Structure Study of Polycrystalline Na₃YSi₃O₉ and Its Substitutes Related to Na₄CaSi₃O₉, Ca₃Al₂O₆ Structure

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The study of the Na₃YSi₃O₉ structure, by x-ray diffraction and infrared spectrum, showed that Na₃YSi₃O₉ is similar to Na₄CaSi₃O₉ except for its being pseudo-cubic instead of cubic. The peaks in the x-ray diffraction pattern of Na₃YSi₃O₉ could therefore be indexed on the basis of the Na₄CaSi₃O₉ cell. Also, modified Na₃MSi₃O₉ (M = Lu, Yb, Tm, Er, Y, Ho, Dy, Gd, Eu, and Sm) type compounds were synthesized by introducing excess sodium, decreasing M(III) concentration, and substituting small amount of phosphorus for silicon. The unit cell parameters of the composition $Na_{3.2}Mo_{.7}Si_{2.9}P_{0.1}O_{8.7}$ were estimated from x-ray powder diffraction patterns using the Cohen method.

Introduction

In 1970 Maki and Sugimura[1] showed that Na₄CaSi₃O₉ is very similar crystallographically to Ca₃Al₂O₆. Both belong to space group Pa3 and have similar unit cell dimensions. The unit cell of Ca₃Al₂O₆ consists of 72 Ca, 48 Al and 144 O. A unit cell of Na₄CaSi₃O₉ consists of 64 Na, 16 Ca, 48 Si, and 144 O. Thus there exist eight additional cations per unit cell in Na₄CaSi₃O₉. Mondal and Jeffery[2] refined the Ca₃Al₂O₆ structure with R = 5.1% and reported that "the structure consists of eight Al₆O₁₈ rings in a unit cell, surrounding holes of radius 1.47 Å at (1/8 1/8 1/8) and its symmetry-related positions, with calcium ions holding the rings together". According to their study, "there are 80 possible holes between the eight Al₆O₁₈ rings in the unit cell and 72 of them are filled up with calcium, leaving eight vacant. The unit cell of Ca₃Al₂O₆ consists of 64 pseudo-cells (a' = a/4). The calcium atoms occupy 56 body-centering positions of the pseudo-cells leaving eight of them vacant, namely (1/8 1/8 1/8) and its symmetry-related positions. The 48 aluminum atoms and the remaining 16 calcium atoms occupy the corners of the pseudo-cells" (See Figure 1 and 2). They emphasized its isomorphic relationship with Na₄CaSi₃O₉, which has Si₆O₁₈ rings. In addition, the replacement of CaO by Na₂O in Ca₃Al₂O₆ has been proved by Regourd et al.[3], because the sizes of calcium ion and sodium ion are comparable and there are eight vacant holes available to replace one calcium ion by two sodium ions.

In 1980, Shannon et al.[4] reported the unit cell of Na₃YSi₃O₉ is similar to those of Ca₃Al₂O₆ and Na₄CaSi₃O₉. However, no evidence was given for that assumption.
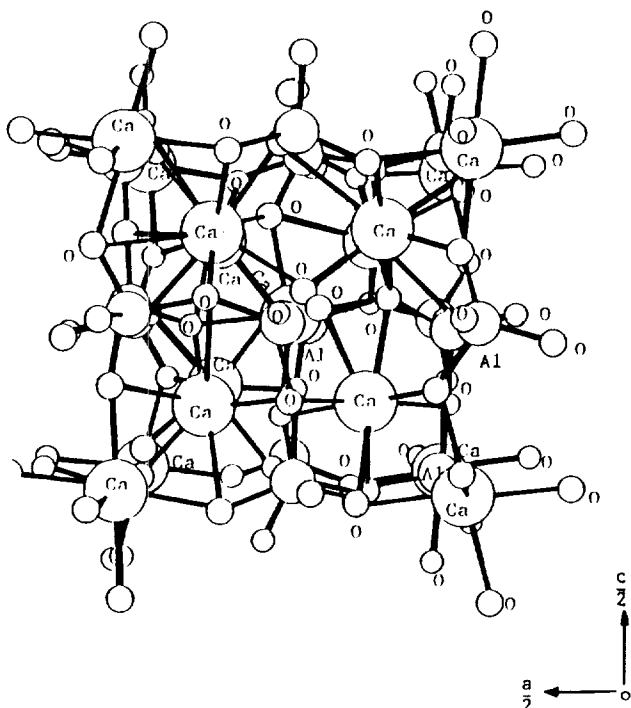
Figure 1. One eighth of the unit cell Ca₃Al₂O₆ viewed along [0̄1̄0]. The origin is at rear, right-hand bottom corner.

