

A New Solution Route to Silicates

Part 1. KHSi_2O_5 , $\text{H}_2\text{Si}_2\text{O}_5$, and $(\text{K,Na,H})_2\text{Si}_2\text{O}_5$

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The reaction of alcoholic potassium hydroxide solution on silicon powder is studied. A redox process leads to an amorphous silicate which can be easily crystallized. This phase is identified by elemental analysis, solid state NMR and XRD as monoclinic KHSi_2O_5 . The same reaction with mixed sodium-potassium alkali solutions results in mixed phases of general formula $(\text{K,Na,H})_2\text{Si}_2\text{O}_5$. Ionic exchange of KHSi_2O_5 in 2 M HCl solution allows to prepare the K-free phase $\text{H}_2\text{Si}_2\text{O}_5$. Thermal processing of amorphous KHSi_2O_5 shows the formation of a second allotropic variety of this compound. Finally, at 1373 K, a colorless, transparent and homogeneous glass is obtained. © 1994 Academic Press, Inc.

INTRODUCTION

The success of sol-gel processes in the synthesis of glasses and ceramic powders is due, in particular, to the possibility of working at a low temperature and attaining good homogeneity in the solution phase. These characteristics are increasingly utilized to produce organic/inorganic hybrid compounds (1). Nevertheless, the preparation of multicomponent materials gives rise to a certain number of problems. The all-alkoxide route requires either synthesizing bi- or trimetallic alkoxides, a process that may be complicated and costly, or using alkoxide mixtures with inherent difficulties due to the marked differences in reactivity of those components. The hybrid routes relying on mixtures of alkoxides and salts or metallic complexes constitute an interesting possibility but products may be soiled by anions that are not easily removed (chlorides for example).

An alternative, at least in the case of silicates and silica glasses, could involve direct reaction of metal with an appropriate reagent. In papers dealing with the etching of circuits on semiconductor wafers, alcoholic potassium hydroxide is a reagent frequently used for etching Si (2-3), GaAs (4) or InP (5). These studies underline the action

of alcoholic solution that corresponds to a two-step oxidation/dissolution process.

In this paper, the reaction of alcoholic alkali solutions on silicon and the characterization of the products obtained are reported.

EXPERIMENTAL

Synthesis

Silicon powder (Aldrich) is added to a molar solution of KOH in methanol (Aldrich). The molar ratio KOH/Si is taken equal to 6. For lower ratios, the reaction is not complete. After 15 mn refluxing, a bulky black-grey solid is formed and occupies almost the whole reaction flask; gas is abundantly released. The product obtained is then filtered, abundantly washed in methanol to remove any excess KOH and then dried at 373 K in a furnace.

The gas produced is collected in an inflatable balloon and analyzed by gas phase chromatography by comparing the chromatogram obtained to those of standard mixtures. The detailed procedure has already been given elsewhere (6).

Characterizations

Chemical analyses were carried out in the Central Department of Microanalysis of the National Centre for Scientific Research (CNRS) in Lyon. The absorption infrared spectra were recorded using a Fourier transform Perkin-Elmer 1725 × spectrometer. Thermal evolution was monitored by thermogravimetry on a SETARAM TG85 setup under air up to 1223 K with a 5° temperature rise per minute. Differential thermal analysis was conducted using a SETARAM MDTA 85 setup. The electron microscopy pictures were taken on a Cambridge type scanning electron microscope. ²⁹Si solid-state NMR measurements were carried out using a Bruker MSL 300 spectrometer operating at 59.6 MHz. MAS spectra were recorded at a spinning frequency of 3.9 kHz. XRD patterns were taken

