Structural characterization of silicon orthophosphate

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Abstract

Silicon phosphate samples have been synthesized at low temperature (200–300 °C) and characterized using various physico-chemical methods. The crystal structure of the silicon phosphate prepared at low temperature and the sample heated at 1000 °C was studied by the Rietveld method. The crystals belong to the hexagonal space group $R\bar{3}$ with $a \simeq 7.8$ and $c \simeq 24.0$ Å. The structure of silicon phosphate in both of these samples is found to be $Si_5O(PO_4)_6$. The asymmetric unit consist of three crystallographically independent silicon atoms of which one is in a tetrahedral environment and the other two have octahedral coordination.

Introduction

Silicon phosphates have been suggested for a wide variety of applications especially in the area of catalysis [1–5]. Although, a large amount of data have been accumulated on the reactions involving SiO_2 and P_2O_5, there exists inconsistency in the structural aspect of the system. Makart [6] and Liebau *et al.* [7] prepared a variety of silicon phosphate phases in the reaction of SiO_2 and H_3PO_4. Our present study focuses on one of these phases, which was reported to belong to the hexagonal system with $a = b \simeq 7.8$ and $c \simeq 24.7$ Å. Makart [6] suggested that the compound is the orthophosphate $Si_3(PO_4)_4$, while Liebau *et al.* [7] proposed that there exists a solid solution system of general composition $Si_{(1+5x)}P_{4(7-x)}O_{72}$, with $x = 2.5–3.5$. The compound $Si_3(PO_4)_4$ is the first member of this series. Mayer [8], on the other hand, prepared single crystals of a silicon phosphate compound from the melt containing a mixture of H_3PO_4 and SiO_2 at 800 °C. These crystals belong to the space group $R\bar{3}$ with unit cell dimensions very close to the values mentioned above. From the crystal structure analysis, the compound was found to $Si_5O(PO_4)_6$, which fits the Liebau formula with $x = 2.68$. These results, otherwise, raise the question about the chemical composition reported for the silicon phosphate phases prepared at lower temperature (200–300 °C).

We have recently prepared a number of silicon phosphate compounds belonging to the same phase, using a slightly modified procedure at temperatures in the range 200–300 °C and characterized them using

XRD, IR, SEM, TG, FT-IR and XPS [9]. Although the unit cell parameters determined for these samples match very well with the above mentioned values, in some cases we have observed significant differences between the low and high temperature phases particularly at the low angle X-ray diffraction data ($16° < 2\theta$). Very importantly the compounds prepared at low temperature have shown weight losses up to and beyond 1000 °C. Thus, it is of interest to determine the structure of the silicon phosphate prepared at 200–300 °C and relate it to the high temperature structure reported by Mayer [8]. Since single crystals cannot be grown at the low temperatures of interest, structure solution was attempted using X-ray powder data. In this paper we demonstrate that the hexagonal phase silicon phosphates prepared at low temperature as well as the sample calcined at 1000 °C have the same structure as that reported by Mayer [8].

Experimental

Sample preparation

Crystalline silicon phosphate samples were synthesized using 85% phosphoric acid (Fischer reagent grade) and silica gel (MIL-D-3716) as sources of phosphorus and silicon, respectively. The sample RB210 was prepared as follows: initially, 85% phosphoric acid was heated at 120 °C for half an hour in a platinum dish and then silica gel was slowly added to the acid. The reaction mixture had a composition Si:P = 1:1.33. The mixture was stirred well and then heated at 200 °C for 5 h. The product was thoroughly washed with acetone

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and dried at 80 °C in an air oven. Sample RB255A was prepared using the same procedure except that the starting reaction composition was Si:P = 1:2.9 and the reaction temperature was 300 °C. The sample RB255C was obtained by calcination of RB255A at 1000 °C for 2 h.

