JOURNAL OF SOLID STATE CHEMISTRY **97**, 163–168 (1992)

Surface-Bound Titania-Induced Selective Growth and Stabilization of Tridymite Aluminum Phosphate

R. DEBNATH AND J. CHAUDHURI

Central Glass and Ceramic Research Institute, Calcutta 700032, India

Received February 5, 1991; in revised form September 19, 1991

The crystallization behavior of amorphous aluminum phosphate ($AlPO_4$) has been studied by X-ray diffraction as a function of the treatment temperature (500–1150°C) in the presence of small amounts of titania (TiO_2) anchored onto its surface. The compound, which like silica can exist in several possible crystalline modifications depending on the treatment temperature, is found to grow in the presence of TiO_2 exclusively in a single phase in the entire range of temperatures studied. The phase has been shown to have the tridymite structure belonging to the orthorhombic system with cell parameters $a = 9.638 \pm 0.0019$, $b = 8.664 \pm 0.0017$, and $c = 18.280 \pm 0036$ Å.

Introduction

Aluminum orthophosphate ($AlPO_4$) is well known for its similar structure and parallel polymorphic transitions to silica. There have been a number of studies (*1–7, 12*) on the polymorphic properties of aluminum phosphate in which the existence of six crystalline modifications are reported. The stability relations among these polymorphs may be summarized as follows.

$$\underset{\alpha \xleftrightarrow{586 \pm 2^\circ\mathrm{C}} \beta}{\text{berlinite}} \xleftrightarrow{705 \pm 7^\circ\mathrm{C}} \underset{\alpha \xleftrightarrow{93 \pm 3} \beta_1 \xleftrightarrow{130^\circ\mathrm{C}(?)} \beta_2}{\text{tridymite}} \xleftrightarrow{1047 \pm 8^\circ\mathrm{C}} \underset{\alpha \xleftrightarrow{210 \pm 5^\circ\mathrm{C}} \beta}{\text{cristobalite}} \xleftrightarrow{1850 \pm 50^\circ\mathrm{C}} \text{Fused } \mathrm{AlPO_4}$$

Recently Byrappa *et al.* reported (*7*) a new monoclinic modification of aluminum phosphate having a structure similar to that of rare-earth orthophosphate.

Among these various modifications, the berlinite variety of $AlPO_4$ has been extensively studied because of its superior piezoelectric properties (*8, 9*) compared to those of quartz. However, reports of many other applications of $AlPO_4$, for example, as catalyst support (*10, 11*), as a microwave substrate (*12*), etc., are also known.

One major obstacle in using aluminum phosphate as a microwave substrate or as other ceramics is the difficulty encountered in sintering the material to a dense ceramic body, because of its nonquenchable $\alpha \rightarrow \beta$ transformation.

Here we report a novel technique of selective growth and stabilization of a crystalline phase of aluminum phosphate that has been shown to have parallel crystallographic properties to those of the γ-tridymite form of silica (*14, 15*).

Experimental

The precursor amorphous aluminum phosphate was prepared by precipitating

0022-4596/92 \$3.00

the compound from an aqueous solution of sodium dihydrogen phosphate (A.R) and aluminum sulfate (A.R) in a molar ratio of 2:1 under a buffer controlled pH of ~6. The precipitate was filtered off and repeatedly washed with distilled water to remove all water-soluble contamination. The compound after rinsing with acetone several times was allowed to dry in air and finally in a desiccator. Chemical analysis of the compound gave the percentage composition as $Al_2O_3 \approx 41.13 \pm 0.41\%$ and $P_2O_5 \approx 59.25 \pm 0.60\%$ (calculated for $AlPO_4$, $Al_2O_3 = 41.8\%$, and $P_2O_5 = 58.2\%$).

