Preparation and X-Ray Diffraction Data for the New Pyrochlores $Pb_2[M_{0.33}Sb_{1.67}]O_{6.5}$ (M = Mg, Ni, Cu, or Zn)

Conchita Cascales and Isidoro Rasines *
Instituto de Química Inorgánica Elhúyar, Serrano 113, E-28006 Madrid, Spain

From mixtures of PbO, Sb_2O_3, and MO (M = Mg, Ni, Cu, or Zn), four new oxide pyrochlores of stoicheiometry $Pb_2[M_{0.33}Sb_{1.67}]O_{6.50}$ have been synthesized. These compounds are coloured powders giving X-ray diffraction patterns typical of cubic pyrochlores, with space group $Fd\bar{3}m$ (no. 227), $Z = 8$, and a values from 10.500 5(2) (M = Ni) to 10.512 9(2) Å (M = Zn). The lowest discrepancy factors R between the observed and calculated intensities were obtained for Pb in 16(c) positions, M and Sb (1 : 5) randomly distributed in 16(d), oxygen atoms in 48(f) and in half of the 8(a) sites, and x values for the oxygen positional parameter (origin at centre, $\bar{3}m$) of 0.430 (M = Cu) and 0.431 (M = Mg, Ni, or Zn). The co-ordination of M and Sb is nearly octahedral. For seven-co-ordinated Pb^{II} the stereochemical influence of the unshared electron pair is demonstrated. Observed interatomic distances are in agreement with those calculated.

Compounds of the general formula $A_2[B_2]O_6O'$ constitute a family of oxides isostructural with the mineral pyrochlore having space group $Fd\bar{3}m$ (no. 227), $Z = 8$. If the centre, ($\bar{3}m$) is chosen as origin, the larger A cations occupy the 16(c) positions, 0, 0, 0, and the smaller B cations are located in 16(d), 0.5, 0.5, 0.5. The oxygen atoms occupy two kinds of positions: 48(f), x, 0.125, 0.125, and 8(a), 0.125, 0.125, 0.125, with only one variable positional parameter, x. In this way the A cations have eight nearest-neighbour oxygen atoms at the vertexes of a scalenohedron, six at the same distance and the other two closer, and the co-ordination polyhedron around the B cations is a trigonal antiprism. These co-ordination polyhedra change shape with x: a value of 0.4375 for x will give regular octahedra around the B cations, and a value of 0.375 will give regular cubes around the A cations. Examples of x values between 0.395 and 0.441 are known,[1,2] and many pyrochlores have $x = 0.420 \pm 0.010$.

We have recently[3] synthesized and studied by X-ray diffraction a new pyrochlore whose composition, $Pb_2[In_{0.5}Sb_{1.5}]O_{6.5}$, was established by taking into account various possibilities, such as the existence of Pb^{IV} in the sublattice of B cations, the variable contents of Sb, and the presence of oxygen vacancies. This pyrochlore has space group $Fd\bar{3}m$ (no. 227), $Z = 8$, $a = 10.589\ 2(1)$ Å, $U = 1\ 187.38(3)$ Å^3, $D_c = 8.48$ Mg m^{-3}, Pb in 16(c) positions, In and Sb (1 : 3) distributed at random in 16(d), oxygen atoms in 48(f) and in one half of the 8(a) sites, oxygen positional parameter $x = 0.429$, and $R = 0.062$. In order to establish the existence of hypothetical pyrochlores containing Pb^{II}, Sb^{V}, and a bivalent metal, we have prepared different materials of composition $Pb_{2-x}[Ni_{0.33}Sb_{1.67}]O_{6.5-x}$ (x = 0, 0.25, or 0.50). Once identified by X-ray diffraction, these materials were found to be mixtures of phases, with the exception of the sample with $x = 0$ which consisted of a cubic pyrochlore. The preparation and crystal study of this pyrochlore and of the isotypic oxides $Pb_2[M_{0.33}Sb_{1.67}]O_{6.5}$ (M = Mg, Cu, or Zn) are reported.

Experimental

The oxides $Pb_2[M_{0.33}Sb_{1.67}]O_{6.5}$ (M = Mg, Ni, Cu, or Zn) were prepared from mixtures of analytical grade PbO, Sb_2O_3, and MO in the molar ratios Pb:M:Sb = 6:1:5, which were heated in air at 953, 1 073, 1 123 K for M = Cu. For M = Mg, Ni, or Zn, further treatments at 1 173 and 1 223 K were performed. After each thermal treatment for 24 h, the materials were quenched, weighed, and ground.

