

Synthesis of $K_2SiSi_3O_9$ with silicon in 4- and 6-coordination

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SUMMARY. Two kinds of vitreous material with composition $K_2GeSi_3O_9$ and $K_2Si_4O_9$ were treated under conditions of high temperature and pressure. The X-ray diffraction patterns of the products were similar to that of $K_2TiSi_3O_9$, which has the wadeite, $K_2ZrSi_3O_9$, structure.

A natural crystal of K-feldspar was also treated under the same conditions. The product was found to consist of three phases, coesite, kyanite, and the above-mentioned $K_2Si_4O_9$. Since Zr ions in wadeite are in a 6-coordinated site, one-quarter of Si ions in $K_2Si_4O_9$ are considered to be in 6-coordination. This is the first silicate in which Si ions occupy sites of 4- and 6-coordinations in one crystal at the same time.

EXPERIMENTS on phase transitions of minerals have proved that the application of high pressures gives rise to an increase in the coordination number of Si ions from four to six. This trend is clearly seen in transitions such as from quartz to stishovite (Stishov and Popova, 1961) and from orthoclase to a hollandite-type phase (Kume *et al.*, 1966; Ringwood *et al.*, 1967); in these cases, however, Si ions occupy either tetrahedral or octahedral sites. This paper reports experimental results on the synthesis of a silicate in which Si ions occur in both tetrahedral and octahedral sites.

Experimental method. Two kinds of starting materials were prepared. Powders of K_2CO_3 , GeO_2 , and silica gel were mixed in the molar ratios of $K_2GeSi_3O_9$ and $K_2Si_4O_9$ and were calcined at 600 °C. The materials obtained in this way were vitreous. A natural crystal of K-feldspar separated from a pegmatite vein in a Mesozoic granite, Tanokamiyama, Shiga Prefecture, was also used.

The starting material of $K_2GeSi_3O_9$ was sealed in a silver capsule and was maintained at 600 °C and 1 kbar for 1 week in a test-tube-type bomb (Roy and Tuttle, 1956). In the case of $K_2Si_4O_9$ and the feldspar crystal, the sample was sealed in a platinum capsule and heated at 900° to 1200 °C under 20 to 90 kbar pressure for 1 hour. The assemblage of the high-pressure cell was similar to that reported by Yanagisawa and Kume (1973).

The cell was compressed using a cubic anvil type apparatus (Osugi *et al.*, 1964). The pressure generated inside the cell was calibrated by the change of electric resistivities of Bi at 25.5 and 77, and of Ba at 55 kbar. No correction was made for the emf of the thermocouple under pressure.

After a run was completed, the sample was quenched to room temperature and taken out of the capsule. The product was examined optically and by X-ray diffraction.

TABLE I. X-ray powder data for hexagonal $K_2SiSi_3O_9$ (a 6.614, c 9.517 Å) and $K_2GeSi_3O_9$ (a 6.697, c 9.704 Å).

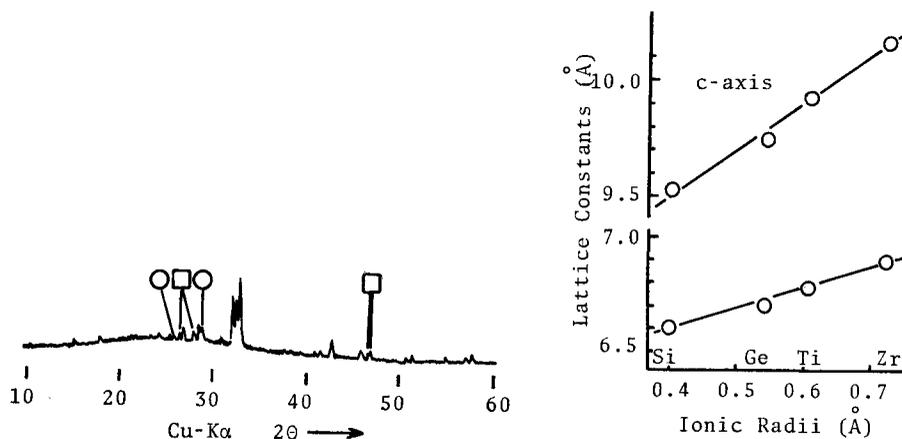
<i>hkl</i>	$K_2SiSi_3O_9$			$K_2GeSi_3O_9$		
	<i>I</i>	d_{obs}	d_{calc}	<i>I</i>	d_{obs}	d_{calc}
100	vw	5.74Å	5.73Å	m	5.80Å	5.80Å
101	w	4.92	4.91	w	4.98	4.98
002	vwv	4.76	4.76	—	—	—
102	vw	3.66	3.66	m	3.72	3.72
110	w	3.31	3.31	m	3.35	3.35
111	m	3.125	2.124	m	3.164	3.165
200	w	2.864	2.864	—	—	—
103	s	2.774	2.775	s	2.825	2.825
201	s	2.743	2.743	s	2.778	2.778
112	vs	2.714	2.716	vs	2.755	2.756
202	—	—	—	vw	2.489	2.489
004	w	2.379	2.379	w	2.427	2.426
113	w	2.291	2.289	vw	2.327	2.326
104	w	2.197	2.197	—	—	—
210	w	2.166	2.166	vw	2.192	2.192
211	m	2.111	2.111	m	2.138	2.138
212	w	1.970	1.971	—	—	—
114	—	—	—	w	1.965	1.965
300	w	1.909	1.909	m	1.934	1.933
204	vw	1.829	1.830	w	1.861	1.861
105	—	—	—	vw	1.839	1.840
213	m	1.788	1.788	w	1.814	1.815
302	m	1.772	1.772	m	1.795	1.796
220	w	1.653	1.654	m	1.673	1.674
214	m	1.601	1.601	m	1.626	1.626
310	vwv	1.589	{ 1.588	w	1.609	1.608
006				{ 1.586	w	1.618
205	m	1.585	1.585	m	1.614	1.613
311	w	1.567	1.567	m	1.587	1.587
222	—	—	—	w	1.582	1.582
106	—	—	—	w	1.557	1.558
312	m	1.507	1.507	m	1.527	1.527
215	m	1.429	1.429	m	1.453	1.453
313	s	1.421	1.421	s	1.440	1.440
206	m	1.387	1.388	s	1.414	1.413

