

# Synthesis and Characterization of New Apatite-Related Phosphates

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New phosphates of the formula  $M^{3+}M_4^{2+}(PO_4)_3O$  ( $M^{3+} = \text{Bi}$  and  $\text{La}$ ;  $M^{2+} = \text{Ca}$  and  $\text{Sr}$ ) are synthesized. The compounds are isostructural with bismuth calcium vanadate,  $\text{BiCa}_4(\text{VO}_4)_3\text{O}$ . A nonlinear increase in both the  $a$  and  $c$  lattice parameters with an increase in strontium content in the solid solution  $\text{BiCa}_{4-x}\text{Sr}_x(\text{PO}_4)_3\text{O}$  ( $x = 1-4$ ) is observed. The compounds are characterized by infrared spectroscopy. © 2000 Academic Press

**Key Words:** bismuth; calcium; strontium; phosphate.

## EXPERIMENTAL

### Synthesis

All the compounds are synthesized by high-temperature solid state reaction. The reactants are high-purity  $\text{Bi}_2\text{O}_3$  (Cerac, 99.9%),  $\text{CaCO}_3$  (Cerac, 99.95%),  $\text{SrCO}_3$  (Cerac, 99.5%), and  $\text{NH}_4\text{H}_2\text{PO}_4$  (Merck, 99%). Stoichiometric mixtures of the reactants are initially heated at  $300^\circ\text{C}$  for 6 h to eliminate water and ammonia. The resultant powder is heated at  $700^\circ\text{C}$  for 12 h and at  $950^\circ\text{C}$  for 24 h with intermittent grindings. The powder samples thus obtained are pelletized and sintered at  $1100^\circ\text{C}$ . The compounds  $\text{LaCa}_4(\text{PO}_4)_3\text{O}$  and  $\text{LaSr}_4(\text{PO}_4)_3\text{O}$  are synthesized from a stoichiometric mixture of preheated  $\text{La}_2\text{O}_3$  (Indian rare earths, 99.99%) and respective carbonates and ammonium dihydrogen phosphate. The heating schedule is the same as that mentioned above.

### Characterization

The compounds are characterized by powder X-ray diffraction (Rich Seifert, Germany,  $\text{CuK}\alpha_1$ ) at room temperature. Potassium chloride is used as an internal standard. The diffraction patterns are indexed using the LAZY PULVERIX (6) program. The lattice parameters are obtained by LSQ fitting of high-angle reflections. IR spectra are recorded in the range  $1500-400\text{ cm}^{-1}$  (Perkin-Elmer 983) using the KBr disc technique.

## RESULTS AND DISCUSSION

### Phase Formation and Structure

Phases of the formula  $\text{BiCa}_4(\text{PO}_4)_3\text{O}$ ,  $\text{BiCa}_{4-x}\text{Sr}_x(\text{PO}_4)_3\text{O}$  ( $x = 1-4$ ),  $\text{LaCa}_4(\text{PO}_4)_3\text{O}$ , and  $\text{LaSr}_4(\text{PO}_4)_3\text{O}$  are synthesized. All the compounds are white in color and are stable with exposure to air and moisture at room temperature. X-ray diffraction patterns of select compounds are given in Fig. 1. Sharp and well-defined powder diffraction patterns are obtained for all the compounds, indicating good crystallinity.

## INTRODUCTION

The structure of the compound  $\text{BiCa}_4(\text{VO}_4)_3\text{O}$  (1) is closely related to the apatite structure (2). The compound crystallizes in hexagonal symmetry with the space group  $P6_3$  ( $a = 9.819\text{ \AA}$ ,  $c = 7.033\text{ \AA}$ ,  $V = 587.2\text{ \AA}^3$ , and  $Z = 2$ ). The unit cell dimensions are found to be similar to those of the apatite  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  (3). However, the space group for apatite is  $P6_3/m$  and there are only two types of calcium atoms.  $\text{BiCa}_4(\text{VO}_4)_3\text{O}$ , on the other hand, is reported to have three types of calcium atoms and the formula can be written as  $\text{Ca}_{0.9}(1)\text{Bi}_{0.1}(1)\text{Ca}_{2.1}(2)\text{Bi}_{0.9}(2)\text{Ca}(3)(\text{VO}_4)_3\text{O}$ . The Ca(1) and Ca(3) atoms occupy  $2b$  crystallographic sites and the Ca(2) atom occupies the  $6c$  crystallographic site. Both Ca(1) and Ca(2) atoms have 6-fold coordination of oxygen and the Ca(3) atom has 9-fold coordination. The Bi atom partially occupies the six-coordinated Ca(1) and Ca(2) sites.

