

Preparation and characterisation of phosphate and arsenate apatites of barium and their solid solution

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Abstract. Phosphate and arsenate apatites of barium and one of their solid solutions were prepared by a wet method and characterized by chemical, x-ray, infrared and thermogravimetric analyses. Chemical analysis gave the stoichiometry of the samples while x-ray and infrared studies confirmed the formation of a solid solution. The range of thermal stabilities of the samples was established through thermogravimetric analysis.

Keywords. Apatites; solid solutions; thermogravimetric analysis.

1. Introduction

Calcium hydroxylapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, the principal inorganic constituent of bones and teeth (Posner 1961) undergoes several cationic and anionic exchange reactions leading to the formation of the corresponding isomorphs. Phosphate and arsenate apatites of barium (abbreviated as BaPA and BaAsA respectively) are important consequent upon the toxicity of elemental barium (Boyd 1962; Deichmann and Gerarde 1962) and arsenic (Stewart and Stolman 1960). The need for a wet method for preparation of BaPA, BaAsA and a representative solid solution was felt since the earlier methods (Narasaraju *et al* 1975; Mayer *et al* 1979) failed and hence the present investigations adopting co-precipitation were undertaken. In addition, the samples were characterized through chemical, x-ray IR and thermogravimetric analyses.

2. Experimental

The samples were prepared by a modification of an existing method (Narasaraju *et al* 1977) used for other apatites and was based on the equation,



where $X = \text{P}$ or As or $(\text{P} + \text{As})$.

While stock solutions ($\approx 0.5 \text{ M}$) of barium acetate, diammonium hydrogen phosphate were prepared in CO_2 -free water, sodium arsenate solution was obtained by dissolving As_2O_5 in sodium hydroxide solution. Barium, phosphorus and arsenic contents of the respective solutions were determined by complexometric (West 1969),

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gravimetric (Washburn and Shear 1932), and iodometric (Narasaraju *et al* 1971–72) methods, respectively. Appropriate volumes of these solutions based on the stoichiometry given in (1), required for ≈ 30 g yield of the desired sample were mixed at 37°C with the required volume of ethylene-diamine to attain a pH of 12. CO_2 -free air was bubbled through the mixture to eliminate the formation of carbonate apatite and to keep it well stirred. The suspension was refluxed for about 3 hr, left overnight and washed till the washings were neutral. The precipitate, suspended in a 2% EDTA solution containing ammonium chloride and ammonium hydroxide (Wier *et al* 1971; Smith *et al* 1974) to maintain a pH of 10, was subjected to rigorous mechanical shaking for about 6 hr. It was filtered through a G_4 sintered glass crucible and washed with double distilled water till the washings were neutral and free from EDTA. A 2% portion of each of the samples was washed with acetone and air-dried, while the rest of the sample was dried to constant weight at 110°C , cooled in a desiccator and analysed (Vogel 1962), for PO_4^{3-} , AsO_4^{3-} and Ba^{2+} . X-ray diffraction patterns of the samples were recorded using CuK_α radiation. The IR absorption spectra in the range, $650\text{--}4000\text{ cm}^{-1}$, were recorded as nujol mulls with a Perkin Elmer IR spectrometer (Model 297) equipped with potassium bromide optics. The densities of the samples were determined by standard methods (Salzberg *et al* 1966). The acetone-washed and air-dried samples were subjected to thermoanalytical investigations using a thermogravimetric furnace (Fertilizer Corporation of India, Sindri, India), upto 800°C .

4. Results and discussion

Chemical analyses gave atomic ratios, $\text{Ba}/(\text{P} + \text{As})$, ranging between 1.66 to 1.68, which are in good agreement with the stoichiometric value, 1.67 (see table 1) indicating the suitability of the methods adopted for the preparation and chemical analyses of the samples.

The lattice parameters a and c were found to be 10.14 and 7.73 Å for BaPA, and 10.66 and 7.92 Å for BaAsA, while the solid solution has intermediate values. A linear dependence of the unit cell volumes of the samples on their arsenate content shows the validity of Vegard's law confirming thereby the homogeneity of the samples. A marginal dilation in the unit cell volumes and hence, the molar volumes of the samples consequent upon the replacement of PO_4^{3-} by AsO_4^{3-} (covalent radii 1.10 and 1.18 Å, respectively, Wells 1950), was observed as expected (see table 2). This is in accordance with the criteria of formation of solid solutions (Azaroff 1960).

