

## High pressure study of phase transitions in $\alpha$ -FePO<sub>4</sub>

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**Abstract.** High pressure behaviour of FePO<sub>4</sub> in berlinite form has been investigated up to 10 GPa using vibrational Raman spectroscopy and energy dispersive x-ray diffraction. Combination of these techniques along with studies on pressure quenched samples reveal structural transitions in this material from its room pressure trigonal phase to a disordered and a crystalline phase near  $3 \pm 0.5$  GPa. The latter is the Cmcm phase which is the equilibrium structure at high pressures. These high pressure phases do not revert back to its initial structure after release of pressure. Irreversibility of these transformations indicates that FeO<sub>4</sub> tetrahedra do not regain their initial coordination. These high pressure transitions can be rationalized in terms of the three level free energy diagram for such systems.

**Keywords.**  $\alpha$ -FePO<sub>4</sub>; phase transition; x-ray diffraction; Raman scattering.

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### 1. Introduction

High pressure behaviour of materials having structures based on tetrahedral framework are of interest because of their relevance to the geophysical problems. These structures display a large number of phase transitions depending on the relative compressibility of the constituent tetrahedra and the nature of inter-tetrahedral linkages [1]. Also the tetrahedral framework does not favour close packing and therefore the effect of pressure in these structures provides an insight into relative importance of close packing and steric hindrances [2]. Prominent among this class of materials, which have attracted much attention of a large number of investigators are  $\alpha$ -quartz (SiO<sub>2</sub>),  $\alpha$ -AlPO<sub>4</sub> and  $\alpha$ -GeO<sub>2</sub>. Of these  $\alpha$ -quartz is perhaps the most investigated material [3, 4] and is known to transform irreversibly to an amorphous phase [5] under a pressure of  $\sim 30$  GPa at room temperature. Both  $\alpha$ -GeO<sub>2</sub> [6] and  $\alpha$ -AlPO<sub>4</sub> [7–10] show reversible or irreversible amorphization depending on the state of stress. Recent studies have shown that  $\alpha$ -quartz and  $\alpha$ -AlPO<sub>4</sub> undergo a precursor crystal to crystal phase transition [5, 10] prior to amorphization. Molecular dynamical simulations on  $\alpha$ -AlPO<sub>4</sub> indicate that though energetics favour a transition to a Cmcm phase, kinetics favour transformation to an amorphous phase at  $\sim 35$  GPa. In the light of these investigations, it would be interesting to study other compounds belonging to the same structural family with different cations. This would provide an opportunity to understand the effect of cation-O interaction on the above mentioned phase transitions. In this

connection  $\alpha$ -FePO<sub>4</sub> which is isostructural to quartz family of compounds would be of interest.

The difference in the cation–O interactions manifests itself even in the structural parameters, such as cation–O–cation angle, at ambient conditions. Earlier studies on  $\alpha$ -SiO<sub>2</sub> and  $\alpha$ -AlPO<sub>4</sub> indicate that phase transformation as well as amorphization is related to a decrease in the non-bonded O–O distances due to the reduction of  $T$ –O– $T$  angle ( $T = \text{Si, Al, Fe, P, etc.}$ ) (see ref. [4] and references therein.) Therefore one would expect that if the initial  $T$ –O– $T$  angle is smaller then these phase transformations will take place at lower pressures. These angles are,  $T$ –O(1)– $T = 144^\circ, 143.1^\circ$  and  $139.2^\circ$  and  $T$ –O(2)– $T = 144^\circ, 142^\circ$ , and  $137.5^\circ$  for  $\alpha$ -SiO<sub>2</sub>,  $\alpha$ -AlPO<sub>4</sub> and  $\alpha$ -FePO<sub>4</sub> respectively [9]. This suggests that  $\alpha$ -FePO<sub>4</sub> will undergo pressure induced phase transformation at lower pressures.

