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Lead Alkali Apatites without Hexad Anion: The Crystal Structure of $Pb_8K_2(PO_4)_6$*

M. MATHEW,† W. E. BROWN,† M. AUSTIN,‡ AND T. NEGAS

Center for Material Science, National Bureau of Standards, Washington, D.C. 20234

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The crystal structure of $Pb_8K_2(PO_4)_6$ has been determined by single-crystal X-ray diffraction. The crystals are hexagonal, space group $P6_3/m$, with $a = 9.827(1)$ and $c = 7.304(1)$ Å. The structure was refined to a final $R = 0.034$ for 551 observed reflections. The structure is that of apatite, $A_6B_4(XO_4)_6Y_2$ with the hexad anion site Y completely vacant. The $6h$ sites are occupied by Pb alone whereas the $4f$ sites contain equal amounts of Pb and K. A short Pb–O distance of 2.24 Å indicates a covalent bond which may account for the incorporation of lead into bone mineral. The presence of lone pairs of electrons from the lead atoms in the vicinity of the hexad site may explain why this site remains empty.

Introduction

Lead in apatites is of interest from two points of view. Lead is known as a "bone seeker" in that it accumulates in bone and tooth mineral. Second, it may contribute to nonstoichiometry of apatites. Nonstoichiometric apatites which deviate from the ideal formula, $A_{10}(XO_4)_6Y_2$ would require charge compensation at one or more sites. A variety of structures have been proposed (*1*) for the cation-deficient apatites, including structures deficient in Y and XO_4 ions and those in which the missing cationic charge is compensated by the presence of protons or by replacement of OH^- ions by water molecules.

Although apatites having vacancies in the anion sites Y have been studied by several investigators (*2–7*), the existence of a pure form retaining the apatite structure has been proposed on the basis of persuasive evidence only in the case of apatites involving lead. For example: $Pb_{10}(PO_4)_4(SiO_4)_2\square_2$ ($\square$ = vacancy) has been proposed to have an apatite structure from a Patterson projection (*2*), whereas the corresponding alkaline earth compounds are of the orthorhombic silicocarnotite type (*7, 8*). Although the formation of $Ca_8Na_2(PO_4)_6\square_2$ has been reported (*6*), this material as well as the analogs of other alkaline earth metals have been found to contain mixtures of different phases (*7*). Thus, the existence of apatites with the anion site Y completely

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† American Dental Association Health Foundation Research Unit, National Bureau of Standards, Washington, D.C. 20234.

‡ Summer Student, College of Notre Dame, Baltimore, Md. 21210.

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vacant has been limited to cations involving lead. Recent studies have shown that silicate apatites containing Bi^{3+}, isoelectronic with Pb^{2+}, also form apatites with deficiency in the Y site (*9*). We undertook a single-crystal X-ray structure analysis of lead potassium apatite $Pb_8K_2(PO_4)_6$, to investigate the apparent unusual ability of lead to form apatites deficient in the Y site.

Experimental

Single-phase powders and single crystals of $Pb_8K_2(PO_4)_6$ were prepared from $Pb_3(PO_4)_2$, KPO_3, and PbO starting materials. Reagent-grade PbO and $PbHPO_4$ (obtained from the Joint Committee for Powder X-ray Diffraction Standards at NBS) were reacted at 600 and at 700°C to produce $Pb_3(PO_4)_2$. The KPO_3 was obtained by heating reagent-grade KH_2PO_4 at 500°C (24 hr) and 600°C (3 hr). The starting materials were stored, weighed, mixed, and loaded into gold tubes within a dry box. These tubes were placed within Pt tubes which were sealed by welding under helium. Polycrystalline powders of apatite were obtained by heating the tubes within the range 600–700°C for 48 hr with periodic remixing. Small single crystals suitable for X-ray precession studies and structural determination were easily prepared using these apatite powders. Samples were sealed within gold tubes, heated at 800°C (24 hr), and withdrawn from the furnace. This treatment provided for significant grain growth without formation of a liquid phase. The product was identified to be a single-phase apatite from X-ray powder pattern. Absence of hydroxyl ion was demonstrated by ir. Similar methods were utilized to synthesize $Pb_8Na_2(PO_4)_6$ powder from $NaPO_3$, $Pb_3(PO_4)_2$, and PbO. Attempts were made to synthesize apatite variants containing more than two alkali cations per unit cell. Coupled substitutions according to formulations, $Pb_{8-x}K_{2+x}(PO_4)_{6-x}(SO_4)_x$, $x = 1,2$; and $Pb_{8-2x}La_xM_{2+x}(PO_4)_6$, M = K, Na and $x = 1$, were not successful.

