

A New Phase in the Sr–Pb–Cu Oxide System: The Crystal Structure of $\text{Sr}_{5-x}\text{Pb}_{3+x}\text{Cu}_y\text{O}_{12-\delta}$

J. S. KIM, X. X. TANG, A. MANTHIRAM, J. S. SWINNEA,
AND H. STEINFINK

Center for Materials Science and Engineering and Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712

Received August 24, 1989

A single crystal with compositions $\text{Sr}_{4.79}\text{Pb}_{3.21}\text{Cu}_{0.66}\text{O}_{11.12}$ was grown from a reaction mixture of nominal composition 2 Pb : 1 Sr : 1 Cu that was fired at 860°C in air. $M_r = 1304.6$, hexagonal, $P62m$, $a = 10.072(3)$ Å, $c = 3.542(3)$ Å, $V = 311.2(4)$ Å³, $Z = 1$, $D_x = 6.96$ g cm⁻³, $\lambda = 0.71069$ Å, $\mu = 645$ cm⁻¹, $F(000) = 553.34$, room temperature, $R = 0.040$ for 323 unique reflections $>5\sigma(F_o)$. The Pb atoms are in octahedral coordination; the octahedra form a chain parallel to c by edge-sharing. Sr is coordinated by nine oxygen atoms that form a capped trigonal prism. The trigonal prisms form a chain parallel to c by face-sharing. The Sr/Pb site is surrounded by seven oxygen ions. The polyhedron can be described as a tricapped trigonal prism with one edge of the prism missing. The octahedra and trigonal prisms articulate by corner sharing into a three-dimensional framework. Two crystallographically independent Cu atoms are disordered and occupy tetrahedral interstices. One oxygen site is partially occupied. The presence of Pb^{2+} on the Pb site distorts the octahedron by lengthening two bonds to 2.44(3) Å; the average of the other four bond lengths is 2.137(19) Å. The Sr–O bond lengths to the six apices of the prism are 2.632(14) and 2.935(3) Å to the three capping atoms. The disordered Sr/Pb atom site has four oxygen neighbors at 2.544(17) Å, two at 2.621(5) Å, and one at 2.42(2) Å. The compound is an electrical insulator. © 1990 Academic Press, Inc.

Introduction

Oxides with the general formula $(\text{AO})_2\text{B}_2\text{CaCu}_2\text{O}_6$ ($A = \text{Bi}$ or Tl , $B = \text{Sr}$, Ba , or Ca , hereafter designated as 2212 phase) have an intergrowth structure consisting of perovskite-type CuO_2 layers alternating with rock-salt-type double layers $(\text{AO})_2$ ($1a-d$). These oxides superconduct with transition temperatures, T_c , ranging from 85–110 K, with the Tl phases having higher values than the Bi compounds. It has been shown that Ca^{2+} can be replaced by Y^{3+} to form $\text{Bi}_2(\text{Sr}_{1.5}\text{Ca}_{0.5})\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_8$ (2) and Bi^{3+} can be replaced by Pb^{2+} provided an equivalent amount of Ca^{2+} is replaced by

Y^{3+} (3). To determine the extent of substitution of Pb for Bi^{3+} the preparation of $\text{Pb}_2(\text{Sr}_{1.5}\text{Ca}_{0.5})\text{YCu}_2\text{O}_8$ was attempted. The X-ray powder diffraction diagram showed no evidence of the formation of a 2212 phase; instead diffraction lines due to $\text{Y}_2\text{Cu}_2\text{O}_5$ and an unknown phase were observed. The unknown phase diffraction pattern did not correspond to any known binary or multinary oxide of Sr, Ca, Pb, and Cu. The specimen was semiconducting with room temperature resistance as high as 10^6 ohm. The same X-ray powder diffraction pattern was also observed while investigating the formation of the compound $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{CoO}_5$ (121) when it was slowly cooled to

room temperature from the reaction temperature at 1020°C (4) and in the reaction product from a nominal reaction mixture ($\text{Pb}_{0.71}\text{Cu}_{0.29}\text{Sr}_2\text{CaCu}_2\text{O}_7$ (1212) (5). The occurrence of this unknown phase in systems of interest in the study of high- T_c superconducting compounds led us to determine its crystal structure and characterize its physical properties.

