Pressure Induced Amorphization of Antiferromagnetic FePO_4 and $\text{Fe}(\text{OH})_2$ *G.Kh. Rozenberg¹, M.P. Pasternak¹, A.P. Milner¹, M. Amanowicz¹, R.D. Taylor²,
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X-ray diffraction studies were performed in $b\text{-FePO}_4$ and $\text{Fe}(\text{OH})_2$. In FePO_4 , at $P=2.5(5)$ GPa, a transformation to a coexisting new crystalline and amorphous phase is observed with about equal abundance. The crystalline phase is identified as VCrO_4 -type where Fe^{III} and Fe^{IV} ions, are six-fold and four-fold coordinated, respectively. The pressure cycle is hysteretic. The onset of pressure-induced amorphization in $\text{Fe}(\text{OH})_2$ is at ~ 1 GPa however is incomplete to the highest pressure ($P \sim 24$ GPa). Evidence exists that anisotropic, short-range-order is involved in the amorphization process. [X-ray diffraction, high pressure, amorphization, FePO_4 , $\text{Fe}(\text{OH})_2$]

1. Introduction.

One of the significant advances of the recent past is the documentation that glasses can be prepared entirely in the solid state, without quenching either from the liquid or the vapor phase. However, there has been only a single case that magnetic glasses have been prepared in such fashion, and this was the case of amorphous fayalite (Fe_2SiO_4) formed at $P > 40$ GPa [1]. In this paper we describe structural and magnetic properties of two antiferromagnetic Fe compounds: berlinite-type FePO_4 ($b\text{-FePO}_4$) and $\text{Fe}(\text{OH})_2$. Our reason for choosing these compounds is that in addition to the X-ray diffraction (XRD) method, which monitors bulk structural changes, we can also use Mössbauer Spectroscopy (MS) to characterize the local structure and bonding character around Fe and the magnetic properties of the amorphous phase. This paper stresses the high pressure XRD studies of both compounds. Results of MS study and description of magnetic properties are described in another paper published in this proceedings [2]

$b\text{-FePO}_4$ is a structural analogue of berlinite ($b\text{-AlPO}_4$) and α -quartz (SiO_2), which belong to *corner-linked polyhedral* (CLP) compounds consisting of chains of XO_4 tetrahedra forming spirals parallel to c-axis. At 20 GPa α -quartz transforms to an amorphous state, and only at 60 GPa is an ordered six-fold coordinated crystalline phase achieved [3]. Similar amorphization features were observed in $b\text{-AlPO}_4$ at 15 GPa, but unlike silica the transformation is reversible, i.e., upon pressure release the crystalline state is fully retrieved at 5 GPa [4], a phenomenon described as *structural memory*. Recent theoretical studies of $b\text{-AlPO}_4$ [5] implied that both the P-driven coordination frustration connected with the AlO_4 unit, i.e. the lack of full four- to six-fold coordination change of Al, and preservation of the PO_4 unit on the other hand, lead to amorphization with pressure increase and also explain the structural memory [4] after decompression.

We report a new phenomenon observed in the P-induced phase transition of $b\text{-FePO}_4$ 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 a new crystalline phase is reported. This finding serves to challenge existing models and

concepts of P-induced amorphization and/or transformations of CLP compounds caused by a displacive mechanism.

$\text{Fe}(\text{OH})_2$ is isostructural with $\text{Ca}(\text{OH})_2$, $\text{Co}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$, all having the trigonal structure ($P\bar{3}m1$), which is isostructural to CdI_2 with OH treated as a single anion [6–9]. These materials are composed of sheets of MeO_6 octahedra interacting through weak hydrogen bonds. The motivation for studying these hydroxides is that the amorphization involves shearing of the octahedral layers, a process apparently quite different from the mechanism of amorphization in the more open, 3-dimensional structures present in $b\text{-FePO}_4$. The hydroxides could therefore play an important role in clarifying some of the diversities in the instability mechanisms that lead to amorphization. Studies with $\text{Ca}(\text{OH})_2$ [7] showed that it undergoes pressure-induced amorphization attributed to frustration in both the O-H layers and in the Ca-OH bonding. This is not the case in the $\text{Co}(\text{OH})_2$ analogue where disorder at high pressure involves only the O-H sublattice [8]. In $\text{Mg}(\text{OH})_2$ the structural change is likely to involve displacement of the H atoms, but does not lead to amorphization of the O-H sublattice [9].