Partial or complete replacement of pentavalent phosphorus by other ions such as  $\text{V}^{5+}$ ,  $\text{As}^{5+}$ , and  $\text{Sb}^{5+}$  has been investigated in the apatite structure (4). Similarly, isostructural phosphate and arsenate of  $\text{BiMg}_2\text{VO}_6$  are reported (5). Thus, in view of the similarity in the structural features of the compound  $\text{BiCa}_4(\text{VO}_4)_3\text{O}$  with the apatite structure, an attempt is made to synthesize the phosphorous analogues of  $\text{BiCa}_4(\text{VO}_4)_3\text{O}$  in the present study. Considering the similar ionic radii of  $\text{Bi}^{3+}$  and  $\text{La}^{3+}$ , synthesis of lanthanum-containing phases,  $\text{LaM}_4^{2+}(\text{PO}_4)_3\text{O}$  ( $M^{2+} = \text{Ca}$  and  $\text{Sr}$ ), is also attempted.

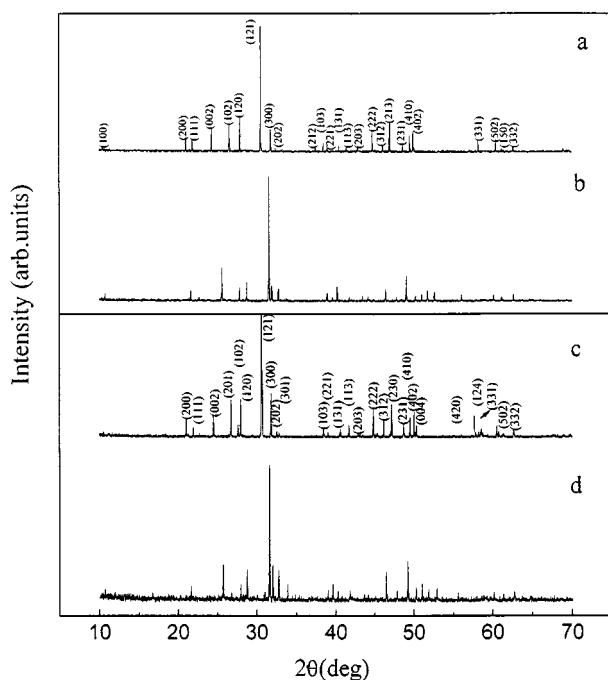


FIG. 1. X-ray diffraction patterns of (a)  $\text{BiSr}_4(\text{PO}_4)_3\text{O}$ ; (b)  $\text{BiCa}_4(\text{PO}_4)_3\text{O}$ ; (c)  $\text{LaSr}_4(\text{PO}_4)_3\text{O}$ ; (d)  $\text{LaCa}_4(\text{PO}_4)_3\text{O}$ .

X-ray diffraction analysis of the phase  $\text{BiCa}_4(\text{PO}_4)_3\text{O}$  indicates that all the reflections can be indexed on the basis of a hexagonal cell and the compound is found to be isostructural with  $\text{BiCa}_4(\text{VO}_4)_3\text{O}$  (1). The unit cell dimensions of the phosphate compound indicate that the substitution of vanadium by phosphorus contracts the cell as one expects on the basis of ionic size. In the structure, the  $\text{VO}_4$  tetrahedra interconnect the chains formed by corner-shared  $\text{Ca}(2)\text{O}_6$  hexahedra and the chains formed by face-shared  $\text{Ca}(1)\text{O}_6$  and  $\text{Ca}(3)\text{O}_9$  polyhedra, and hence both  $a$  and  $c$  lattice parameters decrease when the  $\text{VO}_4$  moiety is replaced by the smaller  $\text{PO}_4$  moiety.

