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Crystal structure of the substituted apatites – deviation from Vegard's Law

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The substituted apatites $Ca_{10}(PO_4)_{6(1-x)}(VO_4)_{6x}(OH)_2$ and $Pb_{10}(PO_4)_{6(1-x)}(VO_4)_{6x}(OH)_2$, where x is the fraction of vanadate, were prepared in the powdered microcrystalline nature. The X-ray diffraction patterns and the infrared spectra of these substituted apatites were recorded. The analysis of the measurements established that the unit cell parameters did not vary smoothly with the degree of substitution as expected by the Vegard's Law. Two different types of linear behaviour in the two regions 0 to 50% and 50 to 100% were present. Hence, this implies the inadequacy of the Vegard's Law when applied to the whole range of substitutions.

1. Introduction

Apatites are essentially phosphates of calcium with chloride, hydroxyl, fluoride or carbonate acting as anions (e.g. $Ca_{10}(OH)_2(PO_4)_6$. They are expected to have a hexagonal crystal structure. A wide range of substitutions is possible among the anions and cations resulting in a broad variety of compounds. This series contains fluorapatite, chlorapatites, hydroxyl apatite, etc. The substituted apatites are important because of their biological significance and have been investigated by many workers [1]. Human bones and teeth contain calcium hydroxyl apatite, $Ca_{10}(PO_4)_6(OH)_2$ as their principal inorganic constituent [2]. The study of the substituted apatites is important in understanding the process of growth and decay of bones or teeth. In the present paper we study the crystal structure of substituted apatites and show that the unit cell parameters deviate substantially from the linear behaviour as a function of the degree of substitutions (as expected from Vegard's Law).

2. X-ray diffraction on substituted apatites

In an isomorphous substitution, it is generally observed that the unit cell parameters (and hence the unit cell volume) change smoothly with the degree of substitution. Vegard's Law in fact, implies a linear relationship between the unit cell parameters and the degree of substitution, this was noticed by several workers. For example, in the substitution of Ca^{++} by Ba^{++} in the calcium hydroxyl apatite [3], a linear dependence of the unit cell parameters on the degree of substitution was established. On closer examination of the data, an impression is gained that Vegard's Law is inadequate for the whole range of substitutions. There is a suspicion that two different types of linear behaviour may be present in the two regions 0 to 50% and 50 to 100%. Hence, a thorough study was undertaken. The apatites selected were calcium and lead hydroxyl apatites (in which phosphate was substituted by vanadate). The levels of substitution are known to a fairly high degree of accuracy ($\sim 0.1\%$).

The substituted apatites could be represented as $Ca_{10}(PO_4)_{6(1-x)}(VO_4)_{6x}(OH)_2$, where x is the molar fraction of vanadate.

The methods of synthesis of the substituted apatites [4, 5] yield the substances in the form of powdered microcrystalline solids. These samples are exposed to Cu$K\alpha$ radiation in the Debye–Scherrer spectrometer.

Now, using Bragg's Law, we have

$$\begin{aligned} \sin^2\theta &= \frac{\lambda^2}{3a^2}(h^2 + hk + k^2) + \frac{\lambda^2}{4c^2}l^2 \\ &= \alpha(h^2 + hk + k^2) + \beta l^2 \qquad (1) \end{aligned}$$

where $\alpha = \lambda^2/3a^2$ and $\beta = \lambda^2/4c^2$,

$$y = \alpha x_1 + \beta x_2 \qquad (2)$$

where $y = \sin^2\theta$, $x_1 = h^2 + hk + k^2$ and $x_2 = l^2$

$$R^2 = \frac{1}{N}\sum |y - (\alpha x_1 + \beta x_2)|^2 \qquad (3)$$

where N is the number of lines observed. The best values (α_0 and β_0) of α and β are those which minimize R^2.