## 2. Experimental details

The berlinite form of FePO<sub>4</sub> belongs to the space group P3<sub>1</sub>21 with three formula units per unit cell. The cell constants of the sample used [11] are,  $a = 5.035 \text{ \AA}$  and  $c = 11.245 \text{ \AA}$  which compare well with the results of Ng *et al* [12] ( $a = 5.036 \text{ \AA}$  and  $c = 11.255 \text{ \AA}$ ). The condensed polycrystallites were used for Raman studies and these were powdered for x-ray diffraction studies. High pressure experiments were performed using fluorescence free Raman quality diamonds (whose second order Raman mode has a signal to noise ratio of  $> 2$ ) with culet sizes of  $\sim 500 \mu$  set in a Syassen–Holzapfel type cell. The sample was loaded along with a ruby chip of size 10–20  $\mu$  in a 200  $\mu$  hole drilled in a steel gasket, preindented to a thickness of  $\sim 100 \mu$ . Methanol–ethanol mixture in the ratio of 4 : 1 was used as pressure transmitting medium, and care was taken to avoid bridging of the sample between the diamond tips. The pressure was measured using the well-known ruby fluorescence technique.

High pressure Raman scattering experiments were carried out with a spectrometer that uses a single-stage double-pass 500 mm Chromex scanning monochromator and a super notch filter from Kaiser optics. This filter permits the observation of Raman modes higher than  $100 \text{ cm}^{-1}$ . We used the 514.5 nm line of a 150 mw Ar-ion laser operated at half the power as the excitation source and some of its plasma lines for calibration purpose. The back scattering geometry was used to obtain Raman spectra. A Nikkor 50 mm lens was employed to collect the scattered radiation and a photomultiplier tube and a computer controlled data acquisition system [13] to record Raman peaks.

X-ray diffraction studies on  $\alpha$ -FePO<sub>4</sub> were carried out using the energy dispersive x-ray diffraction technique that uses a conical slit of cone angle  $5.1^\circ$  and width 200  $\mu$  and a high purity germanium detector [14]. The x-rays from a rotating anode x-ray generator with a molybdenum target, operated at 60 kV and a power of 2.4 kW, were collimated to a size of 200  $\mu$ .

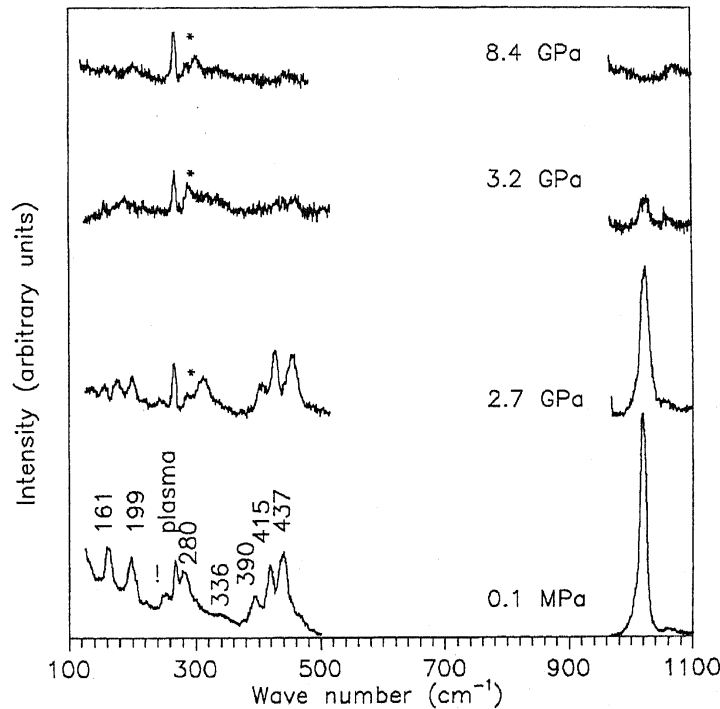
## 3. Results and discussion

As FePO<sub>4</sub> in berlinite form is isostructural to  $\alpha$ -AlPO<sub>4</sub>, its Raman lines can be compared with that of  $\alpha$ -AlPO<sub>4</sub> [15] (see table 1). Raman spectra of  $\alpha$ -FePO<sub>4</sub> at four different

