

Pressure-Induced Concurrent Transformation to an Amorphous and Crystalline Phase in Berlinite-Type FePO_4

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X-ray diffraction, Raman scattering, and Mössbauer spectroscopy provide a diverse description of the high pressure behavior of berlinite-type FePO_4 . At a pressure of 2.5(5) GPa, a transformation to a coexisting new crystalline (*chp*) and amorphous (*ahp*) phase is observed with about equal abundance. The *chp* phase is identified as a VCrO_4 type, where Fe^{II} and P^{V} ions, respectively, are sixfold and fourfold coordinated. In the 6–25 GPa range and after decompression, the relative abundance of the *chp* and *ahp* phases remains unchanged. These phenomena of concurrent amorphous and crystalline transformations at low hydrostatic pressure and stable abundance ratio over a large pressure range are unique in pressure-induced structural transformations of SiO_2 analogs. [S0031-9007(97)04705-4]

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Interest in high pressure phase transitions of silica (SiO_2) [1–3] has resulted in numerous studies aimed at simulating its various phases [4]. The most abundant phase at ambient pressure (P) and temperature (T) is the α -quartz modification. It is a corner-linked polyhedral (CLP) compound with trigonal structure, consisting of chains of SiO_4 tetrahedra forming spirals parallel to the c axis [5]. As it moves towards a denser, higher coordinated state under pressure, α -quartz transforms—possibly via an intermediate metastable polymorph [3]—to an amorphous phase near 20 GPa [1]. At 60 GPa an ordered sixfold coordinated crystalline phase is achieved [4]. Similar amorphization features were observed in the isostructural berlinite AlPO_4 (b - AlPO_4) at 15 GPa, but unlike silica the transformation is *reversible*, i.e., upon pressure release the crystalline state, as well as orientation, was retrieved at 5 GPa [6], a phenomenon described as *structural memory*. A similar result is obtained with b - AlAsO_4 , which amorphizes at 9 GPa [7]. Extensive theoretical studies [8], based on molecular dynamics and *first-principles* local density approximation calculations, have been performed to simulate, explain, and predict the microscopic nature and mechanism of P -induced disorder in the CLP compounds. Recent studies of b - AlPO_4 [9] implied that both of the P -driven coordination frustrations connected with the AlO_4 unit, i.e., the lack of full fourfold to sixfold coordination change of Al on the one hand and the preservation of the PO_4 unit on the other hand, lead to amorphization with pressure increase and also explain the structural memory upon decompression.

In this Letter we report a new phenomenon observed in the P -induced phase transition of a berlinite-type compound, b - FePO_4 , in which, at relatively low pressure (2–

3 GPa), a *simultaneous branching* to an amorphous and a new crystalline phase is observed. This is the first time that a concurrent emergence of an amorphous and crystalline phase is reported. This finding may serve to challenge existing models and concepts of P -induced amorphization and/or transformations of CLP compounds caused by a displacive mechanism.

The high- P structural behavior of FePO_4 was investigated using a combination of synchrotron x-ray diffraction (XRD), Raman spectroscopy (RS), and ^{57}Fe Mössbauer spectroscopy (MS). Polycrystalline FePO_4 was prepared in two ways: (i) $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ starting material was subjected to heat treatment for 48 h at 600 °C, and (ii) a stoichiometric mixture of Fe_2O_3 and $(\text{NH}_4)_2\text{HPO}_4$ was heated gradually to 900 °C. The sample for Mössbauer studies was made with 25% isotopically enriched $^{57}\text{Fe}_2\text{O}_3$. The samples were of berlinite-type single phase, as confirmed by XRD. Pressures up to 26 GPa were generated with diamond anvil cells (DAC) using argon for XRD and MS and a 4:1 mixture of methanol/ethanol for RS. Pressures were determined by the ruby luminescence method. Mössbauer measurements at various T and P were carried out using a top-loading cryostat and a $^{57}\text{Co}(\text{Rh})$ point source [10].