The IR traces (Mayer *et al* 1979) of the solid solution of BaPA and BaAsA exhibited predominant absorption peaks due to PO_4^{3-} , AsO_4^{3-} and OH^- while the end members showed the characteristic peaks of PO_4^{3-} or AsO_4^{3-} along with that of OH^- . The weight loss in each case was found to be uniform upto 500°C beyond which there was the weight became constant. These studies indicated that the samples were thermally stable upto the temperature investigated. In case thermal decomposition is to set in within this range, a discontinuity in the plot depicting weight loss as a function of temperature is anticipated. The uniform weight loss observed as a function of temperature can be attributed to the loss of adsorbed water. The presence of adsorbed water (Rootare *et al* 1962; Chickerur *et al* 1969) in the samples of apatites prepared by these wet methods can be explained on the basis of the large surface area associated with them consequent upon their small particle size.

Table 1. Chemical analyses of phosphate and arsenate apatites of barium and a representative solid solution of the two.

| Samples | Weight (%) [*] | | | | | | g atom ratio Ba/(P + As) | Molecular formula [†] |
|----------------|-------------------------|------------|-------|------------|-------|------------|--------------------------|--|
| | Ba | | P | | As | | | |
| | Found | Calculated | Found | Calculated | Found | Calculated | | |
| BaPA | 69.69 | 69.46 | 9.42 | 9.40 | — | — | 1.67 | Ba _{1.0} (PO ₄) ₆ (OH) ₂ |
| Solid solution | 65.05 | 65.12 | 4.38 | 4.41 | 10.72 | 10.66 | 1.66 | Ba _{1.0} (PO ₄) ₅ (AsO ₄) ₁ (OH) ₂ |
| BaAsA | 60.86 | 61.29 | — | — | 19.75 | 20.06 | 1.68 | Ba _{1.0} (AsO ₄) ₆ (OH) ₂ |

^{*} Mean of six determinations; [†] based exclusively on Ba, P and As contents, (OH⁻) content being assumed stoichiometric.

Table 2. X-ray and IR analyses of phosphate and arsenate apatites of barium and a representative solid solution of the two.

| Sample | Lattice parameters A | | Molar volume ml/mole | | IR data Wave number (cm ⁻¹) | | |
|----------------|----------------------|----------|------------------------|------------|--|--------------------------------|-----------------|
| | <i>a</i> | <i>c</i> | <i>V_m.N</i> | <i>M/d</i> | PO ₄ ³⁻ | AsO ₄ ³⁻ | OH ⁻ |
| BaPA | 10.14 | 7.73 | 414 | 413 | 990 | — | 3560 |
| Solid solution | 10.38 | 7.91 | 444 | 469 | 980 | 800, 870 | 3560 |
| BaAsA | 10.66 | 7.92 | 469 | 502 | — | 800, 870 | 3560 |

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References

- Azaroff L V 1960 *Introduction to solids* (New Delhi: Tata McGraw Hill) p. 90
 Boyd W 1962 *A text book of pathology* (Philadelphia: Lea and Febiger) p. 428
 Chickerur N S, Singh R P and Narasaraju T S B 1969 *Indian J. Chem.* **7** 6
 Deichmann W B and Gerarde H W 1962 *Toxicology of drugs and chemicals* (New York: Academic Press) p. 113
 Mayer I, Wahnon S and Cohen S 1979 *Mater. Res. Bull.* **14** 1479
 Narasaraju T S B, Rao K K, Rai U S and Kapoor B K 1977 *Indian J. Chem.* **15** 1014
 Narasaraju T S B, Rai U S and Rao K K 1971-72 *J. Sci. Res. Banaras Hindu Univ* **22** (2)
 Narasaraju T S B, Rao V L N, Lal Misri and Rai U S 1975 *Indian J. Chem.* **13** 369
 Posner A S 1961 *Phosphorus and its compounds* (ed.) J R Van Wazer (New York: Interscience) p. 1429
 Rootare H M, Dietz V R and Carpenter F G 1962 *J. Coll. Sci.* **17** 179
 Salzberg H W, Marrow J I and Cohen S R 1966 *Laboratory course in physical chemistry* (New York: Academic Press) p. 67
 Smith A N, Posner A M and Quick J P 1974 *J. Colloid Interface Sci.* **48** 442
 Stewart C P and Stolman A 1960 *Toxicology, mechanism and analytical method* (New York: Academic Press) p. 202
 Vogel A I 1962 *A text book of quantitative inorganic analysis, including elementary instrumental analysis* (London: Longmans Green) p. 553
 Washburn M L and Shear M J 1932 *J. Biol. Chem.* **99** 21
 Wells A F 1950 *Structural inorganic chemistry* (Oxford: University Press) p. 50
 West T S 1969 *Complexometry with EDTA and related reagents* 3rd ed. (Bombay: BDH Chemicals Ltd) p. 190
 Wier D R, Chien S H and Black C A 1971 *Soil Science* **111** 107