The solid solutions of the formula  $\text{BiCa}_{4-x}\text{Sr}_x(\text{PO}_4)_3\text{O}$  ( $x = 1-4$ ) are synthesized. All the strontium-substituted phases are found to be isomorphous with  $\text{BiCa}_4(\text{PO}_4)_3\text{O}$ . The latter parameters, cell volume, and  $c/a$  values are listed in Table 1. The substitution of Ca by Sr increases both the  $a$  and  $c$  lattice parameters. The variation in lattice parameters with increasing Sr content is shown in Fig. 2. It is interesting to note that the variation of both  $a$  and  $c$  parameters is nonlinear.

The lanthanum-containing compounds  $\text{LaCa}_4(\text{PO}_4)_3\text{O}$  and  $\text{LaSr}_4(\text{PO}_4)_3\text{O}$  are also found to be isomorphous with  $\text{BiCa}_4(\text{PO}_4)_3\text{O}$ . Similar substitution of the  $\text{Bi}^{3+}$  ion by the  $\text{La}^{3+}$  ion is observed in the eulytine structure (7). The lattice parameters are comparable to those of their bismuth analogues due to the similar sizes of the  $\text{Bi}^{3+}$  and  $\text{La}^{3+}$  ions. The formation of the lanthanum analogues offer the possi-

TABLE 1  
Hexagonal Lattice Parameters of  $M^{3+}M_4^{2+}(\text{PO}_4)_3\text{O}$   
( $M^{3+} = \text{Bi}$  and  $\text{La}$ ;  $M^{2+} = \text{Ca}$  and  $\text{Sr}$ )

Compound	Lattice parameters (Å)		Volume (Å <sup>3</sup> )	$c/a$
	$a$	$c$		
$\text{BiCa}_4(\text{PO}_4)_3\text{O}$	9.461(8)	6.95(1)	538.74	0.735
$\text{BiCa}_3\text{Sr}(\text{PO}_4)_3\text{O}$	9.534(7)	7.032(7)	553.54	0.738
$\text{BiCa}_2\text{Sr}_2(\text{PO}_4)_3\text{O}$	9.605(7)	7.121(8)	568.92	0.741
$\text{BiCaSr}_3(\text{PO}_4)_3\text{O}$	9.669(7)	7.209(8)	583.65	0.746
$\text{BiSr}_4(\text{PO}_4)_3\text{O}$	9.725(8)	7.30(1)	597.88	0.751
$\text{LaCa}_4(\text{PO}_4)_3\text{O}$	9.463(8)	6.92(1)	536.64	0.731
$\text{LaSr}_4(\text{PO}_4)_3\text{O}$	9.71(1)	7.30(1)	596.05	0.751

bility of introducing other lanthanide ions in the  $\text{BiCa}_4(\text{PO}_4)_3\text{O}$  structure. The synthesis of phosphates containing rare earths other than La is underway.

#### Infrared Spectroscopy

The infrared spectra of the compounds of the formula  $\text{BiCa}_{4-x}\text{Sr}_x(\text{PO}_4)_3\text{O}$  ( $x = 1-4$ ) are given in Fig. 3. Table 2 shows the IR spectral assignments for the compounds in the range  $1500-400\text{ cm}^{-1}$ . The broadening of the peaks could be due to minor distortions in the  $\text{PO}_4$  group from the ideal  $T_d$  symmetry.

The IR spectra are analyzed with a view to study the influence of the substituted ions on the vibrational modes of the phosphate groups. The factors considered are the mass of the cation, the size of the cation, and the nature of the cation-anion bond. The effect of the larger size and mass of the Sr ion is evident in the IR spectra. The bands corresponding to antisymmetric stretching  $\nu_{\text{as}}$  ( $1045, 1003\text{ cm}^{-1}$ ) and symmetric stretching  $\nu_{\text{s}}$  ( $942\text{ cm}^{-1}$ ) vibrations of the

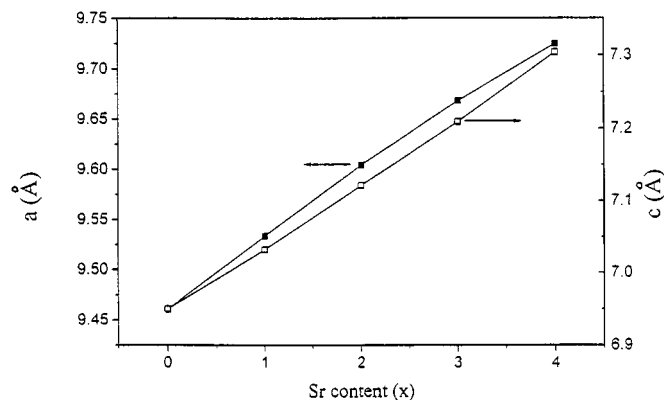


FIG. 2. Variation of the lattice parameters with Sr contents in  $\text{BiCa}_{4-x}\text{Sr}_x(\text{PO}_4)_3\text{O}$ .

