

Fig. 1 — Dependence of lattice parameters of solid solutions of hydroxylapatite and chlorapatite of cadmium on composition

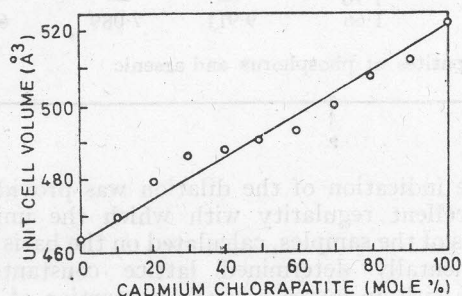


Fig. 2 — Dependence of unit cell volumes of solid solution of hydroxylapatite and chlorapatite of cadmium on composition

composition of the solid solutions confirmed their homogeneity (see Figs 1 and 2).

The similarity of IR spectra of CdHA and CdClA and their solid solutions confirmed the identity of these samples, supplementing thereby the evidence obtained by chemical and X-ray analyses. The predominant absorption peaks recorded in the traces of CdHA and CdClA and their solid solutions were found to be due to the orthophosphate ion and their wavelengths were found to be comparable with those reported^{8,9}. In addition, the samples were found to be free from carbonate-apatite likely to be formed due to atmospheric interaction, if any, during heating. This conclusion was based on the absence of characteristic IR peaks of CO_3^{2-} in the range 1450-1410 and 875-850 cm^{-1} (ref. 10). Further, thermal decomposition likely to be inflicted on the samples of apatites due to sintering at 550° can result in the formation of $\text{P}_2\text{O}_7^{4-}$ groups which show characteristic IR bands at 1152, 1121 and 917 cm^{-1} , the absence of which confirms the thermal stability of the samples at temperature chosen for their preparation. The onset of thermal decomposition of the samples was established on the basis of a precipitous loss of water at temperatures higher than 600° as indicated by the TGA patterns justifying thereby the selection of 550°; as the optimum temperature for the preparation of the samples.

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Preparation & Characterization of Hydroxylapatites of Phosphorus & Arsenic & Their Solid Solutions

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Hydroxylapatites of phosphorus and arsenic and a series of their solid solutions over the entire compositional range were prepared by precipitation adopting conditions specially developed for the purpose. The samples were characterized through chemical, X-ray and infrared analyses. While the homogeneity of the solid solutions could be confirmed by the validity of Vegard's law, extraneous phases were shown to be absent on the basis of the infrared studies.

SAMPLES of arsenic hydroxylapatite (AsHA) $[\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2]$ phosphorus hydroxylapatite (PHA) $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ and a series of their solid solutions over the entire compositional range have been prepared and characterized through chemical, X-ray and IR data. While the preparation of PHA and AsHA were investigated in detail earlier, that of solid solutions needs further investigation since the only method³ available has been of limited utility especially for a rapid preparation of appreciable quantities of homogeneous samples. The chemicals used were either of AR (BDH) or of extra pure (E. Merck) grade. Stock solutions of calcium nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, diammonium hydrogen phosphate, $(\text{NH}_4)_2\text{HPO}_4$ and disodium hydrogen arsenate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ were prepared and their respective calcium, phosphate and arsenate contents were determined complexometrically^{4,5}. The details of precipitation and characterization of the samples by chemical, X-ray and infrared analyses are similar to those reported earlier^{2,6,7}.

The results of analysis (2 determinations) are given in Table 1. Assuming the total number of calcium and hydroxyl ions to remain stoichiometric for the entire series of samples the molecular formulae of the solid solutions were calculated and are also given in

TABLE 1 — CHEMICAL AND X-RAY DATA OF HYDROXYLAPATITES OF PHOSPHORUS AND ARSENIC AND THEIR SOLID SOLUTIONS

Sl No.	Mol. formula	Wt %			g atom ratio Ca/(P+As)	Lattice constant		Unit cell volume (\AA^3) ($\sqrt{3}/2$) a^2c
		Ca	P	As		a	c	
1	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	40.10	18.00	—	1.72	9.425	6.872	528
2	$\text{Ca}_{10}(\text{PO}_4)_{5.4}(\text{AsO}_4)_{0.6}(\text{OH})_2$	38.48	16.21	4.34	1.67	—	—	—
3	$\text{Ca}_{10}(\text{PO}_4)_{4.8}(\text{AsO}_4)_{1.2}(\text{OH})_2$	37.10	13.80	9.00	1.60	9.513	6.914	541
4	$\text{Ca}_{10}(\text{PO}_4)_{4.2}(\text{AsO}_4)_{1.8}(\text{OH})_2$	37.00	12.00	12.60	1.64	—	—	—
5	$\text{Ca}_{10}(\text{PO}_4)_{3.6}(\text{AsO}_4)_{2.4}(\text{OH})_2$	35.70	9.93	16.02	1.68	9.623	6.961	558
6	$\text{Ca}_{10}(\text{PO}_4)_{3.0}(\text{AsO}_4)_{3.0}(\text{OH})_2$	35.90	8.30	20.40	1.67	—	—	—
7	$\text{Ca}_{10}(\text{PO}_4)_{2.4}(\text{AsO}_4)_{3.6}(\text{OH})_2$	35.03	6.31	22.10	1.73	9.736	6.998	574
8	$\text{Ca}_{10}(\text{PO}_4)_{1.8}(\text{AsO}_4)_{4.2}(\text{OH})_2$	35.35	4.78	26.90	1.67	—	—	—
9	$\text{Ca}_{10}(\text{PO}_4)_{1.2}(\text{AsO}_4)_{4.8}(\text{OH})_2$	32.60	3.00	29.20	1.68	9.832	7.039	589
10	$\text{Ca}_{10}(\text{PO}_4)_{0.6}(\text{AsO}_4)_{5.4}(\text{OH})_2$	32.20	1.34	32.13	1.70	—	—	—
11	$\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2$	31.00	—	35.00	1.66	9.911	7.089	600

