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X-Ray Diffraction Studies of Solid Solutions of $M_3(PO_4)_2$ in $Co_3(PO_4)_2$

ANDERS G. NORD

Section of Mineralogy, Swedish Museum of Natural History, P.O. Box 50007, S-104 05 Stockholm 50, Sweden

Solid solutions of $M_3(PO_4)_2$ in $Co_3(PO_4)_2$ have been prepared and equilibrated at 1070 K (M = Mg, Mn, Fe, Ni, Cu, Zn, or Cd). Approximate homogeneity ranges have been determined, and the monoclinic unit cell dimensions are given. The crystallographic properties of the $(Co_{1-z}M_z)_3(PO_4)_2$ solid solutions and the corresponding $(Mg_{1-z}M_z)_3(PO_4)_2$ phases are closely related [$Co_3(PO_4)_2$ is isostructural with $Mg_3(PO_4)_2$]. However, the results indicate that certain $(Co_{1-z}M_z)_3(PO_4)_2$ compositions crystallize with anomalous symmetries so that at least some atoms are incompatible with the space group symmetry reported for pure cobalt orthophosphate.

For structural chemists, geochemists and mineralogists it is of fundamental interest to correlate crystallographic properties of solid solutions such as solubility ranges, unit cell dimensions, cation radii and intra-crystalline cation distributions. Studies with this aim have been published on some important oxosalt structure types, mostly silicates, containing divalent-metal cations like Fe^{2+}, Mg^{2+}, Mn^{2+} and Ca^{2+}, ubiquitous in nature. However, practically all these studies concern only tetrahedral and, in particular, octahedral cationic environments. I have therefore started such investigations on structures containing also five-coordinated M^{2+} cations. To a major extent solid solutions with the "γ-$Zn_3(PO_4)_2$" structure have been used. This crystal structure was determined in 1963 by Calvo;[1] it is here described in the monoclinic space group $P2_1/n$ (No. 14). Two thirds of its cations occupy five-coordinated sites, called M(1), while the rest reside in six-coordinated octahedral sites, M(2).

Two pure orthophosphates are isomorphous with "γ-$Zn_3(PO_4)_2$": The crystal structure of $Mg_3(PO_4)_2$ was published by Nord and Kierkegaard.[2] Later a note on the $Co_3(PO_4)_2$ structure was published,[3] and a detailed structural investigation by Anderson *et al.* appeared shortly afterwards.[4] Some studies based on $(Mg_{1-z}M_z)_3(PO_4)_2$ solid solutions and with the aims mentioned above have already been published.[5-7] An iron-containing magnesium orthophosphate has also been found as a rare mineral, *farringtonite*.[8,9] The present study was undertaken to determine, at least roughly, the homogeneity ranges at about 1070 K for $(Co_{1-z}M_z)_3(PO_4)_2$ solid solutions with M^{2+} cations similar in size to Co^{2+}, *i.e.* M = Mg, Mn, Fe, Ni, Cu, Zn or Cd, each series henceforward abbreviated Co/M. The monoclinic unit cell dimensions have been accurately determined. Finally, these data are discussed in relation to earlier results obtained on the $(Mg_{1-z}M_z)_3(PO_4)_2$ solid solutions.[5-7]

EXPERIMENTAL DETAILS

The preparation of all pure $M_3(PO_4)_2$ orthophosphates involved in this study has already been described.[10] The purity was always checked by X-ray diffraction. Each solid solution between $Co_3(PO_4)_2$ and the $M_3(PO_4)_2$ compound in question was then prepared by heating pellets of stoichiometric mixtures of the two phosphates in an electric furnace. Whenever iron or manganese was included, the sample was heated in an evacuated and sealed Ø 5 mm silica tube to prevent the oxidation of Fe^{2+} or Mn^{2+}. All other mixtures were heated in air in small, open, silica tubes. The heating continued for one month to ensure homogeneity and chemical equilibrium (*cf.* Ref. 7), whereupon the samples were quenched in cold water.

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The equilibrium temperature, about 1070 K (800±10 °C), was the same as in the earlier mentioned studies of $(Mg_{1-z}M_z)_3(PO_4)_2$ solid solutions. This temperature was chosen because it is easily maintained, it is within a temperature region of considerable interest to geochemists and mineralogists, and finally the solid solutions are formed within reasonable time.

X-Ray powder diffraction data of each sample were obtained at 298 K (25±1 °C) with an XDC-700 Guinier-Hägg type focusing camera ($r = 50.00$ mm) using strictly monochromatized Cr$K\alpha_1$ radiation ($\lambda = 2.28975$ Å). Potassium chloride ($a = 6.29294$ Å[11]) was always used as an internal standard.