2. Results and discussion

FePO₄

Measurements were carried out with diamond anvil cells to pressures of 26 GPa. The polycrystalline samples were of berlinite-type single phase as confirmed by XRD. 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 pattern 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. The presence of an amorphous high-P phase, *ahp*, can be inferred from the broad features in the background (see Fig. 1) but is quantitatively measured by MS [2]. Note its absence at 1.6 GPa but its presence with the *chp* phase for increasing P and after decompression. Unlike AlPO_4 , the sample decompressed at 300 K shows no recovery to $b\text{-FePO}_4$. Only upon heating to 700 °C crystalline $b\text{-FePO}_4$ is fully recovered.

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 six-fold

coordination. For comparison, a calculated diffraction pattern of the orthorhombic phase is also shown in Fig. 1(e). We note that Kinomura et al. [10] have earlier obtained a metastable VCrO_4 -type phase of FePO_4 , however, only after simultaneous pressurizing to 5 GPa and heating to 900°C. In our measurements the specific volume ($P = 0$) of the *chp* phase is 21.0(5)% smaller than that of the trigonal modification. We also find an extremely large difference for the bulk moduli of the *clp* and *chp* phases from 24 to 96 GPa, respectively.

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, c, 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) to (d) the background scattering of the empty DAC has been subtracted, otherwise the intensities are as measured except for the indicated reduction factor of 10 in (a). The two broad humps in the background of patterns (b) to (d) are attributed to scattering from the amorphous component.

The presence and the classification of the various phases of FePO_4 are unambiguously distinguishable and their relative abundance A has been quantified by ^{57}Fe MS spectroscopy [2]. It was found that: (i) once the high-pressure phases are created $A(\text{ahp})$ and $A(\text{chp})$ remain equal to the highest pressure, (ii) the close values of Néel temperature (T_N) of *chp* and *ahp* phases suggest [2] 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 [1].

One may wonder why the FePO_4 exhibits such a peculiar behavior under pressure. We may gain some insight from recent high-P diffraction studies of GaPO_4 . Berlinite-type GaPO_4 undergoes a crystalline to amorphous transformation near 9 GPa, retaining the amorphous state at decompression [11]. The cristobalite modification of GaPO_4 , also a CLP compound, shows a nonreversible crystalline to crystalline ($c \rightarrow c'$) phase transformation at about 16 GPa [12]. The new high-P phase belongs to the $Cmcm$ space group similar to *chp* of FePO_4 , with Ga in six-fold coordination [13]. It appears that high-P structural behavior of the Fe and Ga compounds are similar with respect to the occurrence of *ahp* and *chp* components at the same pressure conditions. The key for this phenomenon perhaps can be found in the similarity of their ionic radii, which is also reflected in the very similar metal-oxygen bond length in the low-P phases. The radii of Al and Si are significantly smaller, in keeping 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*- FePO_4 is just a borderline case, ready to go to six-fold coordinated Fe at relatively low P . Nevertheless, even under the low-P conditions there is a kinetic hindrance of the $c \rightarrow c'$ transition, resulting in partial amorphization. Increasing pressure to 25 GPa does not overcome the kinetic barriers.

