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Preparation, IR, and Lattice Constant Measurements of Mixed (Ca + Cu + Zn) Hydroxylapatites

N. K. TRIPATHY AND P. N. PATEL

Department of Chemistry, G.M. College, Sambalpur 768004, India

AND A. PANDA*

P.G. Department of Chemistry, Sambalpur University, Jyoti Vihar, Burla 768 019, India

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Homogeneous solid solutions of calcium, copper, and zinc hydroxylapatites keeping zinc content fixed have been prepared over the entire compositional range by the method of coprecipitation in aqueous media. Frequencies (cm^{-1}) and assignment for the infrared absorption and the lattice constants of the solid solutions have been measured and found to vary linearly with composition.

Introduction

Calcium hydroxylapatite (CaHA), $Ca_{10}(PO_4)_6(OH)_2$, the principal inorganic constituent of human bones and teeth (*1, 2*), belongs to an isomorphous series of compounds known as apatites. Calcium hydroxylapatite (CaHA) also exists in nature as the mineral hydroxylapatite, which is similar if not identical to that in bone mineral; it can be prepared from aqueous media (*3, 4*). The ionic radii (*5*) of calcium (0.99 Å), copper (0.72 Å), and zinc (0.74 Å) are close enough to enable the formation of solid solutions between isomorphous substances containing these ions. Apatite undergoes a series of cationic and anionic replacement reactions (*6*). The $Ca^{2+} \rightarrow Cu^{2+}$ and/or Zn^{2+} replacement reactions in CaHA are of extreme biological significance and, in view of its action on calcified tissue, are interesting. They form the basis of incorporation of Cu^{2+} and Zn^{2+} into the human skeletal system according to

$$Ca_{10}(PO_4)_6(OH)_2 + n\,Cu^{2+} + m\,Zn^{2+} \rightarrow Ca_{10-(n+m)}Cu_nZn_m(PO_4)_6(OH)_2 + (n+m)\,Ca^{2+}.$$

Solid solutions of calcium, copper, and zinc hydroxylapatites were prepared separately earlier (*7*) by firing mixtures containing various proportions of calcium, copper, and zinc hydroxylapatites at about 1300°C. These samples prepared by the solid-state reaction were, however, found to be discontinuous and nonhomogeneous.

Now an attempt has been made at a new method of preparation of the homogeneous

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* To whom correspondence should be addressed.

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solid solutions of mixed (Ca + Cu + Zn) hydroxylapatite over the entire compositional range by the method of coprecipitation.

Materials and Methods

All chemicals used for the preparation of these samples were either AR (BDH) or E. Merck Extra pure grade. Water used in the preparation and in washing was boiled to remove CO_2 and then used immediately.

Preparation

Stoichiometric quantities of ammonium dihydrogen phosphate (Solution A) and a solution containing Ca^{2+}, Cu^{2+}, and Zn^{2+} ions in the proportion desired for the solid solutions (Solution B) were prepared separately in CO_2-free doubly distilled water. The pH's of these solutions were maintained above 11 by the addition of excess of liquor ammonia. Then part of Solution B was transferred into a flask (2 dm^3) fitted with two separating funnels and a delivery tube. Solution A and Solution B were poured individually into the separating funnels and added dropwise to the flask simultaneously. Precipitation was carried out in CO_2-free atmosphere and the precipitation medium was well stirred by bubbling CO_2-free air to prevent the formation of carbonato-apatite.

The precipitate and mother liquor were aged by boiling under reflux for 30 min to improve the homogeneity and crystallinity of the precipitate and maintenance of the desired pH during precipitation was ensured by testing the filtrate after separation of the precipitate, since any alteration of pH of the medium during precipitation leads to the formation of calcium deficient apatites (*8*). The precipitate was washed thoroughly with doubly distilled water to free it from ammonium salts. Samples dried at 100°C for a few hours were analyzed complexometrically (*9*) and their molar volumes were determined by density method using toluene (*10*) as a solvent.

Infrared Absorption Techniques

Samples used for IR studies were washed with acetone and air dried. All the bands were recorded on a grating infrared spectrophotometer Model 577 (Perkin–Elmer) in KBr medium. A few milligrams of the sample was ground with two drops of Nujol in an agate mortar. About 50 mg of a fine polythene powder (Vestolena 6016 Chem. Werke Huels, Germany) was added. The resulting paste was melted rapidly at about 140°C and pressed between glass plates to form a slightly wedge-shaped film with an average thickness of 0.1 mm.

