# PREPARATION AND CHARACTERIZATION OF SOLID SOLUTIONS OF PHOSPHATE AND VANADATE APATITES OF LEAD

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## ABSTRACT

Samples of lead phosphate apatite, lead vanadate apatite and a series of their solid solutions spread over the entire composition range were prepared by a modification of the existing wet method. The samples were characterized through x-ray, electron microscopic and infrared analysis and their stoichiometry confirmed by chemical analyses. Validity of Vegard's law established the formation of solid solutions. Purity and homogeneity of the samples were confirmed by electron microscopic and IR analyses.

## INTRODUCTION

CALCIUM hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$, the principal inorganic constituent[1] of human bones and teeth, has been the subject of extensive investigations by virtue of its biological significance and the remarkable ability to undergo a series of cationic and anionic exchange reactions; important among the former is the replacement[2,3] of $Ca^{2+}$ by $Pb^{2+}$ to form an isomorph, lead phosphate apatite, $Pb_{10}(PO_4)_6(OH)_2$, (abbreviated as LPA). Such an exchange has been shown to be the basis for the incorporation of lead in human skeletal system causing lead poisoning[4,5]. Similarly the replacement of phosphorus by vanadium resulting in another isomorph, lead vanadate apatite, $Pb_{10}(VO_4)_6(OH)_2$, (abbreviated as LVA), leads to vanadium poisoning consequent upon the toxicity[6,7] of the latter. While the preparation of LPA and its solid solutions with calcium hydroxylapatite were investigated[8-10], similar studies of systems involving LPA and LVA were not made. The present investigations deal with the preparation of a series of solid solutions of LPA and LVA by a wet method and their characterizations through x-ray, IR and electron microscopic analyses.

## EXPERIMENTAL

The preparation of the samples was based on the following equations:

$$10\,Pb^{2+} + 6XO_4^{3-} + 2OH^- \Rightarrow Pb_{10}(XO_4)_6(OH)_2$$

where X = P or V or (P + V). While stock solutions of $Pb^{2+}$ and $PO_4^{3-}$ were prepared from lead acetate and diammonium hydrogen phosphate in double distilled water, sodium orthovanadate solution was obtained by dissolving vanadium pentoxide in sodium hydroxide solution. All these solutions were preserved in polyethylene containers. The amounts of lead, phosphorus and vanadium present in the respective solutions were determined by complexometric[11], Washburn and Shear's[12] and iodometric[13] methods respectively. Aqueous solutions of the reactants containing stoichiometric quantities required for an yield of ~ 30 g of the sample were used. An appropriate volume of lead acetate solution added to a required volume of ethylenediamine[10,14,15], to maintain a pH of 12 on dilution to 1000 ml was taken in a 3 litre round bottom flask.

Diammonium hydrogen phosphate and/or sodium orthovanadate solutions stoichiometric with that of $Pb^{2+}$ solution taken were treated with ethylenediamine and diluted to 1000 ml such that the pH of the resulting solution was 12. This solution was added dropwise to that of $Pb^{2+}$. The precipitation was done at 37°C to simulate biological conditions. Air (free from $CO_2$) was bubbled through the medium to eliminate the formation of carbonate apatite. The precipitate was refluxed for about two hours in contact with the mother liquor, left overnight, filtered through a 1G4 sintered glass crucible and washed with water till the washings were neutral. In order to eliminate extraneous phases[16] likely to get co-precipitated with the sample, the latter was equilibrated for about 6 hr with 2% EDTA solution maintained at a pH of 10. The sample was washed with acetone and air dried. A part of the sample was heated to 300°C for 6 hr[14] and cooled in a desiccated atmosphere. This was used for chemical, x-ray and IR analyses. The weight per cents of Pb, P and V of the samples were determined by

**Table 1** *Chemical Analyses of Solid solutions of Phosphate and Vanadate apatites of Lead.*

| Sl. No | Sample | Wt (%) Pb | P | V | g atom ratio, Pb/(P + V) | Molecular formula* |
|---|---|---|---|---|---|---|
| (1) | (2) | (3) | (4) | (5) | (6) | (7) |
| 1 | Lead Phosphate apatite (LPA) | 77.86 | 6.97 | — | 1.67 | $Pb_{10}(PO_4)_6(OH)_2$ |
| 2 | Solid Solution I | 76.61 | 6.19 | 1 16 | 1.66 | $Pb_{10}(PO_4)_{5\ 4}(VO_4)_{0\ 6}(OH)_2$ |
| 3 | Solid solution II | 77.36 | 5 13 | 2.74 | 1.70 | $Pb_{10}(PO_4)_{4\ 5}(VO_4)_{1\ 5}(OH)_2$ |
| 4 | Solid Solution III | 76.69 | 4 15 | 4.22 | 1.71 | $Pb_{10}(PO_4)_{3\ 69}(VO_4)_{2\ 31}(OH)_2$ |
| 5 | Solid Solution IV | 75.46 | 2.99 | 6.40 | 1.64 | $Pb_{10}(PO_4)_{2\ 6}(VO_4)_{3\ 4}(OH)_2$ |
| 6 | Solid Solution V | 75 26 | 2.15 | 7.54 | 1.67 | $Pb_{10}(PO_4)_{1\ 9}(VO_4)_{4\ 1}(OH)_2$ |
| 7 | Solid Solution VI | 75 69 | 1.32 | 8.81 | 1.69 | $Pb_{10}(PO_4)_{1\ 2}(VO_4)_{4\ 8}(OH)_2$ |
| 8 | Lead Vanadate apatite (LVA) | 74.37 | — | 10.80 | 1.69 | $Pb_{10}(VO_4)_6(OH)_2$ |