$\text{Fe}(\text{OH})_2$

$\text{Fe}(\text{OH})_2$ was prepared by precipitation from aqueous solutions of FeCl_2 with KOH in an argon atmosphere. High pressure X-ray diffraction in polycrystalline $\text{Fe}(\text{OH})_2$ attests to the substantial structural change with pressure increase. The diffraction patterns show that the trigonal structure is retained up to the highest pressure of 24.3 GPa (Fig. 2), but the peak intensities decrease continuously by factor of ~ 10 for the pressure range 1–24.3 GPa. The (001) peak is suppressed even more, about 40 times, going down abruptly at $P \sim 8(1)$ GPa (a few small intensity (hkl) peaks with $l \neq 0$ almost disappear at $P > 8$ GPa) [13]. This attests to the substantial anisotropy of the structural alteration along the c -axis.

The relative compression of the unit cell parameters changes significantly at ~ 10 GPa (P_c) (Fig. 3). Similar compression behavior has been documented for other hydroxides [8,9], with an initial extensive compression in the c -direction due to shortening of the hydrogen bonds between the layers of Me-O octahedra. In $\text{Co}(\text{OH})_2$ [8] and $\text{Mg}(\text{OH})_2$ [9] at pressure values very close to the P_c value for $\text{Fe}(\text{OH})_2$, this compression mechanism is saturated, and the structure becomes more isotropically compressible as the hydrogen ions are forced into disordered positions between the octahedra layers. The displacement of the hydrogen ions gives rise to the disordering of the O-H sublattice but does not lead in the above mentioned systems to a long-range disorder, namely, the Me-O sublattice retains its long-range order. This not the case in the $\text{Fe}(\text{OH})_2$ analogue where the significant change of diffraction peaks intensities with rising pressure suggests the Fe-O sublattice is also engaged into a disordering process. It can be assumed that in $\text{Fe}(\text{OH})_2$ at $P < P_c$ the steric strain is minimized by a reduction of the size of the crystallite. This can explain the suppression of diffraction peaks at low

pressure. At higher pressure a Fe-O sublattice short-range-order has to be involved in the amorphization process. The preliminary MS studies confirm this assumption implying the onset of a magnetic glass between 7–13 GPa. Note that for $\text{Ca}(\text{OH})_2$ [7] the amorphization process is rather sharp; for $\text{Fe}(\text{OH})_2$ it is sluggish and at the highest pressure (~24 GPa) the transformation is incomplete. Pressure hysteresis is observed upon decompression.

Fig. 2. Energy-dispersive x-ray diffraction patterns of $\text{Fe}(\text{OH})_2$ at different pressures. The trigonal CdI_2 type structure retains up to the highest pressure of 24.3 GPa, but peak intensities decrease continuously with pressure raise. The lattice index refer to the strongest diffraction lines. A small amount of an unidentified impurities is always present.

Fig. 3. The c/a lattice-parameter ratio for $\text{Fe}(\text{OH})_2$ as a function of pressure. Data for $P=0$ have been taken from the paper [6]. Solid line is to guide the eye.

In our preliminary studies we see no evidence of a discontinuous change in the unit cell volume. A value of the bulk modulus $K_0 = 69.3$ (5.6) GPa was found, assuming $K'_0 = 4$.

3. Concluding remarks

Among the CLP oxides, $b\text{-FePO}_4$ has a quite peculiar response at high pressure, viz., a simultaneous onset of disordered and high pressure crystalline phases near 2.5 GPa is observed. In the *chp* phase Fe becomes six-fold coordinated, which is also the predominant Fe coordination for the amorphous component. The coexisting crystalline and amorphous components show stable relative abundance to these pressures and persist upon fully releasing the pressure at 300 K.

In $\text{Fe}(\text{OH})_2$ in contrast to $\text{Ca}(\text{OH})_2$ the structural transformation is rather sluggish: it starts at ~1 GPa and is incomplete to the highest pressure measured (~24 GPa). It can be postulated that at low pressure ($P < 10$ GPa) the steric strain is minimized by the reduction of the crystallite sizes into smaller ones. At higher pressure after a disordering of the O-H sublattices takes place, the Fe-O sublattices become gradually involved in the amorphization process. In spite of a different transformation mechanism for $\text{Fe}(\text{OH})_2$ and FePO_4 , a kinetic hindrance does not allow complete transformation over the very broad pressure range used.

References

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