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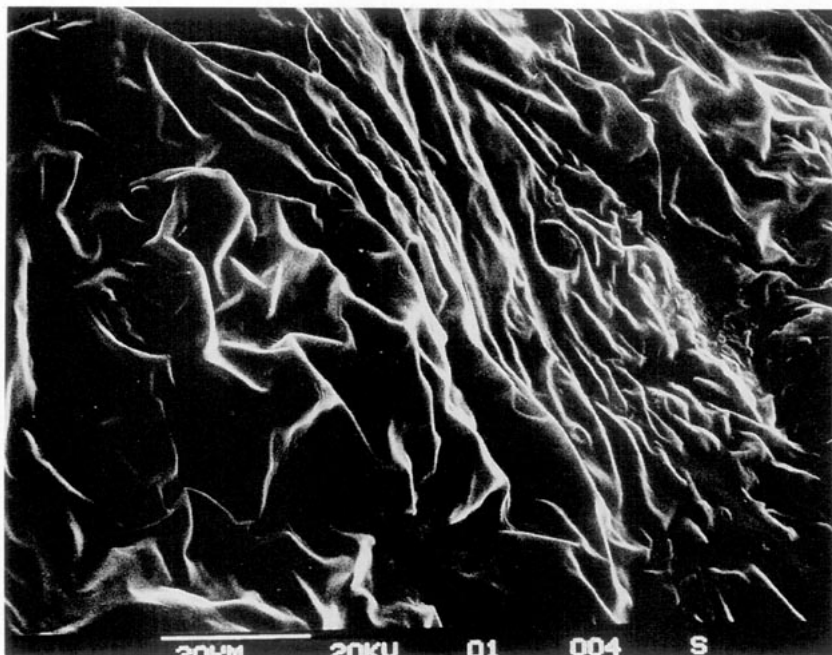


FIG. 1. SEM micrograph of the amorphous phase.

on a Seifert XRD3000 diffractometer using $\text{CuK}\alpha$ radiation, over the range $5 < 2\theta < 50^\circ$ with a scan rate of $1^\circ/2\theta/\text{min}$.

RESULTS AND DISCUSSION

KHSi_2O_5 Synthesis

X-ray diffraction analysis demonstrates that the reaction is complete (all the crystallized silicon powder has been used up) and also shows the product finally obtained to be amorphous. Scanning electron microscopy shows a homogeneous solid with a fabric-like texture (Fig. 1).

The elementary analysis performed on a prepared product leads to the raw formula KHSi_2O_5 (Table 1). Small amounts of methanol are still trapped in the solid (approximately 0.13 methanol per KHSi_2O_5). The IR spectrum

(Fig. 2) exhibits an intense band at 3450 cm^{-1} that can be assigned to the vibrations of the OH group. The absorption band located at 1640 cm^{-1} can be attributed to the vibrations of unbound OH groups. The comparison of the spectrum with those of crystallized KHSi_2O_5 and of an amorphous silica shows a great similarity. In particular the large block centered toward 1100 cm^{-1} and bands at lower frequencies (944 cm^{-1} , 788 cm^{-1} and 458 cm^{-1})

TABLE I
Analytical Results

	Si	H	K	C	O
Experimental	31.40	1.38	20.93	0.87	45.42 ^a
Calculated for KHSi_2O_5	31.86	0.57	22.18	—	45.38

^a Calculated by subtraction to 100.

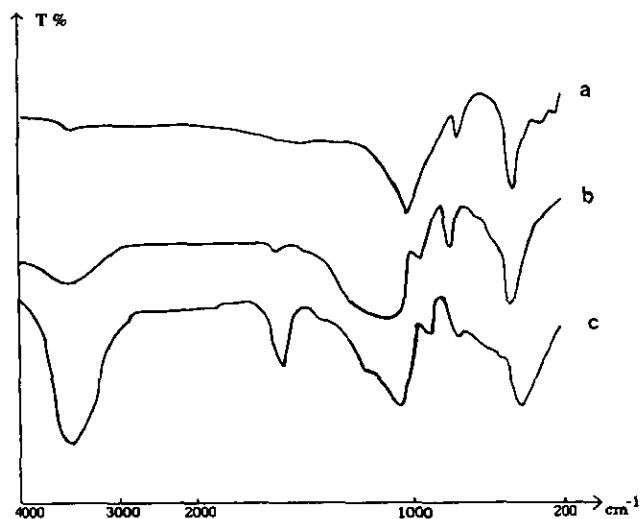


FIG. 2. IR spectra of: (a) crystallized KHSi_2O_5 , (b) amorphous silica, and (c) amorphous KHSi_2O_5 .

correspond to the vibrations of the silicate functional groups (7).