Figure 2. An Al₆O₁₈ puckered ring of Ca₃Al₂O₆ at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ viewed along [1̄1̄1̄].
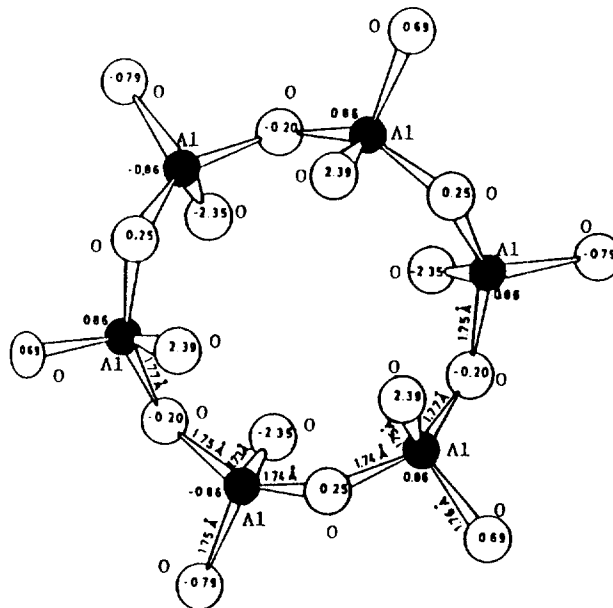
The results of this work could give stronger confirmation about the Na$_3$YSi$_3$O$_9$ structure, which is very similar to Na$_4$CaSi$_3$O$_9$ and CaAl$_2$O$_6$ except that it is orthorhombic close to being pseudo-cubic instead of cubic. Also, samples of composition Na$_{3.2}$M$_{0.7}$Si$_{2.9}$P$_{0.1}$O$_{8.7}$ (M = Lu, Yb, Tm, Er, Y, Ho, Dy, Gd, Eu, and Sm) based on the Na$_3$YSi$_3$O$_9$ composition were synthesized. The unit cell parameters were estimated from x-ray powder diffraction patterns using the Cohen method[5].

Experimental

For the synthesis of Na$_3$YSi$_3$O$_9$ starting materials Na$_2$CO$_3$, Y$_2$O$_3$, and SiO$_2$ were mixed in proper stoichiometric proportion and fired at 1180°C for 18 hours in a furnace. The fired sample was ground and reheated at the same temperature for 5–10 hours. X-ray patterns were obtained on a Philips powder diffractometer using Cu Kα radiation. The indexing of each peak was attempted on the basis of lattice parameter a = 15.215 Å, b = 15.126 Å, and c = 15.036 Å. Also, the infrared spectrum of this specimen was recorded and compared with that of Na$_4$CaSi$_3$O$_9$. The infrared instrument used was the Perkin-Elmer Model No. 337.

For the preparation of Na$_{3.2}$M$_{0.7}$Si$_{2.9}$P$_{0.1}$O$_{8.7}$, the starting materials Na$_2$CO$_3$, SiO$_2$, NH$_4$H$_2$PO$_4$, and M$_2$O$_3$ were weighed and ground in a proper stoichiometric proportion. They were fired for overnight at 890°C–1020°C (1015°C for M = Y; 980°C for M = Dy, Yb; 945°C for M = Ho, Gd, Er; 930°C for M = Eu, Lu, Tm; and 895°C for M = Sm) in covered platinum crucibles. Samples were quenched, reground, reheated at the same temperature for 6–12 hours and quenched in air again. X-ray patterns of products obtained by quenching and by cooling at the natural cooling rate of the furnace were essentially the same.