A small crystal of $Pb_8K_2(PO_4)_6$ with dimensions 0.073 × 0.065 × 0.065 mm was used for the data collection. The crystals were hexagonal, and systematic absences of $000l$ for $l = 2n + 1$ indicated the space group to be $P6_3/m$ or $P6_3$. The cell parameters of $a = 9.827(1)$ and $c = 7.304(1)$ Å, obtained by a least-squares fit of 2θ values of 15 reflections measured on both sides of the primary beam on a Picker[1] four-circle diffractometer with monochromatized Mo$K\alpha_1$ radiation ($\lambda = 0.70932$ Å), are in excellent agreement with the reported values (*10*).

Four equivalent sets of data up to $2\theta = 55°$ were collected using $\theta-2\theta$ scans. The scan rate was 0.5° $\min^{-1}$, and the backgrounds were counted for 40 sec at each end of the scan range. The diffractometer controlling programs were those of Lenhert (*11*). Three standard reflections measured after every 30 reflections showed no significant variation in intensities during data collection. An absorption correction was applied using the equation of Rouse and Copper (*12*). The data were then merged into a set of 695 independent reflections of which 551 with $F > 2\sigma(F)$ were considered observed and used in the structure analysis and refinements. The equivalent reflections agreed within 4% on average.

An initial Fourier synthesis with a lead atom in the column site,[2] $4f$, clearly indicated the position of the second cation in the triangular site, $6h$. The remaining atoms

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[1] Certain commercial equipment, instruments, or material are identified in this paper in order to specify the experimental procedure adequately. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

[2] Cation sites in apatites, space group $P6_3/m$, with Wyckoff notations $4f$ and $6h$ referring to the column sites and triangle sites, respectively.

were located by reiterating Fourier syntheses and least-squares refinements which did not indicate any significant electron density along the hexad axis. Each cation site was assigned an occupancy of 80% Pb^{2+} and 20% K^+ in the initial stages of refinement. Comparison of electron densities and thermal parameters clearly indicated that the triangular sites, 6*h*, were occupied mostly by Pb^{2+} alone whereas the column sites, 4*f*, contained approximately equal amounts of K^+ and Pb^{2+}. Therefore, the occupancies of Pb^{2+} in these positions, 6*h* and 4*f*, were kept at 100 and 50%, respectively, until the final stages of refinement. The distribution of Pb^{2+} and K^+ over these two sites was then refined in the final cycles with the constraints (**a**) the unit cell contained $8Pb^{2+}$ and $2K^+$ ions distributed over the ten cation sites and (**b**) the occupancy of K^+ at each site is one minus the occupancy of Pb^{2+}. Final values of occupancies of Pb^{2+} at the sites, 6*h*, and 4*f*, were 0.971(3) and 0.543(4), respectively. At convergence, the values of $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ and $R_w = \{\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2\}^{1/2}$ were 0.034 and 0.042 respectively for the 551 reflections used in the refinement. The corresponding values were 0.050 and 0.047 for all reflections.

Attempts were made to refine the structure in space group $P6_3$. The distribution of Pb^{2+} and K^+ was allowed to vary in the two nonequivalent column positions of $P6_3$, while the triangular positions were assumed to contain Pb^{2+} ions only. Although a somewhat lower *R* factor was obtained (not significant according to Hamilton's *R*-factor ratio test (*13*)), most of the thermal parameters were physically unreasonable. The correlation coefficients between atoms related by symmetry in space group $P6_3/m$ were very large. Moreover, no significant ordering of Pb^{2+} and K^+ was evident in the two independent column sites. Pb^{2+} and K^+ are thus statistically disordered in the column positions in space group $P6_3/m$.

