JOURNAL OF SOLID STATE CHEMISTRY 46, 363–366 (1983)

Bismuth Substituted Calcium, Strontium, and Lead Apatites

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Received June 21, 1982; and in revised form September 24, 1982

Bismuth substituted apatites of two general types have been prepared: $M_{10-2x}Bi_xNa_x(PO_4)_6Y_2$ (M = Ca, Sr, Pb; Y = F, Cl) and lead apatites with the Y ion completely vacant $Pb_{10-(2x+2)}Bi_xNa_{x+2}(PO_4)_6$. X-ray powder diffraction patterns of all the compounds show the $P6_3/m$ hexagonal apatite type structure. The change of the lattice parameters and c/a values with compositions indicate the preference of the bismuth ions to occupy the 6*h* triangular positions. Bi^{3+} tends to incorporate in apatites with unoccupied halide positions.

Introduction

Apatites with the general formula $M_5(XO_4)_3Y$ (M = Ca, Sr, Ba, Pb; X = P, As, V, Si; Y = F, Cl, OH) are widely investigated because of their biological and industrial applications.

The hexagonal ($P6_3/m$) unit cell of the apatites contains two $M_5(XO_4)_3Y$ formula units. In $M_{10}(XO_4)_6Y_2$ the 10 cations (M) are located at two nonequivalent sites: six of them occupy the 6*h* triangular, and four, the 4*f* column sites. In a substitution process these cation positions can be occupied in a statistical way, or in certain cases the cations might have site preference and consequently the structure becomes ordered. In addition when substitution takes place, the phosphate groups can also be affected by the cations of different size, charge and polarizability producing changes in the internal symmetry of the lattice. Previous studies on Ca, Sr, Ba and Pb apatites (*1–4*) have shown that they can be substituted by the lanthanides and sodium and that structural changes can in fact occur in these compounds.

The present study was undertaken to investigate charge balanced substitution in apatites in which the trivalent substituent is the bismuth ion. Also it was interesting to compare the behavior of these compounds with the results obtained in case of the lanthanide substituted apatites. The bismuth ion is different from the lanthanides in two respects: size and electronic configuration. The ionic radii of Bi^{3+} is 1.17 Å (8 coordination) (*5*), the electronic configuration is similar to that of Pb^{2+} and contains a free electron pair.

Bismuth containing apatites have been reported for a few silicate oxide apatites (*6*). The results obtained in (*6*) indicate that when bismuth is present in Pb or Sr silicate apatites, compounds are formed with the halogen positions empty and that Bi^{3+} prefers to occupy the 6*h* triangle positions of the apatite structure. The incorporation of lanthanide ions in silicate apatites with the halogen positions empty was less success-

0022-4596/83/030363-04$03.00/0

ful. In case of $Pb_4M(PO_4)_3$ type apatites (M = Na, K) substitution by lanthanide ions failed completely (*3*).

Experimental

The compounds were synthesized by solid state reactions. Stoichiometric amounts (250–300 mg) of the starting materials were mixed together and heated in a gold or platinum tube, closed but not sealed. The heating temperature was 1100°C for the Ca and Sr compounds, 900°C for the Pb compounds (chlorides at 600°C), and the duration of heating was 24–48 hr.

The starting materials were reagent grade $Ca_3(PO_4)_2$, CaF_2, $SrCO_3$, $Pb_3(PO_4)_2$, $NH_4H_2PO_4$, SrF_2, $SrCl_2$, NaF, $Na_3PO_4 \cdot 12H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$.

The X-ray diffraction analyses of the powders was performed by a Philips X-ray Diffractometer using monochromatized Cu*K*α radiation. This method served for the phase identification of the compounds and for the determination of their crystal data.

Results

The X-ray patterns of the substituted apatites could be indexed on the basis of a hexagonal unit cell. As a rule, well characterized sharp diffraction peaks were obtained indicating good crystallization of the compounds. The samples were scanned in the 2θ range of 10–70°. About 40 reflections were recorded in each pattern which permitted a fairly accurate determination of the lattice constants.

