purity product for use in fused salt studies. Approximately fifty grams can be prepared in six hours.

The starting material employed was a grade of anhydrous aluminum fluoride whose purity ranged from 93 to 95%. The principal impurities were chiolite and alumina together with small amounts of SiO_2, MgO, Fe_2O_3, CaO, TiO_2, Ga_2O_3 and V_2O_5. The material was calcined at 800° for 30 minutes prior to carrying out the sublimation. There is no reason that reagent grade aluminum fluoride trihydrate would not be as good or better as a starting material provided all the water is removed with a minimum degree of hydrolysis by calcination at 600 to 800° in a stream of dry air.

The vacuum sublimation is conducted in a graphite system consisting of two high density graphite crucibles, each measuring 2.5 inches outside diameter, 1.75 inches inside diameter, and 2.5 inches deep. The lips of the two crucibles are machined in such a manner that the lip of one seats snugly about $^1/_8$ to $^1/_4$ inch into the lip of the second, providing a reasonably tight seal. Sitting vertically, the lower crucible serves as a retort to contain the starting material, and the top inside surface of the upper crucible serves as the condenser.

The crucible assembly is fitted into a type 86 Nichrome cylindrical heating element so that the windings are symmetrical about the mid-point of the assembly. The element is seated directly on a circular block of Insulbrick 4.5 inches in diameter and 2.5 inches thick. A similar Insulbrick block is used for insulation of the top of the assembly. This block is altered by removing a circular section the same diameter as the graphite crucible and 1 inch deep from the center surface. This "cup" is then placed open end down over the top surface of the graphite condenser crucible. The purpose of the removal of this cylinder of insulation is to provide a greater rate of heat loss to maintain a temperature gradient between retort and condenser.

Measurement of temperature gradient during operation is accomplished by two chromel–alumel thermocouples, one in contact with the center of the outside end of the condenser and one at the center of the outside end of the retort. About $^3/_4$ inch of fiber insulation is placed around the sides of the heating element but not on the end nor around the Insulbrick blocks. The furnace can be conveniently contained in a steel or aluminum cylinder 4.5 inches in diameter and 8 to 10 inches long. The geometry of the insulation block over the condenser can be altered slightly if necessary to achieve the correct temperature differential. The entire assembly is then placed into any suitable container which can be evacuated to about 500 μ pressure. A good product and substantial yield can be obtained at a pressure of 500 μ and with a temperature differential of 25 to 30° between the retort and condenser ends. Larger retort–condenser assemblies up to 3 inches diameter and 7 inches over-all length have been used successfully. It is important that the starting material and the entire assembly be bone dry before starting the sublimation.

About 80 g. of the anhydrous starting material is placed into the lower crucible, and the system is assembled. The entire assembly is then pumped down to about 500 μ and the temperature raised until the condenser is at 900° and the retort at approximately 925°. Sublimation is allowed to continue for three to six hours. At the completion of the run the power is turned off and the assembly is cooled to below 100° prior to releasing the vacuum. The product will consist of a dense pad of well-defined crystals on the underside of the top surface of the condenser. No product should be found on the sidewalls.

The pressure may be allowed to vary by $\pm 200\ \mu$ and the retort and condenser temperature by $\pm 25°$. The 25–30° differential should be maintained. The condenser temperature should not rise above about 925°. At 950° the yield is greatly reduced, the product being lost from the system.

The purity of the product varies slightly from batch to batch. A typical spectrographic analysis shows: Si, 0.008; Mn, <0.002; Fe, 0.002; Mg, 0.015; Cu, < 0.001; Na, < 0.05; Ti, <0.006; Ni, 0.001; Cr, 0.002; Ca, <0.06; V, 0.002; graphite, trace.

On the basis of aluminum and fluorine analysis together with trace analysis, the purity appears to be better than 99%. Purity can be increased by resublimation.