Characterization

X-ray powder diffraction patterns were obtained using Seifert-Scintag PAD V and Rigaku RU 200 automated diffractometers with Cu Kα radiation. Scanning electron microphotographs were taken at the Texas A&M Electron microscopy center using a JEOL JSM-25 S-II microscope. The samples were mounted on stainless steel sample holders and were coated with Au–Pd evaporated film. TGA curves were obtained by using a Du Pont (model 951) thermal analyzer. About 30 mg of the sample were placed in a quartz bucket and were heated at a rate of 10 °C/min in the presence of N_2 (flow ~ 60 ml/min). Total analysis of the silicon phosphate samples was carried out by dissolving the sample in hydrofluoric acid and the solutions were then diluted with demineralized water to the desired level. The resulting solution was analyzed for silicon and phosphorus by the ion-coupled plasma method using an ARL 3510 ICP spectrometer.

Data collection and structure refinement

Step scanned X-ray powder data were collected at room temperature on a finely ground sample of silicon phosphate by using a Rigaku RU 200 computer automated diffractometer. The X-ray source was a rotating anode operating at 50 kV and 180 mA with a copper target and graphite monochromated radiation ($\lambda = 1.54184$ Å). Data were collected between 5 and 60° in 2θ with a step size of 0.02 and 0.01° and a count time of 1 and 8 s per step for the low and high temperature phases, respectively. The data were transferred to a DEC Micro-Vax-II computer and the pattern decomposed as described earlier [10]. Indexing was carried out using trial and error [11] methods and refined by least-squares methods [12]. In the case of the sample RB255C, there were 43 unambiguously indexed reflections. This data set was used to generate the normal $F_o(hkl)$ and $\sigma(F_o)$ for structure solution. A Patterson map was computed in the space group $R\bar{3}$ using the program SHELXTL PLUS [13]. The positions of the silicon and phosphorus atoms were derived from this vector map and the oxygen atoms were located from the subsequent difference Fourier maps. When the structure solution was complete, it was found that the positions of the atoms are similar to those of $Si_5O(PO_4)_6$ [8].

These positional parameters were used as a starting model for Rietveld refinement. Using a utility program GRAPH [10] the raw data were transferred to the GSAS program package [14] for the Rietveld method of full-profile refinement. The pairs of peaks arising from the α1 and α2 doublet were treated as separate reflections in the fixed intensity ratio of 2:1. In both cases, the refinement was started with the profile coefficients obtained from the refinement of lanthanum boride powder data which were collected on the same instrument. Initial refinement of the scale, background, unit cell parameters and the zero point error led to a good agreement between the observed and calculated patterns indicating that the starting structural model is correct. Careful refinement of the profile function (no. of coefficients = 11) and increasing the background coefficients to 12 showed a considerable improvement in the calculated pattern ($R_{wp} = 0.18$ and 0.20 for RB210 and RB255C, respectively). Atomic positions were then refined with soft constraints consisting of both Si–O and P–O bond distances and O–O non-bonded distances. P–O distances were constrained to 1.53 Å and Si–O distances for tetrahedral and octahedral silicons were constrained to 1.65 and 1.73 Å, respectively. The allowable refinement bounds in both cases were 0.2 Å. The geometry around Si and P was obtained by the appropriate distances between the bonded oxygen atoms. A total of 14 geometric constraints was included and initially their weight was kept high to maintain a reasonable geometry. As the refinement progressed the soft constraints were assigned less and less weight but they could not be removed completely. The refinement of the atomic positions converged with $R_{wp} = 0.138$ for RB210 and 0.15 for RB255C. In the last stages of refinement the atom isotropic thermal parameters were refined. In the final refinement the shifts in all the parameters were less than their estimated standard deviations. A difference Fourier computed at this stage was featureless. Neutral atomic scattering factors were used for all atoms. No corrections were made for anomalous dispersion, absorption or preferred orientation.