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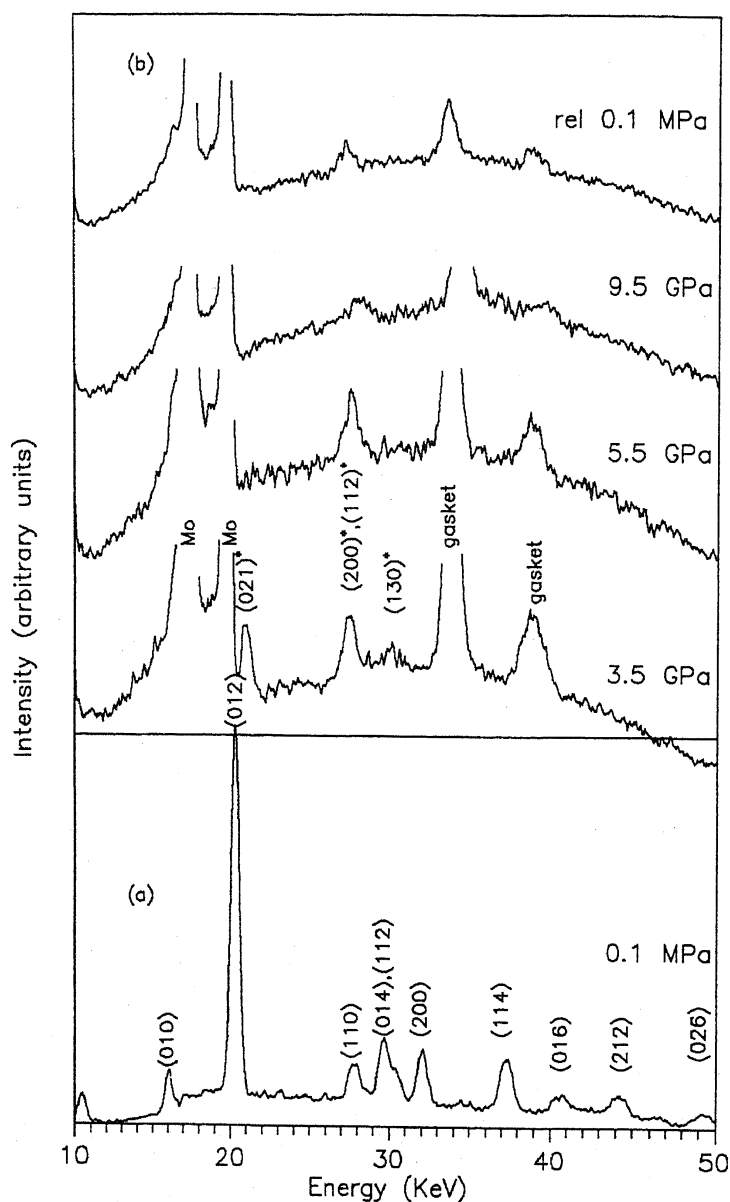
**Table 1.** Comparison of Raman modes of  $\alpha$ -FePO<sub>4</sub> and  $\alpha$ -AlPO<sub>4</sub>.

$\alpha$ -FePO <sub>4</sub>			$\alpha$ -AlPO <sub>4</sub>		
$\nu_i$		$d\nu_i/dP$	$\nu_i$		$d\nu_i/dP$
A <sub>1</sub> modes			A <sub>1</sub> modes		
199		0.1	160		0.0
280		1.5	216		2.6
436		0.6	460		1
1018		0.3	1110		-0.5
E modes			E modes		
161		0.65	116		0.8
336		—	372		-0.1
390		0.45	416		0.4
415		0.4	436		0.9