The solid-state ^{29}Si NMR spectrum (Fig. 3a) shows three peaks resolved at 87.8, 97.2 and 107.8 ppm. These peaks in the ratio 1 : 2 : 0.6 highlight a complex local order in which entities Q^2 , Q^3 and Q^4 coexist (8).

On this basis it is reasonable to assume that the synthesized compound could be the amorphous analogue of the crystallized KHSi_2O_5 species prepared by Von Schweinsberg (9) and Kalt (10). These monoclinic or orthorhombic disilicates were prepared in various ways while still in the crystallized state:

—by adding aqueous potassium hydroxide to a hydrated amorphous silica at 573 K in an autoclave (10)

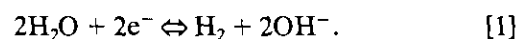
—by processing $\text{K}_2\text{Si}_2\text{O}_5$ in an autoclave at 473 K in anhydrous methanol (11)

—by hydrolysis of variable-composition $\text{K}_2\text{O}-\text{SiO}_2$ glasses in an autoclave between 473 and 723 K (12).

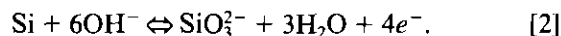
All these reactions differ from the one used here since they occur under pressure at a noticeably higher temperature and with silicon still in the +IV oxidation state in the starting material. To identify more clearly the amorphous phase prepared, we attempted to recrystallize it by heating at 673 K with a drop of water in an evacuated sealed tube for 4 days. The X-ray diffraction spectrum obtained (Fig. 4) shows the onset of crystallization; the diagram could clearly be identified as that of Von Schweinsberg (9, 13) for the KHSi_2O_5 monoclinic variety. A scanning electron microscope examination revealed prismatic layered crystals (Fig. 5). To our knowledge, the crystal structure of this species has never been established.

In this work, metallic silicon has been used as starting

material. A redox reaction therefore occurred, raising the question of the reaction mechanism. It has been shown (14) that in the sodium hydroxide solutions in ethanol, the equilibrium $\text{EtOH} + \text{OH}^- \rightleftharpoons \text{OEt}^- + \text{H}_2\text{O}$ is largely displaced towards the formation of ethoxide (up to 96% of the total base). This remains valid up to the solvent's boiling point and can also be verified in methanol solutions. Gas phase chromatography analysis of the gas released during the reaction clearly showed the presence of hydrogen. The oxygen and nitrogen present in the analysed sample obviously correspond to the initial atmosphere in the reaction flask. Thus it is reasonable to assume that the reduction reaction which occurred was as follows:



To our knowledge, direct oxidation of silicon in a basic medium to obtain $\text{Si}_2\text{O}_3^{2-}$ has not been reported in the literature but the reaction leading to entity SiO_3^{2-} is well known:



Moreover, Funk (11) prepared KHSi_2O_5 by adding methanol at 473 K in an autoclave to K_2SiO_3 . The reaction mechanism may therefore correspond to the reactions [1] and [2] followed by condensation.

The reaction described here occurred over a wide range of conditions. If the potassium hydroxide concentration of the alcoholic solution is increased up to 2 M, the reaction rate is dramatically increased but the resulting product remains the same. On the other hand, if the