Experimental

Several compositions in the Sr–Pb–Cu oxide system were prepared by firing the oxide and carbonate precursors in ceramic boats in air at 780°C for 6 hr; regrinding, and refiring at 860°C for 48 hr in air. Table I lists the results that were obtained when the initial mixtures were close to 5 Sr : 3 Pb : 1 Cu. The X-ray powder diffraction patterns indicated that single phase material could be obtained near that stoichiometry. The room temperature electrical resistance, obtained by a 4-probe measurement on a pressed disk, was 2×10^7 ohms for $\text{Sr}_{4.57}\text{Pb}_{3.43}\text{Cu}_{1.14}\text{O}_{12.3}$ and out of range of the multimeter for $\text{Sr}_{4.8}\text{Pb}_{3.2}\text{Cu}_{0.7}\text{O}_{11.76}$. The oxygen content for these two compositions was determined by iodometric titration with the assumption that Pb and Cu were reduced to Pb^{2+} and Cu^{1+} , respectively, during the de-

termination. The presence of small impurities such as CuO below the limit of detectability by powder X-ray diffraction methods would introduce an error in the oxygen stoichiometry. A TGA experiment did not show any significant loss of oxygen up to a temperature of 750°C.

Single crystals were grown by heating a nominal mixture of composition 2 Pb : 1 Sr : 1 Cu in an alumina boat at 780°C for 5 hr followed by heating at 860°C for 48 hr. The reaction product was slowly cooled to 100°C over an 8-hr interval. Indications of melting were observed under the optical microscope on the surface of the specimen and where it contacted the alumina boat. A reflecting polarizing microscope was used to select a hexagonal, acicular crystal and its composition was approximately 35 Pb : 50 Sr : 15 Cu as determined by standardless EDX (energy dispersive X-ray spectroscopy). Oscillation and Weissenberg photographs showed that the crystal was hexagonal with cell dimensions $a = 10.1 \text{ \AA}$ and $c = 3.5 \text{ \AA}$, diffraction symmetry $6/mmm$ and no systematic absences, consistent with space groups $P6/mmm$, $P622$, $P6mm$, $P6m2$, and $P62m$. A TEM photograph with the electron beam parallel to [001] displayed hexagonal symmetry consistent with the 10-Å cell parameter.

TABLE I
PHASES IDENTIFIED BY POWDER X-RAY DIFFRACTION IN Pb–Sr–Cu OXIDE MIXTURES AFTER FINAL REACTION AT 860°C IN AIR

Sample	Remarks	
$\text{Sr}_3\text{Pb}_3\text{Cu}_{1.5}\text{O}_z$	Unknown impurity	
$\text{Sr}_3\text{Pb}_3\text{Cu}_{1.0}\text{O}_z$	Unknown impurity	
$\text{Sr}_{4.8}\text{Pb}_{3.2}\text{Cu}_{1.6}\text{O}_z$	CuO	
$\text{Sr}_{4.8}\text{Pb}_{3.2}\text{Cu}_{0.7}\text{O}_{11.76}$	Single phase	$a = 10.136(7)$, $c = 3.561(1)$
$\text{Sr}_{4.57}\text{Pb}_{3.43}\text{Cu}_{1.14}\text{O}_{12.3}$	Single phase	$a = 10.099(9)$, $c = 3.555(1)$
$\text{Sr}_4\text{Pb}_4\text{Cu}_{1.0}\text{O}_z$	Unknown impurity	

Note. The stoichiometries of the cations are those of the initial mixture; the known oxygen stoichiometry is from iodometric titration. In each sample the major phase of the product is always $\text{Sr}_{5-x}\text{Pb}_{3+x}\text{Cu}_y\text{O}_z$.

Structure Determination

The single crystal was transferred to a Krisel automated Picker diffractometer equipped with an incident beam monochromator, $\lambda(\text{MoK}\alpha) = 0.71069 \text{ \AA}$. The conditions for the data collection, data reduction, and refinement are shown in Table II. The lattice constants were obtained from a least-squares calculation of precisely determined 2θ values of 10 reflections between

24.5 and 27.2°. The variations in the intensities of the four standard reflections measured after every 60 min fluctuated randomly $\pm 2\%$. Estimated standard deviations, $\sigma(F_o)$, were obtained from counting statistics. The absorption corrections were obtained using ORABS (6). The least-squares calculations were carried out with SHELX76 (7). Atomic scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (8). An extinction correction, g , was applied using the expression $F = F(1 - gF^2/\sin \theta)$.