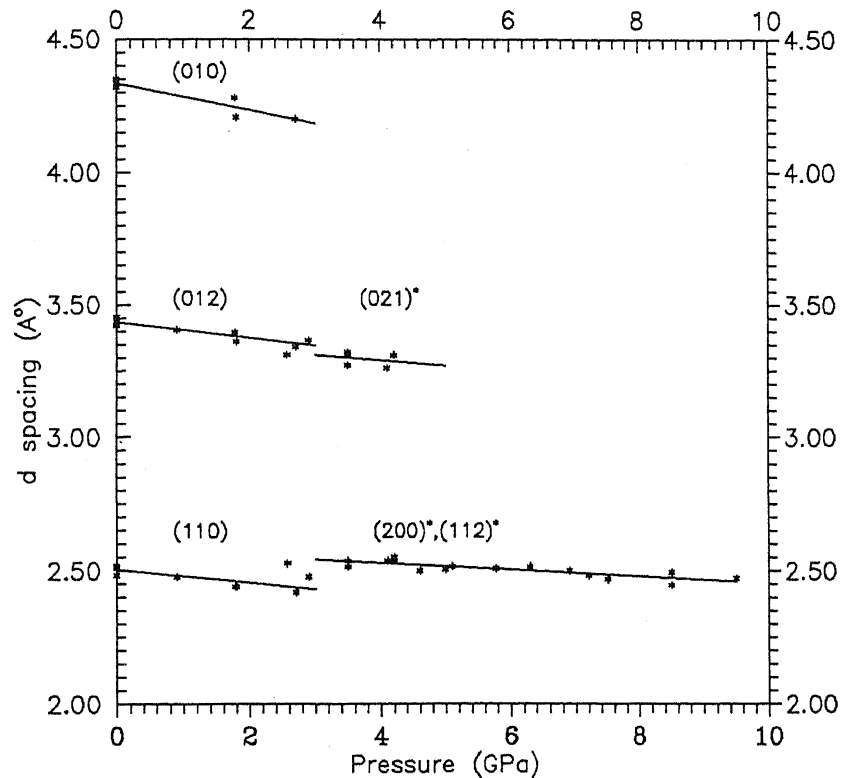
**Figure 1.** The Raman spectra of  $\alpha$ -FePO<sub>4</sub> under different pressures. \* indicates a weak, broad characteristic peak of our Raman system and ! indicates an unidentified peak.

pressures are shown in figure 1. Above  $3 \pm 0.5$  GPa the intensity of all the Raman modes decreases drastically and we observe a discontinuity in the A<sub>1</sub> type ( $199 \pm 1$  cm<sup>-1</sup>) and the E type ( $161 \pm 1$  cm<sup>-1</sup>) modes indicating a structural transition. Above 4 GPa all the Raman modes become very weak. In  $\alpha$ -AlPO<sub>4</sub> the results of Gillette *et al* [10] obtained under hydrostatic conditions show the appearance of some new weak broad bands around 14 GPa in the region of 300–500 cm<sup>-1</sup> accompanied by a simultaneous broadening of the original peaks. This has been interpreted as an indication of a phase



**Figure 2.** X-ray diffraction pattern of  $\alpha$ -FePO<sub>4</sub>; (a) at 0.1 MPa outside the DAC (target: tungsten); (b) in a DAC under different pressures; (target: molybdenum) Peaks marked by \* are indexed on the Cmc<sub>2</sub>m phase. Mo represents molybdenum characteristic peaks.

transformation to a new structure which is a disordered phase. In the case of  $\alpha$ -FePO<sub>4</sub> under both hydrostatic and nonhydrostatic conditions we observe weak broad bands in the region of 100–500 cm<sup>-1</sup> across the transition pressure. The behaviour of A<sub>1</sub> mode at 1018 cm<sup>-1</sup> is similar to the analogous mode in  $\alpha$ -AlPO<sub>4</sub>, which shows substantial loss of intensity across the transition pressure and is comparable to its initial weak shoulder peaks above this pressure. This suggests that the high pressure phase of  $\alpha$ -FePO<sub>4</sub> may also be a disordered crystalline phase where both P–O and Fe–O sublattices are disordered.



**Figure 3.** The  $d$  values of first three Bragg lines of berlinite phase as a function of pressure. Also shown are lines (\*) of the Cmcm phase-data compiled from six different experiments. The spread in  $d$  values at room pressure gives the error in the measurements.

Figure 2 shows the x-ray diffraction pattern of  $\alpha$ -FePO<sub>4</sub> at different pressures. The diffraction pattern of the recovered sample shows that it does not revert back to the berlinite phase, in contrast to memory glass behaviour observed in  $\alpha$ -AlPO<sub>4</sub>. The  $d$  values of the Bragg peaks decrease with pressure up to  $3 \pm 0.5$  GPa (see figure 3). At this pressure the strong (012) peak disappears and a weaker peak emerges close to it. Further, a new broad line appears near the original (110) peak. These changes indicate a structural phase transition. The experiments were repeated several times and similar behaviour was observed. The new peak close to the initial (110) line persists beyond 9.5 GPa (see figures 2 and 3). Because of the limited diffraction data above 3 GPa we could not index the Bragg peaks directly and determine the symmetry of the lattice. However, concurrent studies of this compound using static compression and shock waves [16] gave us a clue. The material recovered from shock experiments (up to 5 GPa) showed the presence of both amorphous and the Cmcm phase. Also, we were able to confirm the above results by carrying out an x-ray diffraction study of pressure quenched samples obtained by compressing the material between tungsten carbide anvils to a pressure of  $\sim 3$  GPa. The colour of the recovered sample was pale yellow while the normal colour of the original material at ambient pressure was creamish white. The Raman spectrum of this pressure quenched material is similar to that of the sample obtained at 3.2 GPa in the diamond anvil cell (see figures 4 and 1). When pressure quenched from a higher pressure  $> 5$  GPa,