Results and discussion

The X-ray powder diffraction patterns of RB210, RB255A and RB255C samples are shown in Fig. 1. The d spacings and the relative intensities of the sample RB210 match well with the corresponding values reported in the literature for silicon orthophosphate [1, 2]. In this sample the reflection at $d = 3.542$ Å has the highest intensity and the intensities of the first three reflections are in the order $2 > 1 > 3$. On the other hand, the sample RB255A shows a highest intensity for the reflection at $d = 8.039$ Å and the relative intensity order for the first three reflections are $1 > 2 > 3$. Upon
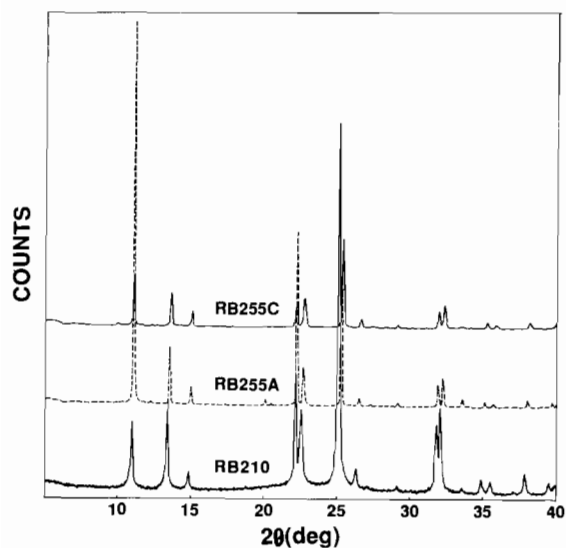
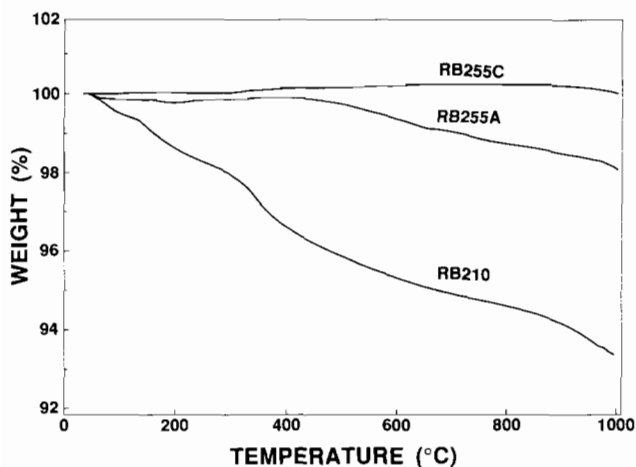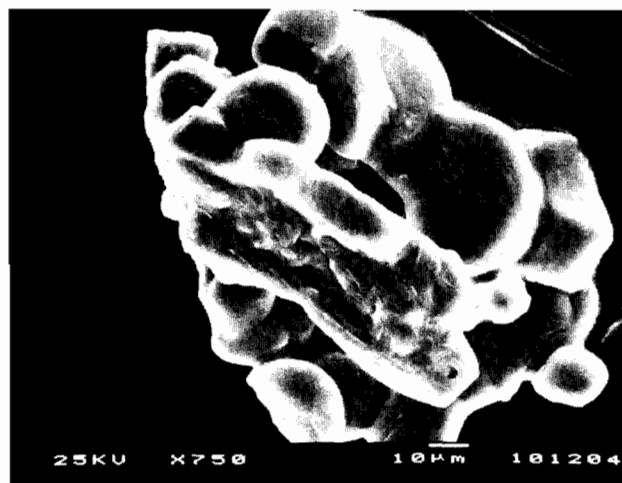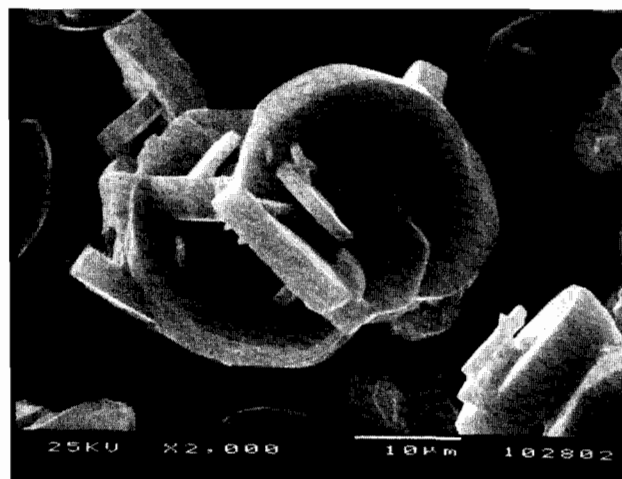Fig. 1. X-ray powder diffraction patterns of RB210, RB255A and RB255C.

