

Solid Solutions of $Pb_8M_2(XO_4)_6$ Lead Alkali Apatites

I. MAYER, S. COHEN, AND J. R. MATALON

Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel

Received November 27, 1979; in revised form June 30, 1980

The $Pb_8Na_{2-x}K_x(PO_4)_6$, $Pb_8Na_{2-x}K_x(AsO_4)_6$, $Pb_8Na_{2-x}Rb_x(PO_4)_6$, and $Pb_8K_{2-x}Rb_x(PO_4)_6$ systems were studied. The compounds crystallize at all compositions in the $P6_3/m$ hexagonal apatite structure and form true solid solutions. The change of the lattice parameters of the composition and of the c/a values and their relation to the ionic radii of the alkali ions are discussed.

The general formula of the apatites is $A_5(XO_4)_3Y$. The hexagonal unit cell of the apatites contains two formula units and therefore the general formula of the unit cell can be written as $A_{10}(XO_4)_6Y_2$. Attempts to prepare phosphate or arsenate apatites ($X = P, As$) with vacancies, especially leaving the Y positions empty, failed. The only system in which compounds could be prepared with the apatite structure and without the second anion Y was the lead system (1). Lead apatites with the general formula $Pb_8M_2(XO_4)_6$ were prepared, M being a monovalent ion, usually Na or K.

The formation of solid solutions between $Pb_8M_2(XO_4)_6$ and other lead apatites has been studied. These studies have revealed the existence of solid solutions of the anion vacant lead apatite with $Pb_{10}(PO_4)_6O$ and $Pb_{10}(PO_4)_6(OH)_2$ (2). Apatites with mixed anions like $Pb_{10}(PO_4)_4(SiO_4)_2$ were investigated as well (3).

In the apatite lattice, cations occupy the $4f$ and $6h$ sites of the $P6_3/m$ lattice. In a very recent work the crystal structure of $Pb_8K_2(PO_4)_6$ was reported (4). The structure is that of an apatite with no deviation

from the symmetry of the $P6_3/m$ space group. The $6h$ sites are occupied by Pb ions only, whereas the $4f$ sites are occupied by equal amounts of Pb and K.

The present work deals with solid solution systems of phosphate and arsenate apatites of the $Pb_8M_2(XO_4)_6$ type, prepared by mixing Na, K, and Rb ions in different compositions. The experiments were aimed to determine whether continuous solid solutions exist when the $4f$ site of the structure is occupied by three different ions of different sizes, the composition at which such solid solutions can be obtained and the size limit of the participating monovalent ions.

Experimental

The starting materials used for the preparation of the composition of the $Pb_8M'_2M''_x(PO_4)_6$ ($M', M'' = Na, K, Rb$), and $Pb_8Na_{2-x}K_x(AsO_4)_6$ systems were commercial $Pb_3(PO_4)_2$, $Na_3PO_4 \cdot 12H_2O$, KPO_3 , PbO , $Na_2HAsO_4 \cdot 7H_2O$, and $KHAsO_4$ all analytical grade. $Pb_3(AsO_4)_2$ was prepared by heating $PbCO_3$ and $NH_4H_2AsO_4$ at $900^\circ C$

overnight. RbNO_3 was prepared by crystallizing a solution in which Rb_2CO_3 was dissolved in HNO_3 .

The reactions were carried out by mixing stoichiometric amounts of the starting materials and heating them in a gold tube. The phosphates were heated 24 hr, ground, and heated for an additional 2 days at 700°C . The arsenates were heated at 500°C 24 hr and after grinding, heated for 2 more days at 700°C . Different compositions were prepared by changing x in the above systems by 0.2, in the range between 0 and 2.

The purity of the samples was checked by X-ray powder diffraction method. The same method was used for crystal data determination. The X-ray diffraction measurements were carried out by a Philips Diffractometer using monochromatized $\text{CuK}\alpha$ radiation. Si was used as external standard for calibration. The samples were scanned at a rate of $\frac{1}{2}(2\theta)/\text{min}$.