Angle-dispersive XRD patterns obtained with increasing pressure and after decompression to ambient P are shown in Fig. 1. Diffraction peaks corresponding to a new crystalline high- P phase (*chp*) first appear at $P \approx 2.5$ GPa, dominating the diffraction patterns at $P > 5$ GPa. The stability range of the *chp* phase extends to at least 26 GPa, as determined by additional energy-dispersive diffraction measurements. Upon decompression to $P = 0$, the *chp* phase continues to be the main crystalline component. The presence of an amorphous high- P phase (*ahp*) can be

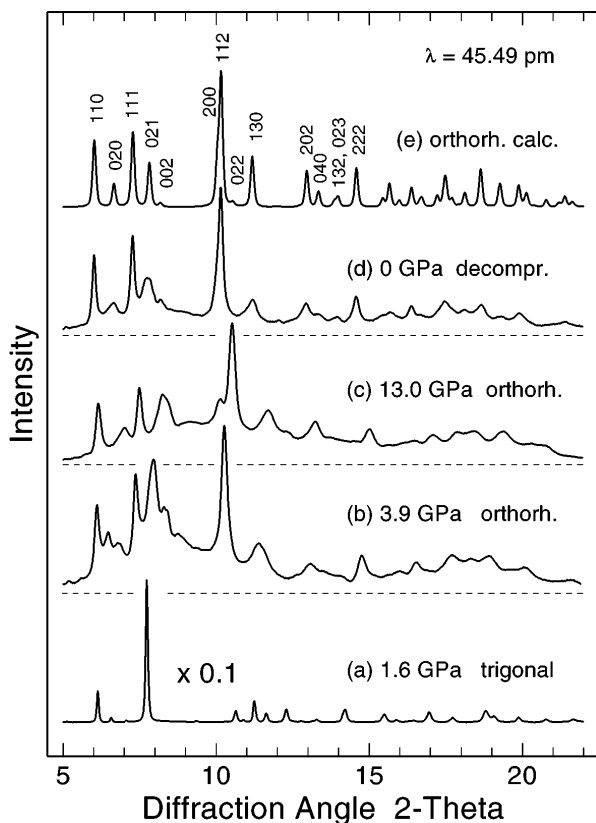


FIG. 1. Angle-dispersive x-ray diffraction patterns of FePO_4 at different pressures and after pressure release. (a) Trigonal berlinite-type phase at 1.6 GPa; (b)–(d) orthorhombic VCrO_4 -type phase at 3.9 GPa (phase transition almost completed), 13.0 GPa, and after decompression; (e) calculated pattern for the metastable orthorhombic phase at 0 GPa. In (a)–(d) the background scattering of the empty DAC (with gasket in place) has been subtracted, otherwise the intensities are represented as measured except for the indicated reduction factor of 10 in (a). The two broad humps in the backgrounds of patterns (b)–(d) are attributed to scattering from the amorphous component.

inferred from the broad features in the background (see Fig. 1). Note its absence at 1.6 GPa but its presence with the *chp* phase for increasing P and after decompression.

The diffraction pattern of the *chp* phase can be indexed in the orthorhombic system. The structure is assigned as VCrO_4 -type (space group $Cmcm$) in which the Fe^{3+} ions acquire a sixfold coordination. For comparison, a calculated diffraction pattern of the orthorhombic phase is also shown in Fig. 1. We note that Kinomura *et al.* [11] have earlier obtained a metastable VCrO_4 -type phase of FePO_4 , however, only after simultaneous application of 5 GPa pressure and a temperature of 900 °C. In our measurements the specific volume ($P = 0$) of the *chp* is 21.0(5)% smaller [12] than that of the trigonal modification. We also find an extremely large difference for the bulk moduli of the *clp* and *chp* phases (24 GPa and 96 GPa, respectively).