Fig. 2. TG curves of RB210, RB255A and RB255C.

(a)

(b)

(c)

Fig. 3. SEM photographs of (a) RB210, (b) RB255A and (c) RB255C.

heating this sample at 1000 °C for 2 h (RB255C), the X-ray diffraction pattern show significant changes in the relative intensities of the reflection in the 2θ range 10–26°. Although the relative intensities of the first three reflections remain unchanged the strongest intensity is now observed for the reflection at $d = 3.542$ Å. Yet, another important observation is the reduction in the relative intensity of the peak at $d = 4.016$ with respect to that at 3.948 ·Å.
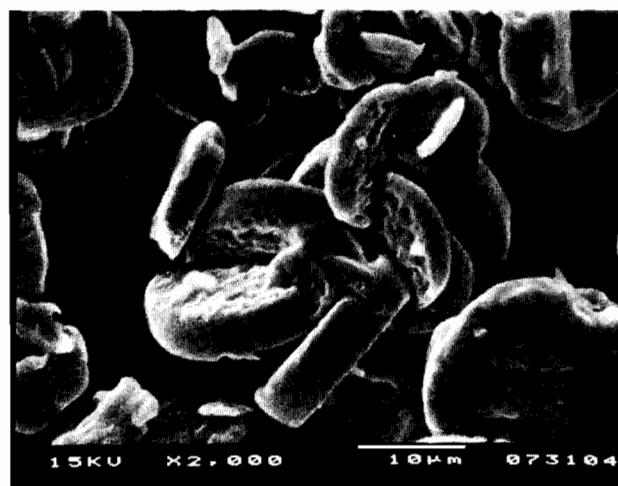
Figure 2 gives the TGA weight loss as a function of temperature. The TG curves of RB210 and RB255A samples show four steps of weight loss. The first step (25–100 °C) and the second step (100–200 °C) are assigned to the desorption of physisorbed and chemically bound water, respectively. The total weight loss due to the first and second step is 2.1 and 0.2% for RB210 and RB255A, respectively. The third weight loss (200–750 °C) seen for both the samples is tentatively

TABLE 1. Crystallographic data for silicon phosphate samples

	Low temp. RB210	High temp. RB255C
Pattern range, 2θ (°)	5–60	5–60
Step scan increment, 2θ (°)	0.01	0.01
Step scan time (s)	1	8
Space group	$R\bar{3}$	$R\bar{3}$
a (Å)	7.8985(5)	7.8481(2)
c (Å)	24.022(2)	24.1780(6)
Z	3	3
No. contributing reflections	182	168
P–O distances and tolerance (Å)	1.53(2)	1.53(2)
Si–O distances and tolerance (Å)	1.75(2), 1.61(2)	1.75(2), 1.61(2)
O–O distance (Å) for PO_4 tetrahedra	2.55(2)	2.55(2)
No. profile parameters	11	11
Statistically expected R_{wp}	0.06	0.04
R_{wp}	0.138	0.15
R_p	0.11	0.12
R_F	0.09	0.08

$R_{wp} = (\Sigma w(I_o - I_c)^2/\Sigma[wI_o^2])^{1/2}$. $R_p = (\Sigma|I_o - I_c|/\Sigma I_c)^{1/2}$. Expected $R_{wp} = R_{wp}/(\chi^2)^{1/2}$; $\chi^2 = \Sigma w(I_o - I_c)^2/(N_{obs} - N_{var})$. $R_F = \langle|F_o| - |F_c|\rangle/\langle|F_o|\rangle$.