Scattering factors, including anomalous dispersion terms, for the neutral atoms were from the International Tables for X-ray Crystallography (*14*). Program RFINE4 (*15*) was used for refinements. The quantity minimized was $\Sigma w(|F_0| - |F_c|)^2$, where $w = (\sigma(F_0))^{-2}$.

Results and Discussion

Final atomic parameters are given in Table I, and a list of observed and calculated structure amplitudes is available.[3]

The results of the refinements indicate that the triangle sites, 6*h*, are occupied by Pb^{2+} ions only (actual values of occupancies 0.971(3) Pb^{2+}, 0.029 K^+) while the column positions, 4*f*, are occupied by nearly equal amounts of Pb^{2+} and K^+ ions (0.543(4) Pb^{2+}, 0.457 K^+) in agreement with those reported for $Pb_8Na_2(PO_4)_6$ (*4*) on the basis of powder pattern analysis. A refinement with fixed occupancies of cations (6*h* site by Pb^{2+} only and 4*f* site by equal amounts of Pb^{2+} and K^+) was not significantly different, according to Hamilton's *R*-factor ratio test (*13*). Thus the apparent difference between the two values for the occupancy of the cations in the two sites has little or no crystal chemical significance.

The unit cell content is illustrated in Fig. 1 and the structural details are listed in Table II. As in the case of other apatites (*16, 17*), each cation in the column site is coordinated to nine oxygen atoms with

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[3] A table of observed and calculated structure factors has been deposited as NAPS Document No. 03592. Order from ASIS/NAPS c/o Microfiche Publications, P. O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance for each NAPS Accession Number. Institutions and organizations may use purchase orders when ordering, however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are \$5.00. Microfiche are \$3.00. Outside the U.S. and Canada postage is \$3.00 for a photocopy or \$1.50 for a fiche.

TABLE I

ATOMIC PARAMETERS ($\times 10^4$) IN $Pb_8K_2(PO_4)_6$[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M(1)[b]	3333	6667	−69(1)	159(4)	U_{11}	135(5)	$U_{11}/2$	0	0
M(2)	2585(1)	33(1)	2500	130(3)	131(3)	185(3)	72(2)	0	0
P	3767(4)	3932(4)	2500	99(12)	136(14)	77(13)	57(11)	0	0
O(1)	4721(13)	3095(13)	2500	172(50)	172(48)	235(58)	118(41)	0	0
O(2)	4859(12)	5715(13)	2500	66(40)	137(46)	311(68)	−21(35)	0	0
O(3)	2695(10)	3498(11)	811(12)	218(35)	283(38)	122(35)	129(32)	−71(31)	−81(32)

[a] The thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Parameters without estimates of standard deviations (in parentheses) are fixed by symmetry.

[b] Pb^{2+} occupancy of $M(1)$ at site $4f$ is 0.543(4) and $M(2)$ at site $6h$ is 0.971(3). In each case, occupancy of K^+ is one minus Pb^{2+} occupancy. $M(2)$ is referred to as Pb throughout the text.

distances in the range of 2.53–2.92 Å. The coordination includes the shared PO_4 edge [O(2)–O(3)]. The upper and lower triangles of oxygen atoms in the coordination geometry are eclipsed and are separated by a staggered triangle (Fig. 1).

The environment of Pb^{2+} in the triangle site (illustrated in Fig. 2) shows that Pb is coordinated to six oxygen atoms including a PO_4 edge. The most obvious geometry of this arrangement corresponds to a pentagonal pyramid. The five Pb · · · O distances in the equatorial plane fall within the narrow range of 2.56–2.67 Å, and the O–Pb–O angles vary from 55.2 to 79.4°, the lower limit corresponding to the PO_4 edge coordination (Table II). The Pb · · · O(2) distance in the axial position is short, 2.24 Å, and is in the range for covalent bonding. The angles between the O(2) and the equatorial oxygen atoms are in the range 81.4–96.9°. The five equatorial oxygen atoms and the Pb atom approximate a plane, none of them lying further than 0.2 Å from the calculated least-squares plane, with the Pb atom displaced 0.2 Å from the plane in a direction opposite to O(2).