PERMANENTE, CALIFORNIA

[CONTRIBUTION FROM THE CANCER RESEARCH INSTITUTE OF THE NEW ENGLAND DEACONESS HOSPITAL]

Strontium–Calcium Hydroxyapatite Solid Solutions: Preparation and Lattice Constant Measurements[1]

BY ROBERT L. COLLIN

RECEIVED APRIL 20, 1959

Homogeneous solid solutions of strontium and calcium hydroxyapatite have been prepared over the entire composition range by heating to 950° precipitates formed by the addition of ammonium phosphate to solutions of calcium and strontium nitrate made strongly basic with ethylenediamine. The lattice constants of the solid solutions have been measured and found to vary linearly with composition between those of the pure end members. The solid samples have a much smaller ratio of strontium to calcium than the solutions from which they are precipitated.

Introduction

The ultimate site and mechanism of strontium incorporation into the bone structure of the body have been of great interest ever since the release of radioactive strontium into the atmosphere from nuclear bomb tests. As part of a more general program of research in this field the feasibility of preparing synthetic solid solutions of strontium in calcium hydroxyapatite has been investigated.

Calcium hydroxyapatite (CaHA), which exists in nature as the mineral hydroxyapatite, and is similar if not identical to bone mineral, can be prepared from aqueous solution.[2,3] Strontium hydroxyapatite (SrHA), although not found naturally, has also been prepared from aqueous solution by a number of workers.[4-6] X-Ray measurements of unit cell dimensions[4,6] indicate that these two hydroxyapatites are probably isomorphous and hence a possibility exists that solid solutions can be formed between the two compounds.

An attempt has been made by Lagergren and Carlström[6] to prepare solid solutions of SrHA and CaHA by precipitation from aqueous solution with subsequent heating above 600° to improve crystallinity. They were not successful and abandoned this procedure in favor of a solid state reaction at

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[1] This work was done under U. S. Atomic Energy Commission Contract AT(30-1)-901 with the New England Deaconess Hospital.

[2] R. Wallaeys and G. Chaudron, *Compt. rend.*, **231**, 355 (1950).

[3] E. Hayek and W. Stadlmann, *Angew. Chem.*, **67**, 327 (1955).

[4] R. Klement, *Z. anorg. allgem. Chem.*, **242**, 215 (1939).

[5] W. Rathje, *Ber.*, **74**, 342 (1941).

[6] C. Lagergren and D. Carlström, *Acta Chem. Scand.*, **11**, 545 (1957).

1300° between the pure components mixed together in various proportions. Using this method, they could prepare solid solutions only over a limited range of composition.

The ionic radii[7] of calcium (0.99 Å.) and strontium (1.13 Å.) are close enough together so that it would not be surprising if solid solutions could be formed between isomorphous substances containing these ions. Indeed, a complete series of solid solutions has been prepared between the orthorhombic structures (aragonite) of calcium and strontium carbonate although solid solution in the hexagonal (calcite) structure does not extend over all compositions.[8] Also, solid solutions of lead and CaHA have been prepared by Müller,[9] at least over part of the composition range. The ionic radius of lead is 1.21 Å.,[7] somewhat larger than that of strontium.

Experimental

Materials.—All chemicals were reagent grade except for the ethylenediamine which was practical grade. Water used in the preparations and in washing was boiled to remove CO_2 and then used immediately. Solutions of calcium and strontium nitrate of known composition were made up by pipetting out the desired volume of a stock solution of calcium nitrate, on which an analysis for calcium had been made,[10] and adding a weighed amount of strontium nitrate dried at 110°.

Preparations.—Many different preparative methods were tried before the necessary conditions of concentration and *p*H were discovered. The required amounts of calcium and strontium nitrate were added to one liter of water maintained at 95° by a water-bath and then 1.5 ml. of 85% ethylenediamine was added. The hot ammonium phosphate solution (2.1 g. $(NH_4)_2HPO_4$ in 500 ml. water) to which 4.5 ml. of 85% ethylenediamine had been added was pumped dropwise into the calcium–strontium solution which was being stirred by a motor-driven stirrer. Both solutions were initially more basic than *p*H 11, and this high basicity was maintained during the precipitation reaction and subsequent digestion. After all the phosphate had been added, the reservoir that had held the phosphate solution was rinsed out with water which was then combined with the original solution to give a total volume of 1700 ml. The precipitate and solution were maintained at 95° with stirring for 6 hr. and then the precipitate was allowed to settle overnight.

