

Mutual phase stabilization of aluminium phosphate and titania in $\text{AlPO}_4\text{-TiO}_2$ binary system

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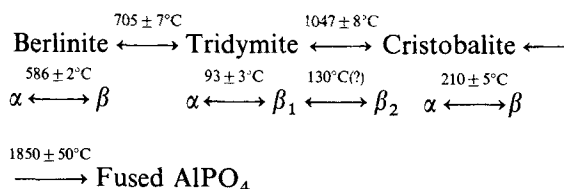
Abstract. Crystallization behaviour of amorphous aluminium phosphate (AlPO_4) and titania (TiO_2) in a mixed system of the two (5:1) has been reviewed in the light of our recent results. The polymorphous aluminium phosphate in such a binary system grows exclusively in a single phase over a temperature range 500–1150°C. The phase is reported to have a tridymite-like structure belonging to orthorhombic system with cell parameters $a = 9.638 \pm 0.0019$, $b = 8.664 \pm 0.0017$ and $c = 18.280 \pm 0.0036$ Å. Titania in the system preferentially retains its anatase phase morphology up to a temperature (950°C) well beyond its normal anatase → rutile transformation temperature showing a phenomenon of stabilization of this phase in such mixture. An interfacial reaction mechanism that can explain the observed phenomenon of mutual phase stabilization has been discussed and implications of this result towards the use of such technique for stabilization of various polymorphous compounds in a single phase has been pointed out.

Keywords. Aluminium phosphate; titania; phase stabilization; γ -tridymite-phase; anatase.

1. Introduction

Polymorphous compounds like silica, aluminium phosphate, titania etc which are frequently used in making special ceramics for various electronic applications (Jhunjhunwala *et al* 1977; Liang and Nakamura 1985), sometimes pose difficulty in sintering these materials into dense ceramic body because of their inherent polymorphic transformations with variations of temperature. Here we review the results of our recent studies on the stabilization of polymorphous aluminium phosphate in a single phase using titania as a nucleating agent.

Aluminium orthophosphate (AlPO_4) exhibits parallel polymorphic transitions to silica. There are six most common crystalline modifications of aluminium phosphate. The stability relations amongst these polymorphs may be summarized as follows.



Titanium dioxide also exists in the three crystalline modifications: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Rutile structure is known to be thermodynamically most stable amongst these three and both anatase and brookite can be transformed to rutile by thermal or even by mechanical methods. However, such transformation temperature varies with the variation of methods of preparation as well as with the presence of impurities in it (Serpone *et al* 1988). Anatase to rutile transformation involves a collapse (Shannon and Pask 1964) of relatively open anatase structure by about 8%. It is, therefore, suggested, that the usual reaction

conditions that removes oxygen ions from anatase structure should facilitate the transformation, conversely the condition that reduces the number of oxygen vacancies or which introduces impurities in the interstitials should inhibit the transformation.

It is interesting to see also how polymorphous titania behaves in the presence of AlPO_4 .

2. Results and discussion

X-ray diffraction spectra of all the TiO_2 contaminated aluminium phosphate of various treatment temperatures (500–1150°C) show prominent peaks at $d = 4.33 \text{ \AA}$, 4.10 \AA and 3.82 \AA which are the characteristics of a tridymite-like structure (Sato 1964; Florke 1967). No change excepting sharpening of these lines and slight variation of their relative intensities was observed with the increase of temperature from 500°C up to 1150°C. However, the XRD of pure aluminium phosphate of identical treatment temperatures exhibit varied characteristics of diffraction peaks showing the presence of different or a mixture of different phases at different temperatures. Thus it is evident from the observed data that in the presence of titania, aluminium phosphate initiates crystallization 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 (Debnath 1991). The phase was found to be stable even up to 1150°C which was in sharp contrast with the normal behaviour of pure AlPO_4 . Long before 1150°C, e.g. at 1050°C aluminium phosphate is expected to transform into a cristobalite phase (Florke 1967). The observed results thus show that the presence of titania in such system not only forces aluminium 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 AlPO_4 phase grown in this process a high resolution diffraction spectrum of the species in the region $2\theta = 15\text{--}80^\circ$ was recorded (figures 1a and b) and the d -values of the observed lines were fed into an automatic indexation program. It is seen from the calculated d -spacings that the data are consistent with orthorhombic unit cell with $a = 9.638 \pm 0.0019$, $b = 8.664 \pm 0.0017$ and $c = 18.280 \pm 0.0036 \text{ \AA}$ and $V = 1526.446 \pm 1.100 \text{ \AA}^3$ (Debnath and Chaudhuri 1992).

