 glass showing hexagonal skeletal development.
E) Crystallized not on the $CaAl_2O_4$-$CaAl_2Si_2O_6$ join but in CaO poor side of the CaO-Al_2O_3-SiO_2 system. Single phase.

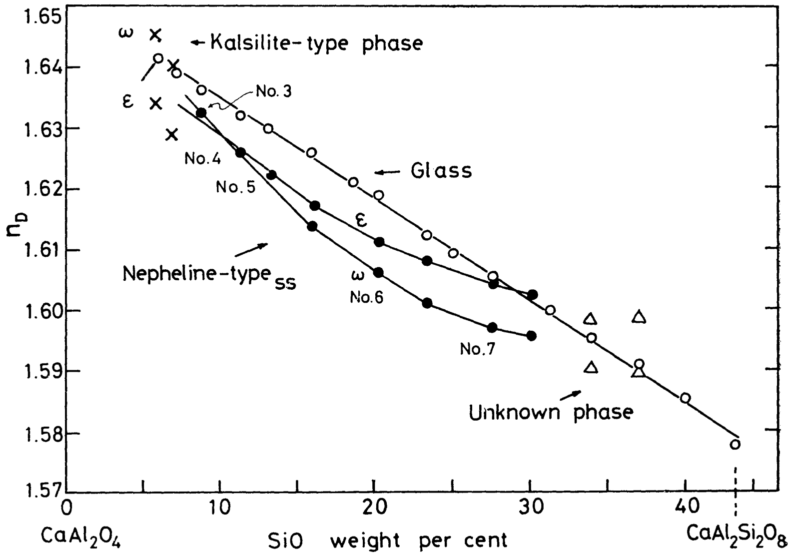

Fig. 4. Refractive index of the phases on the $CaAl_2O_4$-$CaAl_2Si_2O_8$ join. Numbers correspond to those in Table 1 and Fig. 1.

TABLE 4. CELL DIMENSIONS OF THE RELATED CRYSTALS

		a (Å)	c (Å)
Nepheline-type solid solution	Hexagonal	9.95—10.02	8.22—8.24
Nepheline($Ne_{100-30}Ks_{0-70}$)*	Hexagonal	10.0	8.4
High temperature-tridymite*	Hexagonal	5.03	8.22

* Rock-Forming Minerals, vol. 4, (1963), London: Longmans

served.

The nepheline-type solid solution generally shows a weak birefringence. The No. 4 member shows a particularly weak birefringence, but it becomes stronger as the solid solution increases in its SiO_2 content along the join, as is illustrated in Fig. 4. The members with more SiO_2 in the composition than the No. 4 are uniaxially positive. The member crystallized from the glass, No. 3, has an appreciably stronger birefringence than does No. 4, and it is confirmed to be negative. It will be noticed, therefore, that the solid solution changes its optic sign at a certain composition between No. 3 and No. 4. as in the melilite solid solution of the gehlenite-åkermanite series. The refractive index of the phases on the join is illustrated in Fig. 4. The solid solution has a lower refractive index than that of the glass with the same composition. A similar phenomenon appears in Mg-indialite.[11]

Discussion

The cell parameter a of the nepheline-type solid solution is similar to that of nepheline, and it is twice as large as that of the ideal high-temperature tridymite. On the other hand, the parameter c is not consistent with that of nepheline but corresponds to that of the high-temperature tridymite (Table 4). The cell parameter c of the solid solution may be four times the height of a tetrahedron standing on its base, as in the ideal high-temperature tridymite.[12] The reason why, in the solid solution, the repeat distance along the a-axis is twice as large as that in tridymite is uncertain.

The nepheline-type solid solution on the $CaAl_2O_4$–$CaAl_2Si_2O_8$ join may be expressed as $Ca_{8-(1/2)x}\square_{(1/2)x}Al_{16-x}Si_xO_{32}$, where $\square$ means the interstitial vacant site, based on 32 oxygen atoms of the nepheline-unit cell. It is well known that the nepheline solid solution of $Na_{8-y}K_yAl_8Si_8O_{32}$ shows a break in the cell parameter when plotted against the composition at $y=2$ in the chemical formula.[10,13] The composition at which the break appears in the cell parameters of the present solid solution may be compared with that of the ideal nepheline as follows: the ideal composition of nepheline is known to be $Na_6K_2Al_8Si_8O_{32}$, while the present nepheline-type solid solution is represented by the formula $Ca_6\square_2Al_{12}Si_4O_{32}$, in which x is equal to 4. If there are two kinds of interstitial sites in the structure of the present solid solution, as in the nepheline structure,[14,15] six Ca^{2+} ions of the member must be situated in one kind of site, one which corresponds to the smaller Na-sites in the nepheline structure. The variation in the cell parameters in the compositions with x values smaller than 4 may be attributed to the Al–Si substitution and to the omission of Ca^{2+} ions in the larger sites, which correspond to K-sites in the nepheline structure. In the compositions with x values larger than 4, the number of the Ca^{2+} ion should be less than 6 and hence the omission of the Ca^{2+} ion will take place at the other kind of site, namely, at the smaller Na-sites in the typical nepheline structure.

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