X-Ray Diffraction Techniques

Samples dried at 110°C for a few hours were used for X-ray diffraction. The X-ray diffraction patterns of the samples were obtained with Siemens powder diffractometer with NaCl (Tl) counter employing CuK_α (nickel-filtered) radiation with a 2θ scanning speed at 1°/min, using tube voltage of 30 kV and 24 mA.

Lattice Constant Measurements

CaHA, CuHA, and ZnHA are hexagonal with two lattice constants a_0 and c_0. These were determined (*11*) for some of the samples by measuring the diffraction angle 2θ of the three planes: (312), (213), and (321). Each sample was thoroughly mixed with 25% NaCl (recrystallized from HCl) which served as a standard so that the observed values of sin θ for the solid solution lines could be corrected directly for absorption and instrumental errors. The lattice constant of NaCl at 26°C was taken to be 5.6403 Å (*12*). A least-squares calculation on the corrected values of sin θ for the three reflections then gave the two parameters, a_0 and c_0, for each sample. The diffraction angle was read by counting over the top of the peak with the scaling unit and estimating

TABLE I

CHEMICAL ANALYSES OF CALCIUM, COPPER, AND ZINC HYDROXYLAPATITES AND THEIR SOLID SOLUTIONS

Sample	Wt %				Molecular formula	Mol. vol.	G. atom ratio Ca + Cu + Zn/P	Lattice parameter (Å)		Unit cell volume ($(\sqrt{3}/2)a^2c$)	Frequency (cm^{-1})		
	Ca	Cu	Zn	P				a	c		PO_4^{3-} ν_4	PO_4^{3-} ν_3	OH^- ν_3
1	39.89	—	—	18.51	$Ca_{10}(PO_4)_6(OH)_2$	338.271	1.666	9.37	6.86	521.60	570	1075	3450
2	30.22	6.63	5.89	17.52	$Ca_{7.95}Cu_{1.10}Zn_{0.95}(PO_4)_6(OH)_2$	326.675	1.667						
3	26.10	11.69	6.13	17.26	$Ca_{7.01}Cu_{1.98}Zn_{1.01}(PO_4)_6(OH)_2$	322.435	1.667	9.28	6.81	502.44	565	1072	3435
4	22.06	17.11	5.89	16.91	$Ca_{6.05}Cu_{2.96}Zn_{0.99}(PO_4)_6(OH)_2$	323.186	1.666						
5	18.03	22.07	6.11	16.55	$Ca_{5.05}Cu_{3.90}Zn_{1.05}(PO_4)_6(OH_2)$	327.134	1.667	9.22	6.77	498.40	567	1070	3425
6	14.13	27.44	5.76	16.21	$Ca_{4.04}Cu_{4.95}Zn_{1.01}(PO_4)_6(OH_2)$	328.937	1.667						
7	10.34	32.41	5.64	15.88	$Ca_{3.02}Cu_{5.97}Zn_{1.01}(PO_4)_6(OH)_2$	331.053	1.666	9.17	6.72	489.37	560	1086	3415
8	6.75	37.47	5.20	15.57	$Ca_{2.01}Cu_{7.04}Zn_{0.95}(PO_4)_6(OH)_2$	321.535	1.666						
9	3.63	41.20	5.49	15.29	$Ca_{1.1}Cu_{7.88}Zn_{1.02}(PO_4)_6(OH)_2$	325.915	1.667	9.08	6.66	475.53	560	1065	3410
10	—	46.18	5.16	14.97	$Cu_{9.02}Zn_{0.98}(PO_4)_6(OH)_2$	332.103	1.667						
11	—	51.27	—	15.00	$Cu_{10}(PO_4)_6(OH)_2$	347.718	1.666	8.83	6.53	440.93	555	1065	3400
12	—	—	51.99	14.78	$Zn_{10}(PO_4)_6(OH)_2$	347.806	1.667	9.02	6.52	459.4	550	1050	3375

the position of maximum intensity from a plot of intensity against 2θ. The average probable error in unit cell parameter is less than 0.005 Å.