The supernatant was pulled off by an aspirator working through a fritted filter and the precipitate was washed repeatedly in the reaction vessel until the wash water reached *p*H 7. Up to this point CO_2 had been carefully excluded by performing all operations in a closed system behind NaOH traps. Once the wash water had reached neutrality there was not as great a need for these precautions and the precipitate could be washed by decantation in the open until there was no test for calcium or strontium. The precipitate was then filtered, dried at 110°, and part of it heated to 950° for 4 hr. in an electric furnace. X-Ray diffraction patterns were made on all samples and examined for the presence of the β-phosphate phase which would be formed during the heating if the precipitate contained phosphate in excess of the stoichiometric amount.[11] Samples showing even slight amounts of β-phosphate were discarded thus assuring that lattice constant measurements and, more important, strontium determinations were made on a pure apatite phase.

Even for the preparation of pure CaHA an excess of calcium ion was necessary to prevent the uptake of excess phosphate. The necessity for excess cation was even more evident in the preparation of SrHA. Accordingly, a considerable cation excess was used throughout. After the first few preparations it was apparent that calcium tended to precipitate out in preference to strontium and it was necessary to modify the total amount of starting cation present so as not to deplete the calcium entirely before the end of the precipitation. To cover the entire composition range the three different series shown in Table I were used. In series A a total of 0.0473 g. atoms of calcium plus strontium was used, in series B a total of 0.0707 g. atoms and in series C a total of 0.0946 g. atoms was used.

Large amounts of pure CaHA and SrHA for making the standard mixtures needed for the fluorescence analysis procedure were prepared by a modification of the method of Hayek and Stadlmann.[3] Ammonia was replaced with ethylenediamine, an excess amount of cation was always present, and the phosphate was added to the cation rather than *vice versa*. After drying at 110° and then heating 4 hr. at 950° samples were obtained that gave sharp X-ray diffraction patterns of the pure hydroxyapatite phases. Gravimetric determinations of calcium,[10] strontium[12] and phosphate[13] gave the following results. Calcd. for $Ca_{10}(PO_4)_6(OH)_2$: Ca, 39.88; PO_4, 56.71. Found: Ca, 39.84; PO_4, 55.58. Calcd. for $Sr_{10}(PO_4)_6(OH)_2$: Sr, 59.20; PO_4, 38.50. Found: Sr, 59.40; PO_4, 37.10.

Fluorescence Analyses.—The X-ray fluorescence analyses for strontium were made with a General Electric XRD3 unit modified for fluorescence measurements and provided with a lithium fluoride crystal. The sample, after being heated to 950°, was ground in a motor-driven mortar for $^1/_2$ hr. under acetone, then dried and 1.00 g. mixed with 0.50 g. of boric acid. The mixture was compressed at a pressure of 10,000 lb./in.^{2} into a pellet with a $^3/_4$ in. diameter and a thickness greater than $^1/_{16}$ in. in all cases. The boric acid has a very small absorption for Sr Kα X-rays and acts as a lubricant to give nicely compacted pellets. Small variations in pellet weight and ratio of sample to boric acid weight were shown to have no appreciable effect on the fluorescence intensity.

A series of standard pellets was prepared by mixing pure CaHA and SrHA together in various proportions. The Sr Kα intensity was read from these standards each time a series of unknowns was run and a calibration curve relating intensity of the Sr Kα line to atom % strontium[14] prepared from which the atom % strontium in the unknown could be read off with a probable error of ±1%.