To estimate the lattice parameters of each sample pure Si powder as an internal standard, was mixed with all samples and peaks of the samples between the Si peaks were corrected using the interpolation method. Sample peaks used were in the 2θ range of 60–70° since it is practical to deduce accurate values of the lattice constants in the range θ = 30 to 90°; peaks with indices (844), (484), (448), (880), (808), and (088) were
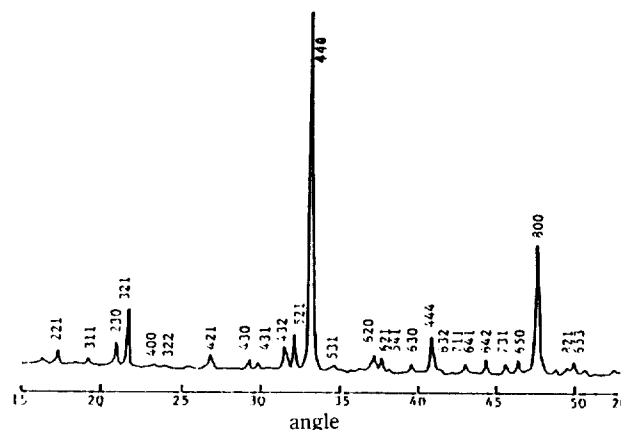
Figure 3. Powder x-ray diffraction pattern of Ca$_3$Al$_2$O$_6$.

chosen because they were clearer than the others. In this work the Cohen's least–square method[5] was employed with angle error term[6]

$$\Delta \sin^2\theta = D \sin^2 2\theta \, (1/\sin\theta + 1/\theta).$$

Peak positions were read within about ±0.04°(2θ) after 3–5 trials. The normal equations established were solved by using the matrix function of a programmable Texas Instrument TI-58C calculator.

Results and Discussion

Figures 3 and 4 show the x–ray powder diffraction patterns of Ca$_3$Al$_2$O$_6$ and Na$_4$CaSi$_3$O$_9$. The diffraction characteristics of these two compounds have been regarded to be essentially similar to each other[1]. Figure 5 shows the x–ray powder diffraction pattern of Na$_3$YSi$_3$O$_9$. The peaks in the Na$_3$YSi$_3$O$_9$ pattern could be indexed on the basis of the Na$_4$CaSi$_3$O$_9$ cell. However, the shape of the peaks in Na$_3$YSi$_3$O$_9$ pattern is less sharp than those of Na$_4$CaSi$_3$O$_9$ due to the pseudo-cubic nature of the cell. In other words, the a, b, and c values are not exactly equal as in a cubic structure, but they are very similar. The X-ray peaks are thus broader due to all possible permutations of (hkl) reflections in the equation $d^{*2} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2}$

Figure 4. Powder x–ray diffraction pattern of Na$_4$CaSi$_3$O$_9$.

Figure 5. Powder x-ray diffraction pattern of $Na_3YSi_3O_9$.

Figure 6. Infrared spectrum of $Na_4CaSi_3O_9$, $Na_{3.2}Y_{0.7}Si_{2.9}P_{0.1}O_{8.7}$ and $Na_3YSi_3O_9$.