All P–O distances are equal within one standard deviation (Table II) and in excellent agreement with the mean value 1.536 Å for orthophosphate groups (*18*). The O–P–O angles vary from 106.7 to 111.8° (Table

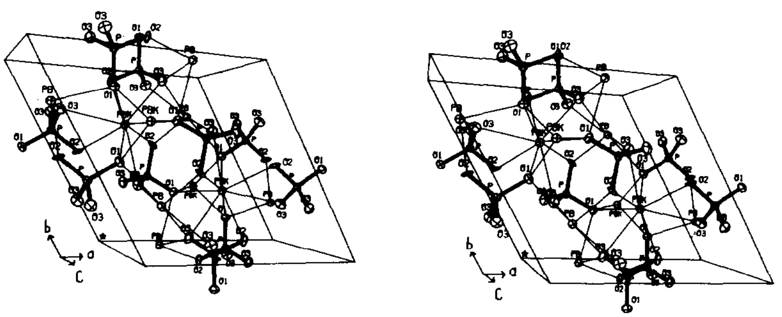

FIG. 1. The unit cell of $Pb_8K_2(PO_4)_6$ representing the apatite structure in general. The cations in column sites (4*f*) are labeled PbK since they contain approximately equal amounts of Pb and K. The origin of the coordinate system is marked by a star. Note that the edges of the cell parallel to *c* are devoid of anions.

TABLE II

SELECTED BOND LENGTHS AND ANGLES IN $Pb_8K_2(PO_4)_6$

1. Cations	
M–O(1)$^{vii, viii, ix}$	2.533(11) Å
M–O(2)$^{i, x, xi}$	2.836(10)
M–O(3)$^{i, x, xi}$	2.924(9)
Pb–O(1)^{i}	2.673(12) Å
Pb–O(2)^{ii}	2.238(13)
Pb–O(3)$^{iii, iv}$	2.558(9)
Pb–O(3)$^{v, vi}$	2.661(11)
O(1)^{i}–Pb–O(3)$^{iii, iv}$	72.8(3)°
O(1)^{i}–Pb–O(3)$^{v, vi}$	152.2(3)
O(3)^{iii}–Pb–O(3)^{v}	79.4(3)
O(3)^{v}–Pb–O(3)^{vi}	55.2(3)
O(2)^{ii}–Pb–O(1)^{i}	96.9(4)°
O(2)^{ii}–Pb–O(3)$^{iii, iv}$	84.0(3)
O(2)^{ii}–Pb–O(3)$^{v, vi}$	81.4(3)
2. Anions	
P–O(1)	1.525(15) Å
P–O(2)	1.531(12)
P–O(3)	1.538(10)
O(1)–O(2)	2.51(2) Å
O(1)–O(3)	2.54(2)
O(2)–O(3)	2.48(2)
O(3)–O(3′)	2.47(2)
O(1)–P–O(2)	110.4(6)°
O(1)–P–O(3)	111.8(6)
O(2)–P–O(3)	108.0(6)
O(3)–P–O(3′)	106.8(6)

Symmetry codes: (1) x, y, z (ii) $1 - y, x - y, z$
(iii) $y, y - x, -z$ (iv) $y, y - x, \frac{1}{2} + z$ (v) $y - x, -x, z$
(vi) $y - x, -x, \frac{1}{2} - z$ (vii) $1 - x, 1 - y, -z$ (viii) $y, y - x + 1, -z$
(ix) $x - y, x, -z$ (x) $1 - y, x - y + 1, z$ (xi) $y - x, 1 - x, z$