Lattice Constant Measurements.—Both CaHA and SrHA are hexagonal with two lattice constants a_0 and c_0. These were determined for all samples by measuring the diffraction angle, 2θ, of the three planes, (312), (213) and (321) using a General Electric XRD3 Spectrogoniometer with nickel-filtered copper radiation. 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 directly corrected for absorption and instrumental errors. The lattice constant of NaCl at 26° was taken to be 5.6403 Å.[15] 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 lines were quite sharp and the diffraction angle was read by counting over the top of the peak with the scaling unit and taking the position of maximum intensity from a plot of intensity *vs.* 2θ. The average probable error in unit cell parameters is less than ±0.003 Å.

Results and Discussion

The precipitates formed from solution and dried at 110° gave X-ray patterns where the line breadth varied in a regular way with the composition of the precipitate and in some cases was fairly large. This line broadening was of a nature that would suggest varying inhomogeneity in the solid solution precipitates. These precipitates

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[7] A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1950, p. 70.

[8] R. Faivre, *Compt. rend.*, **219**, 73 (1944).

[9] M. Müller, *Helv. Chim. Acta*, **30**, 2069 (1947).

[10] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 350.

[11] G. Trömel and H. Möller, *Z. anorg. allgem. Chem.*, **206**, 227 (1932).

[12] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1928, p. 83.

[13] I. M. Kolthoff and E. B. Sandell, ref. 10, p. 395.

[14] Atom % strontium will mean, henceforth, g. atoms strontium/(g. atoms strontium + g. atoms calcium) × 100, and is the atom % calcium replaced by strontium in the phase under discussion.

[15] M. Straumanis and A. Ieviņš, *Z. Phys.*, **109**, 728 (1938).

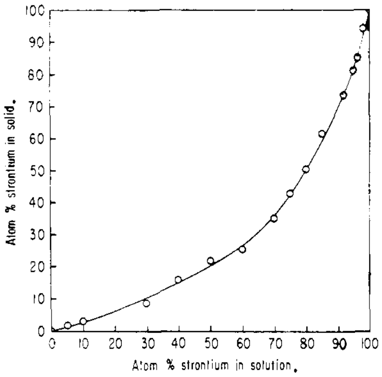

Fig. 1.—Atom % strontium in the solid preparation *vs.* atom % strontium in the initial solution.

also had a higher calcium to strontium ratio than the initial solution as is seen in both Table I and in Fig. 1. This discrimination between calcium and strontium by the precipitate means that the composition of the solution is continuously changing as precipitation occurs and therefore the precipitate composition is also changing. This explains why the precipitates after being dried at 110° are inhomogeneous. On heating to 950° a marked sharpening of the diffraction pattern occurs and in all cases there is no detectable line broadening over that of the two pure end members of the series. The exact mechanism of this crystal growth, or crystal perfection, is not clear but it probably involves, in part at least, a diffusion of strontium and calcium ions through the rather intimate mixture of somewhat similar solid solutions.

TABLE I

COMPOSITION OF INITIAL SOLUTIONS AND PRECIPITATES

Sample no.	Initial solution G. atoms Ca	G. atoms Sr	Atom % Sr	Solid Atom % Sr
A8	0.0473	0.0000	0.0	0.0
A9	.0449	.0024	5.1	1.9
A7	.0426	.0047	9.9	3.2
A6	.0331	.0142	30.0	8.8
A12	.0284	.0189	40.0	16.0
A5	.0236	.0236	50.0	21.9
B6	.0284	.0426	60.0	25.5
B1	.0212	.0495	70.0	35.3
B5	.0178	.0532	74.9	43.1
B2	.0142	.0566	79.9	50.6
B4	.0106	.0604	85.1	61.8
C5[a]	.0076	.0870	92.0	73.5
C4[a]	.0047	.0899	95.0	81.4
C8[a]	.0036	.0908	96.2	85.1
C6[a]	.0019	.0929	98.0	94.4
A17[a]	.0000	.0473	100.0	100.0

In all cases 0.0159 mole (2.10 g.) of $(NH_4)_2HPO_4$ was used.
[a] Double volume of 85% ethylenediamine used.