Indexation and lattice constant calcula-

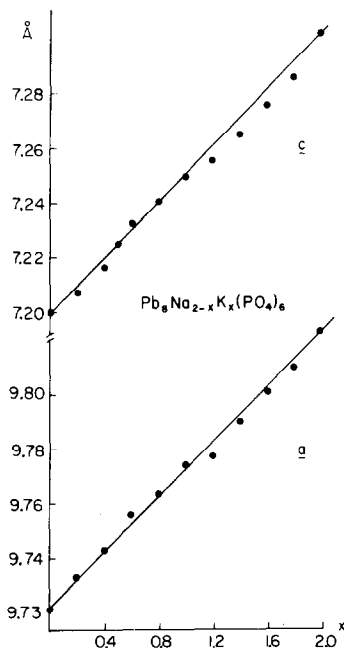


FIG. 1. Lattice constants versus composition in the $\text{Pb}_8\text{Na}_{2-x}\text{K}_x(\text{PO}_4)_6$ system.

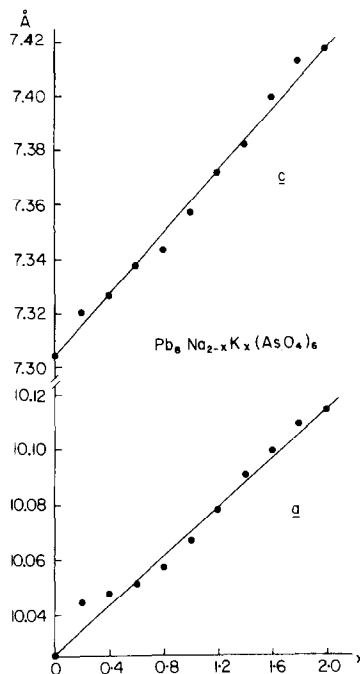


FIG. 2. Lattice constants versus composition in the $\text{Pb}_8\text{Na}_{2-x}\text{K}_x(\text{AsO}_4)_6$ system.

tions were performed on the basis of at least 30 reflections. The data were refined by a least square computer program.

Results and Conclusions

The X-ray patterns of the compounds of the $\text{Pb}_8\text{Na}_{2-x}\text{K}_x(\text{PO}_4)_6$, $\text{Pb}_8\text{Na}_{2-x}\text{K}_x(\text{AsO}_4)_6$, $\text{Pb}_8\text{Na}_{2-x}\text{Rb}_x(\text{PO}_4)_6$, and $\text{Pb}_8\text{K}_{2-x}\text{Rb}_x(\text{PO}_4)_6$ systems were all of one phase and contained well-defined sharp lines. The patterns could be indexed on the basis of the hexagonal apatite structure, known for the endmembers of the system ($x = 0$ or 2). The mean deviations of the lattice constants were $a = 0.001$, $c = 0.001$ Å for the phosphates and $a = 0.001$, $c = 0.002$ Å in the case of the arsenates. In Figs. 1, 2, 3, and 4, the lattice constants versus composition were plotted. The general trend observed in these curves is the increase of the lattice constants with

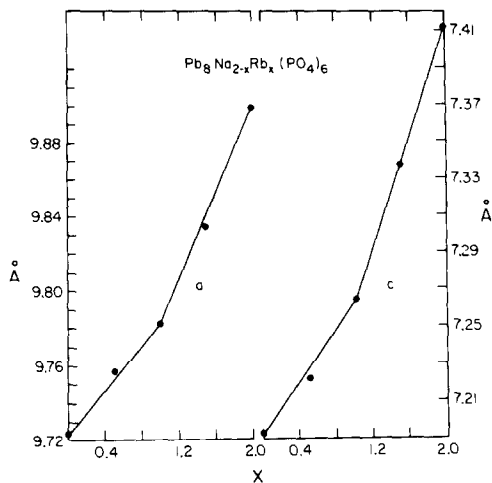


FIG. 3. Lattice constants versus composition in the $\text{Pb}_8\text{Na}_{2-x}\text{Rb}_x(\text{PO}_4)_6$ system.