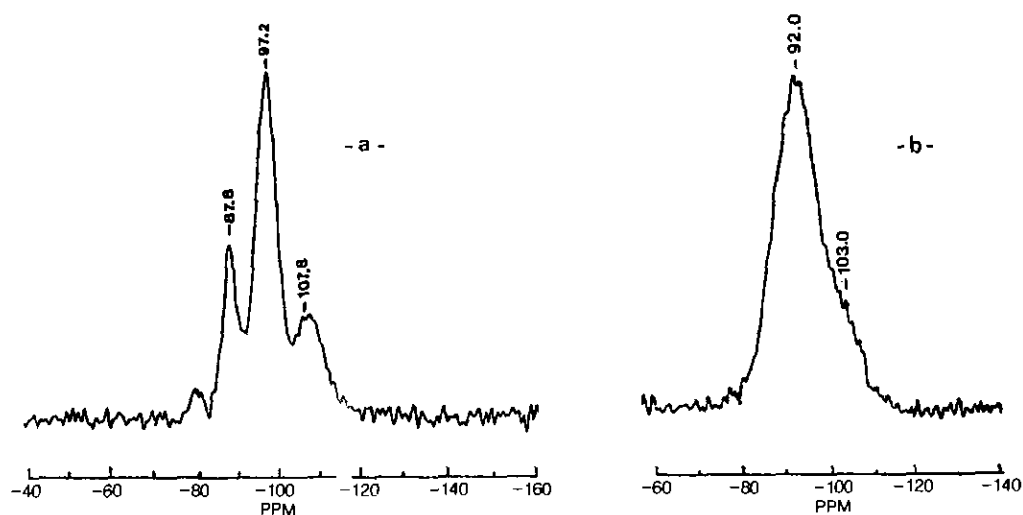


FIG. 3. Solid-state ^{29}Si NMR spectrum of: (a) the amorphous KHSi_2O_5 , (b) the glass obtained at 1373 K.

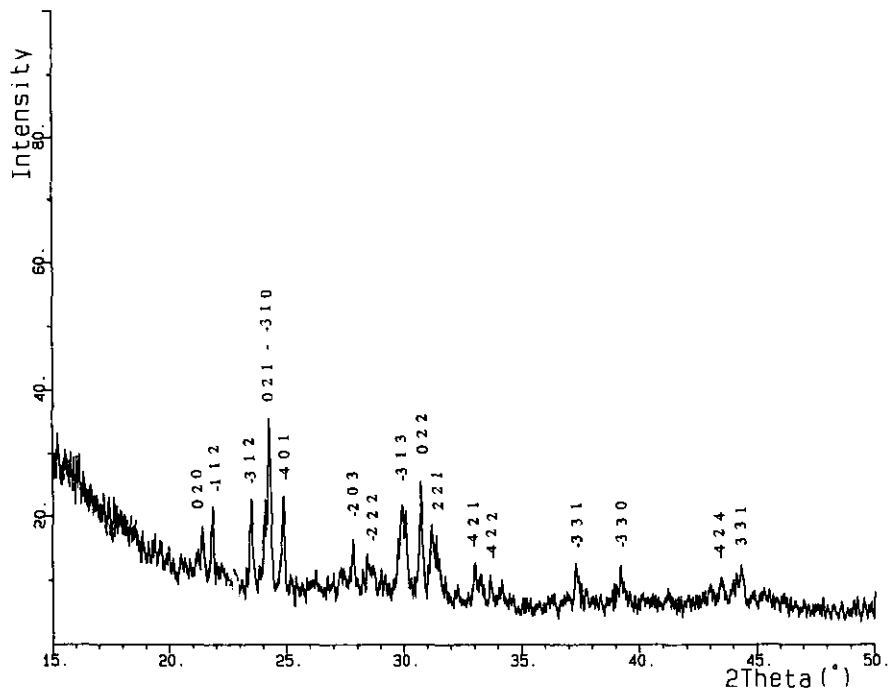


FIG. 4. XRD spectrum of the monoclinic crystals.

concentration is lowered to 0.5 *M*, the reaction no longer takes place even if the KOH/Si ratio is maintained equal to 6.

This reaction occurred in an identical way in a 1 *M*

ethanol solution of potassium hydroxide. Likewise hybrid compounds containing K^+ and Na^+ can be obtained, starting from a 1 *M* KOH methanolic solution in which sodium hydroxide has been dissolved. For example, starting with