In some cases, mainly with the Sr compounds, additional lines not belonging to the hexagonal phase were observed. These lines matched very well with the lines of the eulytin type cubic phase (*7*). The additional compound formed must be therefore $Sr_3Bi(PO_4)_3$ (*8*).

TABLE I

Lattice Constants of the Compounds[a] in the $Ca_{10-2x}Bi_xNa_x(PO_4)_6F_2$ and $Sr_{10-2x}Bi_xNa_x(PO_4)_6F_2$ Systems

Compound	*a* (Å)	*c* (Å)	*c*/*a*
$Ca_{10}(PO_4)_6F_2$	9.374	6.882	0.734
$Ca_8BiNa(PO_4)_6F_2$	9.396	6.914	0.736
$Ca_6Bi_2Na_2(PO_4)_6F_2$	9.449	6.952	0.736
$Ca_4Bi_3Na_3(PO_4)_6F_2$	9.465	6.968	0.736
$Sr_{10}(PO_4)_6F_2$	9.776	7.270	0.744
$Sr_8BiNa(PO_4)_6F_2$	9.733	7.290	0.749
$Sr_6Bi_2Na_2(PO_4)_6F_2$	9.670	7.246	0.749

[a] Standard deviations in the lattice constants are ± 0.002.

Attempts to prepare the corresponding Ba compounds failed.

Table I lists the lattice constants of the Bi substituted Ca and Sr compounds and Table II those of the lead compounds. The X-ray reflections and the lattice constants of the compounds are characteristic of the apatite type $P6_3/m$ structure. The *c*/*a* (Tables I and II) values remain almost constant for the different compositions, but differ signifi-

TABLE II

Lattice Constants of Bi Substituted Lead Compounds[a]

Compound	*a* (Å)	*c* (Å)	*c*/*a*
$Pb_{10}(PO_4)_6F_2$	9.771	7.301	0.747
$Pb_8BiNa(PO_4)_6F_2$	9.732	7.246	0.742
$Pb_6Bi_2Na_2(PO_4)_6F_2$	9.690	7.183	0.741
$Pb_4Bi_3Na_3(PO_4)_6F_2$	9.653	7.149	0.741
$Pb_{10}(PO_4)_6Cl_2$	9.934	7.327	0.738
$Pb_8BiNa(PO_4)_6Cl_2$	9.888	7.217	0.730
$Pb_6Bi_2Na_2(PO_4)_6Cl_2$	9.849	7.195	0.731
$Pb_8Na_2(PO_4)_6$	9.722	7.193	0.740
$Pb_6Na_3Bi(PO_4)_6$	9.689	7.154	0.738
$Pb_4Na_4Bi_2(PO_4)_6$	9.657	7.079	0.733
$Pb_6KNa_2Bi(PO_4)_6$	9.725	7.146	0.735

[a] Standard deviations in the lattice constants are ±0.002.

cantly from their values in the nonsubstituted compounds.

An important finding of this work is the formation of $Pb_4M(PO_4)_3$ type apatites substitutes with Bi^{3+}. The maximum amounts of bismuth, sodium and potassium which could be inserted in this type of compounds corresponded to the compositions $Pb_4Na_4Bi_2(PO_4)_6$ and $Pb_6KNa_2Bi(PO_4)_6$. The increase in the amount of Na^+ and Bi^{3+} caused a decrease of the lattice constants and the *c*/*a* values.