an increase in the amount of ions with larger ionic radii. The points of Figs. 1 and 2 lie close to the line connecting the two points representing the lattice constants of the endmembers of the two systems. The changes in the lattice parameters of these systems can be considered therefore to be generally linear and regular in both the phosphate and the arsenate systems with the exception of the relatively large deviation from linearity of

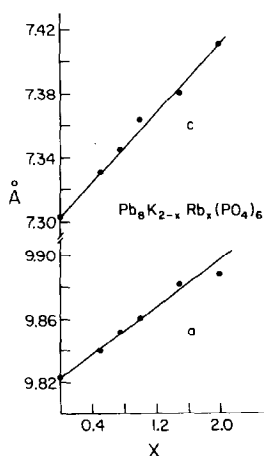


FIG. 4. Lattice constants versus composition in the $\text{Pb}_8\text{K}_{2-x}\text{Rb}_x(\text{PO}_4)_6$ system.

the a parameter in the arsenate system at low potassium content. The curves representing the changes of the lattice constants in the $\text{Pb}_8\text{Na}_{2-x}\text{Rb}_x(\text{PO}_4)_6$ system (Fig. 3) show a break at about the composition of $\text{Pb}_8\text{NaRb}(\text{PO}_4)_6$, namely, the changes being steeper at compositions richer in Rb. A similar trend can be seen in the changes of the a constant in the $\text{Pb}_8\text{K}_{2-x}\text{Rb}_x(\text{PO}_4)_6$ system (Fig. 4). In Table I, the lattice constants of compounds with different compositions are listed.

Solid solutions of the $\text{Pb}_8M_2(\text{XO}_4)_6$ system were investigated in this work. The monovalent alkali ions appearing in the compounds have the following ionic radii: Na^+ (1.24 Å), K^+ (1.55 Å), and Rb^+ (1.63 Å), all at nine coordination, while that of Pb^{2+} is 1.35 Å (5). The results show that: (a) true solid solutions have been obtained for all proportions of M and that the crystal structure of the compounds was always the $P6_3/m$ hexagonal structure of the apatites,

TABLE I

LATTICE CONSTANTS OF THE COMPOUNDS OF THE $\text{Pb}_8M'_2-xM''_x(\text{XO}_4)_6$ SYSTEMS ($M', M'' = \text{Na, K, Rb; X = P, As}$)

	a (Å)	c (Å)	c/a
$\text{Pb}_8\text{Na}_2(\text{PO}_4)_6$	9.722	7.913	0.740
$\text{Pb}_8\text{Na}_{1.5}\text{K}_{0.5}(\text{PO}_4)_6$	9.752	7.225	0.741
$\text{Pb}_8\text{Na}_{1.0}\text{K}_{1.0}(\text{PO}_4)_6$	9.774	7.250	0.742
$\text{Pb}_8\text{Na}_{0.6}\text{K}_{1.4}(\text{PO}_4)_6$	9.790	7.266	0.742
$\text{Pb}_8\text{K}_2(\text{PO}_4)_6$	9.823	7.303	0.744
$\text{Pb}_8\text{Na}_2(\text{AsO}_4)_6$	10.026	7.305	0.729
$\text{Pb}_8\text{Na}_{1.4}\text{K}_{0.6}(\text{AsO}_4)_6$	10.051	7.338	0.730
$\text{Pb}_8\text{Na}_{1.0}\text{K}_{1.0}(\text{AsO}_4)_6$	10.067	7.357	0.731
$\text{Pb}_8\text{Na}_{0.4}\text{K}_{1.6}(\text{AsO}_4)_6$	10.100	7.400	0.733
$\text{Pb}_8\text{K}_2(\text{AsO}_4)_6$	10.114	7.418	0.733
$\text{Pb}_8\text{K}_{1.5}\text{Rb}_{0.5}(\text{PO}_4)_6$	9.840	7.331	0.745
$\text{Pb}_8\text{K}_{1.0}\text{Rb}_{1.0}(\text{PO}_4)_6$	9.861	7.364	0.747
$\text{Pb}_8\text{K}_{0.5}\text{Rb}_{1.5}(\text{PO}_4)_6$	9.882	7.381	0.747
$\text{Pb}_8\text{Rb}_2(\text{PO}_4)_6$	9.888	7.412	0.750
$\text{Pb}_8\text{Na}_{1.5}\text{Rb}_{1.5}(\text{PO}_4)_6$	9.757	7.222	0.740
$\text{Pb}_8\text{Na}_{1.0}\text{Rb}_{1.0}(\text{PO}_4)_6$	9.782	7.264	0.743
$\text{Pb}_8\text{Na}_{0.5}\text{Rb}_{1.5}(\text{PO}_4)_6$	9.834	7.337	0.746