UNIT CELL DIMENSIONS

The visually observed readings of the Guinier photographs were corrected using the internal standard technique as described by Westman and Magnéli.[12] The dimensions of the monoclinic unit cell for all Co/M compounds were refined by a traditional least-squares procedure on a NOVA 4/X computer (program CELREF by A. G. Nord); 25–30 unambiguously single-indexed reflections were used in each refinement. The results are given in Table 1, which also indicates the homogeneity ranges, within ±3 atom per cent, for the Co/M solid solution series. The observed change in unit cell volume with composition for each Co/M series is mainly due to the changes in the monoclinic b axis length, while a, c and the β angle change comparatively little. For clarity, the unit cell volumes $V\,(Z=2)$ for the $(Co_{1-z}M_z)_3(PO_4)_2$ phosphates have been plotted *versus* the composition z in Fig. 1. Note that Vegard's law is clearly not obeyed in some cases.

Each Co/M series may be sorted into one of three groups: (1) low solubility of M^{2+} in $Co_3(PO_4)_2$ [M = Ni or Cd], (2) moderate solubility of the incorporated cation [M = Cu, Fe or Mn], and (3) complete or almost complete solubility of $M_3(PO_4)_2$ in cobalt orthophosphate over the whole composition range [M = Zn or Mg]. The Co/M series are

Table 1. Unit cell dimensions ($Z=2$) at 298 K for some $(Co_{1-z}M_z)_3(PO_4)_2$ solid solutions, equilibrated at 1070 K.

z	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
$Co_3(PO_4)_2$					
	7.556(1)	8.374(1)	5.062(1)	94.03(2)	319.6(1)
$(Co_{1-z}Cd_2)_3(PO_4)_2$					
0.03	7.566(2)	8.406(2)	5.064(2)	93.89(2)	321.4(2)
$(Co_{1-z}Mn_z)_3(PO_4)_2$					
0.05	7.575(4)	8.392(3)	5.072(3)	94.00(6)	321.6(4)
0.10	7.587(2)	8.419(2)	5.073(1)	93.96(2)	323.3(2)
0.15	7.593(3)	8.434(3)	5.075(2)	93.94(2)	324.2(3)
0.20	7.596(4)	8.445(4)	5.079(2)	93.92(4)	325.0(3)
0.25	7.603(2)	8.458(3)	5.079(2)	93.90(3)	325.9(2)
0.30	7.609(5)	8.470(5)	5.080(3)	93.86(5)	326.6(4)
$(Co_{1-z}Fe_z)_3(PO_4)_2$					
0.05	7.573(5)	8.389(3)	5.071(2)	94.00(5)	321.3(4)
0.10	7.574(2)	8.392(2)	5.072(1)	94.08(2)	321.6(2)
0.20	7.581(2)	8.405(1)	5.077(1)	94.06(2)	322.7(1)
0.30	7.590(2)	8.421(1)	5.081(1)	94.09(2)	323.9(1)
0.40	7.597(1)	8.428(1)	5.088(1)	94.09(2)	325.0(1)
$(Co_{1-z}Cu_z)_3(PO_4)_2$					
0.10	7.565(2)	8.326(2)	5.074(1)	93.72(2)	318.9(1)
0.15	7.569(3)	8.295(4)	5.080(2)	93.55(3)	318.3(3)
0.20	7.573(3)	8.264(2)	5.085(1)	93.30(3)	317.8(3)
0.25	7.578(3)	8.237(2)	5.093(1)	93.00(4)	317.4(3)
$(Co_{1-z}Ni_z)_3(PO_4)_2$					
0.05	7.558(3)	8.365(2)	5.067(1)	93.99(3)	319.5(2)
0.10	7.553(2)	8.346(2)	5.069(1)	93.92(2)	318.8(2)
0.15	7.557(5)	8.349(5)	5.074(3)	93.93(5)	319.3(5)

