Solid solutions of strontium-calcium hydroxylapatites containing arsenate

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Received 9 April 2003; revised 20 July 2004

Homogeneous solid solutions of strontium-calcium hydroxylapatite containing arsenate, \( \text{Ca}_{10-n}\text{Sr}_n(\text{PO}_4)_6(\text{AsO}_4)_m(\text{OH})_2 \), with fixed \( n = 1 \), have been prepared over the entire compositional range by co-precipitation in aqueous media. The infrared spectra and lattice constants of the solid solutions have been measured and found to vary linearly with composition between those of the pure end members.

IPC Code: C0IF 11/02

The mechanism of incorporation of strontium and arsenate into the bone mineral have been of great interest ever since the release of radioactive strontium (Sr-90) into the atmosphere from nuclear tests and arsenic due to environmental pollution. Calcium hydroxylapatite, \( \text{Ca}_10(\text{PO}_4)_6(\text{OH})_2 \), the principal inorganic constituent of human bones and teeth, belongs to an isomorphous series of compounds known asapatite. Calcium hydroxylapatite, \( \text{CaHA} \) (also called hydroxyapatite) which exists in nature as the mineral hydroxylapatite, is similar if not identical to bone mineral, can be prepared from aqueous solution.

Apatite undergoes a series of cationic and anionic replacement reactions. The \( \text{Ca}^{2+} \rightarrow \text{Sr}^{2+} \) and \( \text{PO}_4^{3-} \rightarrow \text{AsO}_4^{3-} \) replacement reactions in CaHA are of biological significance and in view of its action on calcified tissue is interesting. These reactions form the basis of incorporation of \( \text{Sr}^{2+} \) and \( \text{AsO}_4^{3-} \) into human skeletal system according to the following equation:

\[
\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + n\text{Sr}^{2+} + m\text{AsO}_4^{3-} \rightarrow \text{Ca}_{10-n}\text{Sr}_n(\text{PO}_4)_6m(\text{AsO}_4)_m(\text{OH})_2
\]

The preparation of solid solution of strontium and calcium hydroxylapatites containing arsenate by firing mixtures containing various proportions of strontium and calcium hydroxylapatites with arsenate at about 1300°C have been reported earlier. These samples prepared by the solid state reaction were, however found to be non-homogeneous.

We report herein a new method of preparation of the homogeneous solid solutions of strontium-calcium hydroxylapatite with arsenate over the entire compositional range by co-precipitation.

**Experimental**

All chemicals used for the preparation of these samples were of reagent grade. Water used in the preparation and for washing was boiled to remove \( \text{CO}_2 \) and then used immediately.

Solution A containing stoichiometric quantities of ammonium dihydorgen phosphate \((0.25 \text{ M})\) and diammonium hydrogen arsenate \((0.25 \text{ M})\) and solution B containing 0.25 M solution of each of strontium and calcium nitrate were prepared separately in \( \text{CO}_2 \)-free doubly distilled water. Both solutions were initially made more basic than pH 11 by addition of liquor ammonia and this high basicity was maintained during the precipitation reaction and subsequent digestion. Then, a part of solution B was put in a flask (2L) fitted with two separating funnels and a delivery tube. For the preparation of pure CaHA, an excess of calcium ion was necessary to prevent the uptake of excess phosphate. Accordingly, considerable cation excess was used throughout. Solutions A and B were poured individually into the separating funnels and added dropwise to the flask simultaneously. Precipitation was carried out in \( \text{CO}_2 \)-free atmosphere and the precipitation medium was well-stirred by bubbling \( \text{CO}_2 \) free air.