Experimental conditions and details on the analysis of the X-ray diffraction data have been described elsewhere.[3] The unit-cell parameters were refined from the 2θ values of the last seven reflections. The intensities were calculated with the program LAZY-PULVERIX[4] using scattering factors for neutral atoms, Debye–Waller, Lorentz, and polarization factors, and correction for anomalous dispersion. The arbitrarily chosen Debye–Waller factors, B_j, for calculation of the intensities were 0.01 and 0.80 Å^2 for Pb and oxygen atoms, respectively. The values 0.38 (Sb), 0.77 (Mg), 0.63 (Ni), 0.61 (Cu), and 0.60 Å^2 (Zn) were obtained from those for Pb and oxygen by interpolation of the corresponding atomic masses. The discrepancy factor between the observed and calculated intensities, $R = (\Sigma|I_o^{\frac{1}{2}} - I_c^{\frac{1}{2}}|)/\Sigma I_o^{\frac{1}{2}}$, was computed after setting $\Sigma I_o = \Sigma I_c$, and taking into account all the reflections with $I_o > 5$. For each compound the x value taken as observed was that leading to the smallest value of R.

Results and Discussion

The oxides $Pb_2[M_{0.33}Sb_{1.67}]O_{6.5}$ were obtained as powders either strong orange (M = Mg, Ni, or Zn) or strong yellowish brown (M = Cu), which gave good X-ray diffraction patterns. The observed interplanar d spacings are included in Table 1 and indicate cubic pyrochlores, having space group $Fd\bar{3}m$ (no. 227), $Z = 8$. The samples were always obtained as single-phase pyrochlores, *i.e.* the presence of other phases was never detected. The observed, I_o, and calculated, I_c, intensities are also included in Table 1. The lowest discrepancy factors R were obtained for Pb in 16(c) positions, origin at centre, ($\bar{3}m$), M and Sb randomly distributed (M:Sb = 1:5) in 16(d), and oxygen atoms in 48(f) and one half of the 8(a) positions. Table 2 contains the relevant crystal data, a, U, D_c, and oxygen positional parameters, x. Table 3 shows the apparent interatomic distances for the observed a and x values, the observed Pb–O distance being the weighted average of six (c)–(f) and one (c)–(a) distances. Table 4 gives the angles of the co-ordination polyhedra around the cations for the compound of Mg and that of Cu. In the cases of the other two oxides, these angles are the same as for Mg, since $x = 0.431$ for M = Mg, Ni, or Zn. The Figure shows the co-ordination polyhedra: a scalenohedron around the lead(II) cations, and a trigonal antiprism, nearly a regular octahedron, for [M,Sb] cations.

The results obtained indicate that $Pb_2[M_{0.33}Sb_{1.67}]O_{6.5}$ (M = Mg, Ni, Cu, or Zn) and $Pb_2[In_{0.5}Sb_{1.5}]O_{6.5}$ are very

Table 1. *X*-Ray diffraction data for the pyrochlores $Pb_2[M_{0.33}Sb_{1.67}]O_{6.5}$ (M = Mg, Ni, Cu, or Zn)

	M = Mg			M = Ni		
hkl	d_o	I_o	I_c	d_o	I_o	I_c
111	6.03	47.2	57.4	6.09	46.1	46.5
311	3.15	55.1	55.5	3.17	45.9	46.7
222	3.01	1 076.0	1 000.0	3.030	1 106.1	1 000.0
400	2.61	389.2	382.4	2.626	388.1	384.0
331	2.40	65.9	72.4	2.410	60.5	64.6
511—333	2.025	31.4	40.3	2.022	27.7	35.7
440	1.858	476.4	421.2	1.856	431.6	418.6
531	1.778	21.7	28.4	1.776	22.4	24.7
622	1.584	465.0	434.2	1.583	418.3	431.5
444	1.518	124.0	117.6	1.5152	118.2	116.9
800	1.3141	60.2	63.1	1.3128	74.3	62.5
662	1.2057	174.8	174.6	1.2041	197.2	172.8
840	1.1752	157.0	156.7	1.1738	169.0	155.2
844	1.0727	118.8	125.3	1.0717	127.6	123.9
10 22—666	1.0113	146.2	154.8	1.0104	148.9	153.1
880	0.9291	47.6	54.2	0.9282	48.8	53.6
10 62	0.888 25	202.1	237.8	0.887 43	178.2	235.2
12 00—884	0.875 85	132.3	160.4	0.875 03	119.4	158.6
12 40	0.830 93	127.9	158.7	0.830 15	139.5	157.3
10 66	0.801 39	187.8	205.3	0.800 63	175.8	204.6