Figure 2 shows Raman spectra of FePO_4 measured at increasing pressures up to 18 GPa and after pressure release. The Raman modes of the berlinite-type phase (see

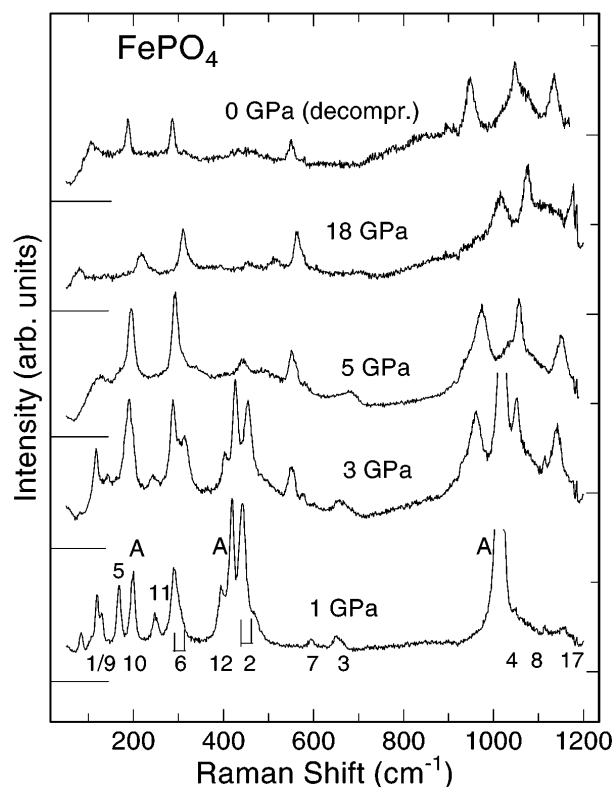


FIG. 2. Raman spectra of polycrystalline FePO_4 at different pressures up to 18 GPa and after pressure release. The horizontal lines indicate the base lines for the different spectra. The most prominent Raman line of the low pressure phase near 1015 cm^{-1} has been cut in intensity in order to show more clearly the weaker lines. A mode assignment is indicated for the spectrum at 1 GPa (see text).

spectrum at 1 GPa) are well separated into two groups, high frequency stretching modes above 900 cm^{-1} and mostly bending modes below 500 cm^{-1} . Based on the analysis of vibrational spectra of the related *b*- AlPO_4 [13], we assign the modes observed for *b*- FePO_4 as indicated in Fig. 2. The E_g modes are numbered according to Table II of Ref. [13]. Near 2.5 GPa, additional Raman modes appear, indicating the onset of the structural transition. The very intense A_g mode of the low- P berlinite-type phase (1015 cm^{-1} at $P = 0$) is not resolved anymore above 4.5 GPa.

For the *chp* phase, nine Raman lines can be clearly seen. A detailed discussion of these modes and a comparison with vibrational spectra of related VCrO_4 -type compounds [14] will be given elsewhere. The features important in the present context are (1) the Raman lines of *b*- FePO_4 between 900 and 1200 cm^{-1} involve stretching vibrations of the PO_4 tetrahedra. The high- P phase also shows a group of strong Raman lines in this frequency range, indicating that the P^{V} ions retain their fourfold coordination in the *chp* modification. This is consistent with the proposed VCrO_4 -type structure with P^{V} ions in distorted tetrahedral coordination (C_{2v} site symmetry). (2) Two broadbands centered at about 300 cm^{-1} and

1100 cm^{-1} are observed and attributed to an amorphous component. Upon decompression, both the *chp* and the *ahp* phases are evident from the corresponding spectrum in Fig. 2.

The presence and the classification of the various phases of FePO_4 are unambiguously distinguishable, and their relative abundance can be quantified by ^{57}Fe MS spectroscopy, based on the well-established Néel temperatures (T_N) and hyperfine interaction parameters of the low- and high- P phases. The *b*- FePO_4 is an antiferromagnet below $T_N = 24\text{ K}$, and at 4.2 K the MS spectrum displays a magnetic splitting with a small quadrupole shift [15]. The VCrO_4 -type FePO_4 was synthesized by Battle *et al.* [16] by the high- P -high- T process described earlier [11]. The authors derived its magnetic properties ($T_N = 60\text{ K}$) and hyperfine interaction parameters from ^{57}Fe MS studies.