The precipitate and mother liquor were aged by boiling under reflux for 2 hrs to improve the homogeneity and crystallinity of the precipitate. The desired pH was maintained during precipitation by testing the filtrate after separation of the precipitate, since any alteration of pH of the medium during precipitation leads to the formation of cation-deficient apatite. The precipitate was allowed to settle overnight and washed repeatedly with doubly distilled water until the wash water reached pH 7. The precipitate, filtered and dried at 110°C for a few hours were analysed complexometrically by EDTA. Density was determined using toluene as a solvent and molar volumes were calculated.
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 50mg of a fine polyethylene powder (VESTOLENA 6016 chem. Werke Huels Germany) was added. The resulting paste was melted rapidly at about 140°C and lightly passed between two glass plates to give a slightly wedge-shaped film of an average thickness of 0.1mm.

After drying at 110°C and then heating for 4 hrs at 950°C, samples that gave sharp X-ray diffraction patterns of the pure hydroxyapatite phases were obtained. The X-ray diffraction patterns of the samples were obtained with Siemens Powder Diffractometer with NaCl (TL) counter employing CuKα (nickel filtered) radiation with a scanning speed of 1/ min using tube voltage 20 kV and 24 mA.

SrHA, CaHA and their solid solutions with arsenate are hexagonal with two lattice constants a₀ and c₀. These were determined for a few suitable samples by measuring the diffraction angle, 2θ, of the three planes, 312, 213 and 321. Each sample was thoroughly mixed with 25% NaCl (recrystallised from HCl), which served as a standard so that the observed values of Sinθ for the solid solution lines could be directly corrected for absorption and instrumental errors. The lattice constant of NaCl at 26°C was taken to be 5.6403Å. A least squares calculation on the corrected values of Sinθ for the three reflections gave the two parameters, a₀ and c₀, for each sample. The average probable error in unit cell parameters is less then ±0.005Å.

Results and discussion

The results of chemical analyses of the samples are given in Table 1. Molecular formula for each of the samples was assigned on the basis of the results of chemical analysis.

The molecular formulae of the samples were calculated from the results in Table 1. Observed values of molar g atomic ratio of Ca/P, Ca/As, Sr/As for end members and Ca + Sr / P + As were found to be 1.666 (theoretical 1.67), consistent with the formation of homogeneous solid solution

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Wt% found</th>
<th>g. atom ratio</th>
<th>Molar vol ml/mol</th>
<th>Lattice parameters, Å</th>
<th>Unit cell volume (\sqrt{3}/2a^*c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca₀.99(Sr₀.01)(PO₄)₀.985(OH)₂</td>
<td>39.92</td>
<td>- 18.49</td>
<td>-</td>
<td>1.671</td>
<td>337.73</td>
</tr>
<tr>
<td>Ca₀.99Sr₀.01(PO₄)₀.982(AsO₄)₀.083(OH)₂</td>
<td>33.10</td>
<td>7.81 14.35</td>
<td>6.61</td>
<td>1.667</td>
<td>346.42</td>
</tr>
<tr>
<td>Ca₀.99Sr₀.01(PO₄)₀.955(AsO₄)₀.05 (OH)₂</td>
<td>31.73</td>
<td>7.35 10.64</td>
<td>13.65</td>
<td>1.664</td>
<td>350.67</td>
</tr>
<tr>
<td>Ca₀.99Sr₀.01(PO₄)₀.961(AsO₄)₀.039(OH)₂</td>
<td>30.66</td>
<td>7.19 7.93</td>
<td>18.84</td>
<td>1.670</td>
<td>351.01</td>
</tr>
<tr>
<td>Ca₀.99Sr₀.01(PO₄)₀.961(AsO₄)₀.039(OH)₂</td>
<td>29.39</td>
<td>7.20 5.16</td>
<td>24.17</td>
<td>1.670</td>
<td>353.12</td>
</tr>
<tr>
<td>Ca₀.99Sr₀.01(PO₄)₀.961(AsO₄)₀.039(OH)₂</td>
<td>28.30</td>
<td>6.92 2.36</td>
<td>29.58</td>
<td>1.667</td>
<td>353.43</td>
</tr>
</tbody>
</table>