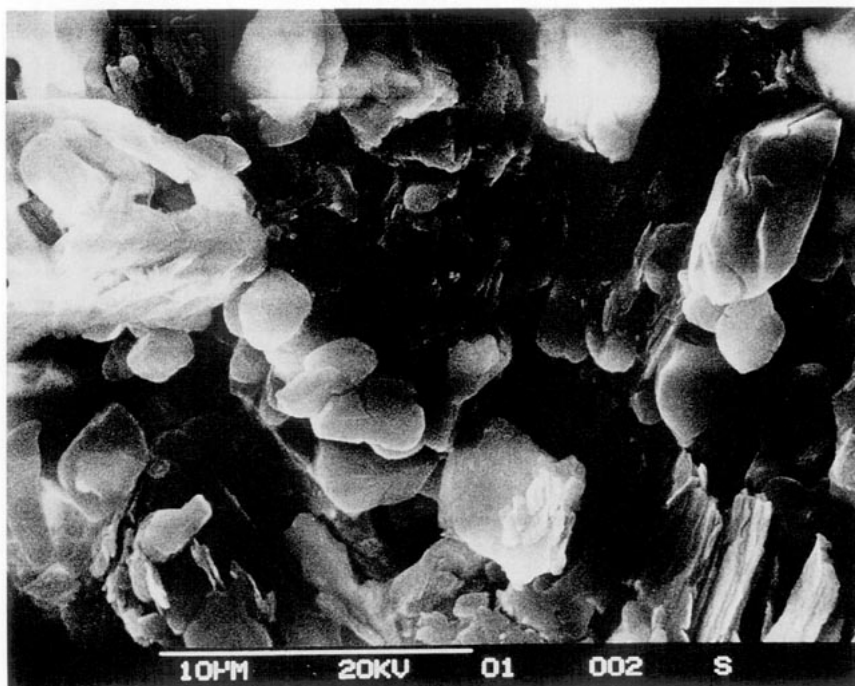


FIG. 5. SEM micrograph of the monoclinic crystals.