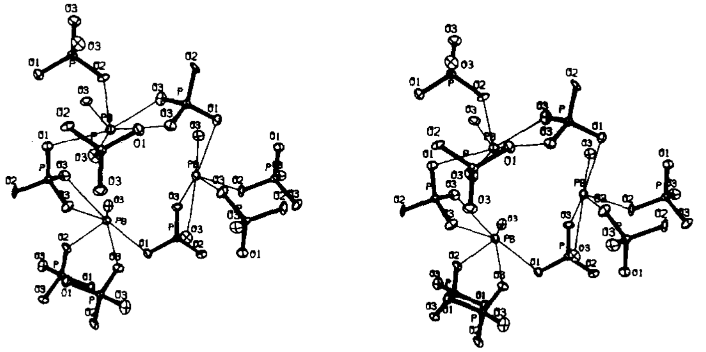

FIG. 2. The environment of Pb^{2+} at the triangular sites. Some PO_4 groups have been omitted for clarity.

II), the smaller angles corresponding to PO_4 edge coordinations.

Although the arrangement of oxygen atoms around the triangular Pb^{2+} corresponds to a distorted pentagonal pyramid, the geometry may be described as a distorted pentagonal bipyramid, if a stereochemical position is assigned to the lone pair of electrons. The assignment of a stereochemical position to the lone pair of electrons has been used to describe the various geometries of lead coordination (*19, 20*) (for example: trigonal bipyramidal geometry with a lone pair at the equatorial position; an octahedral arrangement and a pentagonal bipyramid with a lone pair in the equatorial position (*19*)). In the present study, however, the lone pair of electrons appears to be in the axial position, opposite to the Pb–O(2).

The PbO_6E group (E denotes a lone pair of electrons) exhibits, at least qualitatively, the general effect characteristic of the lone pair–bond pair interactions on the bond lengths: bonds most remote from the lone pair tend to be shorter than the adjacent bonds. Thus, in the PbO_6E group, the axial bond Pb–O(2) remote from the proposed lone pair is shorter than the equatorial Pb–O distances by about 0.4 Å (Table II). Although pentagonal bipyramidal geometry with the lone pair in the axial position has not been observed in Pb(II) coordinations, this shortening of the Pb–O bond is of the same magnitude as observed in the PbS_6E group in lead(II) diisopropylphosphorodithioate (*19*) with the lone pair in the equatorial plane. A pentagonal bipyramidal arrangement with the lone pair occupying an axial site has been observed in trisoxalatoantimonate(III) anion, SbO_6E group, where the axial Sb–O bond is shorter than the equatorial Sb–O bond by 0.2 Å (*21*).

The length of Pb ··· Pb distance, 4.373 Å, in the triangle sites also lends support to the presence of a stereochemically active lone pair of electrons. The edge of the Pb triangle in this study is approximately the same as that found in the Ba triangle in $Ba_{10}(PO_4)_6F_2$ (*22*) (Ba ··· Ba = 4.384 Å) with the F^- ion approximately at the center of the triangle. Since the ionic radius of Pb^{2+} is about 0.2 Å, smaller than that of Ba^{2+} (*23*), and the center of the triangle in $Pb_8K_2(PO_4)_6\square_2$ is vacant, the expected distance of Pb ··· Pb would be significantly smaller than that of the Ba triangle. The expansion of the Pb triangle in the present study (compared to ionic radii) may be attributed to the repulsion due to lone-pair orbitals directed approximately along the edge of the triangle.

The Pb–O(2) bond length, 2.24 Å, corresponds to the Pb–O covalent bond distance, for example, Pb–O distances of 2.30 Å in tetragonal PbO (*24*); 2.21(12) Å in orthorhombic PbO (*25, 26*); and 2.29(1) Å in $Pb_6O(OH)_6(ClO_4)_4 \cdot H_2O$ (*27*). The ordering of Pb^{2+} in the triangle positions in lead alkali apatites has been attributed to its tendency to form bonds with partial covalent character (*28*). However, it is difficult to assess the importance or contribution of the covalent character of the Pb–O bond relative to the lone pair–bond pair interactions on the shortening of the Pb–O(2) bond.