A comparison of these parameters with those of various modifications of silica shows that the AlPO_4 -phase that grows in the presence of TiO_2 has parallel physical properties to those of γ -tridymite form of silica (Bereznoi 1960; Sato 1964).

The X-ray diffraction patterns of titania in such system for samples of different treatment-temperatures were also recorded and the fraction of rutile calculated by using the method of Spurr and Myers (1957) was plotted as a function of temperature in figure 2. It is discernible from the plot that the anatase \rightarrow rutile transformation begins here only after 900°C although the same process in the case of pure titania prepared from the same source and by the same method initiates just after 500°C (figure 2). The anatase structure of TiO_2 thus becomes stable in the presence of AlPO_4 (Debnath and Chaudhuri 1992).

To understand the mechanism of this mutual phase stabilization effect we studied the Raman spectra of titania in the system. However, the Raman spectrum of only rutile phase was found to be more informative. Such a spectrum is shown in figure 3 along with that of pure rutile. The spectrum of rutile in contact with AlPO_4 exhibits bands at 609 cm^{-1} , 450 cm^{-1} , 230 cm^{-1} and 147 cm^{-1} . From earlier studies (Balachandran and

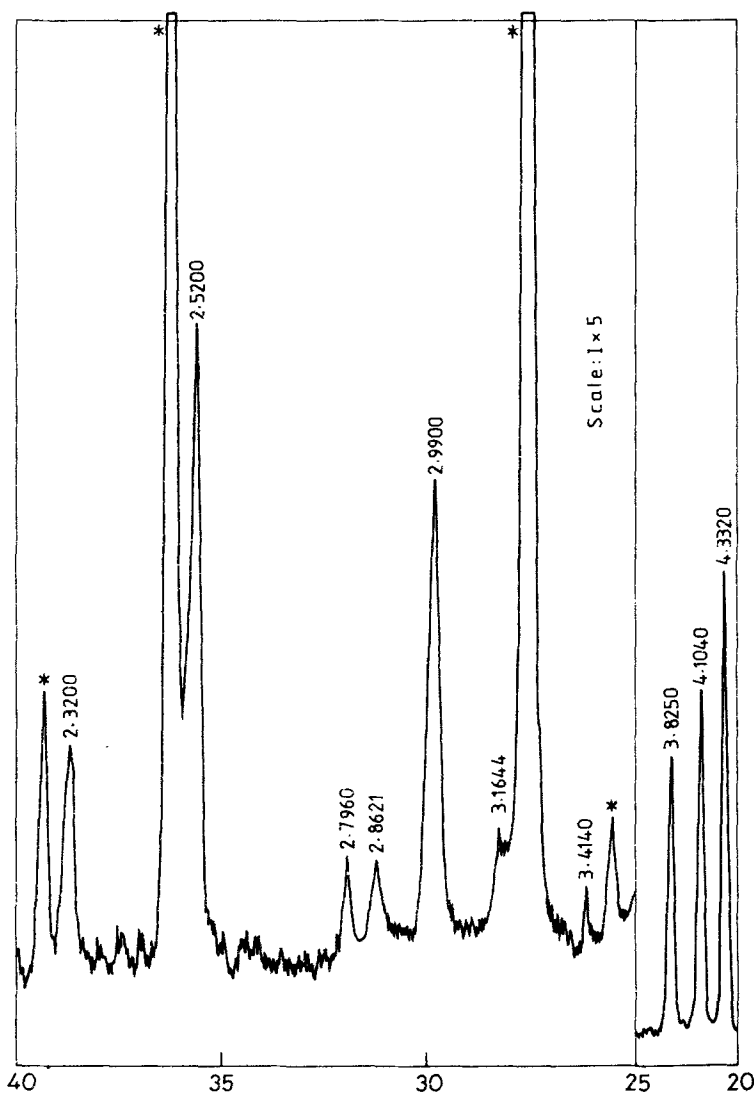


Figure 1a. Highly resolved X-ray diffraction spectrum of tridymite AlPO_4 grown in the presence of TiO_2 in the 2θ range $20\text{--}40^\circ$. Star indicates TiO_2 lines.

Error 1982; Babovich and Tsenter 1987) the 609 cm^{-1} band can be easily identified as the A_{1g} mode, the 450 cm^{-1} band as the E_g mode, and the weak sharp band at 147 cm^{-1} as the B_{1g} mode, while the broad band around 230 cm^{-1} may be considered as a disordered induced Raman effect. A comparative study of this spectrum with that of the pure rutile shows the following distinctive features:

(i) Although the temperature of both the spectra is the same (300 K), the bands (specially E_g and A_{1g}) in the $\text{AlPO}_4\text{-TiO}_2$ -spectrum occur with narrower widths than those of the corresponding bands of pure rutile. In the case of pure rutile, FWHM (full width at half maximum) of A_{1g} and E_g modes are $\sim 48\text{ cm}^{-1}$ and 46.5 cm^{-1}

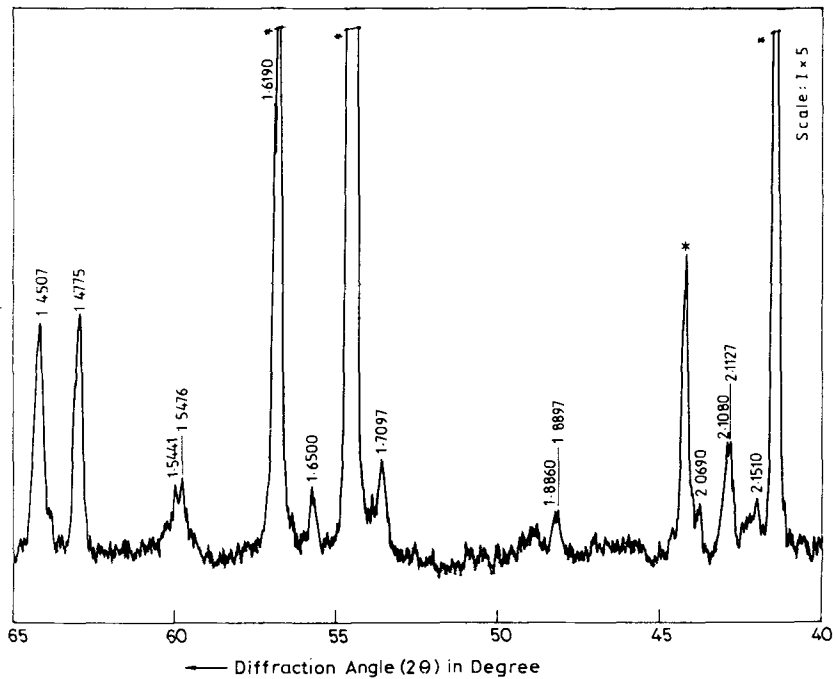


Figure 1b. Highly resolved X-ray diffraction spectrum of tridymite AlPO_4 grown in the presence of TiO_2 in the 2θ range $40\text{--}65^\circ$. Star indicates TiO_2 lines.