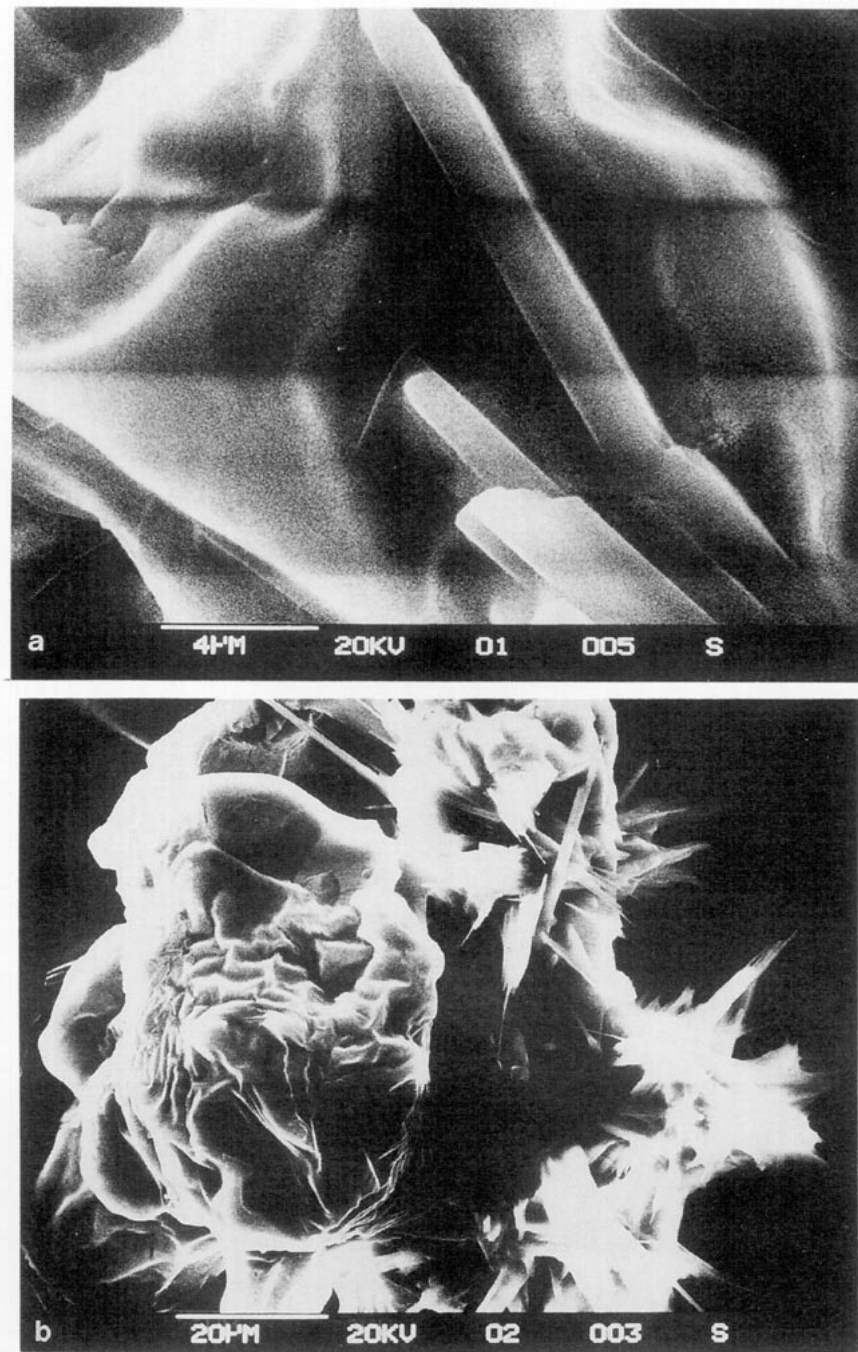


FIG. 6. SEM micrographs of the crystals formed in air: at 373 K (a), and at 873 K (b).

a molar ratio $K/Na = 2.5$, the compound $K_{0.43}Na_{0.18}H_{1.4}Si_2O_5$ has been obtained, a formulation analogous to the phases $K_xH_{2-x}Si_2O_5$ and $(NH_4)_xH_{2-x}Si_2O_5$ obtained by Hubert (15) and Kalt (16). Conversely it is apparently not possible to prepare a compound containing sodium only as the reaction does not occur with sodium hydroxide alcoholic solutions.

In addition, it is possible to exchange, partially or fully, potassium ions with protons (17). The formation of

$H_2Si_2O_5$, totally free of K^+ ions, is obtained by an exchange reaction stirring the starting product in HCl 2 M for 8 hr.

Thermal Processing of $KHSi_2O_5$

The amorphous product obtained shows a complex thermal behavior. Heating in air produces a low-temperature crystallization. At 373 K, some prismatic needles start to appear at the expense of the amorphous phase

(Fig. 6a). The differential thermal analysis shows an endothermic peak at 408 K which could correspond to this crystallization. The phase obtained remains minor as shown by scanning microscopy of the product annealed at 873 K (Fig. 6b). Microdiffraction and diffraction spectrum of these crystals remained ambiguous because of the poor quality of crystallization. However, the diffraction spectrum showed features similar to those of $\text{H}_2\text{Si}_2\text{O}_5$ (JCPDS No. 27-606) and of the orthorhombic variety of KHSi_2O_5 (JCPDS No. 19-968). These two compounds crystallize with the same spatial group and comparable cell parameters so that most probably (since the crystal structure of $\text{H}_2\text{Si}_2\text{O}_5$ is not known) they are isostructural. Thus, the phase observed in this work could be an orthorhombic variety of $\text{K}_x\text{H}_{2-x}\text{Si}_2\text{O}_5$.

If heating in air is continued these crystals decompose at 1073 K. The product turns amorphous a second time and melts at 1223 K to yield glass. At 1373 K a homogeneous glass which is both transparent and colorless is attained. Air quenching brings it back to ambient temperature without devitrification.

The chemical composition of the product changes during this temperature rise. The thermogram shows a continuous weight loss of 22% between 383 and 703 K. The elemental analysis of glass heated at 1373 K yields an atomic ratio K/Si close to 0.65 (average over several preparations) which is significantly higher than the value observed for the amorphous starting material (0.5). This result is surprising and not understood but fully reproducible.

This change in chemical composition is accompanied by a change in structure as shown in the ^{29}Si NMR spectrum taken from the glass (Fig. 3b). The spectrum shows

a main peak at 92.0 ppm and a shoulder located at about 103 ppm. Their respective intensities lead to a distribution of approx. 73% Q^3 units and 27% Q^4 units. This is in good agreement with those obtained from binary alkali silica glasses containing sodium (8).

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