A search of the CAN/SND crystallographic data base (9) using only the cell parameters $a = b$, c , $\gamma = 120^\circ$ without any other restrictions yielded a listing for Ca_2IrO_4 , $P\bar{6}2m$. Babel *et al.* (10) solved this structure and discuss its close relationship to Sr_2PbO_4 , $P2_12_12_1$, and Na_2CuF_4 , $P2_1/c$. These crystal structures contain common features and it was decided to merge our data set on the basis of monoclinic, orthorhombic, and hexagonal symmetry to look for possible solutions to the structure by examining the three-dimensional Patterson functions. The first two crystal systems produced structures that had a hexagonal motif for the cations. Refinements stopped at R about 15% and oscillated thereafter. The same lack of success resulted when a structure solution was attempted in $P6/mmm$. The placement of Pb and Sr on the basis of the Ca_2IrO_4 structure in $P\bar{6}2m$ provided electron density maps that led to the correct assignments of Sr and Pb positions to yield $R = 8\%$. Difference electron density maps revealed all oxygen and the disordered Cu atom positions. The positional parameters, thermal displacement parameters, and variable occupancy factors, as shown in Table III, the inclusion of an extinction parameter, and the omission of (002), yielded a final $R = 3.97\%$. A refinement of the inverse structure converged

TABLE II
SUMMARY OF DATA COLLECTION AND STRUCTURE REFINEMENT

Formula	$\text{Sr}_{4.79}\text{Pb}_{3.21}\text{Cu}_{0.66}\text{O}_{11.12}$
Formula weight	1304.6
Crystal system	Hexagonal
a , \AA	10.072(3)
c , \AA	3.542(3)
V , \AA^3	311.2(4)
Space group	$P\bar{6}2m$
Z	1
D_x , g cm^{-3}	6.96
μ , cm^{-1}	645
λ , \AA	0.71069
$F(000)$	553.34
Dimensions, mm	$0.427 \times 0.055 \times 0.036$
Mode	ω
Max 2θ	60
Scan rate, deg min^{-1}	4
Scan width	$2 + 0.70 \tan \theta$
Background	2.5 s at high and low ω
$h k l$, min	-14, -14, 0
$h k l$, max	14, 14, 5
Reflections measured	2099
Reflections unique	382
R_{int}	0.075
$\geq 5\sigma(F)$	323
Transmission factor range	0.129–0.059
Standard reflections	$5\bar{1}1$, 411 , $5\bar{1}\bar{1}$, $4\bar{1}\bar{1}$
Number of variables	26
w^{-1}	$\sigma^2(F_o) + 0.0004 F_o^2$
Goodness of fit, S	1.54
Function minimized	$\sum w (F_o - F_c)^2$
R , wR ; all data: R , wR , max shift/esd	0.040, 0.039; 0.059, 0.048 0.001
$\Delta\rho$, max, min, e \AA^{-3}	6.0, -4.3
Extinction parameter	2.63×10^{-7}

TABLE III
 ATOMIC AND THERMAL DISPLACEMENT (\AA^2) PARAMETERS FOR $\text{Sr}_{4.79}\text{Pb}_{3.21}\text{Cu}_{0.66}\text{O}_{11.12}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{eq}
Pb1	0.3368(1)	0	0	0.0119(5)	0.0073(6)	0.0165(5)	0.0037(3)	0.0124(4)
Sr1	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{2}$	0.0164(18)	U_{11}	0.0067(26)	0.0082(9)	0.0132(15)
Sr2 ^a	0.7005(5)	0	$\frac{1}{2}$	0.0107(12)	0.0065(13)	0.0198(22)	0.0033(6)	0.0128(11)
Pb2 ^b	0.7005	0	$\frac{1}{2}$	0.0107	0.0065	0.0198	0.0033	
Cu1 ^c	0	0	0.371(8)	0.009(6)				
Cu2 ^c	0	0	0.112(9)	0.009				
O1 ^d	0.170(4)	0	$\frac{1}{2}$	0.043(16)				
O2	0.4604(20)	0	$\frac{1}{2}$	0.012(4)				
O3	0.2412(16)	0.4446(21)	0	0.020(3)				

Note. Numbers in parentheses are the uncertainties in the last digits. The thermal displacement parameter is of the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk)]$. U_{eq} from $\frac{1}{3} \sum U_{ii}$ of the diagonalized tensor.

