

Manganese in apatites, chemical, ligand-field and electron paramagnetic resonance spectroscopy studies

I. MAYER, H. DIAB

Department of Inorganic and Analytical Chemistry, The Hebrew University, Jerusalem, Israel

D. REINEN, Ch. ALBRECHT

Fachbereich Chemie, Philipps Universität Marburg, Marburg, Germany

Hydroxapatites precipitated with different amounts of carbonate and Mn^{2+} were studied. Infrared spectra, X-ray diffraction lattice parameters and thermal behaviour indicate that the presence of Mn^{2+} does not have any effect on the formation and properties of the carbonate apatites obtained. Interaction of apatite with a Mn^{2+} -containing aqueous solution reveals that the molar uptake of Mn^{2+} by the apatite is higher than the Ca^{2+} released by it. Ligand-field and electron paramagnetic resonance spectroscopy results show that in Mn^{2+} -doped $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$, Mn^{2+} replaces Ca^{2+} in the apatite lattice, but in precipitated carbonate apatite it is in an MnO phase. The conclusion that Mn^{2+} in precipitated carbonate apatites is not incorporated in the apatite crystal is discussed in the light of the size differences between Mn^{2+} and Ca^{2+} .

1. Introduction

The mineral constituent of teeth and bones is closely related to calcium hydroxy apatite, but contains numerous trace elements which may have considerable influence on the chemical and physical properties of these apatites. Manganese appears in biological apatites like bones and teeth. Studies have indicated positive correlation between manganese and dental caries [1]. The way manganese acts in cases of dental caries and how manganese is incorporated in dental enamel is not yet well understood. The uptake of manganese by bone and its effect on the growth and development of bone have been studied [2]. The most important results of these studies are that manganese in bone causes decreased bone resorption.

Hydroxy apatite crystallizes in the hexagonal $\text{P6}_3/\text{m}$ structure, with two formula units in a unit cell. In $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$ the ten Ca^{2+} ions are distributed among two crystallographically non-equivalent positions. Six $\text{Ca}(2)$ ions are arranged in two triangles around the six-fold c -axis, and four other $\text{Ca}(1)$ ions in the so-called column positions [3].

Fluoride apatites substituted by Mn^{2+} were studied by electron paramagnetic resonance (EPR) measurements [4–7]. These studies resulted in a structure in which Mn^{2+} preferably occupied $\text{Ca}(1)$ positions; in some cases, location in both the $\text{Ca}(1)$ and $\text{Ca}(2)$ sites was also found. The formation of solid-solution Ca-Mn -hydroxy apatites were reported recently [8].

The above results show the limited incorporation of Mn^{2+} in fluoride apatites prepared at elevated temperatures. The purpose of the present work was to

study Mn^{2+} in precipitated carbonate apatites and in a series of cadmium apatites prepared at high temperatures in order to obtain information on its chemical form and possible incorporation in apatites.

2. Materials and methods

The method of preparation of the carbonated apatites used in this work was as described previously [9]: Na_2HPO_4 solution (5.2 g in 200 ml) of triply distilled water (TDW) was added drop-wise to a $\text{Ca}(\text{NO}_3)_2$ solution (14.5 g in 200 ml TDW) under reflux at 87°C . Carbonate was added to the phosphate solution from an NaHCO_3 stock solution (20 ml at concentrations up to 20 mmol). Manganese was added to the calcium solution from an MnSO_4 solution (20 ml, in the concentration range 2.5–10 mg). The pH was maintained constant during the precipitation at 7 or 9, by adding concentrated NH_4OH solution. The precipitation was carried out for 2 h and following this the temperature was raised to boiling point and the system refluxed for a further 2 h. After this the sample was thoroughly washed by TDW and dried overnight in an electric furnace in air at 120°C . Manganese was determined by atomic absorption spectroscopy. Thermal properties were studied by heating the samples in an electric furnace.

Single crystals of Mn^{2+} -doped $\text{Cd}_5(\text{PO}_4)_3\text{Cl}$ were prepared by heating $\text{Cd}_{5-x}\text{Mn}_x(\text{PO}_4)_3\text{Cl}$ (x between 0.03 and 0.15) with a large excess of CdCl_2 in a sealed platinum capsule at 900°C for 2 h and slowly cooling. The powder compound was synthesized by sintering

$\text{Cd}_3(\text{PO}_4)_2$ and $\text{Mn}_3(\text{PO}_4)_3$ in the respective molar ratios with CdCl_2 (slight excess) in an evacuated quartz tube at 800°C .