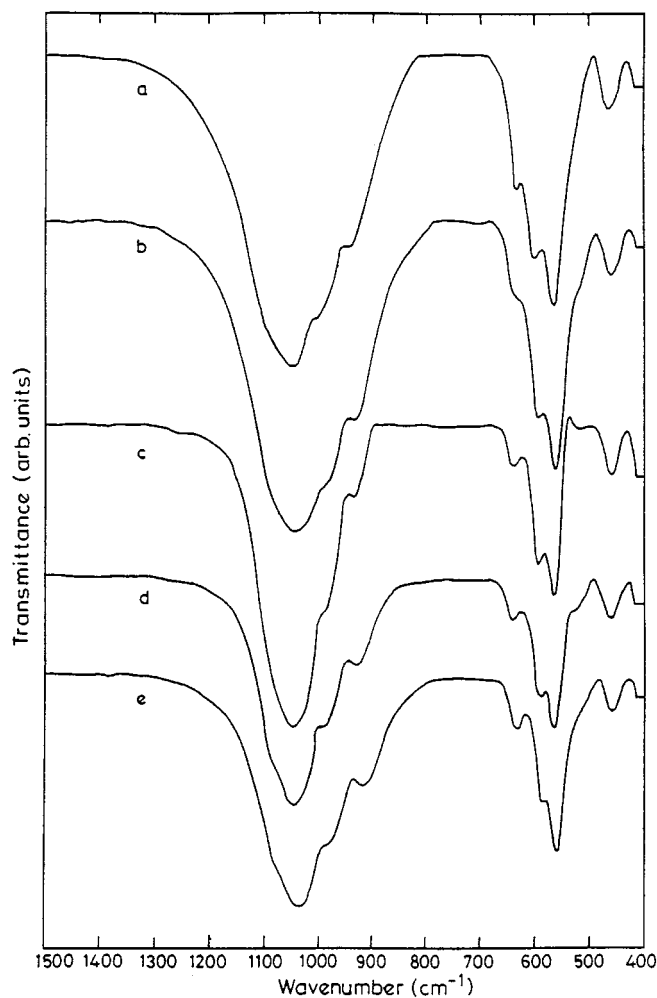


FIG. 3. Infrared spectra of (a)  $\text{BiCa}_4(\text{PO}_4)_3\text{O}$ ; (b)  $\text{BiCa}_3\text{Sr}(\text{PO}_4)_3\text{O}$ ; (c)  $\text{BiCa}_2\text{Sr}_2(\text{PO}_4)_3\text{O}$ ; (d)  $\text{BiCaSr}_3(\text{PO}_4)_3\text{O}$ ; (e)  $\text{BiSr}_4(\text{PO}_4)_3\text{O}$ .

$\text{PO}_4$  group of  $\text{BiCa}_4(\text{PO}_4)_3\text{O}$  are shifted to lower wave numbers ( $\nu_{\text{as}}$ ,  $1036, 987 \text{ cm}^{-1}$ ,  $\nu_{\text{s}}$ ,  $919 \text{ cm}^{-1}$ ) in the case of the Sr analogue. A similar observation is made in the case of