TABLE 2. Positional parameters for sample RB210 (low temperature) and sample RB255C (high temperature)

Atom	x	y	z	U_{iso} (Å)
RB210				
Si1	0	0	0	0.005(7)
Si2	0	0	0.1801(6)	0.001(5)
Si3	0	0	0.4290(6)	0.023(5)
P	0.2979(9)	0.2557(7)	0.0885(3)	0.001(3)
O1	0	0	0.5	0.028(15)
O2	0.1397(16)	0.2039(17)	0.1332(4)	0.028[a]
O3	0.2207(13)	0.1386(16)	0.0389(4)	0.028[a]
O4	0.3585(19)	0.4838(10)	0.0719(4)	0.028[a]
O5	0.4812(14)	0.2740(20)	0.1076(4)	0.028[a]
RB255C				
Si1	0	0	0	0.008(4)
Si2	0	0	0.1824(4)	0.006(3)
Si3	0	0	0.4313(3)	0.024(3)
P	0.2891(6)	0.2721(5)	0.0924(2)	0.017(2)
O1	0	0	0.5	0.007(7)
O2	0.1324(12)	0.2117(11)	0.1376(3)	0.010(3)
O3	0.2148(9)	0.1448(12)	0.0405(2)	0.005(3)
O4	0.3593(11)	0.4873(9)	0.0775(3)	0.017(3)
O5	0.4612(12)	0.2473(11)	0.1116(3)	0.007(3)

[a]Constrained to be equal to U of O(1).

TABLE 3. Bond distances (Å) and angles (°) for sample RB210

Si octahedra					
Si1–O3	1.789(5)	6×	O3–Si1–O3	180.00	3×
			O3–Si1–O3	95.2(5)	6×
			O3–Si1–O3	84.8(5)	6×
Si octahedra					
Si2–O2	1.818(6)	3×	O2–Si2–O2	85.6(9)	3×
Si2–O5	1.697(10)	3×	O2–Si2–O5	95.6(9)	3×
Av.	1.758		O2–Si2–O5	95.6(5)	3×
			O2–Si2–O5	178.1(11)	3×
			O5–Si2–O5	82.8(8)	3×
Si tetrahedra					
Si3–O1	1.706(14)	1×	O4–Si3–O1	110.1(6)	3×
Si3–O4	1.654(6)	3×	O4–Si3–O4	108.8(6)	3×
Av.	1.680			109.5	
Phosphate group					
P–O2	1.526(6)		O2–P–O3	109.0(6)	
P–O3	1.518(6)		O2–P–O4	110.0(7)	
P–O4	1.518(6)		O2–P–O5	113.0(7)	
P–O5	1.525(6)		O3–P–O4	111.3(7)	
			O3–P–O5	105.9(7)	
			O4–P–O5	107.6(7)	
Av.	1.522			109.5	

assigned to the dehydroxylation of surface –OH groups. Based on the SEM results it appears that this phenomenon may be associated with the desorption of the surface phosphorus species. The weight loss due to the third step is 3.0% for the RB210 and 0.8% for the RB255A sample. The fourth weight loss (above 900 °C) is present in both RB210 and RB255A but not in RB255C. The amount desorbed is 1.3 and 0.7% for RB210 and RB255A, respectively. The X-ray pattern of RB255C shows that the sample retains its crystal structure, it is therefore concluded that the weight loss above 900 °C corresponds to the volatilization of chemically bound phosphorus species.

The SEM photograph of RB210 shows a hexagonal shape for the crystals with irregular shape and poorly defined edges with sizes ranging from 10 to 30 μm in diameter (Fig. 3). The crystals of the RB255A sample are also hexagonal with dimensions 12–15 μm in diameter and about 5 μm in thickness. The surface of the crystals seems to be very smooth. On calcination