For the samples heated to 950° all lines out to at least 50° 2θ could be indexed on a hexagonal unit cell with a_0 and c_0 values between those of pure CaHA and SrHA. The lattice constants are plotted in Fig. 2 against atom % strontium and are seen to lie on a straight line joining the two end members, to within the probable errors of the lattice constants and the composition determinations. This, of course, is the real evidence for solid solution in this series and clearly shows that these preparations are not mixtures of two components or one component with adsorbed material.

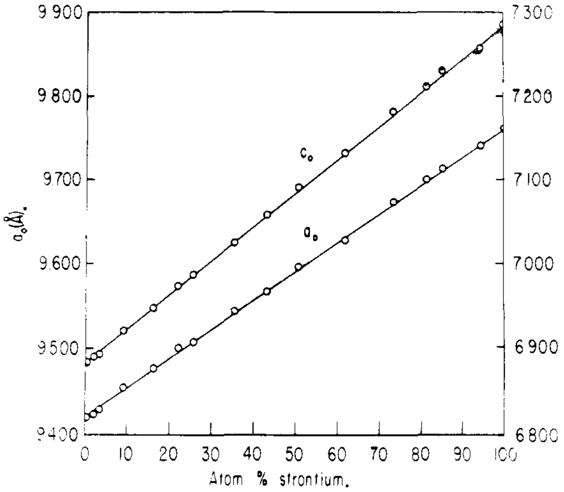

Fig. 2.—Lattice constants of solid solutions *vs.* atom % strontium.

It might be appropriate here to indulge in some speculation on the experiments of Lagergren and Carlström[6] and their inability to prepare a complete solid solution series by heating a mechanical mixture of CaHA and SrHA. Certainly from the present work it would appear that in the process of heating to 950° diffusion of strontium and calcium can occur to change an inhomogeneous solid solution into a homogeneous one. However, here, the mixture is exceedingly intimate and consists of solid solutions within a limited range of composition. It would be expected that in the experiments of Lagergren and Carlström the pure CaHA and SrHA particles were in contact at only a relatively few points and diffusion occurred only across these few boundaries. They were, however, able to prepare a homogeneous phase, with sharp diffraction lines, of 50 atom % strontium although compositions on either side were inhomogeneous. This is not surprising if it is realized that at a grain boundary the equiatom phase is the one that would tend to form by diffusion, other things being equal, and that this would be further augmented if one started with an equimolar mixture of CaHA and SrHA. It does not seem necessary to postulate, as Lagergren and Carlström have done, any special property of the 50 atom % phase, such as superlattice formation.

A comparison of lattice constants from this work with those of Lagergren and Carlström for the solid solutions that they were able to prepare is not feasible since their samples were heated to 1300° which, as they showed for pure CaHA, causes an appreciable decrease in lattice constant. However, the lattice constants they obtained for pure CaHA and SrHA heated to 900° can be compared with those found in this work and this is done in Table II. The agreement is quite satisfactory.

Conclusions

Homogeneous solid solutions can be formed in all proportions between CaHA and SrHA by

TABLE II

LATTICE CONSTANTS OF PURE CALCIUM AND STRONTIUM HYDROXYAPATITE IN Å.

		This work	Lagergren and Carlström[6]
CaHA	a_0	9.418 ± 3	9.423
	c_0	6.883	6.884
SrHA	a_0	9.760	9.761
	c_0	7.284	7.277

precipitation from basic solution with subsequent heating to 950°. Under the conditions of these experiments there is a marked discrimination against strontium in the precipitate. An extension of these data to processes occurring in biological systems of vastly different concentrations and *p*H is not yet possible. However, nothing has been brought out in this work that would indicate solid solutions of strontium in bone mineral are either unlikely or impossible.

Acknowledgment.—The assistance of Carlton Nelson and Paul Shanley in the experimental work is gratefully acknowledged.

BOSTON, MASS.