Typical MS spectra recorded at $T = 35\text{ K}$, a temperature at which the *b*- FePO_4 is still paramagnetic and the *chp* phase is antiferromagnetic, are shown in Fig. 3. Whereas the low- P regime reveals a pure quadrupole splitting doublet, with increasing P to 2.5 GPa , a well-defined magnetic splitting is detected (dashed curve) which, based on its hyperfine parameters and T_N [16], we assign to the *chp*- FePO_4 . This component is superimposed on a very broad absorption line (dotted curve) and a quadrupole-split (QS) doublet. The broad line is a manifestation of a disordered spin arrangement, on an atomic scale, arising from a wide distribution of exchange and superexchange interactions. We assign it to the amorphous component. The close values of T_N deduced from T -dependent measurements suggest that the *ahp*- FePO_4 is more closely related to the *chp* than the *clp* phase. We note that identical values of T_N of P -induced amorphous and crystalline antiferromagnets were also found in Fe_2SiO_4 (fayalite) [17].

The abundance of the *ahp* and *chp* components increase further to about 7 GPa (see Fig. 3), then to the highest pressure measured, 25 GPa , no significant changes are observed anymore in the MS spectra. The presence of a QS doublet component to the highest pressure and upon decompression is attributed to remnants (13% abundance) of the low- P *b*- FePO_4 phase coexisting with the high- P phases. The correspondence between the *b*- FePO_4 and the high- P QS component is based on both the hyperfine parameters and T_N , which were found to be identical with those of *b*- FePO_4 [see Fig. 3(d)]. No remnant of this phase could be unambiguously identified in XRD and RS spectra. We can not reject the possibility that this phase contributes a small fraction to the total noncrystalline diffraction. We suggest that chains of corner-linked polyhedra clusters with sizes in the range of 10 nm are still present in the high- P regime, coexisting with the higher coordination amorphous and crystalline FePO_4 of macroscopic scale. The sample decompressed at 300 K shows no recovery to *b*- FePO_4 . Only upon heating to $700\text{ }^\circ\text{C}$ is the crystalline *b*- FePO_4 fully recovered.

The P dependence of the abundances n_i of the three phase components were determined from the relative areas