The crystal phases were characterized by powder X-ray diffraction (XRD) and infrared (IR) methods. The IR spectra of the samples were taken with a Perkin-Elmer model 457. Samples of ≈ 1 mg were pressed into pellets with ≈ 150 mg KBr. The carbonate content of the samples was estimated by IR analysis using the extinction ratio values of the carbonate (1420 cm^{-1}) and phosphate (575 cm^{-1}) bands [10].

XRD analyses were carried out on powdered samples by a Philips Diffractometer using monochromatic CuK_α radiation. The samples were scanned in the 2θ range at 20 – 60°C . The lattice parameters were calculated by a least-square computer program.

The powder-reflection ligand-field spectra at 295 and 5 K were recorded with a Zeiss spectrophotometer PMQ II (reflectance accessory RA2, liquid helium device). Dry MgO was used as a standard. The EPR experiments were performed with a Varian E15 spectrometer at Q-band frequency (35 GHz) at 295 and 130 K. DPPH ($g = 2.0036$) was used as an internal standard.

The interaction of Mn^{2+} with apatite was studied by mixing 0.2 g apatite sample with 100 ml solution containing 100 or 500 p.p.m. Mn^{2+} for 2, 5, 24 h and 8 days. At the end of each of these time intervals the solution was filtered. The solid residue was dried at 120°C and the manganese content of the solution determined.

3. Results

The compounds studied were apatites prepared by precipitation in the presence of Mn^{2+} at pH 7.0 and

9.0 and with different amounts of carbonate. The infrared spectra of all the compounds were similar and contained the bands characteristic of apatites. The carbonate bands of the spectrum (1420 and 1456 cm^{-1}) have shown that carbonate replaces phosphate in the apatites (B-type). No changes caused by the presence of Mn^{2+} ions could be observed.

The powder XRD patterns reveal that these compounds crystallize in a hexagonal unit cell, the one known for apatites. Table I lists the lattice constants obtained for the different compounds depending on carbonate content. The lattice constant a decreases with the increase in carbonate content. The manganese content does not seem to have any effect on these constants. Table II summarizes the carbonate content and lattice constants after the above samples were heated to 400 and 700°C . The carbonate content, estimated from the IR results decreases with an increase in the temperature. The samples loose carbonate to a very small extent until 400°C and more rapidly at 700°C . The lattice constants decrease at 400°C , most probably because of the loss of absorbed water, and increase towards 700°C , reaching values close to that of carbonate-free hydroxyapatites.

The effect of Mn^{2+} ions on apatites was studied also by their interaction in an aqueous solution with solid-phase apatites. The interaction was studied in solutions at two different Mn^{2+} concentrations and at different time intervals. The results of these experiments are given in Table III. The molar ratios between Mn^{2+} , taken up from the solution and found in the apatite and Ca^{2+} removed from the apatite and found in solution, indicate that more Mn^{2+} is taken up by the apatite than Ca^{2+} leaving it, thus only some of the manganese ions replace calcium in the apatite lattice. The table shows also that, when the Mn^{2+} concentra-

TABLE I Lattice constants and carbonate content of manganese-containing apatites

Sample	pH of preparation	Mn^{2+} input (mg)	Carbonate content (%)	Lattice constants	
				a (nm)	c (nm)
BS ₀	9	–	0.3	0.9431	0.6890
S-2	7	10	2.4	0.9413	0.6875
S-3	7	2.5	2.6	0.9408	0.6885
S-4	9	2.5	4.1	0.9395	0.6888
S-5	9	5.0	4.1	0.9395	0.6891
S-6	7	5.0	Traces	0.9420	0.6878
S-7	9	5.0	0.9	0.9422	0.6887

TABLE II Lattice constant and carbonate content of manganese-containing apatites after heating to 400 and 700°C

Sample	400°C		700°C			
	Carbonate content (%)	Lattice constants		Carbonate content (%)	Lattice constants	
		a (nm)	c (nm)		a (nm)	c (nm)
S-2	2.1	0.9401	0.6895	0.4	0.9421	0.6878
S-3	2.2	0.9403	0.6885	0.6	0.9415	0.6880
S-4	3.5	0.9377	0.6892	1.7	0.9418	0.6887
S-5	3.6	0.9390	0.6898	1.5	0.9419	0.6889
S-6	Traces	0.9420	0.6883	Traces	Decomposes	
S-7	Traces	0.9402	0.6888		0.9411	0.6893