With the notation, $\langle\ \rangle$ denoting the average values

$$\alpha_0 = \frac{\langle x_2^2\rangle\langle x_1 y\rangle - \langle x_1 x_2\rangle\langle x_2 y\rangle}{\langle x_1^2\rangle\langle x_2^2\rangle - \langle x_1 x_2\rangle^2} \qquad (4)$$

$$\beta_0 = \frac{\langle x_1^2\rangle\langle x_2 y\rangle - \langle x_1 x_2\rangle\langle x_1 y\rangle}{\langle x_2^2\rangle\langle x_1^2\rangle - \langle x_1 x_2\rangle^2} \qquad (5)$$

$$\begin{aligned} \langle R^2\rangle_{\min} &= \langle y^2\rangle - \alpha_0^2\langle x_1^2\rangle - \beta_0\langle x_2^2\rangle \\ &\quad - 2\alpha_0\beta_0\langle x_1 x_2\rangle \qquad (6) \end{aligned}$$

$$\begin{aligned} R^2(\alpha, \beta) &= \langle R^2\rangle_{\min} + (\alpha - \alpha_0)^2\langle x_1^2\rangle \\ &\quad + (\beta - \beta_0)\langle x_2^2\rangle \\ &\quad + 2(\alpha - \alpha_0)(\beta - \beta_0)\langle x_1 x_2\rangle \qquad (7) \end{aligned}$$

The error estimates are given by

$$\Delta\alpha = [R_{\min}^2/\langle x_1^2\rangle(N - 2)]^{1/2} \qquad (8)$$

$$\Delta\beta = [R_{\min}^2/\langle x_2^2\rangle(N - 2)]^{1/2} \qquad (9)$$

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TABLE I Best values of a and c together with their estimated errors

Sample no.	Substitution of vanadate (%)	a_o (nm)	Error in a_0 (nm)	c_0 (nm)	Error in c_0 (nm)
1.	0.00	0.9464	0.0028	0.6913	0.0036
2.	5.70	0.9419	0.0009	0.6886	0.0008
3.	10.00	0.9343	0.0112	0.6956	0.00622
4.	18.30	0.9463	0.0065	0.6993	0.00749
5.	36.67	0.9498	0.0039	0.6920	0.00333
6.	37.50	0.9488	0.0043	0.6903	0.0034
7.	49.16	0.9790	0.0104	0.7240	0.0055
8.	61.33	0.9632	0.00744	0.7080	0.0052
9.	74.17	0.9780	0.0075	0.7023	0.0070
10.	86.66	0.9731	0.0056	0.7037	0.0060
11.	100.00	0.98059	0.0033	0.6969	0.0066

Once α_0 and β_0 were determined, best values of a and c (a_0 and c_0) could be found. The errors in a and c are given as

$$a_0 = \frac{\lambda}{(3\alpha_0)^{1/2}} \tag{10}$$

and

$$c_0 = \frac{\lambda}{(4\beta_0)^{1/2}} \tag{11}$$

$$\left(\frac{\Delta a}{a_0}\right) = \frac{1}{2}\left(\frac{\Delta\alpha}{\alpha}\right), \tag{12}$$

$$\left(\frac{\Delta c}{c_0}\right) = \frac{1}{2}\left(\frac{\Delta\beta}{\beta}\right) \tag{13}$$

The best values of a_0 and c_0 (Table I) obtained at different levels of substitution were examined to determine their relation with the degree of substitution. To test this, the entire series of substituted compounds were grouped into two parts, i.e. 0 to 50% and 50 to 100%. For the sake of comparison, the slopes and intercepts of the two lines at 50% were determined.

The method of least squares [6] was adopted to obtain the value of the slope, intercept and the errors in them.

The intercept, b, the slope, m, and their errors, r_b and r_m, in the intercept and slope, respectively, were given by the following equations

$$b = \frac{\Sigma y\,(\Sigma x^2) - \Sigma x \Sigma xy}{D} \tag{14}$$

where

$$D = n(\Sigma x^2) - (\Sigma x)^2$$

$$r_b = r_e\left(\frac{\Sigma x^2}{D}\right)^{1/2} \tag{15}$$

$$m = \frac{n(\Sigma xy) - (\Sigma x)(\Sigma y)}{D} \tag{16}$$

$$r_m = r_e\left(\frac{n}{D}\right)^{1/2} \tag{17}$$

where x is the degree of substitution $-$ 50%, y is the lattice constant (a), r_e is the probable error of the point as calculated by external consistency,

$$r_e = 0.6745\left(\frac{\Sigma v^2}{n-2}\right)^{1/2} \tag{18}$$

where ΣV^2 is the sum of the squares of the $|y_{obs} - y_{exp}|^2$, and n is the number of substituted compounds.