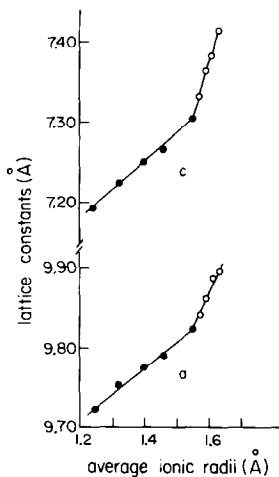


FIG. 5. Lattice constants versus average ionic radii in the $\text{Pb}_8\text{M}_2(\text{PO}_4)_6$ system. Full circles $\text{Pb}_8\text{Na}_{2-x}\text{K}_x(\text{PO}_4)_6$ compositions, empty circles $\text{Pb}_8\text{K}_{2-x}\text{Rb}_x(\text{PO}_4)_6$ compositions.

(b) the c/a values increase for successive substitution of alkali ions of larger radii, but the change is more rapid when K^+ is replaced by Rb^+ rather than for K^+ replacing Na^+ . These findings indicate that all the compounds investigated have the same overall structure including the Rb-containing compositions; namely, that of $\text{Pb}_4\text{K}(\text{PO}_4)_3$ (4) in which the alkali ions were found to be distributed randomly with the lead ions in the $4f$ site. In Fig. 5, the variation of the lattice constants versus the ionic radii of the monovalent ions was plotted. In the case of mixed cations, the

average radii were calculated according to the proportions of the ions. The points on these curves are arranged along two different lines; the line containing the moderate changes in the lattice constants extends between the ionic radii of Na^+ and K^+ , while the more rapidly changing lattice parameters arrange themselves along the line between the sizes of K^+ and Rb^+ . This is a somewhat surprising observation, since one would expect that the lattice constants of the $\text{Pb}_8\text{Na}_{2-x}\text{K}_x$ system should grow faster because the ionic radii increase in this region faster (1.24–1.55) than between K^+ and Rb^+ (1.55–1.63 Å). The immediate conclusion at this point must be, therefore, that when Rb^+ is inserted, the symmetry and overall structure is the same as found for $\text{Pb}_4\text{K}(\text{PO}_4)_3$, but some internal structural changes occur which cause the sharp increase in the lattice dimensions of Rb-containing compounds.

References

1. L. MERKER AND H. WONDRA TSCHKEK, *Z. Kristallogr.* **109**, 110 (1957).
2. G. ENGEL, *J. Solid State Chem.* **6**, 293 (1973).
3. L. MERKER AND H. WONDRA TSCHKEK, *Z. Kristallogr.* **113**, 475 (1960).
4. M. MATHEW AND W. E. BROWN, American Crystallographic Association, Winter Meeting, Honolulu, 1979, Abstract G8.
5. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32**, 751 (1976).