* Based exclusively on Pb, $PO_4^{3-}$ and $VO_4^{3-}$ contents, ($OH^-$) content being assumed to be stoichiometric.

methods[17] specially worked out by us for the purpose and reported in columns 3, 4, 5 of table 1. From these results the molecular formulae were calculated and given in column 7 of the table. The g atom ratio, Pb/(P + V) was calculated and included in column 6. The samples were characterized through x-ray and infrared analyses, the experimental details being the same as those described elsewhere[16]. Using a microcomputer the lattice parameters and unit cell volumes were refined by least squares[14] and given in table 2. The electron micrographs of the air dried samples were obtained with water as dispersion medium and carbon as back ground. The IR data of the samples are also given in table 2.

## RESULTS AND DISCUSSION

The data in table 1 show that g atom ratios, Pb/(P + V), vary between 1.64 to 1.71, the theoretical value being 1.67. A striking agreement between the experimental g atom ratios, Pb/(P + V), of the samples with the stoichiometric value justifies the suitability of the methods adopted for preparation as well as for chemical analyses of the samples.

The criteria[18] for formation of solid solutions among isomorphs are (i) the charges of the replaced and replaceable ions should be the same and (ii) the ionic radii of the pair of ions involved should be comparable. While a fulfilment of the desired criteria justifies the formation of solid solutions of LPA and LVA over the entire compositional range, a marginal dilation in the unit cell volume, consequent upon the replacement of $PO_4^{3-}$ by $VO_4^{3-}$ in LPA lattice, resulting in the formation of solid solutions over the entire compositional range has been substantiated by the validity of Vegard's law as indicated by a linear dependence of the unit cell volumes on the composition of the samples as shown in figure 1 and column 4 of table 2. The IR traces[20, 21] of the solid solutions of LPA and LVA exhibited predominant absorption peaks due to $PO_4^{3-}$, $VO_4^{3-}$ and $OH^-$ while the end members showed the characteristic peaks of $PO_4^{3-}$ or $VO_4^{3-}$ along with that of $OH^-$. In addition, absence of extraneous peaks in the patterns eliminated the possibility of contamination of the samples.

The electron micrographs of LPA, LVA and a few representative solid solutions indicated that the individual crystals of the samples were mostly either tabular or ribbon-like in shape tending to look like elongated flattened hexagonal prisms[22]; the crystals existed individually as well as in clusters. Based on the identity of the shape of the individual crystals, evidence for the absence of phases other than that of apatite could be obtained confirming thereby, the homogeneity of the samples. For electron microscopic investigations, air-dried samples were found to be better suited than those heated to high temperatures as the latter operation was found to lead to fusion of the crystals[23].

Preference for co-precipitation technique to crystal-

**Table 2** *X-ray and IR analyses of Solid Solutions of Phosphate and Vanadate apatites of Lead.*

| | X-ray Data | | | | IR Data Wave number ($Cm^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | Lattice Parameters (Å) | | Unit cell volume, $V_{uc}$ | Molar volume | | | |
| Samples* No. | a | c | $(\sqrt{3}/2)a^2c$ $(Å)^3$** | $V_{uc}.N$ (ml/mole) | $PO_4^{3-}$ | $VO_4^{3-}$ | $OH^-$ |
| (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) |
| 1 | 9.8877 | 7.4476 | 630.6 (629.7) | 379.8 | 1040(m),975(s) | — | 3560(s) |
| 2 | 9.9172 | 7.4477 | 634.4 (634.7) | 382.1 | 1040(m),980(s) | 780(m) | 3560(s) |
| 3 | 9.9614 | 7.4478 | 640.0 (641.7) | 385.5 | 1040(m),980(s) | 780(m),760(s) | 3540(m) |
| 4 | 9.9997 | 7.4479 | 645.0 (642.9) | 388.5 | 1050(m),980(s) | 800(m),750(s) | 3520(m) |
| 5 | 10.0557 | 7.4480 | 652.2 (652.5) | 392.8 | 1050(m),980(s) | 800(m),750(s) | 3540(w) |
| 6 | 10.0911 | 7.4481 | 656.8 (657.4) | 395.6 | 1050(m),980(s) | 810(m),750(s) | 3540(m) |
| 7 | 10.1235 | 7.4482 | 661.1 (664.1) | 398.2 | 1050(m),965(s) | 800(m),750(s) | 3540(w) |
| 8 | 10.1825 | 7.4483 | 668.8 (666.1) | 402.8 | — | 800(m),740(s) | 3515(w) |

* Details are given in colum 2 of table 1; ** Experimental values are given in parentheses. s = strong; m = medium; w = weak.