To prepare the titania-anchored samples a 5-g portion of the powdered compound was impregnated with a sufficient amount of 50% acetone solution of titanium tetra-2 propoxide [$Ti(Pr^iO)_4$] (Fluka AG); the excess liquid was decanted off and the mixture was then exposed to air for complete hydrolysis of the absorbed [$Ti(Pr^iO)_4$]. The hydrolyzed product was then fired in air at 500°C in a tube furnace until all organic matter in the mixture was completely burnt out. The concentration of titania in the resulting mixture was estimated colorimetrically and was found to be approximately 16.00 ± 0.15 wt%. Samples treated at higher temperatures (700, 900, 1050, and 1150°C) were prepared from the product of 500°C treatment by taking a fraction from the latter and heat-treating it in air for 1 hr at the respective temperature. A similar set of samples of aluminum phosphate without the addition of titania was also prepared for comparative study. The XRD spectra of all samples were recorded in a Philips X-ray diffractometer (Model PW 1730) fitted with a goniometer and provided with nickel-filtered Cu*K*α-line (1.54178 Å) X-ray source. Indexing of the observed lines and calculation of the related cell parameters were accomplished with the help of program POWD (version 2.2) devised by E. Wu (*13*).

Results and Discussion

Figures 1a and 1b show the X-ray diffraction patterns of titania containing aluminum phosphate samples (ALPT series) in the region $20° < 2\theta < 40°$ of different treatment temperatures while Figs. 2a and 2b exhibit those of pure aluminum phosphate of identical treatment temperatures (ALP series). Aluminum phosphate samples of the ALPT series of all temperatures (500–1150°C) show prominent peaks at $d = 4.33$, 4.10 and 3.82 Å (Figs. 1a and 1b) which are the characteristics of a tridymite-like structure (*3, 6, 14, 15*). The samples of the ALP series of identical treatment temperatures exhibit (Figs. 2a and 2b) varied characteristics of diffraction peaks showing the presence of a mixture of different phases at all temperatures. For example at 500°C, weak growth of a tridymite-like structure is indicated by the lines at $d = 4.33$ and 4.13 Å but the line at $d = 3.90$ Å does not show the characteristics of any definite phase. It appears from its broadness that a line of some other emerging phase (possibly the $d = 4.04$ Å line of cristobalite) mingled here with the $d = 3.82$ Å line of tridymite. On increasing the temperature to 700°C the same feature prevails. At 900°C and above a cristobalite phase with $d = 4.04$, 3.12, 2.84, and 2.50 Å (*3*) emerges as a major phase, although the presence of a small fraction of the tridymite phase ($d \approx 3.79$ Å) and a characteristic (*2*) of a mixture of tridymite and cristobalite ($d = 4.27$ Å) are also evident.

In the case of ALPT samples no change except the sharpening of the observed lines and a slight variation in their relative intensities was observed in the spectra with the increase of temperature from 500 to 1050°C. However, the spectra of the 1150°C sample show an indication of the emergence of a

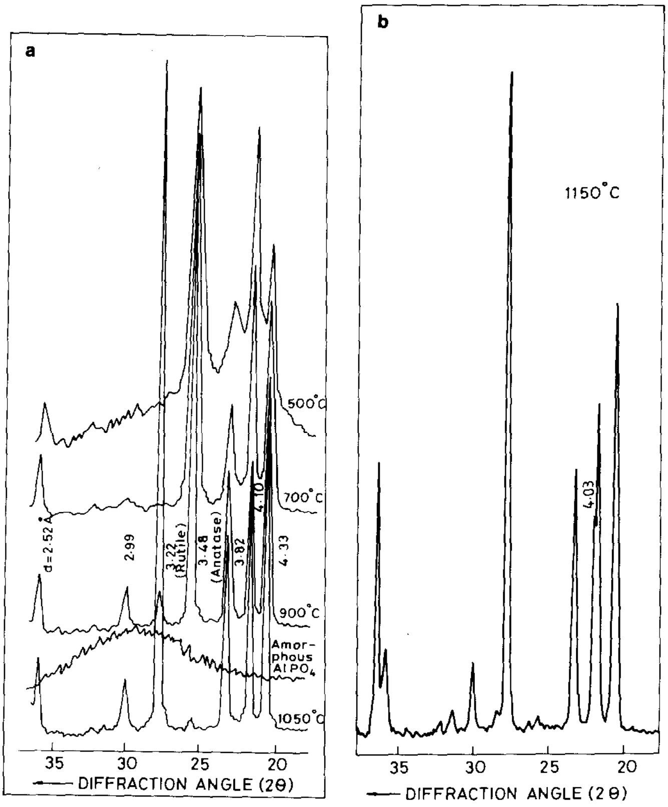

FIG. 1. (a) XRD pattern of tridymite aluminum phosphate grown in the presence of titania at various temperatures along with that of pure amorphous AlPO$_4$ used as starting materials. (b) XRD pattern of tridymite aluminum phosphate heat treated at 1150°C.