^a The site occupancy is 0.930(13) and Pb2 is 1–0.930.

^b The absence of esd's denotes that the parameters are set equal to those of another atom.

^c Site occupancy for Cu1 is 0.197(19) and for Cu2 it is 0.134(15).

^d Site occupancy is 0.71(9).

to $R = 4.55\%$ and was rejected. A table of F_o , F_c , and $\sigma(F_o)$ has been deposited.¹

Discussion

In Table IV are listed bond lengths and angles. The Pb1 atom is in a somewhat distorted octahedral coordination with O3 occupying the apical positions. The four bond lengths to O3 and O2 do not differ significantly but the two to O1 are significantly longer. The stoichiometry of the compound obtained from the structure refinement requires the presence of Pb^{2+} (2.46 Pb^{4+} and 0.75 Pb^{2+}). The statistically occupied 3g Sr2 site contains 0.21 Pb^{2+} (0.07 per site) and the fully occupied 3f Pb1 site contains 0.54

Pb^{2+} (0.18 per site). The admixture of Pb^{2+} into the Pb^{4+} site is supported by the observation of a 2.44 \AA Pb–O bond length. The lengthening of this bond due to the presence of the lone electron pair in the Pb^{2+} ion is also seen in PbO (11). The Sr2/Pb2 site occupant is bonded to seven O^{2-} ions. The coordination polyhedron is an incomplete tricapped trigonal prism. The four O3 constitute one square face of a trigonal prism whose edge is missing. The O2 and two O1 ions are in the capping positions. The Sr1 site is fully occupied and its coordination polyhedron consists of a tricapped trigonal prism. A least-squares refinement of the occupancy factor converged to unity.

The Pb1 octahedra form an infinite chain parallel to *c* by edge sharing; the Sr1 trigonal prisms propagate parallel to *c* by face sharing. The articulations between these polyhedra are illustrated in Fig. 1. They occur through corner sharing of each of the six trigonal prism O3 atoms with six surrounding Pb1 octahedra; the O3 are at the apices of the octahedron. The Sr/Pb is in an interstice formed by seven oxygen atoms. The crystallographically equivalent metal

¹ See NAPS document No. 04751 for 5 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy. \$7.75 up to 20 pages plus \$0.30 for each additional page. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling, for the first 20 pages, and \$1.00 for additional 10 pages of material, \$1.50 for postage of any microfiche orders.

TABLE IV
BOND LENGTHS (Å) AND ANGLES (Deg) FOR $\text{Sr}_{4.79}\text{Pb}_{3.21}\text{Cu}_{0.66}\text{O}_{11.12}$

Pb1-2 × O3	2.108(15)	4 × O3-Pb1-O1	87.6(4)
-2 × O2	2.165(11)	2 × O2-Pb1-O1	171.6(9)
-2 × O1	2.44(3)	2 × O2-Pb1-O1	78.6(9)
		O1-Pb1-O1	173(1)
Sr1-6 × O3	2.632(14)	O2-Pb1-O2	109.8(9)
-3 × O2	2.935(3)		
		3 × O1-Cu1-O1	113.7(8)
Sr2/Pb2-4 × O3	2.544(17)	3 × O1-Cu1-"Cu2" ^a	105(1)
- O2	2.42(2)		
2 × O1	2.621(5)	3 × O1-Cu2-O1	85(1)
		O1-Cu2-"Cu1" ^a	129(1)
Cu1-3 × O1	1.77(4)		
Cu2-3 × O1	2.20(4)		
O1-2 × O2	3.074(19)		
-2 × O2	3.195(18)		
2 × O1	3.156(24)		
O2-O1	2.92(5)		
O1-2 × O1	2.97(7)		
Cu1-Cu1	0.91(6)		
-Cu1	2.63(6)		
-Cu2	0.92(4)		
-Cu2	2.62(4)		
-Cu2	1.71(4)		
-Cu2	1.83(4)		
Cu2-Cu2	0.80(6)		
-Cu2	2.75(6)		

^a These are oxygen atoms when the interstice is occupied by Cu1 or Cu2, respectively.