The present investigation has shown that K^+ ions occupy the columnar site, 4*f*, as expected from the larger size of the K^+ ion and the higher coordination number. But in the corresponding sodium lead apatite, $Pb_8Na_2(PO_4)_6\square_2$, the Na^+ ions are reported to occupy the column positions (*4*) and this cannot be accounted for by the cation size alone. However, this can be explained on the basis of electrostatic repulsion, as in the case of Ln/Na-coupled substitution for barium in barium fluorapatite (*22*) and La/Ca occupancy of column sites in $Ca_2La_8(SiO_4)_6O_2$ (*29*). Although no tripositive ions are involved in $Pb_8K_2(PO_4)_6\square_2$, the short separation of the cations within a column ($c/2 = 3.65$ Å) will be an important factor considering the larger ionic radii of Pb^{2+} and K^+ compared to Ln^{3+} and Na^+ or Ca^{2+}.

The triangle sites, 6*h*, in $Pb_8K_2(PO_4)_6\square_2$ are occupied by Pb^{2+} ions. Similar ordering or preferred occupancy of Pb^{2+} ions in the triangle sites has been predicted in other lead-bearing apatites and related compounds on the basis of powder diffraction data and from variations in the cell constants (*4, 28*). For the system $(Pb,Ca)_{10}(PO_4)_6(OH)_2$, a break in the curve for the cell constant *c* was observed for the composition $Pb_6Ca_4(PO_4)_6(OH)_2$; this, together with calculations of X-ray intensities, reveals ordering of Pb^{2+} on the 6*h* sites and Ca^{2+} on the 4*f* sites (*28*). However, for the Ca–Sr apatites, a linear relationship exists for both *a* and *c*, indicating a statistical disordering of Ca^{2+} and Sr^{2+} ions in both 6*h* and 4*f* sites (*30, 31*). Since the radii of Pb^{2+} and Sr^{2+} are approximately equal (*23*), the ordering of Pb^{2+} in the 6*h* sites has been related to a special property of Pb^{2+}, probably its ability to form covalent bonds (*28*). Pb–O bond lengths support this view. Ordering of Pb^{2+} ions in the 6*h* sites has been observed in nasonite, $Pb_6Ca_4(Si_2O_7)_3Cl_2$, a mineral which is related to apatite (*32, 33*). Three Pb–O distances in nasonite (mean 2.35 Å) lie between the sum of the covalent radii and ionic radii, indicating partial covalent character. In $Pb_8K_2(PO_4)_6\square_2$, however, apparent covalent character is limited to only one Pb–O bond. In the apatitic mineral, caracolite, $Pb_4Na_6(SO_4)_6Cl_2$, the column positions are occupied by Na^+ ions; and the four Pb^{2+} ions, together with the remaining two Na^+ ions, occupy the 6*h* sites (*34*). Since Pb^{2+} and Na^+ ions are statistically disordered in 6*h* positions, Pb/Na–O distances are closer to that of an ionic bond. Another example for the ordering of Pb^{2+} in 6*h* is the fluoroberyllate apatite $Pb_4Na_6(BeF_4)_6F_2$ (*35*).

The preferred occupancy of Pb^{2+} in the triangle site may be due to its apparent ability to form covalent bonds. The unique feature of Pb^{2+} ions to form apatites with the anion site *Y* vacant may be related to the fact that it has a lone pair of electrons near that site, and this can be satisfied only at the 6*h* positions. Thus, the substitution of Pb^{2+} in apatites should occur preferentially at 6*h* sites.

The largest concentration of Pb in the human body is usually in bones and teeth, where it is in a nondiffusible form (*36*). The covalent nature of Pb–O bonding may be a contributing factor in the accumulation of Pb in bones and teeth. Although the question of whether Pb is concentrated in the superficial layers or in the body of dentin and enamel still remains (*37, 38*), the preferred site in the apatite lattice appears to be 6*h*. Too little is known about the chemistry of lead-containing biological apatites to speculate on the possibility that its incorporation may be coupled with substitution of Na^+ for Ca^{2+} and the formation of a vacancy in the hexad anion site.