Similarly, the method was applied for the lattice constant (c_0) and the unit cell volume (V).

Analysis of the X-ray diffraction data of the substituted apatites showed that the lattice constants (a and c) followed different behaviours in the two regions. The variation between the lattice constants obtained from our analysis with respect to the degree of substitution is presented in the Figs 1 and 2. As seen from Table II, there was a marked difference in the slopes of the two lines for both the constants. The differences between the two intercepts were not significantly larger than the uncertainties (for both a and c) in them.

3. Infrared spectroscopic studies on substituted apatites

To support the results obtained from the previous sections, infrared absorption spectroscopy has been applied to the analysis of a different series of substituted apatites. The substituted apatites chosen could be represented as $Pb_{10}(PO_4)_{6(1-x)}(VO_4)_{6x}(OH)_2$, where x is the fraction of vanadate.

The spectra of the substituted apatites recorded by

TABLE II Slopes and intercepts of the calculated lattice constants a and c in two different regions (i.e. 0 to 50% and 50 to 100%)

	Lattice constants				Unit cell volume	
	a_0 (nm)	Error (nm)	c_0 (nm)	Error (nm)	V_0 (nm^3)	Error (nm^3)
Intercept (< 50%)	0.9651	0.00480	0.70823	0.0052	0.571600	0.009400
Intercept (> 50%)	0.9720	0.00400	0.71803	0.00279	0.588000	0.006200
Difference	0.0069	0.0062	0.00980	0.0059	0.016400	0.011300
Slope (< 50%)	0.00057	0.00015	0.00040	0.00016	0.000974	0.000288
Slope (> 50%)	0.00011	−0.00013	−0.00046	0.00010	−0.000255	0.000206
Difference	0.00046	0.00020	0.00086	0.00018	0.001229	0.000354

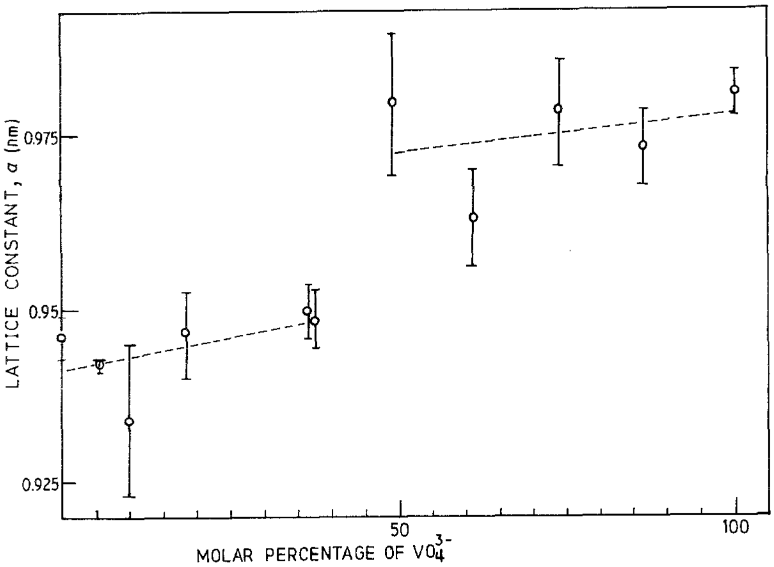

Figure 1 The behaviour of the lattice constant a obtained from our analysis plotted against the molar % of VO_4^{3-} together with the best fit straight line.

using the Perkin–Elmer Model 983 spectrophotometer with a dedicated data processor. Our spectra were taken in the double beam mode. After the radiation passed through the sample, a monochromator was used to produce a spectrum of a fixed frequency (expressed in wave number units) during the recording period. The range of the spectra is studied in the range 180 to 4000 cm^{-1}.

The samples were prepared by applying the Nujol technique. The technique [7] is preferable compared to the potassium bromide pellet technique in the sense that there might be a possibility of an exchange reaction with KBr. Moreover, the material under investigation may also undergo changes in crystalline form as a result of the high mechanical pressure (10 000 p.s.i., 68.9 N mm^{-2}) used in the pelleting process.