weak cristobalite peak in addition to the major features of the tridymite phase.

Thus it is evident from the observed data that in the presence of titania, aluminum phophosphate crystallizes in a tridymite-like structure from the very inception of the crystallization process. With the rise in temperature the phase suffers no morphological change; on the contrary, it becomes more and more well defined and was found to be considerably stable even up to 1150°C (Fig. 1b) which is in sharp contrast with the normal behavior of pure AlPO$_4$. Long before 1150°C, e.g., at 1050°C aluminum phosphate is expected to transform into a cristobalite phase. The observed results thus show that the presence of titania in such systems not only forces aluminum phosphate to grow in a selective phase (tridymite) but also helps in retaining the same structure over a wide range of temperatures. For the precise identification of the AlPO$_4$ phase grown in this process we have recorded a high resolution diffraction spectrum of the species in the region $2\theta = 15$–$80°$. The complete indexed powder pattern of the phase is given in Table I. It can be seen from the calculated d-spacings that the data are consistent with an orthorhombic unit cell with $a = 9.638 \pm 0.0019$, $b = 8.664 \pm 0.0017$, and $c = 18.280 \pm 0.0036$ Å and $V = 1526.446 \pm 1.100$ Å^3.

A comparison of these parameters with

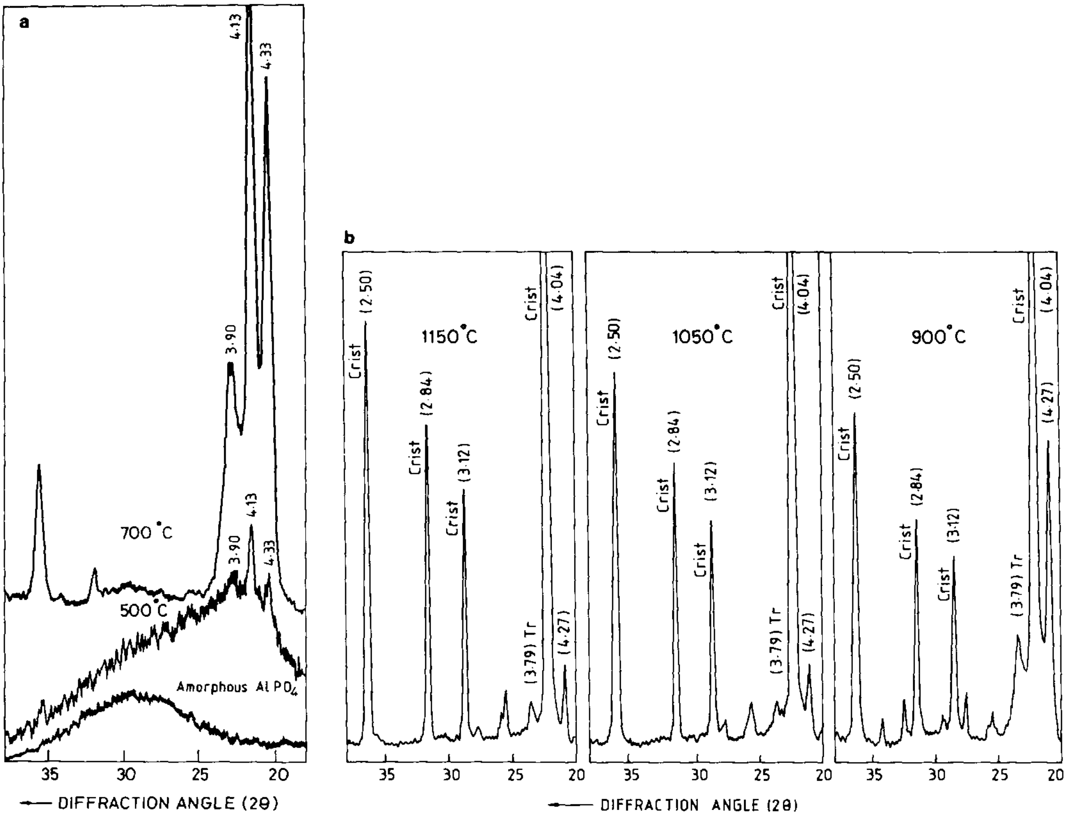

FIG. 2. (a) XRD pattern of a mixture of phases (tridymite + cristobalite) of $AlPO_4$ grown on heat-treated pure aluminum phosphate (without the addition of titania) at temperatures of 500 and 700°C along with that of amorphous $AlPO_4$. (b) XRD pattern of a mixture of phases (tridymite + cristobalite) of $AlPO_4$ grown at temperatures of 900, 1050, and 1150°C. Cr, cristobalite; Tr, tridymite.

those of various modifications of silica shows that the observed $AlPO_4$ phase has parallel crystallographic parameters to those of the γ-tridymite form of silica (*14, 15*) (Table II). The sample could not readily be separated from contaminated TiO_2, so it was not possible to measure its density. However, on the basis of the above similarity the number of $AlPO_4$ molecules per unit cell of the phase can be estimated to be 16, which yields a value of X-ray density D_X = 2.13 g/cm^3. Since two silica molecules are almost equal to a molecule of aluminum phosphate in weight, the estimated density of