	M = Cu			M = Zn		
	d_o	I_o	I_c	d_o	I_o	I_c
111	6.08	39.4	45.4	6.09	32.8	43.6
311	3.172	49.6	44.9	3.171	41.5	44.1
222	3.031	1 098.5	1 000.0	3.032	1 042.0	1 000.0
400	2.627	406.0	383.3	2.629	364.1	384.7
331	2.411	46.3	62.7	2.413	52.8	62.2
511—333	2.024	24.3	34.7	—	25.0	34.2
440	1.8576	423.9	420.5	1.8584	456.3	419.0
531	1.7765	16.5	23.8	1.7775	14.6	23.4
622	1.5835	425.7	431.9	1.5843	457.7	432.6
444	1.5170	114.8	116.3	1.5174	118.1	117.2
800	1.3136	60.2	62.6	1.3141	64.5	62.6
662	1.2053	180.4	172.9	1.2059	170.1	173.3
840	1.1749	144.1	154.8	1.1754	155.8	155.6
844	1.0722	119.5	124.4	1.0729	124.1	124.2
10 22—666	1.011 08	150.6	152.9	1.0116	155.1	153.1
880	0.928 73	51.2	53.6	0.929 23	51.7	53.5
10 62	0.888 03	208.1	234.5	0.888 50	205.8	234.4
12 00—884	0.875 61	140.0	157.7	0.876 08	154.6	157.9
12 40	0.830 67	144.2	156.1	0.831 10	144.6	155.9
10 66	0.801 19	191.3	202.6	0.801 58	201.8	201.4

Table 2. Crystal data for the pyrochlores $Pb_2[M_{0.33}Sb_{1.67}]O_{6.5}$ with estimated standard deviations in parentheses

M	*a*/Å	*U*/Å^3	D_c/ Mg m^{-3}	*x**	*R*
Mg	10.501 2(2)	1 161.00(6)	8.34	0.431	0.046
Ni	10.500 5(2)	1 157.77(5)	8.52	0.431	0.048
Cu	10.507 3(1)	1 160.06(4)	8.50	0.430	0.048
Zn	10.512 9(2)	1 161.90(7)	8.47	0.431	0.033

* Origin at centre, ($\bar{3}m$).

Table 3. Observed and calculated interatomic distances (Å) for $Pb_2[M_{0.33}Sb_{1.67}]O_{6.5}$

	M = Mg	Ni	Cu	Zn
Pb–O_o	2.61	2.60	2.60	2.61
Pb–O_c	2.61	2.61	2.61	2.61
M,Sb–O_o	2.00	1.99	2.00	2.00
M,Sb–O_c	2.00	2.00	2.00	2.00

similar chemical species. They only differ in the M:Sb ratio, 1:5 and 1:3, respectively. All of these oxides are definite compounds, with Pb fully occupying the sublattice of A cations, and vacancies at half of the O′ positions. These vacancies indicate the stereochemical influence of the non-bonded pair of electrons of Pb^{II}. The co-ordination polyhedron of this cation in the five mentioned pyrochlores is a scalenohedron with seven vertexes occupied by six (f) and one (a) oxygen atoms, while the lone pair of electrons (⊙) occupies the remaining eighth vertex at the vacant (a) position. For this reason, the observed interatomic distances in Table 3 are comparable with the sums of the Shannon[5] effective ionic radii, if Pb^{II} is considered to be seven-co-ordinated. As for the [M,Sb] cations, nearly regular octahedra are found in the five cases, since the oxygen positional parameters, *x*, have values close to 0.4375.

The $6s^2$ cation Pb^{II} shows various co-ordinations to oxygen atoms in its compounds, but the stereochemical influence of the non-bonded electron pair is always present, *e.g.* the ψ-tetragonal and ψ-trigonal pyramids[6] of PbO and Pb_3O_4

Table 4. Angles (°) of co-ordination polyhedra around the cations for the pyrochlores $Pb_2[M_{0.33}Sb_{1.67}]O_{6.5}$ (M = Mg or Cu)

	M = Mg	M = Cu
$O(1^{i})-Pb-O(1^{ii})$	62.4	62.5
$O(1^{i})-Pb-O(1^{iii})$	117.6	117.5
$O(1^{i})-Pb-O(1^{iv})$	180.0	180.0
$O(1^{i})-Pb-O(2^{vii})$	80.9	80.8
$O(1^{iv})-Pb-O(2^{vii})$	99.1	99.2
$O(2^{vii})-Pb-\odot(2^{viii})$	180.0	180.0
$O(1^{ix})-M,Sb-O(1^{x})$	87.4	87.0
$O(1^{ix})-M,Sb-O(1^{xii})$	92.6	93.0
$O(1^{ix})-M,Sb-O(1^{xiii})$	180.0	180.0