Sl. Nos 2 to 10 are the solid solutions of hydroxylapatites of phosphorus and arsenic

Table 1. In addition, the g atom ratio, Ca/(P or As or both), were calculated for each sample and are given in Table 1, the ratio was found to vary between 1.60 and 1.73, the theoretical value being 1.67. It is evident that pH of the medium of precipitation is an important parameter in deciding the proportions of the different dissociation products of orthophosphoric and orthoarsenic acids. It could be shown from considerations of the dissociation constants⁸⁻¹¹ of H_3PO_4 and H_3AsO_4 that at the chosen dilutions and pH (about 12) prevalent in the media of precipitation of the samples, the third stage of dissociation of these acids was predominant. The various aspects¹² of experimental conditions chosen for the precipitation of the samples were such that relatively large crystals of the samples having a high order of purity were obtained, the crystal imperfections being restricted to the minimum possible. The particle size of precipitates of PHA, AsHA and their solid solutions is usually in the range of colloidal dimensions possessing consequently a pronounced surface activity leading to the introduction of surface impurities during precipitation which could be eliminated by washing the samples with EDTA¹³ and ammonium chloride^{14,15}. Another important parameter among the post-precipitatorial operations was the sintering of the samples for about 6 hr at 900° to drive out volatile impurities, to facilitate the lattice formation of the desired solid solution and to enhance the crystal dimensions. Care was taken to see that the conditions chosen for the preparation were kept scrupulously the same for all the samples so that the alteration in their properties could be attributed exclusively to the replacement of phosphorus by arsenic.

Results of X-ray diffraction studies of the samples which belong to the hexagonal group are also included in Table 1. Based on considerations of atomic dimensions of P and As (tetrahedral covalent radii 1.10 and 1.18 Å respectively) as well as of the isomorphism³ existing between PHA and AsHA the possibility for the formation of a series of solid solutions over the entire compositional range could be anticipated. In addition, a marginal dilation in the unit cell volume is likely due to the replacement of P by As. A more

decisive indication of the dilation was provided by the excellent regularity with which the unit cell volumes of the samples, calculated on the basis of the experimentally determined lattice constants, increased with an increase in the proportion of AsHA as shown in Table 1. The homogeneity of the solid solutions could thus be substantiated by the validity of Vegard's law over the entire compositional range of the solid solutions.

In addition to the nujol bands at 2920, 1462, 1378 and 719 cm^{-1} , the IR spectra of all the samples showed a peak at 3570 cm^{-1} , characteristic of the νOH^{16} . The predominant absorption peaks¹⁷ in the spectra of PHA and AsHA were found to be due to orthophosphate and orthoarsenate in the ranges 1050-960 cm^{-1} and 880-837 cm^{-1} respectively. The patterns of the solid solutions contained both these sets of peaks, the area under the peaks being approximately proportional to the relative amounts of PO_4^{3-} and AsO_4^{3-} in the samples. The non-appearance of peaks due to pyrophosphate, pyroarsenate and carbonate confirmed the absence of such a set of likely impurities in the samples.

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Structure & Ferroelectric Studies of a New Type of Perovskite[†] [$x\text{BaTiO}_3 + (1-x)\text{Ba}(\text{La}_{0.5}\text{Ta}_{0.5})\text{O}_3$]

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Structural and ferroelectric properties of a new type of perovskite $\text{BaTi}_x(\text{La}_{0.5}\text{Ta}_{0.5})_{1-x}\text{O}_3$ ($0 \leq x \leq 1$) are reported. Compounds with $x \geq 0.8$ only crystallize with the ferroelectric perovskite phase. The highest value of spontaneous polarization (P_s) in this phase is obtained ($4.90 \mu\text{C}/\text{cm}^2$) for the composition with $x = 0.9$, with a Curie-point of 105°C .