the tridymite aluminum phosphate should also be comparable to that of γ-tridymite SiO_2. In practice, that is also found to be true (shown in Table II). Another interesting feature observed in the crystallization process of such a mixture is that the titania (TiO_2) which in the pure state readily transforms (*16, 17*) from its anatase morphology to a rutile structure above 500–600°C remains unchanged under such condition up to a temperature as high as 950°C; i.e., on the surface of aluminum phosphate the anatase structure of titania also becomes stable possibly through a reciprocating mechanism. Although further experiments should be done before one could achieve a conclu-

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR TRIDYMITE $AlPO_4$ GROWN IN THE PRESENCE OF TiO_2 AT 1050°C

Orthorhombic system d-spacing (Å)		F_{23} = 4.2(0.016,344)			
			Indices		
Observed	Calculated	I/I_0	h	k	l
4.3320	4.3320	100	0	2	0
4.1040	4.1040	75	2	1	1
3.8250	3.8250	61	2	1	2
3.4140	3.4184	3	1	0	5
3.1644	3.1643	4	3	0	1
2.9900	2.9890	17	1	2	4
2.8621	2.8610	6	3	1	2
2.7960	2.7940	5	0	2	5
2.5200	2.5206	24	1	0	7
2.3200	2.3215	11	4	1	0
2.1510	2.1510	2	0	4	1
2.1127	2.1133	5	1	4	0
2.1080	2.1083	5	3	2	5
2.0690	2.0698	2	4	1	4
1.8897	1.8900	2	4	0	6
1.8860	1.8862	2	5	0	2
1.7097	1.7092	5	2	0	10
1.6500	1.6508	3	4	3	5
1.6190	1.6202	23	0	5	4
1.5476	1.5472	4	3	4	6
1.5441	1.5446	4	0	3	10
1.4775	1.4769	13	2	2	11
1.4507	1.4500	12	6	1	5

sive understanding of the process of this mutual phase stabilization effect, we suggest the following tentative mechanism.

During the process of ignition (500°C) of titanium isopropoxide-impregnated $AlPO_4$, nascent TiO_2 molecules are generated. Since titania here is generated a a combustion product of an organotitanium compound the resulting product will definitely suffer from deficiencies in oxygen. Consequently it seems that at the subsequent stages of its crystallization it will try to incorporate oxygen into its structure to reduce its oxygen vacancies taking a share from the neighboring oxygen source, i.e., the contiguous $AlPO_4$ molecules, so that at the experimental temperature of 500°C thermodynamically stable anatase crystals are generated. The experimentally observed abnormally high thermal stability of the resulting anatase crystal supports the above view. Moreover since the $AlPO_4$ is slightly ionic in character the idea of its sharing oxygen with anatase crystals is not unreasonable.