TABLE III Interaction in solutions at two different Mn^{2+} concentrations

Sample	CO_3^{2-} (%)	Amount of Mn^{2+} in 100 ml (p.p.m.)	Time of interaction (h)	Mn^{2+} uptake from solution by apatite (10^{-5} mol)	Ca^{2+} removed from apatite and found in solution (10^{-5} mol)	Mole ratio Mn^{2+}/Ca^{2+}
BS ₀	0.3	500	2	18.7	5.31	3.52
BS ₀	0.3	500	5	15.1	5.81	2.60
BS ₀	0.3	500	24	18.7	5.76	3.25
BS ₀	0.3	100	24	8.37	3.99	2.10
BS ₀	0.3	100	192	10.2	8.23	1.24
H-18	3.0	100	24	9.28	5.98	1.55
H-19	4.1	100	24	8.37	4.24	1.97

tion increases in the solution, its uptake in the apatite increases as well, and the time of interaction has very little effect.

Ligand-field and EPR spectroscopy measurements were carried out on a representative manganese-containing carbonate apatite (S-5 and S-7) after being heated to 400 °C and on Mn^{2+} -doped $Cd_5(PO_4)_3Cl$.

The typical ligand-field spectrum of the S-5 sample (Fig. 1) is similar to that of MnO [11] with octahedrally-coordinated Mn^{2+} ions, but with much less resolved $d-d$ transitions even at 5 K. Only the ${}^6A_{1g} \rightarrow a^4T_{1g}$ band is distinct, while the usually sharp transitions to the nearly degenerate a^4E_g and ${}^4A_{1g}$ states is rather broad, indicating that the sample crystallinity is poor. In the spectra of Mn^{2+} -doped $Cd_5(PO_4)_3Cl$, more transitions are observed than in Fig. 1, due to the presence of two cadmium positions and their lower site symmetries. Although it cannot be totally excluded that the spectrum of sample S-5 is due to Mn^{2+} in a Ca^{2+} site of the the apatite lattice, the presence in an impurity phase with octahedral coordination seems to be much more probable.

The investigation by EPR spectroscopy provides more detailed information about the geometry of the Mn^{2+} site. Fig. 2 shows the EPR spectrum of Mn^{2+} -doped $Cd_5(PO_4)_3Cl$ (powdered single crystals). It closely resembles that of Mn^{2+} in $Ca_5(PO_4)_3F$ [4] and shows the typical symmetry features of the Cd(I) position, with a nicely resolved fine and hyperfine structure. The five groups of six lines are due to the allowed transitions between the fine-structure components of $S = 5/2$. The calculated axial zero-field splitting parameter is estimated to be $D \approx 457G$, which is somewhat larger than the value reported for $Ca_5(PO_4)_3F$ ($D = 428 G^2$). The hyperfine splitting resulting from the interaction with the manganese nucleus ($I = \frac{5}{2}$) is $A = 92 G$ ($g = 2.00_5$). The presence of manganese preferentially on site I is also in accord with single-crystal EPR studies [5].

The EPR spectra of samples S-5 and S-7 (Fig. 3) are representative for Mn^{2+} in carbonate apatite compounds. The observed sextet is clearly due to the hyperfine interaction with the manganese nucleus. The hyperfine parameter ($A \approx 90 G$) is practically identical with the one cited above. A fine structure splitting is very small or not present, indicating that Mn^{2+} is in a site with nearly cubic symmetry. This supports the suggestion that Mn^{2+} is not incorporated into the Ca^{2+} positions of the apatite lattice, but is present in

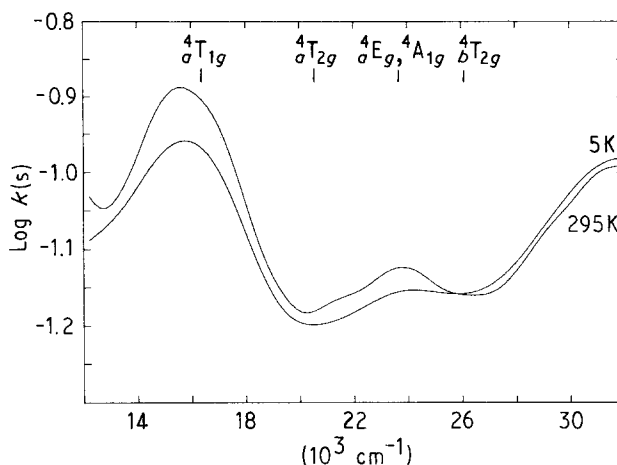


Figure 1 Ligand-field transitions of sample S-5 (400 °C). Assignments and given band positions are those of MnO ($\Delta = 10400 cm^{-1}$, $B = 655 cm^{-1}$ ($\beta = 0.87_5$), $C/B = 5.2$) [11].

an impurity phase with presumably octahedral coordination. The small splitting of the hyperfine lines (Fig. 3) might indicate the presence of two impurity phases with Mn^{2+} .