where $d^* = 1/d$, $a^* = 1/a$, $b^* = 1/b$, and $c^* = 1/c$. For example, cubic peaks with indices (230), (203), (320), (302), (023), and (032) have the same 'd' value and are located at the same 2θ va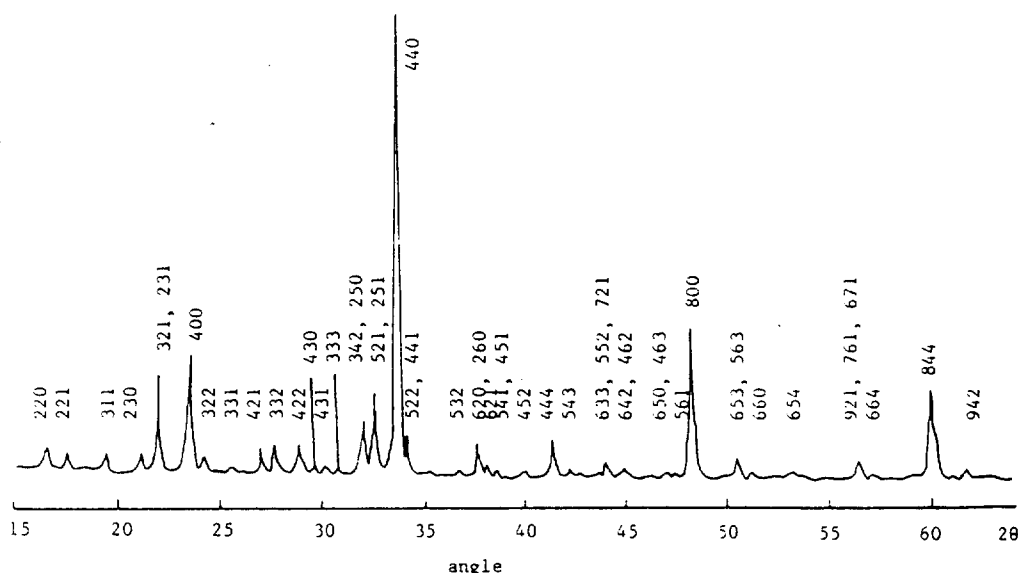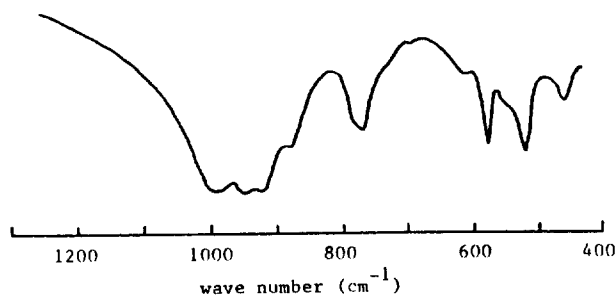lue. However, in the orthorhombic structure, their d values are different and if the lattice constants are very similar, the peaks will be located very closely to each other, thereby giving rise to one broad peak. The indices expressed with brackets < > indicate all or part of the possible (hkl) permutations. Among the indices shown in Figure 5, only (444) has no other permutation except for itself. It thus gives a sharp peak compared to the other peaks.

Figure 6 shows the infrared spectra of $Na_3YSi_3O_9$, $Na_4CaSi_3O_9$, and $Na_{3.2}Y_{0.7}Si_{2.9}P_{0.1}O_{8.7}$. The spectra are essentially similar to each other, indicating similar structural relation

between the compounds. From the Hooke's law expression, the frequency is given by:

$$\nu = \frac{1}{2\pi c}[\frac{k}{u}]^{1/2}$$

where c is the velocity of light ($=3 \times 10^{10}$ cm/sec), k the force constant in dyne/cm, and u is the reduced mass. This equation can be used to calculate the approximate position of a band in the infrared spectrum by assuming that k for the Si-O bond is about 5×10^5 dyne/cm. This force constant was calculated numerically for the Si_6O_{18} ring type by Saksena et al.[7]. Then the stretching frequency of Si-O bond should be 917 cm^{-1} approximately. However, mixing of the vibrations

Table 1. Estimation of $Na_{3.2}Yb_{0.7}Si_{2.9}P_{0.1}O_{8.7}$ Lattice Constants

Plane	α	β	γ	d	$\sin^2\theta_{exp}$	$\sin^2\theta_{calc}$
844	64	16	16	1.524539994	0.2495466873	0.2489426977
484	16	64	16	1.525305197	0.2503023608	0.2499244288
448	16	16	64	1.526888148	0.2518917482	0.2616644883
880	64	64	0	1.564803973	0.3318632289	0.3316166987
808	64	0	64	1.564797559	0.3342487213	0.3338371249
088	0	64	64	1.56476074	0.3358139363	0.3352370672