The net result is the anchoring of aluminum phosphate molecules of the contact layer into the structure of the freshly grown anatase crystals, which leads to the following two effects: (a) structural stuffing of anatase crystals inhibiting their transition to ru-

TABLE II

A COMPARISON OF CRYSTALLOGRAPHIC PARAMETERS OF OUR TRIDYMITE $AlPO_4$ TO THOSE OF γ-TRIDYMITE SILICA

Cell parameters (Å)	γ-Tridymite SiO_2		Tridymite $AlPO_4$ reported here
a	10.04[a]	9.91[b]	9.64
b	17.28	17.18	1/2 × 17.32
c	1/2 × 16.40	16.30	18.28
Z (No. of molecules/unit cell)	32	64	16.00[c]
D_X (g/cm^3)	2.24	2.31	2.13

[a] Ref. 15.

[b] Ref. 14.

[c] Estimated on the basis "two silica molecules in the cell equivalent to one aluminum phosphate molecule."

tile and (b) diminution in the degree of freedom of the surface-lying molecules of $AlPO_4$.

Since aluminum phosphate is a relatively slow crystallizing system compared to TiO_2, it is reasonable to assume that the crystallization of the contact layer of aluminum phosphate in the mixture should occur at a later stage under the influence of the surface-bound anatase crystals. This possibly favors the selective growth of tridymite $AlPO_4$. Once the surface layer of $AlPO_4$ crystallizes in a definite modification, it then acts as seeds for the bulk materials and hence the whole aluminum phosphate crystallizes with the same structure.

Acknowledgments

The authors express their thanks to the Director, C. G. & C. R. I., Calcutta, India, for his kind permission to publish this work. Thanks are also due to Mr. D. K. Ghosh, C. G. & C. R. I., for recording the XRD spectra.

References

1. W. R. Beck, *J. Am. Ceram. Soc.* **32,** 147 (1949).
2. F. D'Yvoire, *Bull. Soc. Chim. France* **10,** 1762 (1961).
3. O. W. Florke, *Z. Kristallogr.* **125,** 134 (1967).
4. B. M. Kobtsev, A. G. Kotlova, N. I. Shchepochkina, and B. V. Strizhkov, *Inorg. Mater.* **8,** 348 (1972).
5. W. F. Horn and F. A. Hummel, *Trans. J. Br. Ceram. Soc.* **77,** 158 (1978).
6. D. Vasoric' and D. Stojakovic', *J. Am. Ceram. Soc.* **70,** C-23 (1987).
7. K. Byrappa, S. Srikantaswamy, and P. Shashidhara, *J. Mater. Sci. Lett.* **5,** 690 (1986).
8. J. M. Stanley, *Ind. Eng. Chem.* **46,** 1684 (1954).
9. A. Jhunjhunwala, J. F. Vetelino, and J. C. Field; *J. Appl. Phys.* **48,** 887 (1977).
10. S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannon, and E. M. Flanigen, *J. Am. Chem. Soc.* **104,** 1146 (1982).
11. R. Debnath and J. Chaudhuri, *J. Mater. Sci. Lett.* **10,** 494 (1991).
12. R. Liang and T. Nakamura, *Mater. Res. Bull.* **20,** 1253 (1985).
13. E. Wu, POWD (Version 2.2), School of Physical Sciences, Flinders University, South Australia.
14. A. S. Bereznoi, *in* "Silica and Its Binary Systems," P-20 Consultant Bureau, New York (1960).
15. M. Sato, *Mineral J.* (*Japan*) **4,** 215 (1964).
16. S. Nishimoto, B. Otani, H. Kajiwara, and T. Kagiya, *J. Chem. Soc. Faraday Trans. 1* **81,** 61 (1985).
17. R. Debnath and J. Chaudhuri, submitted for publication.