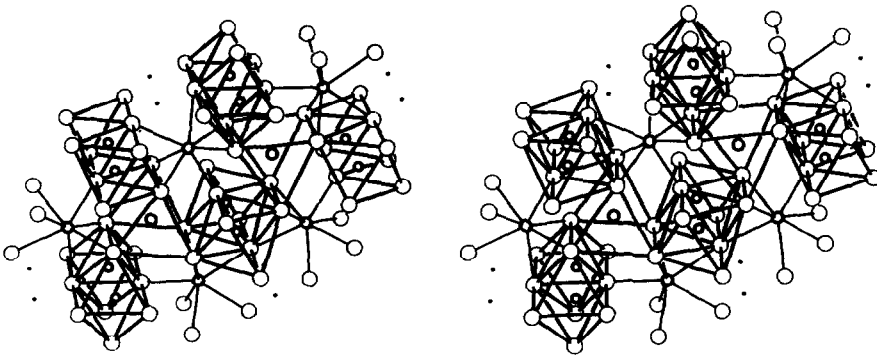


FIG. 1. Stereoscopic view of the structure of $\text{Sr}_{4.79}\text{Pb}_{3.21}\text{Cu}_{0.66}\text{O}_{11.12}$. The small dots show the direction of c and outline the hexagonal cell. Large circles represent oxygen, small circles Pb, and intermediate circles the Sr and Sr/Pb atoms. The lightly drawn bonds show the coordination from the Sr/Pb site to oxygen.

atoms within chains are separated by the c -axis dimension and intrachain separations exceed 3.3 Å so that no cation–cation interactions occur. This is consistent with the insulating electrical resistance values observed in this compound.

The crystal structure of this compound is very closely related to that of Ca_2IrO_4 (10). In the latter compound the $2d$ and $3g$ sites are occupied by Ca while in this phase Sr1 and Sr2/Pb2 are located in these sites. Ir is in the $3f$ site and Pb1 takes its place in this structure. The six Ir–O bond distances are equal while in this structure two of the Pb–O distances have significantly lengthened because of the influence of the lone electron pair of Pb^{2+} . In Ca_2IrO_4 the shared edge between IrO_6 octahedra, O1–O2, is very short, 2.48(2) Å, while in this structure it is equal to the ionic diameter, 2.92(5) Å. The oxygen ions in both structures occupy the same sites in the space group. The spatial parameter values of Table III are close to the values reported for Ca_2IrO_4 . A single Ca atom occupies the $1a$ site of $P\bar{6}2m$ placing it into an octahedral interstice. This position is not occupied in this compound. The placement of Cu at the origin raises R by several percent. The difference Fourier map definitely shows that the origin is not occupied. Two peaks in the difference Fouriers located on the c -axis were assigned to Cu atoms and refinement converged to the positions and occupancies shown in Table III. These two Cu locations represent tetrahedral interstices. If Cu1 is present three O1 atoms at 1.77(4) Å constitute the base of the tetrahedron and the apex oxygen atom is at the “Cu2” site at $z = -0.112$, at a distance of 1.71(4) Å. When Cu2 is present the three O1 atoms, now at 2.20(4) Å, again constitute the base of a tetrahedron and the apex oxygen is at the “Cu1” site at $z = -0.371$, at a distance of 1.71(4) Å. If Cu were at the origin it would form six equal Cu–O bonds of 2.20 Å. When Cu^{2+} is in octahedral coordination

the apical bond lengths are usually lengthened because of the Jahn–Teller effect. This may be the reason that in this structure Cu^{2+} avoids the origin site. A tetrahedral site for Cu is not common but does occur, e.g., in CuCr_2O_4 (12). The Cu1 is in a less distorted tetrahedron than Cu2 and this may be the reason that the former site is slightly favored.