Normal equations

$12800A$ $+$ $6400B$ $+$ $6400C$ $+$ $346.7001512D$ $=$ 66.63725854

$6400A$ $+$ $12800B$ $+$ $6400C$ $+$ $346.7345246D$ $=$ 66.77370463

$6400A$ $+$ $6400B$ $+$ $12800C$ $+$ $346.8100957D$ $=$ 67.00266673

$346.7001512A$ $+$ $346.7345246B$ $+$ $346.8100957C$ $+$ $14.3278446D$ $=$ 2.714642868

$A = 0.0025796$ $\qquad$ $B = 0.0026010$ $\qquad$ $C = 0.0026367$

$a = 15.165$ $\qquad$ $b = 15.103$ $\qquad$ $c = 15.000$

Normal equations for calculation of error

$12800\Delta A$ $+$ $6400\Delta B$ $+$ $6400\Delta C$ $+$ $346.7001512D$ $=$ ± 0.0904576

$6400\Delta A$ $+$ $12800\Delta B$ $+$ $6400\Delta C$ $+$ $346.7345246D$ $=$ ± 0.090184

$6400\Delta A$ $+$ $6400\Delta B$ $+$ $12800\Delta C$ $+$ $346.8100957D$ $=$ ± 0.0935216

$346.7001512\Delta A$ $+$ $346.7345246\Delta B$ $+$ $346.8100957\Delta C$ $+$ $14.3278446D$ $=$ ± 0.0037768

$\Delta A = \pm 0.00000014$ $\qquad$ $\Delta B = \pm 0.00000022$ $\qquad$ $\Delta C = \pm 0.00000030$

$\Delta a = \pm 0.001$ $\qquad$ $\Delta b = \pm 0.001$ $\qquad$ $\Delta c = \pm 0.001$

Lattice constants

$\qquad$ $a = 15.165 \pm 0.001$ Å

$\qquad$ $b = 15.103 \pm 0.001$ Å

$\qquad$ $c = 15.000 \pm 0.001$ Å

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Figure 7. Infrared spectrum of $Cu_6Si_6O_{18} \cdot 6H_2O$.

Table 2. $Na_{3.2}M^{III}_{0.7}Si_{2.9}P_{0.1}O_{8.7}$

Formula	Lattice Constants (Å)
$Na_{3.2}Lu_{0.7}Si_{2.9}P_{0.1}O_{8.7}$	$a = 15.160 \pm 0.006$
	$b = 15.076 \pm 0.004$
	$c = 14.989 \pm 0.005$
$Na_{3.2}Yb_{0.7}Si_{2.9}P_{0.1}O_{8.7}$	$a = 15.165 \pm 0.001$
	$b = 15.103 \pm 0.001$
	$c = 15.000 \pm 0.001$
$Na_{3.2}Tm_{0.7}Si_{2.9}P_{0.1}O_{8.7}$	$a = 15.192 \pm 0.006$
	$b = 15.095 \pm 0.020$
	$c = 15.011 \pm 0.015$
$Na_{3.2}Er_{0.7}Si_{2.9}P_{0.1}O_{8.7}$	$a = 15.193 \pm 0.008$
	$b = 15.108 \pm 0.019$
	$c = 15.011 \pm 0.016$
$Na_{3.2}Y_{0.7}Si_{2.9}P_{0.1}O_{8.7}$	$a = 15.211 \pm 0.002$
	$b = 15.118 \pm 0.001$
	$c = 15.017 \pm 0.001$
$Na_{3.2}Ho_{0.7}Si_{2.9}P_{0.1}O_{8.7}$	$a = 15.197 \pm 0.003$
	$b = 15.124 \pm 0.001$
	$c = 15.034 \pm 0.001$
$Na_{3.2}Dy_{0.7}Si_{2.9}P_{0.1}O_{8.7}$	$a = 15.218 \pm 0.002$
	$b = 15.146 \pm 0.001$
	$c = 15.040 \pm 0.002$
$Na_{3.2}Gd_{0.7}Si_{2.9}P_{0.1}O_{8.7}$	$a = 15.241 \pm 0.001$
	$b = 15.175 \pm 0.002$
	$c = 15.064 \pm 0.002$
$Na_{3.2}Eu_{0.7}Si_{2.9}P_{0.1}O_{8.7}$	$a = 15.300 \pm 0.004$
	$b = 15.201 \pm 0.005$
	$c = 15.074 \pm 0.004$