[CONTRIBUTION NO. 1043 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Magnesium–Cadmium Alloys. X. Heat Capacity of MgCd between 20 and 270° and a Final Evaluation of the Residual Entropy of the MgCd Superlattice[1,]

BY K. F. STERRETT, W. G. SABA AND R. S. CRAIG

RECEIVED APRIL 25, 1959

The heat capacity of MgCd has been measured between 25 and 270° by adiabatic calorimetric techniques permitting a precision of 0.1 to 0.2% in the measurements. The data show a sharp first degree transition at about 251° superimposed upon a broad second degree "order-disorder" transition of the type customary for such alloys. With the aid of the heat capacity data, the residual entropy of MgCd has been calculated to be 0.035 ± 0.04 e.u./g. atom. Standard heats, free energies and entropies of formation of the alloy at 270°, which were reported earlier, have been corrected to 25°. Transition energy and temperature agree well with values reported by other investigators.

In paper V of this series heat capacity data for MgCd between 12 and 320°K. were presented.[3] The entropy of formation of this substance at 270° had been determined[4] by the electrochemical cell method and in paper V the two sets of data were used to evaluate the residual entropy of the compound MgCd. The required thermal data above 320°K. for MgCd and for the pure metals were taken from the literature.

In this paper heat capacity data for MgCd from 20 to 270° are presented. These data together with heat capacities of the pure metals[5] recently determined in the same apparatus and the entropy of formation at 270° of MgCd are used to evaluate the residual entropy of the MgCd superlattice.

Experimental

Apparatus.—Full descriptions of the calorimetric equipment used may be found elsewhere.[6-9]

Materials Used.—The sample employed was the same as had been used in the earlier work.[3] Its composition was 50.52 ± 0.04 atomic % cadmium. The mass of the sample was 429.281 g. (*in vacuo*) or 6.2375 gram atoms of alloy.

Method of Measurement.—The intermittent heating technique has been used in this study. Heat is applied to the sample for a carefully measured interval of time of 5 to 15 minutes resulting in a temperature increment of roughly 5°. Temperature is then measured until it becomes constant, or at least until the drift is very small (10^{-5} deg./min.).

In contrast to the long equilibration times experienced with $MgCd_3$ and Mg_3Cd, as described in paper VIII[9] of this series, "normal" equilibration times of 20 to 30 minutes were observed in the measurements on MgCd below and above the "order-disorder" Curie point at 251°.

Transition Experiments.—The transition temperature could not be determined by a single direct measurement. The sample absorbed a large amount of energy from 251.08 to 251.30°. This range was obtained from the results of four partial heatings into the transition in which the heating was stopped periodically and the equilibrium temperature determined.

The energy absorbed by the sample in this 0.22° region was measured in two separate experiments. In each experiment the sample was continuously heated from a temperature below the transition to a temperature above the transition. The energy absorbed from 251.08 to 251.30° could then be calculated from a knowledge of the appropriate heat capacities of the sample below and above the transition.

Results

The data for MgCd were obtained in 15 series of measurements including transition point experiments involving a total of 126 determinations. The experimental details of each series of determinations are too numerous to relate here.[10]

Smoothed values for the heat capacities are given in Table I. Excluding the region immediately below the transition, where the heat capacity is rising sharply, the precision of the measurements is 0.1 to 0.2% as judged from the scatter of points from a smooth curve.

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[1] This work was supported by a grant from the U. S. Atomic Energy Commission.

[2] From a thesis submitted by K. F. Sterrett in partial fulfillment of the requirements for the Ph.D. degree at the University of Pittsburgh, June, 1957.

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[6] W. V. Johnston, Ph.D. Thesis, University of Pittsburgh, August 1955.

[7] K. F. Sterrett, Ph.D. Thesis, University of Pittsburgh, June 1957.

[8] W. E. Wallace, R. S. Craig and W. V. Johnston, U. S. Atomic Energy Commission Report, No. NYO-6328, Oct. 1955. This document is available from the U. S. Government Printing Office.

[9] W. V. Johnston, K. F. Sterrett, R. S. Craig and W. E. Wallace, THIS JOURNAL, **79**, 3633 (1957).

[10] These details are given in ref. 7.