4. Discussion

The results obtained in the present study suggest that the addition of Mn^{2+} does not cause any changes in the basic properties of these compounds when carbonate apatites are precipitated in the presence of Mn^{2+} ions. This has been indicated by the carbonate uptake in the compounds at different pH values, which was of the same order as without manganese. This was also indicated by the IR and XRD results. The IR spectra had characteristic bands of a B-type carbonate apatite, and the XRD patterns showed the reflections of an apatite-type hexagonal structure. The changes of the lattice constants of the different compounds can be attributed to the change in the carbonate content of the compound and seem not to be affected by the Mn^{2+} added to them.

The thermal behaviour of the compounds was very similar to what is known for synthetic carbonate apatites [12]. This was demonstrated by the carbonate loss during heating, which was complete at 700 °C. The changes in the lattice constants indicate that at 400 °C the samples are free of water and at 700 °C they are free of carbonate. Decomposition by heating to $\beta-Ca_3(PO_4)_2$ was observed only with samples which

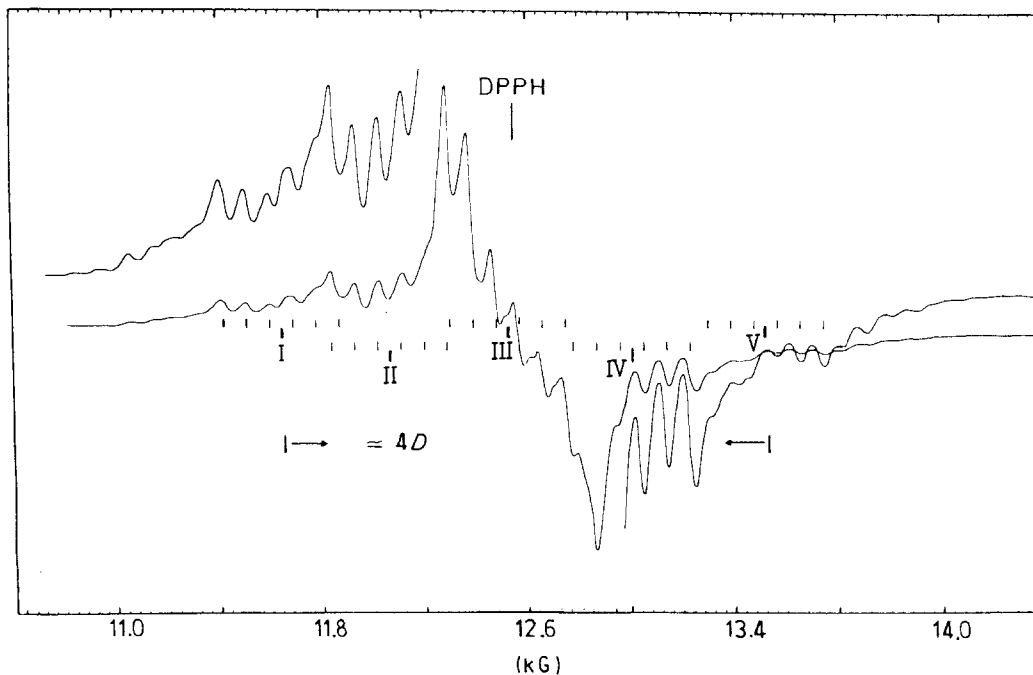


Figure 2 EPR powder spectrum of Mn^{2+} -doped $\text{Cd}_3(\text{PO}_4)_2\text{Cl}$ (295 K). The five groups of lines indicated are due to transitions $M_s =$ (I) $\pm \frac{3}{2} \rightleftharpoons \pm \frac{1}{2}$, (II) $\pm \frac{1}{2} \rightleftharpoons \pm \frac{3}{2}$, (III) $\pm \frac{1}{2} \rightleftharpoons \pm$, (IV) $\pm \frac{3}{2} \rightleftharpoons \pm \frac{1}{2}$, (V) $\pm \frac{3}{2} \rightleftharpoons \pm \frac{3}{2}$ in the perpendicular orientation, and to $M_s = \pm \frac{3}{2} \rightleftharpoons \pm \frac{1}{2} \rightleftharpoons \pm \frac{3}{2}$ (overlap with I and V, respectively) in the parallel direction. "Parallel" and "perpendicular" refers to the C_3 axis of site I.

