Short Communication

A High-Pressure Phase of Manganese(II) Orthophosphate, $Mn_3(PO_4)_2$

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The manganese(II) orthophosphate modification thermodynamically stable at room temperature (1 bar) is structurally related to β–$Zn_3(PO_4)_2$, although with a superstructure. It is usually denoted β′–$Mn_3(PO_4)_2$. It crystallizes in the monoclinic space group $P2_1/c$ with three six- and six five-coordinated metal ion sites and with V/Z = 156.0(1) Å^3.[1,2] It is isomorphous with β′–$Cd_3(PO_4)_2$.[3] When the Mn^{2+} ions are partly replaced by other divalent M^{2+} metal ions, solid solutions of the form $(Mn_{1-x}M_x)_3(PO_4)_2$ are formed. These are often isomorphous with graftonite,[2] a naturally occurring mineral with the chemical composition $(Fe,Mn,Ca,Mg)_3(PO_4)_2$. Graftonite crystallizes in space group $P2_1/c$ and contains one six- and two distinct five-coordinated metal ion sites.[4] On the other hand, pure "manganese graftonite" seems never to have been prepared. Its unit cell volume, should this phase exist, may be inferred by extrapolation of the cell data for the graftonite-type $(Mn_{1-x}M_x)_3(PO_4)_2$ phases[2] to be 620 Å^3, i.e. $V/Z = 155$ Å^3.

Among divalent-metal $M_3(PO_4)_2$ orthophosphates, many high-pressure modifications have been prepared (cf. below). The present study was undertaken to see whether Mn-graftonite or some other structure type was formed on applying high pressure to β′–$Mn_3(PO_4)_2$.

Experimental

Manganese orthophosphate was prepared by heating equimolar amounts of MnO (Merck, Darmstadt) and $Mn_2P_2O_7$, prepared as described earlier,[5] in an evacuated silica tube at 1100 K for two weeks. The purity of the product was checked by means of X-ray powder diffraction, confirming the β′ form. High pressure was then applied [25 kbar (2.5 GPa), 600 °C, 24 h] in a solid media press of the type described by Boyd and England.[6] Accurate X-ray powder diffraction data were obtained with a Guinier-Hägg type focusing camera using Cr$K\alpha_1$ radiation (λ = 2.8975 Å, r = 50.00 mm, KCl internal standard, t = 25 °C).

Results and discussion

The powder diffraction pattern clearly indicated the high-pressure phase to have the graftonite structure. The indexed powder data are given in Table 1. The refined unit cell parameters are: a = 8.788(3), b = 11.434(2), c = 6.255(1) Å, β = 98.98(2)° and V = 620.8(4) Å^3. Since there are four formula units per unit cell (Z = 4), V/Z is equal to 155.2(1) Å^3, which is only slightly less than the corresponding value for β′–$Mn_3(PO_4)_2$, viz. 156.0(1) Å^3. The smaller value may be compared with the V/Z value of 150.4 Å^3 for synthetic $Fe_3(PO_4)_2$-graftonite.[7] The solid solution $(Mn_{0.90}Fe_{0.10})_3(PO_4)_2$-graftonite may readily be

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Table 1. X-Ray powder diffraction data for the high-pressure modification of $Mn_3(PO_4)_2$ (space group $P2_1/c$). Relative intensities (I): st = strong, m = medium, w = weak, vw = very weak.

h	k	l	d/Å	I	h	k	l	d/Å	I
1	0	0	8.703	vw	1	0	−2	3.065	m
1	1	1	4.345	w	1	3	1	2.960	st
2	1	0	4.054	vw	2	2	1	2.869	st
2	1	−1	3.645	vw	0	4	0	2.858	vw
1	3	0	3.492	st	1	0	2	2.777	vw
0	3	1	3.243	vw	2	0	−2	2.726	vw
2	2	−1	3.191	vw	1	4	0	2.716	m
0	0	2	3.088	w	1	1	2	2.698	w

prepared at 1 bar, 1100 K, thus showing that the graftonite structure is easily obtained.