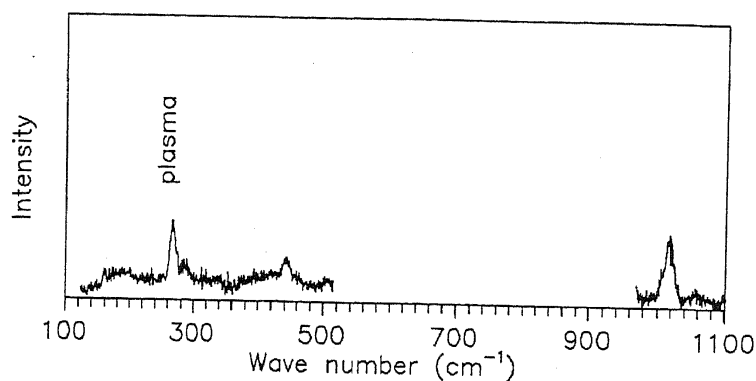


Figure 4. Raman spectrum of pressure quenched sample.

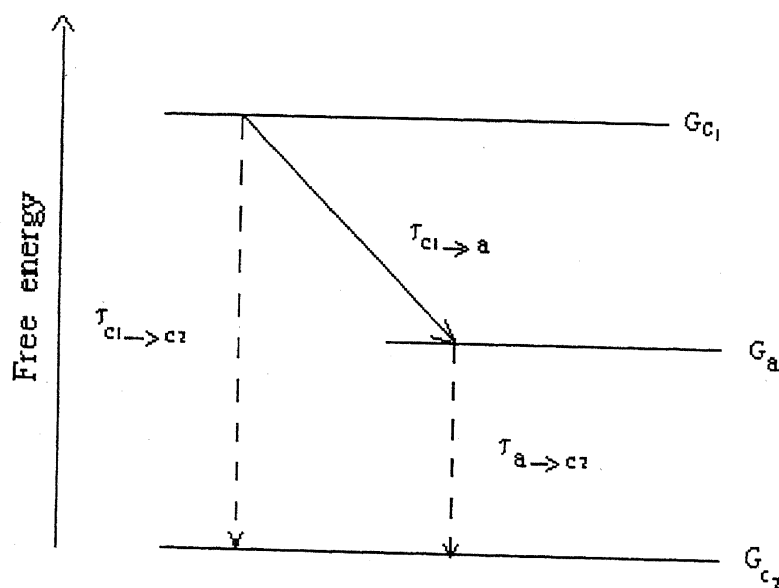


Figure 5. A schematic three level diagram for  $c \rightarrow a$  transformations.

the samples were brownish black in colour and its Raman spectrum had a very high background, which we believe is due to amorphization. The x-ray diffraction pattern of the shock recovered material shows a hump at the expected  $2\theta$  region [16] corresponding to the strongest peaks of the Cmcm phase. Following this lead we assign the diffraction peak observed above 3 GPa (shown in figure 3) at  $3.1 \text{ \AA}$  as  $(021)^*$  and the broad peak at  $2.55 \text{ \AA}$  as a doublet  $(200)^*$  and  $(112)^*$  and at  $2.32 \text{ \AA}$  as  $(130)^*$  which are the strongest peaks of the Cmcm phase.