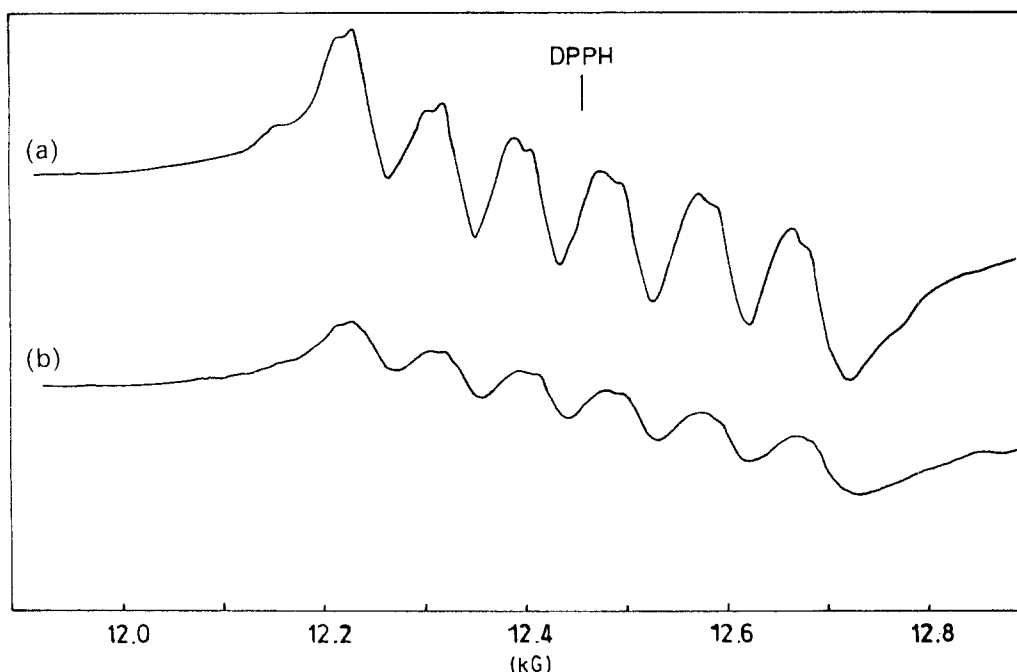


Figure 3 EPR powder spectra of samples (a) S-5, 400 °C and (b) S-7, 400 °C, $g \approx 2.00$; $A \approx 90$ G.

were prepared at pH 7.0 and low in carbonate content, similar to other carbonate apatites.

The interaction of precipitated apatites with an Mn^{2+} -containing solution has shown that more moles of Mn^{2+} are taken up by the apatite from the solution than moles of Ca^{2+} are released from the apatite. Apparently only a very small amount of Mn^{2+} , equivalent to the Ca^{2+} released from the apatite, is incorporated in the apatite lattice. Most of it is surface-adsorbed on the apatites.

The ligand field spectroscopy and EPR results reveal the incorporation of Mn^{2+} in the apatite only in the case of the cadmium apatites prepared at high

temperatures. In the precipitated carbonate apatites, Mn^{2+} is present presumably in an octahedral coordination, but with certainty, in a high symmetry site, which might correspond to MnO rather than to the phosphate phase.

In conclusion, it can be stated that the results obtained in this work all point in the same direction, namely that Mn^{2+} added during the precipitation of a carbonate apatite does not become incorporated in the apatite crystal. Apparently, the size difference between Mn^{2+} (0.096 nm) and Ca^{2+} (0.112 nm) in 8-coordination [13] is too large to achieve isomorphous substitution of Ca^{2+} in the apatite structure.

Even with high-temperature synthesis, such a substitution was found only to a very limited extent [14] or partially with the bigger Cd^{2+} ion (0.110 nm). In a recent work dealing with Fe^{3+} in carbonate apatites, similar results were obtained. Iron was found to be in the FeOOH phase and not in the calcium site of the apatite lattice [15].

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