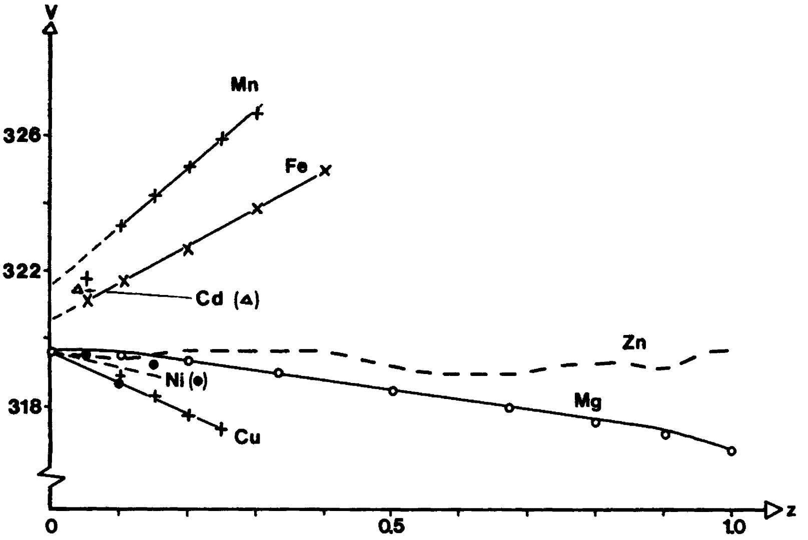

Fig. 1. Unit cell volumes V (in Å^3) *versus* composition z for the $(Co_{1-z}M_z)_3(PO_4)_2$ solid solutions. The Co/Mg data are based on Ref. 6, and the Co/Zn data, indicated by a dashed curve, on Ref. 15.

discussed below in the order mentioned. The divalent cation radii cited within parentheses (r_M) are those published by Shannon and Prewitt[13] for octahedral coordination with oxygen ligands (r_{Co} is 0.74 Å for Co^{2+}). All solubility ranges are given at about 1070 K.

Ni^{2+} is the smallest of the cations involved in this study ($r_{Ni}=0.70$ Å). The solubility in $Co_3(PO_4)_2$ is surprisingly low, considering that Ni^{2+} and Co^{2+} oxosalt compounds are often isostructural (*e.g.* see Ref. 10); there is, however, a pronounced difference in crystal field stabilization energy between the two cations.[14] Cd^{2+} is the largest cation to be incorporated in cobalt orthophosphate ($r_{Cd}=0.95$ Å). The solubility of cadmium is very slight, probably as a result of the size effect. The Co/Cu orthophosphates clearly obey Vegard's law. The unit cell volume smoothly decreases as the slightly smaller copper ions ($r_{Cu}=0.73$ Å) replace cobalt. Divalent iron ($r_{Fe}=0.77$ Å) and manganese ($r_{Mn}=0.82$ Å) have a solubility in $Co_3(PO_4)_2$ around 35 atom per cent. The unit cell volume in each series (Co/Fe and Co/Mn) increases linearly with the composition z. However, both curves show discontinuities in the vicinity of pure $Co_3(PO_4)_2$. This effect will be discussed in the next section.

The magnesium and zinc (γ-phase) orthophosphates are isomorphous with cobalt orthophosphate, and it is therefore natural that Mg^{2+} and Zn^{2+} are the most soluble cations in $Co_3(PO_4)_2$. The former ion ($r_{Mg}=0.72$ Å) is, in fact, continuously soluble over the whole composition range (at 1070 K). The unit cell dimensions have already been published,[6] and they are included in Fig. 1. As regards zinc ($r_{Zn}=0.75$ Å), up to 97 % of the cobalt may be replaced by this metal. The Co/Zn "cell volume" curve (Fig. 1) is almost linear. The slight discontinuities will be looked into more closely in a forthcoming paper on γ-$(Zn_{1-z}M_z)_3(PO_4)_2$ solid solutions.[15]

DISCUSSION

The crystal structure of $Co_3(PO_4)_2$ is built up of distorted trigonal bipyramids, $M(1)O_5$, and almost regular $M(2)O_6$ octahedra and PO_4 tetrahedra.[2,4,10] The Co/M solid solutions and $Co_3(PO_4)_2$ are isostructural or at least closely related. The homogeneity region for each Co/M series at 1070 K is rather similar to that of the corresponding Mg/M series (see Table 2). Ca^{2+} is too large to be incorporated in $Co_3(PO_4)_2$. Neither can calcium replace magnesium in $Mg_3(PO_4)_2$.[16] However, as pointed out earlier, the cobalt and magnesium orthophosphates are isostructural, and Co^{2+} and Mg^{2+} are similar in size. X-Ray diffraction studies of $Co_2Mg(PO_4)_2$ and $(Co_{0.5}Mg_{0.5})_3(PO_4)_2$ have

Table 2. Approximate homogeneity ranges, in atom per cent, for the $(Co_{1-z}M_z)_3(PO_4)_2$ and $(Mg_{1-z}M_z)_3$-$(PO_4)_2$ solid solution series at about 1070 K. The cation radii, r_M, are from Shannon and Prewitt[13] for octahedral M^{2+} coordination of oxygen ligands.