Symmetry code: (i) $\frac{1}{4} - x, \frac{1}{4} - y, z$; (ii) $\bar{z}, x - \frac{1}{4}, y - \frac{1}{4}$; (iii) $z, \frac{1}{4} - x, \frac{1}{4} - y$; (iv) $x - \frac{1}{4}, y - \frac{1}{4}, \bar{z}$; (v) $\frac{1}{4} - y, z, \frac{1}{4} - x$; (vi) $y - \frac{1}{4}, \bar{z}, x - \frac{1}{4}$; (vii) $\bar{x}, \bar{y}, \bar{z}$; (viii) x, y, z; (ix) $x, \frac{1}{2} + y, \frac{1}{2} + z$; (x) $\frac{1}{2} - z, 1 - x, \frac{1}{2} - y$; (xi) $\frac{1}{2} - y, \frac{1}{2} - z, 1 - x$; (xii) $\frac{1}{2} + z, x, \frac{1}{2} + y$; (xiii) $1 - x, \frac{1}{2} - y, \frac{1}{2} - z$; (xiv) $\frac{1}{2} + y, \frac{1}{2} + z, x$.

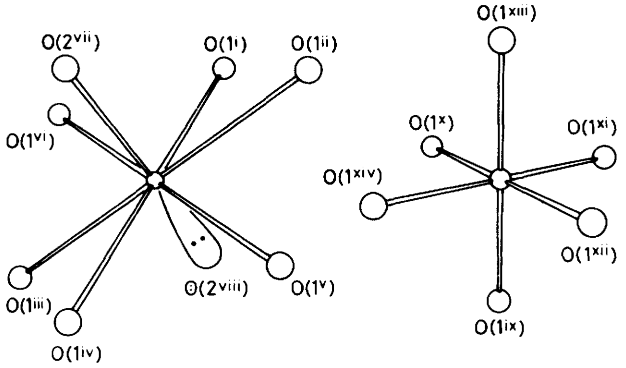

Figure. Co-ordination of A (left) and B (right) cations

respectively, the distorted ψ-trigonal bipyramid of $Pb(O_2PPh_2)_2$,[7] the seven- and nine-fold co-ordination of $PbTi_3O_7$[8] and PbV_2O_6[9] respectively, and the irregular eight- or nine-co-ordinations of both natural and synthetic $Pb_2V_2O_7$.[10,11] Similarly, in the case of the pyrochlores $Pb_2[M_{0.33}Sb_{1.67}]O_{6.5}$ (M = Mg, Ni, Cu or Zn) and $Pb_2[In_{0.5}Sb_{1.5}]O_{6.5}$ the co-ordination polyhedron of Pb^{II} is the above mentioned scalenohedron with seven vertexes occupied by oxygen atoms, and the unshared pair of electrons at the eighth vertex on a vacant (a) position.

Acknowledgements

The authors acknowledge one scholarship and financial aid from the Consejo Superior de Investigaciones Cientificas.

References

1 M. A. Subramanian, G. Aravamudan, and G. V. Subba Rao, *Prog. Solid State Chem.*, 1983, **15**, 55.
2 B. C. Chakoumakos, *J. Solid State Chem.*, 1984, **53**, 120.
3 C. Cascales and I. Rasines, *Z. Anorg. Allg. Chem.*, 1985, **529**, 229.
4 R. Yvon, W. Jeitschko, and E. Parthé, *J. Appl. Crystallogr.*, 1977, **10**, 73.
5 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
6 A. F. Wells, 'Structural Inorganic Chemistry,' 5th edn., Clarendon Press, Oxford, 1984, p. 558.
7 P. Colamarino, P. L. Orioli, W. D. Benzinger, and H. D. Gillman, *Inorg. Chem.*, 1976, **15**, 800.
8 K. Kato, I. Kawada, and K. Muramatsu, *Acta Crystallogr., Sect. B*, 1974, **30**, 1634.
9 B. D. Jordan and C. Calvo, *Can. J. Chem.*, 1974, **52**, 2701.
10 A. Kawahara, *Bull. Soc. Fr. Minéral. Cristallogr.*, 1967, **90**, 279.
11 R. D. Shannon and C. Calvo, *Can. J. Chem.*, 1973, **51**, 70.

Received 5th August 1985; *Paper* 5/1361