TABLE 2  
Assignments ( $\text{cm}^{-1}$ ) of IR Spectra

Compound	$\nu_3$ , $\nu_{\text{as}}(\text{P-O})$	$\nu_1$ , $\nu_{\text{s}}(\text{P-O})$	$\nu_4$ , $\delta(\text{P-O})$	$\nu_2(\text{P-O})$
$\text{BiCa}_4(\text{PO}_4)_3\text{O}$	1045 b, 1003 sh	942 sh	597 sh, 563 s	460 s
$\text{BiCa}_3\text{Sr}(\text{PO}_4)_3\text{O}$	1045 b, 987 sh	935 m	594 sh, 563 s	461 s
$\text{BiCa}_2\text{Sr}_2(\text{PO}_4)_3\text{O}$	1046 b, 990 sh	935 m	593 sh, 566 s	460 s
$\text{BiCaSr}_3(\text{PO}_4)_3\text{O}$	1041 b, 990 sh	929 m	589 sh, 564 s	457 s
$\text{BiSr}_4(\text{PO}_4)_3\text{O}$	1036 b, 987 sh	919 m	984 sh, 562 s	460 s
$\text{LaCa}_4(\text{PO}_4)_3\text{O}$	1097 sh, 1051 s	—	602 s, 572 s	513 s, 459 s
$\text{LaSr}_4(\text{PO}_4)_3\text{O}$	1085 sh, 1041 s	948 sh	591 s, 566 s	513 sh, 460 s

Note: s = sharp, m = medium, b = broad, and sh = shoulder.

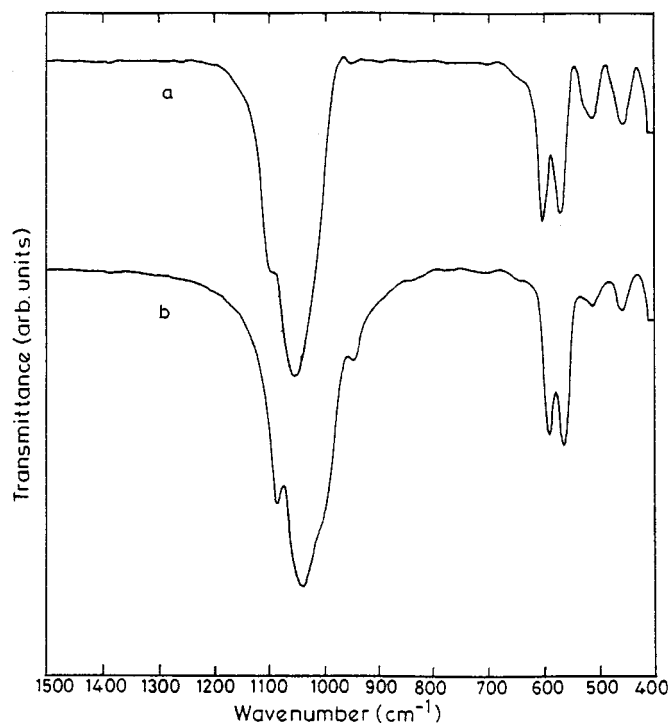


FIG. 4. Infrared spectra of (a)  $\text{LaCa}_4(\text{PO}_4)_3\text{O}$ ; (b)  $\text{LaSr}_4(\text{PO}_4)_3\text{O}$ .

Ca apatites when  $\text{Ca}^{2+}$  is replaced by the larger  $\text{Ba}^{2+}$  ion (8). The increase in unit cell dimensions upon substitution of Sr in the present study affects the P-O bond distance and consequently the frequency of the absorption bands. The band around  $630 \text{ cm}^{-1}$  is due to the Bi-O vibrations (9). It is noted that this band is not observed in the lanthanum-containing phases.

IR spectra of  $\text{LaCa}_4(\text{PO}_4)_3\text{O}$  and  $\text{LaSr}_4(\text{PO}_4)_3\text{O}$  are given in Fig. 4. Replacement of the heavier Bi atom by the lighter lanthanum atom shifts the antisymmetric and symmetric (P-O) stretching vibrations to higher frequencies. As observed in the case of bismuth analogues, substitution of Sr shifts the antisymmetric and symmetric stretching vibrations to lower frequencies.

## CONCLUSION

A series of new phosphate compounds of the formula  $M^{3+}M_4^{2+}(\text{PO}_4)_3\text{O}$  ( $M^{3+} = \text{Bi}$  and  $\text{La}$ ;  $M^{2+} = \text{Ca}$  and  $\text{Sr}$ ) isostructural with  $\text{BiCa}_4(\text{PO}_4)_3\text{O}$  are synthesized. The isostructural nature of all the compounds listed here indicates that the structural motif of  $\text{BiCa}_4(\text{PO}_4)_3\text{O}$  lends itself to the replacement of the  $\text{VO}_4$  moiety by the  $\text{PO}_4$  tetrahedral group and Bi by other trivalent ions of similar size.

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