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References

1. A. S. Posner and A. Perloff, *J. Res. Nat. Bur. Stand.* **58**, 279, (1957).
2. H. Wondratschek and L. Merker, *Naturwissenschaften* **43**, 494 (1956).
3. L. Merker and H. Wondratschek, *Z. Kristallogr.* **109**, 110 (1957).
4. H. Wondratschek, *Neues Jb. Mineral. Abh.*, **99**, 113 (1963).
5. G. Engel and H. Jäckle, *Z. Anorg. Allg. Chem.* **448**, 71 (1979).
6. R. Klement and R. Harth, *Chem. Ber.* **94**, 1452 (1961).
7. E. R. Kreidler, Ph.D. thesis, The Pennsylvania State University (1967).

8. B. Dickens and W. E. Brown, *Tschermak's Mineral. Petrogr. Mitt.*, **16,** 1 (1971).

9. G. Engel, W. Götz, and R. Eger, *Z. Anorg. Allg. Chem.* **449,** 127 (1979).

10. G. Engel, *J. Solid State Chem.* **6,** 293 (1973).

11. P. G. Lenhert, *J. Appl. Crystallogr.* **8,** 568 (1975).

12. K. D. Rouse and M. J. Cooper, *Acta Crystallogr. A* **26,** 682 (1970).

13. W. E. Hamilton, *Acta Crystallogr.* **18,** 502 (1965).

14. "International Tables for X-ray Crystallography," Vol. IV, pp. 99–101, 149–150, Kynoch Press, Birmingham (1974).

15. L. W. Finger and E. Prince, *Nat. Bur. Stand. (U.S.) Tech. Note* **854,** 1–733 (1975).

16. M. I. Kay, R. A. Young, and A. S. Posner, *Nature (London)* **204,** 1050 (1964).

17. M. Sudarsanan, P. E. Mackie, and R. A. Young, *Mater. Res. Bull.* **7,** 1331 (1972).

18. W. H. Baur, *Acta Crystallogr. B* **30,** 1195 (1974).

19. S. L. Lawton and G. J. Kokotailo, *Inorg. Chem.* **11,** 363 (1972).

20. E. I. Lerner and S. J. Lippard, *Inorg. Chem.* **16,** 1537 (1977).

21. M. C. Poore and D. R. Russel, *Chem. Commun.*, 18 (1971).

22. M. Mathew, I. Mayer, B. Dickens, and L. W. Schroeder, *J. Solid State Chem.* **28,** 79 (1979).

23. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. B* **25,** 925 (1969).

24. J. Leciejewicz, *Acta Crystallogr.* **14,** 1304 (1961).

25. J. Leciejewicz, *Acta Crystallogr.* **14,** 66 (1961).

26. M. I. Kay, *Acta Crystallogr.* **14,** 80 (1961).

27. T. G. Spiro, D. H. Templeton, and A. Zalkin, *Inorg. Chem.* **8,** 856 (1969).

28. G. Engel, F. Krieg, and G. Reif, *J. Solid State Chem.* **15,** 117 (1975).

29. L. W. Schroeder and M. Mathew, *J. Solid State Chem.* **26,** 387 (1978).

30. R. L. Collin, *J. Amer. Chem. Soc.* **81,** 5275 (1959).

31. R. L. Collin, *J. Amer. Chem. Soc.* **82,** 5067 (1960).

32. G. Guiseppetti, G. Rossi, and C. Tadini, *Amer. Mineral.* **56,** 1174 (1971).

33. C. Frondel and L. H. Bauer, *Amer. Mineral.* **36,** 534 (1951).

34. W. Schneider, *N. Jb. Miner. Monatsh.*, 284 (1967).

35. G. Engel, *Mater. Res. Bull.* **13,** 43 (1978).

36. R. A. Goyer and P. Mushak, *Advan. Mod. Toxicol.* **2,** 41 (1977).

37. F. Brudevold and L. T. Steadman, *J. Dent. Res.* **35,** 430 (1956).

38. K. G. Carroll, H. Needleman, O. C. Tencay, and I. M. Shapiro, *Experientia* **28,** 434 (1972).