TABLE 4. Bond distances (Å) and angles (°) for sample RB255C

Si octahedra					
Si1–O3	1.783(5)	6×	O3–Si1–O3	180.00	3×
			O3–Si1–O3	92.7(3)	6×
			O3–Si1–O3	87.3(3)	6×
Si octahedra					
Si2–O2	1.813(7)	3×	O2–Si2–O2	88.0(4)	3×
Si2–O5	1.696(7)	3×	O2–Si2–O5	91.9(4)	3×
Av.	1.754		O2–Si2–O5	88.6(3)	3×
			O2–Si2–O5	176.6(5)	3×
			O5–Si2–O5	91.5(5)	3×
Si tetrahedra					
Si3–O1	1.659(8)	1×	O4–Si3–O1	108.1(4)	3×
Si3–O4	1.599(6)	3×	O4–Si3–O4	110.8(4)	3×
Av.	1.629			109.5	
Phosphate group					
P–O2	1.533(7)		O2–P–O3	113.5(4)	
P–O3	1.525(7)		O2–P–O4	107.3(5)	
P–O4	1.535(6)		O2–P–O5	111.5(5)	
P–O5	1.529(7)		O3–P–O4	109.8(5)	
			O3–P–O5	103.8(6)	
			O4–P–O5	110.9(5)	
Av.	1.530			109.5	

at 1000 °C for 2 h, the surface of the crystals becomes very rough and they have no definite shape. It appears that the crystals have lost material not only from the surface but also from the bulk of the crystals.

Refinement results

The crystallographic data are presented in Table 1. Final positional parameters are given in Table 2 and important bond distances and angles are presented in Tables 3 and 4. The observed and calculated patterns are shown in Figs. 4 and 5.

As can be seen by the reasonably good Rietveld profile fit for the low temperature (Fig. 4) and high temperature data (Fig. 5), there can be no doubt about the structure of silicon phosphate in these temperature ranges. The unit cell dimensions as well as positional parameters for these two phases are similar and are comparable to the results obtained by the single crystal study [8].

There are three crystallographically distinct silicon atoms in the structure (Figs. 6 and 7), all positioned along the *c* axis of the crystal. Si(1) lies on a three-fold axis and is octahedrally coordinated by symmetry related O(3) atoms. Si(2) lies on a three-fold axis and its six coordination sites are occupied by symmetry related O(2) and O(5) atoms. Si(1) and Si(2) are bridged to each other by three phosphate groups. Si(3) also lies on a three-fold axis and is bridged to the symmetry related Si(3) by an Si–O–Si bond of angle 180°. The tetrahedral coordination of Si(3) is completed by symmetry related O(4) atoms. These tetrahedrally bonded silicons are centered at *c* = 1/2. Si(3) and Si(2) are indirectly connected through octahedrally bonded silicon groups and this arrangement leads to small voids
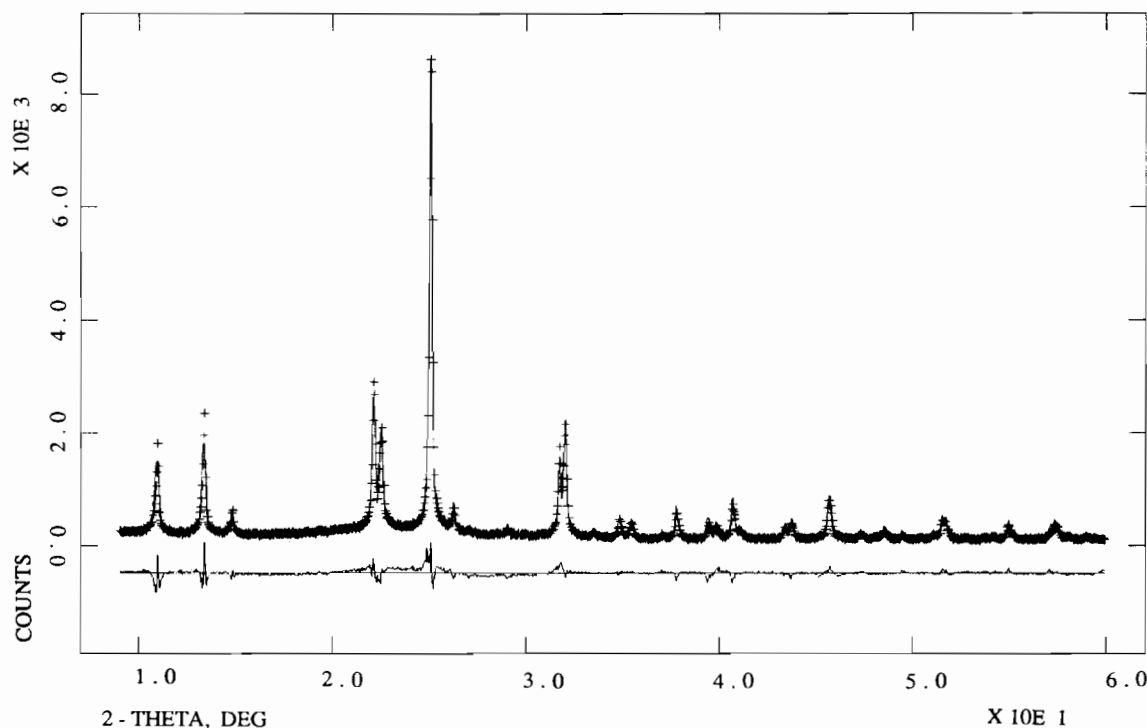