The high-pressure modifications of some divalent-metal orthophosphates are listed in Table 2. The values of V/Z, cation coordination numbers (CN) when known, and cation radii for octahedral coordination of oxygen ligands[8] are included, as well as the decrease in cell volume for the transformation from low- to high-pressure phase. The data show clearly that there is a strong correlation between decrease in cell volume and increase in metal ion coordination number for the orthophosphate systems; this is briefly discussed below.

At 1 bar, magnesium orthophosphate crystallizes with the so-called farringtonite structure, with five- and six-coordinated metal ions.[9] It may be compressed to a high-pressure form with the olivine-related sarcopside structure having two distinct six-coordinated cations.[10] For this transformation the decrease in unit cell volume is 9.3 %. $Co_3(PO_4)_2$ is isomorphous with $Mg_3(PO_4)_2$, but its high-pressure structure (decrease in cell volume 10.2 %) is unknown.[11] A third modification of cobalt(II) orthophosphate, isostructural with sarcopside and with the high-pressure phase of magnesium orthophosphate, has been described in the literature.[12] This phase is almost as closely packed as the high-pressure modification of $Co_3(PO_4)_2$ of unknown structure.

$Fe_3(PO_4)_2$ crystallizes at 1 bar with the graftonite structure (CN = 6, 5 and 5)[7] and with V/Z = 150.4 Å^3. Hydrothermal treatment gives a sarcopside modification (CN = 6 and 6) with an almost identical volume per formula unit (V/Z = 150.6 Å^3), so this phase can hardly be regarded as a high-pressure phase.[13] β–$Ca_3(PO_4)_2$ (CN = 6, 8, 8, 8 and 9)[14] can be converted to a high-press-

Table 2. Data for divalent-metal $M_3(PO_4)_2$ orthophosphates and respective high-pressure modifications. CN stands for cation coordination number, r_M is the cation radius (Å) after Shannon.[8] Relevant references are mentioned in the text. ΔV is the decrease in cell volume from low- to high-pressure phase.

M	r_M (Å)	Low-pressure phase V/Z (Å^3)	CN	High-pressure phase V/Z (Å^3)	CN	ΔV/%
Mg	0.72	158.3	5, 6	143.5	6, 6	9.3
Co	0.745	159.4	5, 6	143.1	?	10.2
Mn	0.83	156.0	6, 6, 6, 5, 5, 5, 5, 5, 5	155.2	6, 5, 5	0.5
Cd	0.95	170.0	6, 6, 6, 6, 6, 5 5, 5, 5	165.1	7, 5, 5	2.9
Ca	1.00	168.0	6, 8, 8, 8, 9	148.4	10, 12	11.7

ure phase called $Ca_3(PO_4)_2$–II. The latter structure contains one ten- and one twelve-coordinated calcium ion,[15] and the decrease in cell volume is as large as 11.7 %.

As mentioned above, β'–$Mn_3(PO_4)_2$ and β'–$Cd_3(PO_4)_2$ are isomorphous at 1 bar.[1,3] As shown by Bonel and Roux[16] for cadmium orthophosphate and by the present authors for manganese orthophosphate, these compounds form high-pressure phases having the graftonite structure. In graftonite, as well as in β'–$Mn_3(PO_4)_2$, two-thirds of the cations are five-coordinated, while in β'–$Cd_3(PO_4)_2$ only 4/9 (~44 %) of the metal atoms are five-coordinated; the rest are six-coordinated. Accordingly, the decrease in cell volume occurring when these two orthophosphates are transformed into denser high-pressure modifications is more noticeable for the cadmium compound (2.9 %) than for manganese orthophosphate (0.5 %), since two-thirds of the cations in both $Mn_3(PO_4)_2$ forms are five-coordinated and thus give almost the same structural packing.

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