Cation	r_M/Å	Homogeneity ranges (atom %)	
		Co/M[a]	Mg/M[b]
Ni^{2+}	0.70	15	10
Mg^{2+}	0.72	100	–
Cu^{2+}	0.73	25	15
Co^{2+}	0.74	–	100
Zn^{2+}	0.75	97	97
Fe^{2+}	0.77	40	60
Mn^{2+}	0.82	30	33
Cd^{2+}	0.95	3	10
Ca^{2+}	1.00	0	0[c]

[a] This work. [b] Ref. 6. [c] Ref. 16.

also shown that the cation distribution was close to random but with a slight predominance for Co^{2+} at the M(1) sites.[7] These facts may, partly, explain the similar solubility ranges for Co/M and Mg/M. A difference, though, is noted for Cu^{2+}: the solubility in $Co_3(PO_4)_2$ is moderate, but low in magnesium orthophosphate. The latter fact is curious, since Cu^{2+} has a large tendency to enter into very distorted environments such as five-coordinated sites. Another significant difference is noted for Fe^{2+}, where the solubility situation is reversed: greater solubility in $Mg_3(PO_4)_2$ than in $Co_3(PO_4)_2$. This effect is consistent with the results of cation distribution studies performed on $(Mg_{1-z}M_z)_3(PO_4)_2$ solid solutions, which show that the M(1) site preference order in this structure is $Co^{2+} > Fe^{2+} > Mg^{2+}$, although with very small differences.[6] In Mg/Fe, iron therefore has better possibilities to enter into the more numerous five-coordinated M(1) sites, while in Co/Fe the converse is true: Co^{2+} preferentially occupies the M(1) sites thus leaving the less numerous M(2) sites for the major part of the Fe^{2+} ions. However, there is also another effect observed in the Co/Fe phases to take into consideration, which will be discussed below.

In contrast to the Mg/M series,[6] it is obvious that some of the Co/M solid solution series slightly disobey Vegard's law, *viz.* Co/Zn, Co/Fe and Co/Mn. The two latter series display similar anomalies: the plots of unit cell volume *versus* composition z for the two $(Co_{1-z}M_z)_3(PO_4)_2$ series are principally linear but show a discontinuity close to $z=0$ (Fig. 1). I assume that, upon substitution of some cobalt for Fe^{2+} or Mn^{2+}, the structure changes slightly so that at least some of the atoms no longer conform to the centrosymmetric space group reported for pure cobalt orthophosphate. Atomic displacements may be implied by a superstructure or by some other symmetry change. However, experiments with a Giebe-Scheibe piezoelectric tester could not produce any definite results as regards the existence or not of a center of symmetry in Co/Mn or Co/Fe. Some Co/Fe Guinier photographs have been evaluated by means of a computer-controlled film scanner. For each phase only two very weak reflections out of thirty-two (at $d \approx 2.97$ Å and $d \approx 2.56$ Å) could not be indexed assuming $P2_1/n$ symmetry. [These two reflections do not originate from an impurity of $Fe_3(PO_4)_2$ which might otherwise be suspected, considering the preparation method.] Any structural changes must therefore be very slight; this is also indicated by the small irregular increases in the unit cell dimensions close to $z=0$.

Mössbauer spectroscopy studies of some Co/Fe compounds have also been performed.[17] The preliminary results show three distinct Fe^{2+} doublets in each spectrum. Two of the doublets (one strong and one weak) closely correspond to those obtained in an earlier study of some $(Mg_{1-z}Fe_z)_3$-$(PO_4)_2$ and γ-$(Zn_{1-z}Fe_z)_3(PO_4)_2$ solid solutions, isomorphous with $Mg_3(PO_4)_2$ and $Co_3(PO_4)_2$.[5] The third "extra" doublet of Co/Fe is quite strong and with much lower quadrupole splitting. The above results thus indicate that the Co/Fe phases contain at least three crystallographically non-equivalent M^{2+} cation positions rather than two as in pure cobalt orthophosphate.

Finally, another difference in structural behaviour between $Co_3(PO_4)_2$ and $Mg_3(PO_4)_2$ will be pointed out. Pure and iron-doped magnesium orthophosphate contracts to a denser high-pressure phase at about 25 kbar;[18] the new structure is that of the mineral *sarcopside*[19] or nickel orthophosphate.[20] However, when high pressures are applied to pure and iron-doped $Co_3(PO_4)_2$, another phase is formed.[17] The X-ray powder diffraction patterns of the two latter compounds are similar, but the high-pressure structure in question is so far unknown. Further Mössbauer and neutron diffraction studies of some $(Co_{1-z}Fe_z)_3(PO_4)_2$ phases are in progress.

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