The spectra of the substituted apatites showed vanadate peaks at 724 and 808 cm^{-1}. At 724 cm^{-1}, there was an overlap with the Nujol peak and hence correction was done when the area under the vanadate peaks was estimated.

The location of the phosphate peaks in the spectra was also noted for the whole series of substituted apatites. The two peaks occurred around 972 and 1154 cm^{-1}, and the areas under these peaks were measured. Besides measuring the areas under the phosphate and vanadate peaks, their heights from the background were determined. Apart from a slight drift in the peak frequencies, the heights of the peaks are expected to reflect the changes in the crystal structure. It is expected that there should be a linear proportionality of the areas under the peaks with the amounts of substitution. In the case of isomorphous substitution, it is expected that the area under the phosphate (or vanadate) peak will represent the fraction of phosphate (or vanadate). A graph of $Y = (A_v - A_p)/(A_v + A_p)$ (where A_v is the area under the vanadate peak and A_p is the area under phosphate peak) against the degree of substitution clearly supports the linear behaviour as shown in Fig. 3.

On the other hand, a similar analysis of the heights of the peaks rather than the areas, shows some clear-cut systematic changes in crystal structure. The plot of

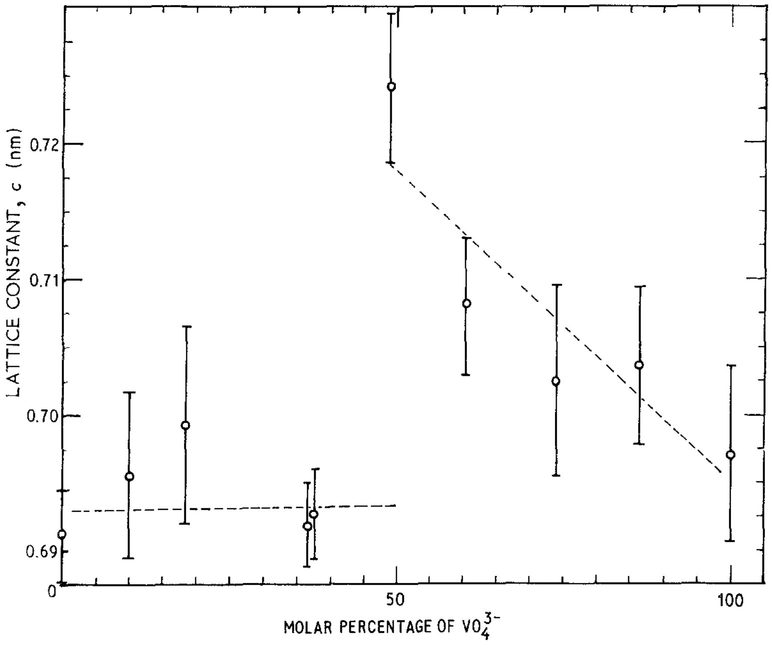

Figure 2 The behaviour of the lattice constant c obtained from our analysis plotted against the molar % of VO_4^{3-} together with the best fit straight line.

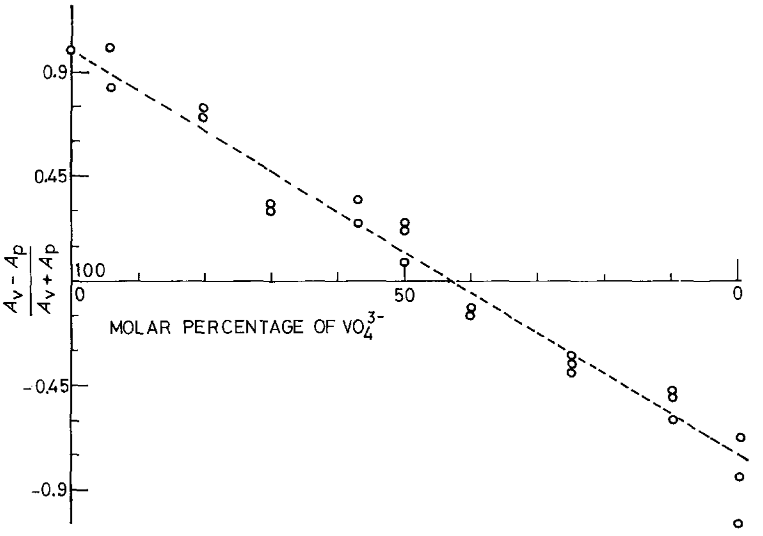

Figure 3 The linear relationship between the areas under the phosphate and vanadate infrared absorption peaks and the degree of substitution by vanadate.