Fig. 4. Observed (+) and calculated (−) profiles (X-ray intensity vs. 2θ) for the Rietveld refinement of the low temperature phase (RB210). The bottom curve is the difference plot on the same intensity scale.
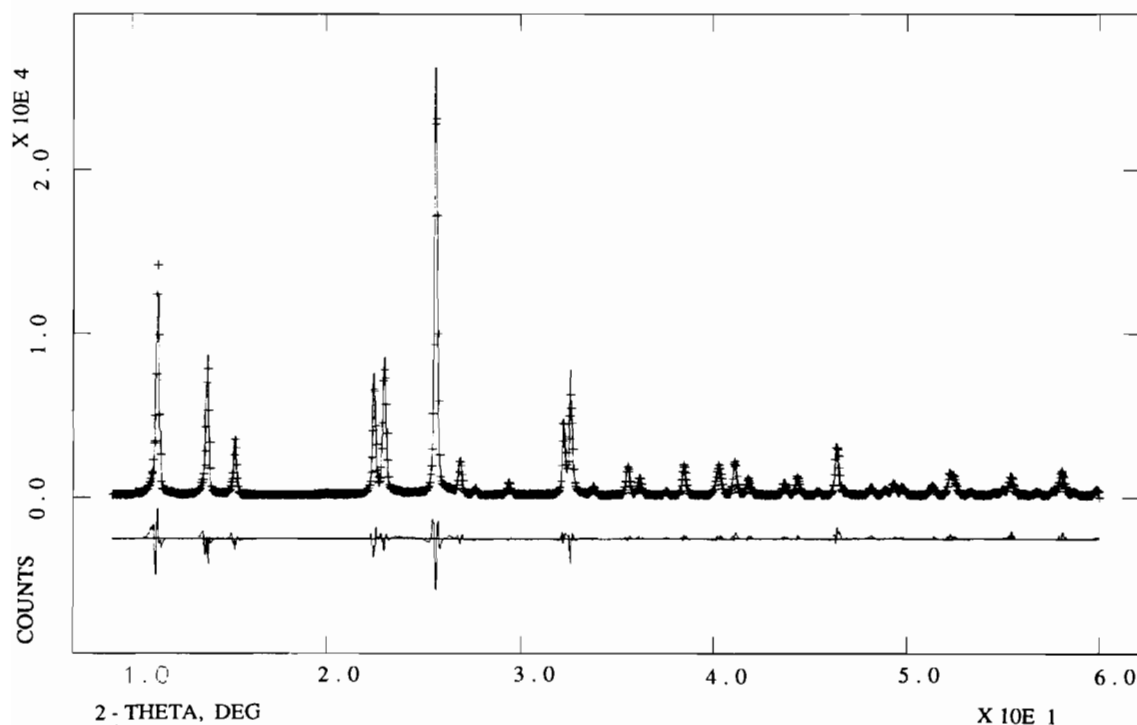
Fig. 5. Observed (+) and calculated (−) profiles (X-ray intensity vs. 2θ) for the Rietveld refinement of the high temperature phase (RB255C). The bottom curve is the difference plot on the same intensity scale.
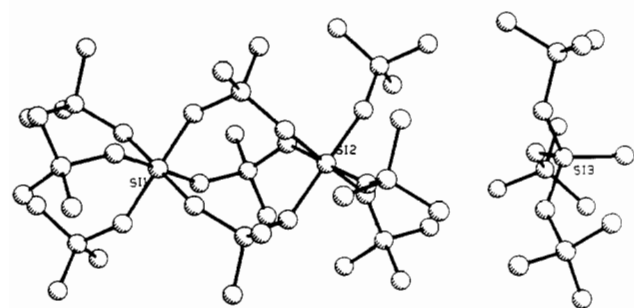