occurs in spectra of Si_6O_{18} anions and it is probable that the assignment of a considerably higher frequency[8] than that resulting from calculation is associated with the difficulty in clearly distinguishing the frequencies of the complex anion. It is supposed[9] that the appearance of a high frequency band is due largely to special features in the dynamics of the anion. The infrared spectrum of dioptase ($Cu_6Si_6O_{18} \cdot 6H_2O$), in which the Si_6O_{18} ring is a nonplanar structure, has been studied[9,10]. Figure 7 shows the frequencies of the asymmetric Si-O-Si stretching at about 1000 cm⁻¹ and those of symmetric Si-O-Si stretching at about 770 cm⁻¹. In a planar ring the Si-O-Si angle increases. This makes asymmetric stretching energetically favorable and the asymmetric Si-O-Si vibration increases. It was therefore expected that a planar ring might have higher asymmetric Si-O-Si vibrational frequency and lower symmetric Si-O-Si vibrational frequency[9]. As can be

seen in Figure 2, the six bridging oxygen atoms are almost coplanar thus the absorption bands in the 900-1080 cm⁻¹ and 750 cm⁻¹ region for $Na_3YSi_3O_9$ may be expected to be due to the Si-O-Si vibration in Si_6O_{18} anion structure.

Even though the synthesis of the $Na_3YSi_3O_9$ single crystal by solid solution method was not successful, the similarities in powder x-ray diffraction pattern and infrared spectra as mentioned above give the idea that $Na_3YSi_3O_9$ and $Na_4CaSi_3O_9$ are nearly isostructural. The unit cell contents of $Na_3YSi_3O_9$ are: 48 Na, 16Y, 48 Si, and 144 O.

The 48 Na and 16Y would occupy 64 sites holding eight Si_6O_{18} rings coordinated by six SiO_4 tetrahedra, leaving 16 vacant holes.

The x-ray patterns of $Na_{3.2}M_{0.7}Si_{2.9}P_{0.1}O_{8.7}$ (M = Lu, Yb, Tm, Er, Y, Ho, Dy, Gd, Eu, and Sm) showed that they are isostructural with $Na_3YSi_3O_9$. Only some shifts in the position of the peaks depending on the size of M(III) ion were observed. For estimation of the orthorhombic $Na_{3.2}M_{0.7}Si_{2.9}P_{0.1}O_{8.7}$ lattice constants the following equation was employed:

$$\alpha A + \beta B + \gamma C + \delta D = \sin^2\theta$$

were $\alpha = h^2$, $\beta = k^2$, $\gamma = l^2$, $\delta = \sin^2 2\theta$ $(1/\sin\theta + 1/\theta)$, $A = \lambda^2/4a^2$, $B = \lambda^2/4b^2$, $C = \lambda^2/4c^2$, and $\lambda_{Cu K\alpha} = 1.5405$ Å. The combination of the various observational equations led to a set of four normal equations:

$$A\Sigma\alpha^2 + B\Sigma\alpha\beta + C\Sigma\alpha\gamma + D\Sigma\alpha\delta = \Sigma\alpha \sin^2\theta$$
$$A\Sigma\alpha\beta + B\Sigma\beta^2 + C\Sigma\beta\gamma + D\Sigma\beta\delta = \Sigma\beta \sin^2\theta$$
$$A\Sigma\alpha\gamma + B\Sigma\beta\gamma + C\Sigma\gamma^2 + D\Sigma\gamma\delta = \Sigma\gamma \sin^2\theta$$
$$A\Sigma\alpha\delta + B\Sigma\beta\delta + C\Sigma\gamma\delta + D\Sigma\delta^2 = \Sigma\delta \sin^2\theta$$

ΔA, ΔB, and ΔC were then calculated with the same method suggested by Cohen. Table 1 shows the procedure estimated for $Na_{3.2}Yb_{0.7}Si_{2.9}P_{0.1}O_{8.7}$. Table 2 is the result for $Na_{3.2}M_{0.7}Si_{2.9}P_{0.1}O_{8.7}$ using the same procedure described above.

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