FOR studying the relation between structure and ferroelectricity, ABO_3 type of compounds with BaTiO_3 as the typical example provide a very good starting point. Apparently, one of the important features of the ABO_3 perovskite lattices is the BO_6 octahedra¹. Perovskite type of compounds with more than one kind of ions at the B site have been reported^{2,3}. A general example of compounds with two different metal ions at the B position for specific A and B valences is $\text{A}^{2+}(\text{B}_I)_{0.5}^{3+}(\text{B}_{II})_{0.5}^{5+}\text{O}_3$. Ferroelectricity is found to occur in the perovskite type of compounds^{4,5} with $\text{A}^{2+} = \text{Pb}^{2+}$, $\text{B}_I = \text{Fe}^{3+}$, Sc^{3+} ,

and $\text{B}_{II} = \text{Nb}^{5+}$, Ta^{5+} . In all these perovskite type ferroelectrics the empirical rule framed by Mathias⁶ that the B -ion(s) within the oxygen octahedra should have the noble gas configurations formed by the removal of the s or d electrons from the B atom(s) is usually obeyed. Not many compounds with Ln^{3+} ions as one of the ions at the B site are known. Galasso and Darby⁷ reported on the structural properties of some compounds with Ln^{3+} and Nb^{5+} compositions at the B site. In the present study the preparation, structure and the ferroelectric properties of $\text{Ba}(\text{La}_{0.5}\text{Ta}_{0.5})\text{O}_3$ and those of its solid solutions with BaTiO_3 are described.

The pure compound, $\text{Ba}(\text{La}_{0.5}\text{Ta}_{0.5})\text{O}_3$ ($x=0$) and its solid solutions with BaTiO_3 were prepared by the usual ceramic techniques described earlier⁸. Debye-Scherrer powder photographs were taken on a 14 cm diameter camera using $\text{Cu}/\text{Mo}(\text{K}\alpha)$ radiation. The ferroelectric and dielectric properties were measured on a modified apparatus⁹ devised in this laboratory. Dielectric constant (ϵ), loss tangent ($\tan \delta$), spontaneous polarization (P_s), remnant polarization (P_r) and Curie-point (T_c) were measured.

The pure phase ($x=0$) crystallizes with the orthorhombic symmetry. The orthorhombic strain (b/a) is 1.003. Table 1 shows the unit cell variations for different compositions in this series.

Considering the pure phase, one can see from a consideration of the ionic size of the ions ($r\text{Ba}^{2+} = 1.35 \text{ \AA}$, $r\text{La}^{3+} = 1.15 \text{ \AA}$, and $r\text{Ta}^{5+} = 0.73 \text{ \AA}$) that the difference in the size of the La^{3+} and the Ba^{2+} ions is about 20%, while that between La^{3+} and Ta^{5+} is of the order of 40%. It would hence appear probable that La^{3+} ions would enter the A sites in this compound. However, intensity calculations (i) using the unit cell parameters obtained from the diffraction pattern lines and (ii) using the ordered arrangement of Ta^{5+} and La^{3+} ions at the B site, agreed well with the observed intensities, thereby ruling out the entry of La^{3+} ions at A sites. The measured density values also suggest an arrangement of the La and Ta ions at the B site only.

The orthorhombic distortion of the pure phase disappears with the addition of about 20 mol % of

TABLE 1—UNIT CELL PARAMETERS OF $x\text{BaTiO}_3 + (1-x)\text{Ba}(\text{La}_{0.5}\text{Ta}_{0.5})\text{O}_3$

Composition	Symmetry*	Å			c/a	V Å ³
		a	b	c		
$\text{Ba}(\text{La}_{0.5}\text{Ta}_{0.5})\text{O}_3$	O ($Z = 4$)	8.62	8.64	8.77	1.017	647.8
$\text{Ba}(\text{Ti}_{0.2}\text{La}_{0.4}\text{Ta}_{0.4})\text{O}_3$	M	8.58	8.62	8.75	1.020	647.2
		4.03	3.94	3.94	0.977	64.0
$\text{Ba}(\text{Ti}_{0.4}\text{La}_{0.3}\text{Ta}_{0.3})\text{O}_3$	M	8.53	8.58	8.72	1.022	638.2
		4.00	3.98	3.98	0.995	63.7
$\text{Ba}(\text{Ti}_{0.5}\text{La}_{0.25}\text{Ta}_{0.25})\text{O}_3$	M	8.50	8.56	8.68	1.021	631.6
		3.96	4.03	4.03	1.018	63.2
$\text{Ba}(\text{Ti}_{0.6}\text{La}_{0.2}\text{Ta}_{0.2})\text{O}_3$	M	8.45	8.50	8.64	1.023	620.6
		3.94	4.08	4.08	1.036	63.3
$\text{Ba}(\text{Ti}_{0.8}\text{La}_{0.1}\text{Ta}_{0.1})\text{O}_3$	BT ($Z = 4$)	3.96	3.96	4.11	1.038	64.4
$\text{Ba}(\text{Ti}_{0.9}\text{La}_{0.05}\text{Ta}_{0.05})\text{O}_3$	BT ($Z = 1$)	3.98	3.98	4.08	1.025	64.6
BaTiO_3	BT ($Z = 1$)	3.99	3.99	4.04	1.013	64.3

*O = orthorhombic; M = mixed phase; and BT = BaTiO_3 phase.

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