Fig. 6. Coordination around the silicon atoms showing octahedral coordination for Si(1), Si(2) and tetrahedral coordination for Si(3).

Fig. 7. Three-dimensional structure of $Si_5O(PO_4)_6$. The view is down the *b* axis. Note the voids formed by the way in which the octahedral Si groupings connect to the tetrahedral silicon groups.

between Si(2) and Si(3) groups as shown in Fig. 7. All the phosphate oxygens are bonded to silicon as well, so that there are no Si–OH or P–OH groups in the structure. These may exist at the surface because of unfulfilled bridging.

The PO_4 group in both cases shows regular geometry with average bond lengths and angles. The P–O distances range between 1.52 and 1.53 Å and the tetrahedral angles are in the range 103–114°. The angles about the Si(3) atom are very typical of tetrahedral geometry and the average Si(3)–O distance is 1.68 Å in RB210 and 1.63 Å in RB255C. Si(1) and Si(2) display regular octahedral geometry in both cases. The average Si–O bond length for these atoms is 1.78 and 1.76 Å for RB210 and RB255C, respectively. The *cis* angles in
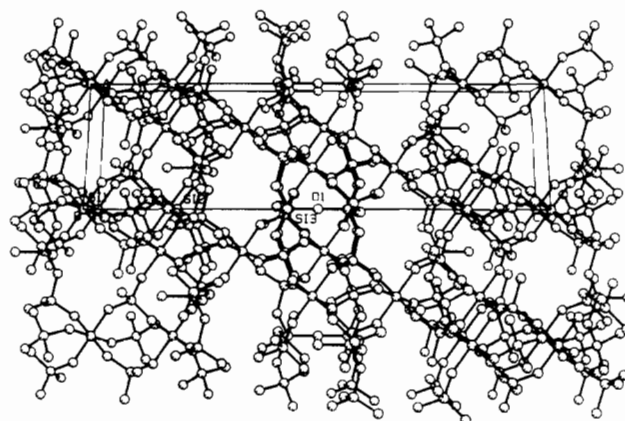
these cases range between 83 and 96° while the *trans* angles are very close to 180°.

As described in 'Experimental', the sample RB255A was prepared at 300 °C with a higher P/Si ratio. This material shows considerable differences in the low angle X-ray diffraction data ([003] and [006] reflections), although the high angle data are remarkably similar to RB210 or RB255C. Again the unit cell parameters are very close to those found for RB210 and RB255C. We have also processed and refined this data using

the positional parameters for $Si_5O(PO_4)_6$ and found that the large intensities of [001] reflections at low angle are mainly due to preferred orientation effects. On heating this sample to 1000 °C (RB255C) this effect is not seen in the X-ray data as shown in Fig. 1.

Conclusions

The most important result of the X-ray study is that the chemical composition of silicon orthophosphate is $Si_5O(PO_4)_6$ contrary to the formula $Si_3(PO_4)_4$ suggested by Liebau *et al.* The successful refinement of this structure for both the low and high temperature phase X-ray powder data further allow us to conclude that the lattice structure remains intact in this temperature (200–1000 °C) range and that the compound does not exist as a solid solution system as proposed by Liebau *et al.* [7]. The true ratio P/Si is 1.2 and not 1.33. Since the high and low temperature preparations have the same structure, the weight loss observed for low temperature preparations must be due to condensation of P–OH groups and volatilization of H_3PO_4 and phosphorus polymers from the surface. Both octahedral and tetrahedral silicon are present in this structure which is quite unusual.

Acknowledgement

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