The maximum Cu content of this phase should be 1 with the two sites about equally occupied. If the more symmetric tetrahedral interstice is energetically slightly more favorable prolonged annealing may cause this site to be fully occupied and concomitantly fill the O1 site, resulting in an idealized formula $\text{Pb}_3\text{Sr}_5\text{CuO}_{12}$. Except for the $\text{Cu}_{1.14}$ sample the prereacted mixtures with Cu compositions exceeding 1 showed impurity phases in the reaction products, Table I. It is quite likely that the excess CuO that is probably present is below the limit of detectability of the powder X-ray diffraction technique. The oxygen content in excess of 12 is also indicative of such an impurity. The phase with the same cation composition as the single crystal but oxygen stoichiometry 11.76 has slightly different lattice constants than those of the single crystal. The oxygen content implies that Pb is essentially tetravalent leading to six equal Pb–O bond lengths. The preparative conditions for the powder shown in Table I and for the single crystal were not the same and the differences in oxygen composition and, therefore, oxidation states of Pb may depend on the thermal history of the sample.

Acknowledgments

This research was supported by NSF Grant DMR 8520028, The Robert A. Welch Foundation of Houston, Texas, and the Microelectronics and Computer Technology Corporation (MCC), Austin, Texas.

References

1. (a) R. M. HAZEN, C. T. PREWITT, R. J. ANGEL, N. L. ROSS, L. W. FINGER, C. G. HADIDIACOS,

- D. R. WEBLEN, P. J. HEANEY, P. H. HOR, R. L. MENG, Y. Y. SUN, Y. Q. WANG, Y. Y. XUE, Z. L. HUANG, L. GAO, J. BECHTOLD, AND C. W. CHU, *Phys. Rev. Lett.* **60**, 1174 (1988); (b) M. A. SUBRAMANIAN, C. C. TORARDI, J. C. CALABRESE, J. GOPALAKRISHNAN, K. J. MORRISSEY, T. R. ASKEW, R. B. FLIPPEN, U. CHOWDHRY, AND A. W. SLEIGHT, *Science* **239**, 1015 (1988); (c) J. M. TARASCON, Y. LEPAGE, P. BARBOUX, B. G. BAGLEY, L. H. GREENE, W. R. MCKINNON, G. W. HULL, M. GIROUD, AND D. M. HWANG, *Phys. Rev. B* **37**, 9382 (1988); (d) S. A. SUNSHINE, T. SIEGRIST, L. F. SCHNEEMEYER, D. W. MURPHY, R. J. CAVA, B. BATLOGG, R. B. VAN DOVER, R. M. FLEMING, S. H. GLARUM, S. NAKAHARA, R. FARROW, J. J. KRAJEWSKI, S. M. ZAHURAK, J. V. WASZCZAK, J. H. MARSHALL, P. MARSH, L. W. RUPP, JR., AND W. F. PECK, *Phys. Rev. B* **38**, 893 (1988).
2. A. MANTHIRAM AND J. B. GOODENOUGH, *Appl. Phys. Lett.* **53**, 420 (1988).
 3. A. MANTHIRAM AND J. B. GOODENOUGH, *Appl. Phys. Lett.* **53**, 2695 (1988).
 4. J. S. KIM, J. S. SWINNEA, AND H. STEINFINK, *J. Less-Commons Met.*, in press.
 5. J. Y. LEE, J. S. KIM, J. S. SWINNEA, AND H. STEINFINK, *J. Solid State Chem.*, submitted.
 6. D. J. Wehe, W. R. Busing, and H. A. Levy, "Program ORABS," ORNL TM 229, Oak Ridge, TN (1962).
 7. G. M. Sheldrick, SHELX76 Program for Crystal Structure Determination," University of Cambridge, England (1976).
 8. "International Tables for X-ray Crystallography," Vol. IV, Kynock Press, Birmingham (1974). (Present distributor Kluwer Academic Publishers, Dordrech.)
 9. CRYSTDAT, crystallographic data base operated by the Canada Institute for Scientific and Technical Information (CISTI), a division of the National Research Council Canada (NRCC), Ottawa, Canada.
 10. D. BABEL, W. RÜDORFF, AND R. TSCHÖPP, *Z. Anorg. Allge. Chem.* **347**, 282 (1966).
 11. A. F. WELLS, "Structural Inorganic Chemistry," 5th ed. p. 558, Clarendon Press, Oxford (1984).
 12. A. F. WELLS, "Structural Inorganic Chemistry," 5th ed. p. 1137, Clarendon Press, Oxford (1984).