As the Cmcm phase is the equilibrium phase under pressure for this family of compounds [17] we invoke the three level free energy diagram (see figure 5) to explain the behaviour. Accordingly the compressed berlinite phase ( $c_1$ ) energetically prefers to transform to the Cmcm phase ( $c_2$ ) above 3 GPa, but the kinetics impedes this. Instead a transformation to the amorphous ( $a$ ) phase occurs, which then transforms to the equilibrium phase. This behaviour is similar to that of quartz  $\text{SiO}_2$ , where the  $c \rightarrow a$  transition occurs at 21 GPa and at 70 GPa traces of the equilibrium stishovite phase are detected [1]. The fact that both the transitions occur in a small pressure interval suggests

that the energy barriers for  $c_1 \rightarrow a$  or  $a \rightarrow c_2$  are of similar magnitude. Also we cannot rule out the direct transformation of  $c_1 \rightarrow c_2$ .

Our experimental data show that  $c/a$  ratio of  $\alpha$ -FePO<sub>4</sub> increases to a value of  $\sim 2.3$  around 2 GPa, before it undergoes the phase transition. This feature is very similar to what is observed in this class of materials [1]. As anticipated from structural crystal chemistry, the pressure at which the compounds of this family exhibit a phase transition is correlated with the ambient values of  $T-O-T$  angle, referred to in the introduction.

In most of these compounds, it has been shown, through IR absorption measurements as well as molecular dynamics calculations, that crystal to amorphous ( $c \rightarrow a$ ) transformations are closely related to coordination increase as a function of pressure. In the present case the presence of Cmcm phase in the pressure released samples indicates that Fe atoms which is six coordinated to oxygens in the Cmcm phase do not regain their initial four coordination to neighbouring oxygens.

## References

- [1] R M Hazen and L W Finger, *Phase Trans.* **1**, 1 (1979); *Am. Sci.* **72**, 143 (1984); *Sci. Am.* **252**, 110 (1985)  
W G Moffat, G W Pearsall and J Wulff, *The structure and properties of materials* (Wiley Eastern Limited, New Delhi, 1980) vol. 1, Ch. 5
- [2] S K Sikka, Surinder M Sharma and R Chidambaram, *High pressure science and technology* edited by S C Schmidt, J W Shaner, G A Samara and M Ross (AIP Press, 1994) 213
- [3] R J Hemley, C T Prewitt, K J Kingma, *Silica, reviews in mineralogy* edited by P J Heaney, C T Prewitt and G V Gibbs (Minerological Society of America, Washington, DC, 1994) vol. 29, p. 241
- [4] Surinder M Sharma and S K Sikka, *Progress in materials science* **40**, 1-77 (1996) and references therein
- [5] K J Kingma, R J Hemley, H K Mao and D R Veblen, *Phys. Rev. Lett.* **70**, 3927 (1993)
- [6] M S Somayazulu, Nandini Garg, Surinder M Sharma and S K Sikka, *Pramana - J. Phys.* **43**, 1 (1994)
- [7] H Sankaran, Surinder M Sharma, S K Sikka and R Chidambaram, *Pramana - J. Phys.* **35**, 177 (1990)
- [8] M B Krugger and R Jeanloz, *Science* **249**, 647 (1990)
- [9] P Cordier, J C Doukhan and J Peyronneau, *Phys. Chem. Miner.* **21**, 133 (1994)
- [10] P Gillet, J Badro, B Varrel and P F Macmillan, *Phys. Rev.* **B51**, 11262 (1995)
- [11] M M Gadgil and S K Kulshreshtha, *J. Solid. State. Chem.* **111**, 357 (1994)
- [12] H N Ng and C Calvo, *J. Chem.* **53**, 2064 (1975)
- [13] S N Momin and R Siva Bhaskar (unpublished)
- [14] S K Sikka, H Sankaran, S M Sharma, V Vijaykumar, B K Godwal and R Chidambaram, *Indian J. Pure Appl. Phys.* **27**, 47 (1989)
- [15] A Jayaraman, D L Wood and R G Maines, *Phys. Rev.* **B35**, 8316 (1987)
- [16] K D Joshi, N Suresh, G Jyoti, S K Kulshreshtha, S C Gupta and S K Sikka (under publication in Shock Waves)  
G Kh Rozenberg, M P Pasternak, A P Milner and K E Brister, abstracts, ICCMHP-India (1996)
- [17] S M Sharma and S K Sikka, *Phys. Rev. Lett.* **74**, 3301 (1995)