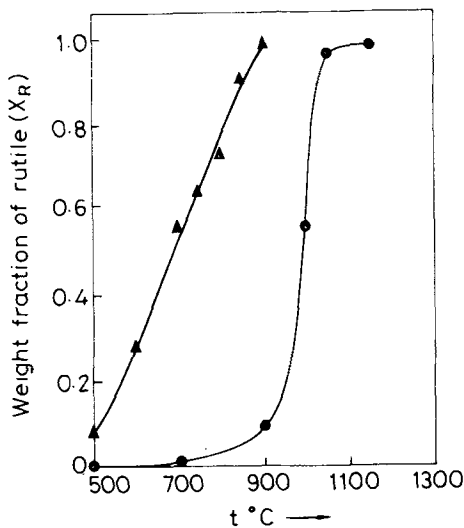


Figure 2. Weight fraction of rutile as a function of treatment temperatures corresponding to different titania systems: $\blacktriangle\blacktriangle\blacktriangle$, pure titania; $\bullet\bullet\bullet$, $\text{AlPO}_4\text{--TiO}_2$ system ($C_{\text{TiO}_2} \approx 16.04\text{ wt}\%$).

respectively while those in the case of $\text{AlPO}_4\text{--TiO}_2$ system they are found to be 45 cm^{-1} and 40.5 cm^{-1} .

(ii) The intensity ratio of anharmonicity mode (230 cm^{-1}) to E_g mode decreases in the spectrum as one goes from pure system to $\text{AlPO}_4\text{--TiO}_2$ system (0.38 to 0.23).

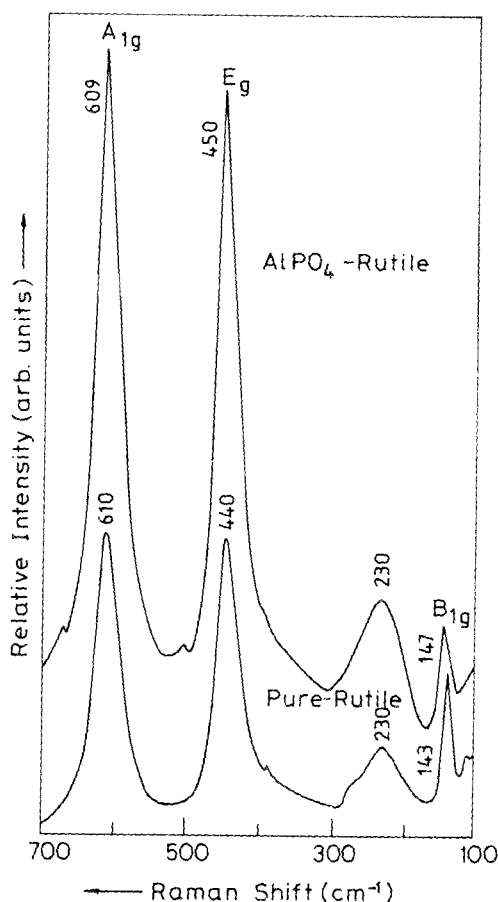


Figure 3. Raman spectrum of rutile in $\text{AlPO}_4\text{-TiO}_2$ system (obtained at 1150°C) along with that of pure rutile obtained from the same source at 900°C .

In a recent study Betsch *et al* (1991) showed that at any particular temperature stoichiometric rutile crystal markedly differs in Raman behaviour from that of its oxygen-deficient counterpart. They argued that structural defect in a rutile crystal may arise due to two reasons: (a) dynamic disordering of the Ti^{+4} ion i.e. due to off-centre displacement of Ti^{+4} ion which can be minimized by lowering the temperature of the crystal and (b) randomizing the effect of oxygen vacancies. Thus, at any particular temperature, the possibility of dynamic disordering of Ti^{+4} remaining the same, the stoichiometric crystal is expected to behave more harmonic in its vibrations than the vibronic behaviour of an oxygen-deficient crystal; in other words the intensity of the anharmonicity band (230 cm^{-1}) as well as the disordered-induced broadening of the bands will be less pronounced in a stoichiometric crystal compared to those in a nonstoichiometric one. Thus, the observed spectral differences between the Raman features of the pure rutile and of the rutile prepared in contact with AlPO_4 in the present case show a parallelism to the spectral differences observed (Betsch *et al* 1991) in the case of a nonstoichiometric and a stoichiometric rutile crystal. It is logical to argue, therefore, that the rutile generated on the surface of AlPO_4 has much more Ti:O stoichiometry than that of pure rutile prepared from the same source following the