Results and Discussion

The results of the chemical analysis of the samples are given in Table I. Based on the fact that 1 mole of each sample has a total of 10 G-atoms of calcium and/or copper and/or zinc the molecular formulas of the samples were calculated from the results of columns 2–4 and included in column 6 of Table I. The G-atom ratio (Ca + Cu + Zn)/P in 1 mole of each sample was calculated from the results of columns 2–5 and is given in column 8 of the table. The fact that the observed value of molar G-atom ratios of Ca/P, Cu/P, Zn/P for the end members and (Ca + Cu + Zn)/P were found to be equal to 1.66 (theoretical 1.67) is consistent with the formation of homogeneous solid solution (*12*). This was further supported by the closeness of values of molar volumes of end members and those of the intermediate samples which lie within the range of end members.

The formation of solid solutions can be further confirmed by the X-ray diffraction analysis. It is well established that all members of the apatite series belong to the hexagonal–dipyramidal class 6/*m* (space group $P6/_{3/m}$ (*13, 14*). Lattice parameters showed unit cell contraction consequent upon the introduction of smaller ions Cu^{2+} and Zn^{2+} in place of two Ca^{2+} ions in the apatite lattice. Such contraction with the proportion of Ca–Cu–ZnHA is evidence that the unit cell volumes of the samples calculated on the basis of the experimentally determined lattice constant decrease with the proportion of copper and zinc content in Ca–Cu–ZnHA.

The lattice constants are plotted in Fig. 1 against molar ratio Ca/Cu + Zn in the mixed hydroxylapatites, seen to lie on a straight line within the probable errors of the lattice constants. This, of course, is the real evidence for solid solutions in the series and clearly shows that these preparations are not mixtures of two components or one component with absorbed material.

The CaHA and its solid solutions with copper and zinc have hexagonal crystalline structure and are interesting examples of the solid state of fairly simple molecules of tetrahedral symmetry where bands are allowed due to relaxation of the molecular symmetry (*15*) selection rules due to the in-

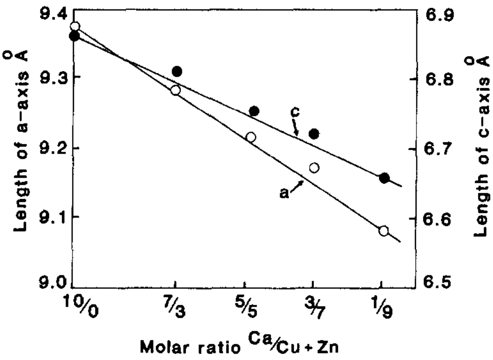

FIGURE 1.

fluence of site symmetry. The ideal symmetry of tribasic phosphate ion in the free or undistorted state is tetrahedral—a member of Td point group. Under this ideal symmetry condition only a few absorption bands corresponding to ν_4 (570 cm^{-1}) and ν_3 (1075 cm^{-1}) of PO_4^{3-} and ν_3 (3450 cm^{-1}) of OH^- were clearly observed. From the spectra of the samples it can be seen that the ν_3 and ν_4 frequencies corresponding to PO_4^{3-} ion and ν_1 and ν_3 corresponding to OH^- ion are shifted to lower frequencies and the shape of the peaks was affected by the introduction of copper and zinc ion into the samples. The shift of the ν_3 and ν_4 of PO_4^{3-} vibration to lower frequencies in general may be due to the effect of binding energy and atomic mass. The lowering of frequency of OH^- indicates the presence of a hydroxyl group in the apatite (*16*). This hydroxyl group in the hydroxylapatite lies in the internuclear axis coincident with sixfold screw axis. In Barnes's (*17*) expression

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}},$$

which gives a relationship between frequency, atomic mass, and force constant. The vibrational frequencies are dependent on the reduced mass μ of the participating atoms and restoring forces K between atoms, all other terms remaining constant. When the equilibrium distance between the positive and the negative atoms of the molecule is decreased K generally increases in the above equation. This equilibrium distance depends on the ionic radii of the participating atoms in the molecule. Substitution of Ca^{2+} with a nucleus like Cu^{2+} and/or Zn^{2+} gives rise to a stronger coordination of PO_4^{3-} group through oxygen. This in turn weakens the P–O bond, lowering K (increasing P–O bond length), and the frequency is lowered. The PO_4^{3-} binding is normally around 520 cm^{-1} and the bending mode does not shift very much under these conditions, but here the substitution is more complex, presumably because of the splitting of the triply degenerate mode at 600 cm^{-1}, and thus there is an increase in the frequency from 520 to 570 cm^{-1}. This theoretical explanation agrees well with the experimental data.

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