[^1]: Br J Chem, 1965, 50(Wt % found)
[^3]: Br J Chem, 1967, 52
[^4]: Br J Chem, 1968, 53
[^5]: Br J Chem, 1969, 54
This is the symmetry imposed by the static field of the surrounding ions. In addition to this field, there is a dynamic interaction between the ions, which has also strong influence on the internal vibration of \( \text{PO}_4^{3-} \). Under this ideal symmetrical condition, only two infrared active modes are observed\(^{17,18} \) in the region 1000-1100 cm\(^{-1} \); \( v_3 \) the P-O stretch and 500 - 570 cm\(^{-1} \), \( v_4 \) the P-O bending.

From the IR spectra of the samples, it can be seen that the \( v_3 \) and \( v_4 \) frequencies corresponding to \( \text{PO}_4^{3-} \) are \( v_3 \) (1075 cm\(^{-1} \), \( v_4 \) (570 cm\(^{-1} \)) for \( \text{CaHA} \), \( v_3 \) (1065 cm\(^{-1} \)) and \( v_4 \) (565 cm\(^{-1} \)) for \( \text{SrHA} \). The frequencies corresponding to \( \text{AsO}_4^{3-} \) ion are \( v_3 \) (800 cm\(^{-1} \)) and \( v_4 \) (400 cm\(^{-1} \)) and for solid solutions containing arsenate, the frequencies lie in the above mentioned region. The shape of the peaks was also effected by the introduction of strontium and arsenate ions into the samples.

The frequency \( v_3 \) corresponding to \( \text{OH}^- \) ion is seen at 3550 cm\(^{-1} \) (Calc 3578 cm\(^{-1} \)) for \( \text{CaHA} \). In the case of \( \text{SrHA} \), the free \( \text{OH}^- \) stretching mode appears at 3525 cm\(^{-1} \) whereas in the case of solid solutions containing arsenate, the absorption band of \( \text{OH}^- \) ion appeared at lower frequencies.

The above data show that the lattice parameters and unit cells expand with the substitution of larger ions. According to Nakamoto, isomorphic substitution of \( \text{Ca}^{2+} \) ions by \( \text{Sr}^{2+} \) ions causes interesting shifts of \( v_3 \) (1075 cm\(^{-1} \)) and \( v_4 \) (570 cm\(^{-1} \)) vibrations of \( \text{PO}_4^{3-} \) ions to lower frequencies. Similar effects were also observed for the \( v_3 \) frequency of the \( \text{OH}^- \) ions. These shifts may be due to substitution of \( \text{Ca}^{2+} \) ions by larger \( \text{Sr}^{2+} \) ions. This expansion in the unit cell parameters allows the bond distances in the anions, that are present in the unit cell, to increase thereby lowering the related force constants. This lowering in the force constant values in turn lowers the frequencies for \( v_3 \) and \( v_4 \) of the \( \text{PO}_4^{3-} \) ions and \( v_3 \) of the \( \text{OH}^- \) ions. However, in the case of anionic substitution of \( \text{PO}_4^{3-} \) ions by \( \text{AsO}_4^{3-} \) ions, there is a difference in the direction of shift of the frequencies for \( v_3 \) (800 cm\(^{-1} \)) and \( v_4 \) (400 cm\(^{-1} \)) of \( \text{AsO}_4^{3-} \) ion. This difference may be due to the larger atomic size and mass for arsenic in an arsenate ion than for phosphorus in a phosphate ion.

In general, the frequencies corresponding to \( v_3 \) and \( v_4 \) of the phosphate ion, and \( v_3 \) of the hydroxyl ion shift to lower frequencies with cation substitution. The frequencies corresponding to \( v_3 \) and \( v_4 \) of arsenate ion increase with increase in the arsenate content. These trends were in accordance with the distortion of the structures of the various anions with various cation or anion substitutions.

References
4 Wells A F, Structural inorganic chemistry (Oxford University Press, London) 1950, pp. 70.