Discussion

The results obtained in this work prove that charge-coupled substitution of the apatites by tri- and monovalent ions can be achieved through Bi^{3+} and Na^+ ions. Bismuth thus behaves in this respect like the rare-earth ions which have been found as substituents in many phosphate apatite systems. Still, bismuth differs from the rare earths in two ways: (a) no Bi substituted Ba apatites could be obtained; (b) Bi^{3+} can substitute for Pb^{2+} in $Pb_4M(PO_4)_3$ type apatites, unlike the rare-earth ions (*3*). This last property of the Bi^{3+} ions is most probably due to the isoelectronic configuration of Bi^{3+} and Pb^{2+}. The presence of a free electron pair enables the Bi^{3+} to be incorporated in apatites in which the halogen positions are vacant, the free electron pair completes the coordination sphere of Bi^{3+}. Results in case of silicate apatites have shown (*6*) similar behavior of Bi^{3+} and that this ion unlike the rare earths prefers to form apatites with vacant halide positions and occupy preferentially the 6*h* triangle positions of the $P6_3/m$ space group.

Examination of the lattice constants (Tables I and II) shows that as a rule these constants are different from those of the nonsubstituted compounds. The general trend in their variation can be related to the size and amount of the substituted ions. When Bi^{3+} and Na^+ substitute for Ca^{2+} the lattice expands, while in case of the Sr and Pb apatites the lattice contracts by insertion of the same ions.

Conclusions about preferential changes along one of the crystallographical axes may be drawn by examining the changes in the *c*/*a* values. Comparison of the *c*/*a* values in the $Sr_{10-2x}Bi_xNa_x(PO_4)_6F_2$ and $Pb_{10-2x}Bi_xNa_x(PO_4)_6F_2$ systems demonstrate relatively large differences between these values in the substituted and nonsubstituted compounds. Interestingly, these changes proceed in the opposite way in the two systems, namely they increase in the Sr and decrease in the Pb system. It has been pointed out that bismuth ions prefer to occupy the triangle sites parallel to the *a* axis and therefore it can be assumed that if such a preference exists the ions will be distributed so that in the column positions there will be no Bi^{3+} but only Sr^{2+} and Na^+ ions. Such an arrangement of the structure leads to relatively large *c* constants, i.e., high *c*/*a* values. In the Pb system, because of the similarity in the chemical properties of Pb^{2+} and Bi^{3+}, no preferential site occupancy is expected by the Bi^{3+} ions, consequently the insertion of Bi^{3+} in the lattice causes its contraction in the same proportion along the two axes.

The results obtained in the case of the lead chloride apatites show similar trend as was found for the corresponding fluoride apatites.

The change of the lattice parameters of the lead apatites with the halogen positions vacant, show a different behavior from the fluoride and chloride apatites. This change is expressed in the relatively large drop in the *c* value observed and also in the decrease of *c*/*a* (Table II, $Pb_4Na_4Bi_2(PO_4)_6$). The reasoning pointed out already, namely that Pb^{2+} and Bi^{3+} ions prefer the 6*h* triangle positions, might cause the column sites to be mainly occupied by sodium ions. The relatively large contraction of the lattice along the *c* axis must be a result of this effect.

Acknowledgment

The authors extend their thanks to Mrs. P. Odenitz for her assistance in the preparation of compounds.

References

1. I. Mayer, R. S. Roth, and W. E. Brown, *J. Solid State Chem.* **11,** 33 (1974).
2. M. Matthew, I. Mayer, B. Dickens, and L. N. Schroeder, *J. Solid State Chem.* **28,** 79 (1979).
3. I. Mayer, A. Semadja, and V. Weiss, *J. Solid State Chem.* **34,** 223 (1980).
4. B. Eiberger and M. Greenblatt, *J. Solid State Chem.* **41,** 44 (1982).
5. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
6. G. Engel, W. Goetz, and R. Eger, *Z. Anorg. Allg. Chem.* **449,** 127 (1979).
7. "Powder Diffraction File," International Centre for Powder Diffraction Data, Swarthmore, Pa., Card No. 29-1306 (1981).
8. G. Engel, *Z. Anorg. Allgem. Chem.* **443,** 23 (1979).