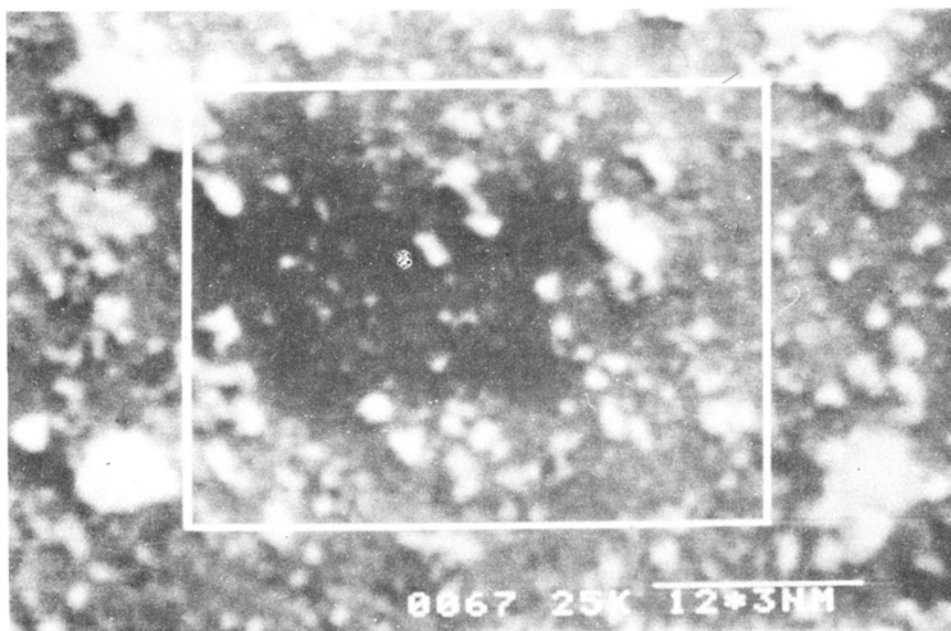


Figure 4. Electron micrograph showing highly dispersed anatase titania on the surface of AlPO_4 . (Sample heat treated at 700°C for 1 h)

same method. The result stated above seems to be quite obvious if we consider the following reaction mechanism.

During the process of ignition of titanium isopropoxide impregnated aluminium phosphate, TiO_2 molecules deficient in oxygen are generated. As a consequence, when such amorphous titania crystallizes to anatase it will have the tendency to incorporate oxygen into its structure taking oxygen from the nearest available source. The aluminium phosphate being slightly ionic, its molecules in the contact layer can contribute oxygen to the vacancies of contiguous anatase crystals by extending the oxygen of P-O deep into the structure of the latter. The net result is generation of anatase crystals having better Ti:O stoichiometry, those remain anchored/bound on the surface of AlPO_4 through P-O...Ti type linkage. The electron micrograph of such samples of treatment temperature below 900°C in fact, shows the presence of widely dispersed anatase crystals embedded on the surface of AlPO_4 (figure 4). Such an anatase crystal having a relatively larger stuffed structure is expected to transform into rutile at much higher temperature compared to the oxygen-deficient crystals obtained in the case of pure system and hence the product obtained on transforming such anatase crystals into rutile is also expected to show better Ti:O stoichiometry.

Under such condition, however, the possibility of existence of some sort of restriction in the mobility of molecules of AlPO_4 in the contact layer is also expected and aluminium phosphate being a relatively slow crystallizing system compared to TiO_2 , crystallization of its contact layer in the mixture should occur at a later stage under the influence of surface bound anatase crystal. This favours 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 material and hence the whole aluminium phosphate crystallizes with the same structure.

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