The diffractometer was scanned at a speed of 0.5° per minute and powder data were recorded using Ni-filtered Cu- $K\alpha$ radiation with silicon as an internal standard. The error in the calculated d -spacings is estimated to be within ± 0.003 Å. The density was determined by weighing a 111.74 mg sample in air and water.

Results. When $K_2GeSi_3O_9$ and $K_2Si_4O_9$ glasses were treated under the conditions mentioned above, the products always consisted of a single phase, the X-ray powder pattern of which could be completely indexed assuming hexagonal symmetry (Table I).

The X-ray data correlate well in both spacings and relative intensities with $K_2TiSi_3O_9$ with wadeite-type structure (Choisnet *et al.*, 1973).

The measured and calculated densities of $K_2Si_4O_9$ were 3.00 and 3.08 g cm^{-3} respectively. When $K_2Si_4O_9$ once crystallized to the wadeite-type structure was reheated at 700°C in air for 6 hours, it reverted to a glassy state.



FIGS. 1 and 2: FIG. 1 (left), X-ray diffraction of K-feldspar treated at 950°C and 85 kbar for 1 hour. In this pattern the diffractions marked with circles are assigned to coesite, those with squares to kyanite. The remainder are all assigned to a wadeite-type phase. FIG. 2 (right), Relation between lattice constants and ionic radii of tetraivalent cations in $K_2MSi_3O_9$ ($M = \text{Si, Ge, Ti, Zr}$) with wadeite-type structure. The lattice constants obtained by Choisnet *et al.* (1973) are used for $M = \text{Ti and Zr}$.

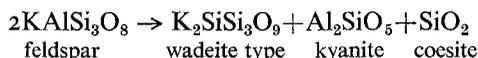
When K-feldspar was subjected to 950°C and 85 kbar, the X-ray powder pattern of the product was as shown in fig. 1. This pattern was interpreted as a mixture of coesite, kyanite, and a wadeite-type phase. When some water was added to the starting powder of the feldspar, a cymrite-type phase appeared, as has been reported by Seki and Kennedy (1964).

Discussion. The results of the high-pressure syntheses show that $K_2GeSi_3O_9$ and $K_2Si_4O_9$ crystallize with a structure similar to wadeite. The measured density of the high-pressure product of $K_2Si_4O_9$ is consistent with the value calculated from X-ray data and this is further confirmation that the phase is isostructural with wadeite.

Henshaw (1955) has suggested that Zr is in octahedral and Si is in tetrahedral sites in wadeite. The present result indicates that $K_2Si_4O_9$ is isostructural with wadeite. Consequently it is suggested that a quarter of Si ions in $K_2Si_4O_9$ are located in octahedral and three-quarters in tetrahedral sites. The formula should be written $K_2SiSi_3O_9$. When the lattice constants of several compounds with the wadeite type structure are plotted against the ionic radii of cations in octahedral sites, a linear relation is observed, as illustrated in fig. 2; this is additional evidence that one-quarter of the Si in $K_2SiSi_3O_9$ occupies in the same site as Ge, Ti, and Zr. No mineral has previously been found nor synthesized in which Si ions simultaneously occupy two sites with different kinds of coordinations in one crystal.

Goranson and Kracek (1932) reported the existence of a crystalline phase of $K_2Si_4O_9$ with density 2.335 g cm^{-3} . Schweinsberg and Liebeau (1972) have synthesized a crystalline phase of $K_2Si_4O_9$ and determined its structure to have triclinic symmetry with a 12.43, b 4.959, c 8.423 Å, α 90.80°, β 110.82°, γ 89.95°, and $Z = 2$. With these data, the density of this phase is calculated to be 2.29. When this value is compared to that obtained in the present experiment, the indication is that the wadeite-type phase is a dense phase of $K_2Si_4O_9$. It is seen here that the dense phase converts to a glassy state on heating in air. The difficulty of crystallization of $K_2Si_4O_9$ in air is probably due to high viscosity of the glass as has been pointed out by Goranson and Kracek (1932).

K-feldspar decomposes to three phases under pressure, the reaction being:



The decrease in volume due to this reaction is about 21 %. The volume change associated with the direct transition from feldspar to a hollandite-type phase is 35 % (Kume *et al.*, 1966). The above decomposition is thus probably an intermediate step in the transition of feldspar to the hollandite type. Although there has been very little discussion on the possible existence of silicate such as $K_2SiSi_3O_9$ in nature, the coexistence of 4- and 6-coordinated Si ions in one mineral may occur in some part of the Earth's mantle.

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