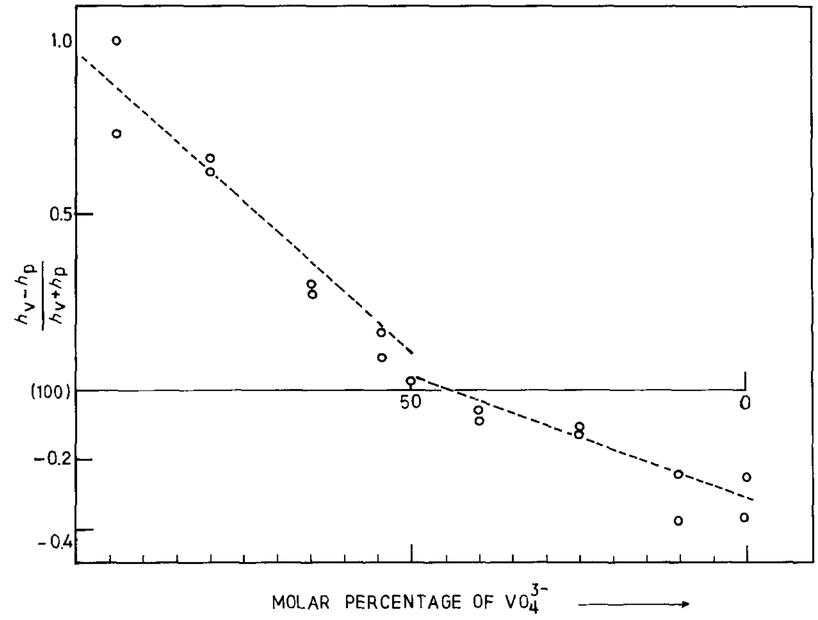

Figure 4 The behaviour of the infrared absorption peak heights of phosphate and vanadate with the degree of substitution..

$Z = (h_v - h_p)/(h_v + h_p)$ (where h_v is the peak height at VO_4^{3-} frequency, h_p is the peak height at PO_4^{3-} frequency) against the degree of substitution (Fig. 4) shows marked deviation from the linear behaviour. This shows two distinct types of linear behaviour in the two regions 100 to 50% and 50 to 0%. The least square fit estimates of the intercepts at 50% and the slopes together with their error estimates are given in Table III.

4. Conclusions

Analysis of the X-ray and infrared data of the synthesized apatites $Ca_{10}(PO_4)_6(OH)_2$ and $Pb_{10}(PO_4)_6(OH)_2$ at different degrees of substitution of PO_4^{3-} by VO_4^{3-} (in both cases) clearly indicated the inadequacy of Vegard's Law for the whole range of substitution. The results obtained from the analysis of the two different sets of data were very consistent, as both separately showed that there was a different linear behaviour in the two regions 0 to 50% and 50 to 100%. In both cases there was a marked deviation in the slopes when the best fit was done in the two regions. Hence, this is a direct contradiction to Vegard's Law.

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TABLE III Slopes and intercepts of the ratios of the infrared absorption peak heights of vanadate and phosphates in two different regions (i.e. 100 to 50% and 50 to 0%)

Range* (%)	Intercept ($\times 10^{-2}$)	Error in intercept ($\times 10^{-2}$)	Difference in intercept ($\times 10^{-2}$)	Error in the difference	Slope ($\times 10^{-2}$)	Error in the slope ($\times 10^{-2}$)	Difference in slopes ($\times 10^{-2}$)	Error in the difference ($\times 10^{-2}$)
50- 0	9.023	1.538	2.144	1.729	0.941	0.0502	0.778	0.0568
100-50	11.167	0.791			1.719	0.0265		

*Ranges of the regions relative to the degree of substitution of VO_4^{3-}.

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