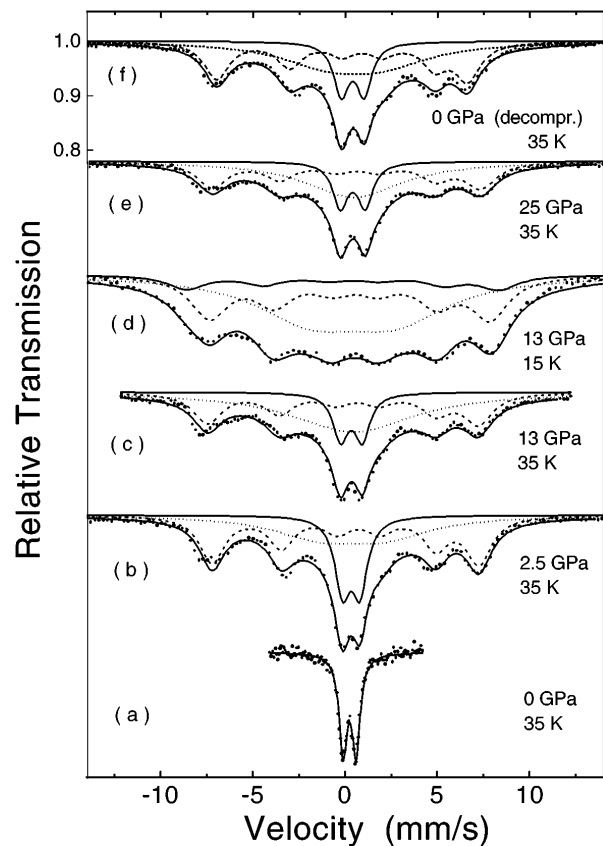


FIG. 3. Mössbauer spectra of FePO_4 recorded at several pressures: (a) Typical absorption spectrum of paramagnetic berlinite-type $^{57}\text{FePO}_4$ characterized by its quadrupole doublet. (b),(c),(e) Spectra recorded at various pressures at 35 K . The fitted solid line through the experimental points is a convolution of three spectral components: a paramagnetic doublet (solid lines) arising from remnants of the *clp* phase, a magnetic sextet (dashed lines) arising from the *chp* phase, and a broad component arising from the *ahp* phase. (d) Spectrum recorded at 13 GPa and 15 K showing the magnetic splitting of the *clp* phase admixture. (f) Spectrum recorded after decompression from 25 GPa to ambient pressure.

A_i of their respective MS spectral components. For a thin absorber, A_i is proportional to $f_i \cdot n_i$ [18], where f_i is the recoil-free fraction of the i th component [19]. We find that at 7 GPa $n(\text{ahp} + \text{chp})$ and $n(\text{ahp})$ reach a value of $0.87(5)$ and $0.40(5)$, respectively, and retain those values to the highest pressure and after decompression.

One may wonder why the FePO_4 exhibits such a peculiar behavior under pressure. We may gain some insight from the recent high- P diffraction studies of GaPO_4 . Berlinite-type GaPO_4 undergoes a $c \rightarrow a$ phase transition near 9 GPa , retaining the amorphous state at decompression [20]. The α -cristobalite modification of GaPO_4 , also a CLP compound, shows a nonreversible $c \rightarrow c$ phase transition at about 16 GPa [21]. The new high- P phase belongs to the $Cmcm$ space group (as the *chp* of FePO_4) with Ga in sixfold coordination [21]. It looks like the high- P structural behavior of the Fe and Ga compounds are similar with regard to the occurrence of *ahp* and *chp*

components at the same pressure conditions. The key for this phenomenon can perhaps be found in the similarity of their ionic radii [22], which is also reflected in the very similar metal-oxygen bond lengths in the low- P phases. The radii of Al and Si are significantly smaller, going along with a stronger preference for low coordination. In InPO_4 the trivalent ion radius is the largest, and it crystallizes in the VCrO_4 -type structure at $P = 0$. Thus, $b\text{-FePO}_4$ is just a borderline case, ready to go to sixfold coordinated Fe at relatively low P . Nevertheless, even under the low- P conditions there is a kinetical hindrance of the $c \rightarrow c$ transition, resulting in partial amorphization. Increasing pressure to 25 GPa does not help to overcome the kinetical barriers. We emphasize that amorphization in FePO_4 occurs under fully hydrostatic pressure conditions. This is different from the high- P behavior of AlPO_4 : Raman studies indicate that nonhydrostatic stress is a major factor in driving the amorphization of berlinite upon compression [23].

In conclusion, among CLP oxides showing P -induced crystalline to amorphous phase transitions, berlinite-type FePO_4 exhibits a quite peculiar response at high pressure. Using a combination of experimental methods probing different length scales—XRD, RS, and MS—we have observed the *simultaneous* onset of disordered and high pressure crystalline phases near 2.5(5) GPa. In the *chp* phase, Fe becomes sixfold coordinated, which is also the predominant Fe coordination for the amorphous component. A small amount of Fe in fourfold coordination is retained up to at least 25 GPa. The coexisting crystalline and amorphous components show stable relative abundance to these pressures, and persist upon fully releasing the pressure at 300 K. We suggest that differences in the bonding characteristics between the trivalent metal and oxygen play a major role in determining the course of pressure-induced amorphization in berlinite-type compounds.

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