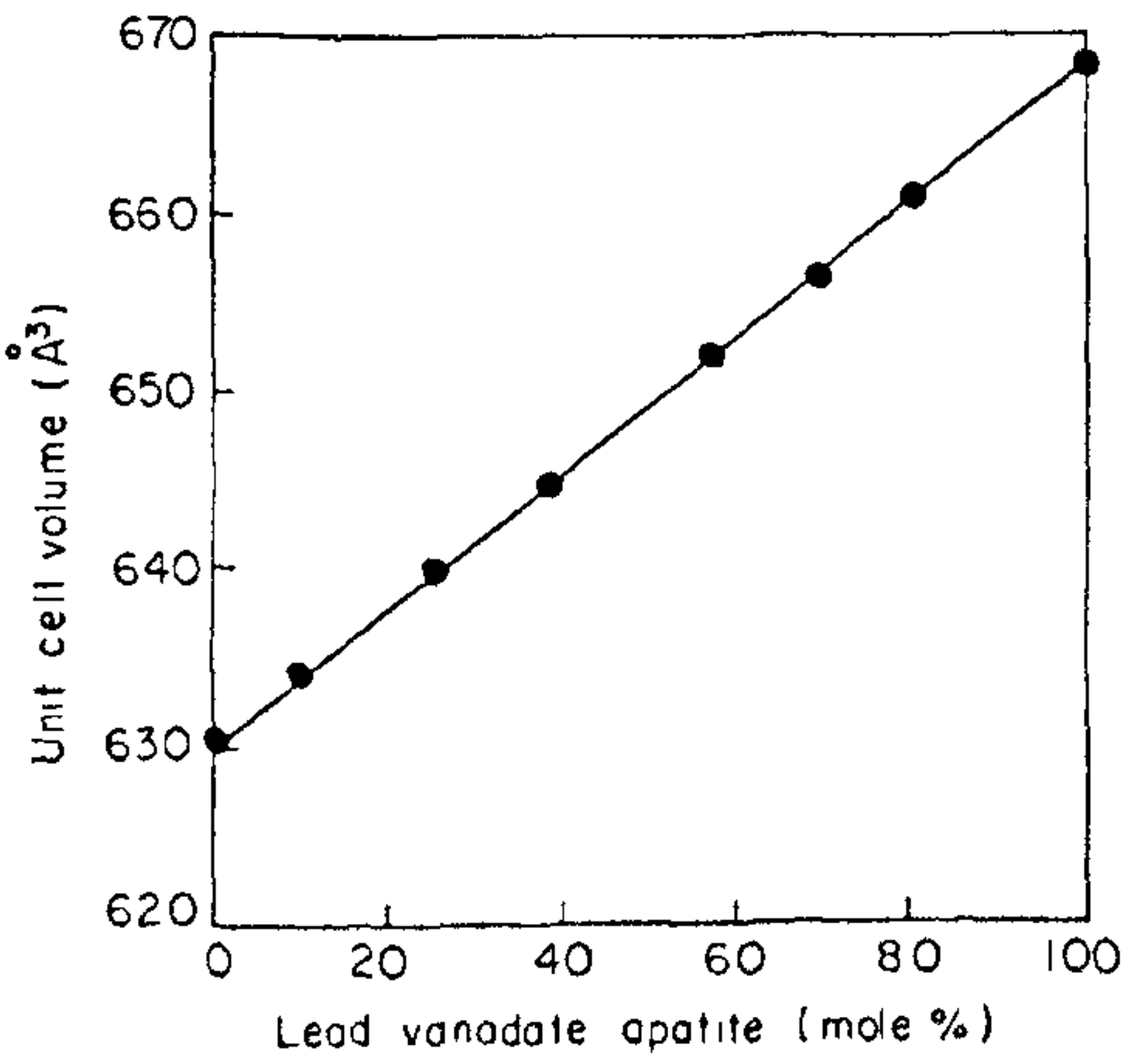


**Figure 1.** Dependence of unit cell volume on mole per cent of lead vanadate apatite

lization from fused mixtures for the preparation of the solid solutions was based on the consideration that fusion needs different temperatures for the end-members resulting in decomposition due to inequalities in individual thermal stabilities. Formation of the tertiary phosphates of heavy metals through a conventional precipitation from aqueous media was complicated due to co-precipitation of their hydroxides and acid phosphates[3]. Among the methods available for elimination of such a co-precipitation[24,25], that of Hayek[24] involving complexing of the heavy metal ions with an appropriate ligand was found to be suitable. It was shown by Keller and Eyke[16] that lead forms well-defined soluble complexes with ethylenediamine and its monosubstituted derivatives. The lead ions present in the solution used for the preparation of the samples were thus retained as soluble complexes to prevent their precipitation as hydroxide at pH ~ 12 chosen for the preparation. The mechanism of precipitation of LPA, LVA and their solid solutions was based on the consideration that the lead

complex dissociated setting free $Pb^{2+}$ ions thus facilitating the precipitation on availability of $PO_4^{3-}$ and $VO_4^{3-}$ ions.

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