Tableau 2. *Distances* (Å) *et angles intératomiques* (°)

(a) Groupements PO_3H

P(1)–O(11)	1,49 (3)	P(2)–O(21)	1,54 (2)
P(1)–O(12)	1,52 (3)	P(2)–O(22)	1,54 (3)
P(1)–O(13)	1,58 (3)	P(2)–O(23)	1,59 (3)
P(1)–H(1)	1,38	P(2)–H(2)	1,35
		O(12)···O(23)	2,87 (4)

O(11)–P(1)–O(12)	112 (2)	O(21)–P(2)–O(22)	116 (2)
O(11)–P(1)–O(13)	109 (2)	O(21)–P(2)–O(23)	108 (2)
O(12)–P(1)–O(13)	101 (2)	O(22)–P(2)–O(23)	106 (1)
O(11)–P(1)–H(1)	110	O(21)–P(2)–H(2)	105
O(12)–P(1)–H(1)	114	O(22)–P(2)–H(2)	116
O(13)–P(1)–H(1)	102	O(23)–P(2)–H(2)	106

(b) Groupement NdO_8

Nd···O(21)	2,33 (2)	Nd···O(11)	2,49 (2)
Nd···O(23)	2,39 (3)	Nd···W(1)	2,50 (3)
Nd···O(12)	2,44 (2)	Nd···O(22)	2,52 (2)
Nd···O(22)	2,45 (3)	Nd···O(23)	2,60 (3)

(c) Molécules d'eau

	$W(1)···W(2)$	2,63 (4)	
$W(1)···O(11)$	2,81 (4)	$W(2)···O(21)$	2,91 (4)
$W(1)···O(12)$	2,87 (4)	$W(2)···O(12)$	2,97 (4)
$W(1)···O(22)$	2,92 (3)		

valeurs déjà trouvées (Loub *et al.*, 1978; Rafiq *et al.*, 1982; Larbot *et al.*, 1984).

L'ion néodyme est au centre d'un antiprisme à base carrée. Cet environnement 8 est constitué par sept atomes d'oxygène de groupements PO_3H^{2-} et l'atome d'oxygène de la molécule d'eau $W(1)$. L'arête O(22)··· O(23) est commune entre cet antiprisme et un tétraèdre PO_3H^{2-}. Ce type d'environnement est couramment rencontré avec les éléments des terres rares. Les distances Nd–O sont comprises entre 2,33 et 2,60 Å.

Les molécules d'eau assurent, avec le cation Nd^{3+}, la cohésion de l'édifice structural. Les atomes d'hydrogène de ces molécules n'ont pas été positionnés, et les plus courtes distances $W···O$ ne permettent pas de prédire

les directions de ces liaisons hydrogène (Tableau 2c). On observe pour $W(1)$ une distance très courte $W(1)–W(2) = 2,63$ Å et trois distances plus longues (entre 2,81 et 2,92 Å) révélatrices d'un réseau complexe de liaisons hydrogène faibles. Pour $W(2)$, mise à part la distance courte $W(1)···W(2)$, deux autres atomes d'oxygène se trouvent à des distances longues 2,97 et 2,91 Å. Ici aussi ces liaisons hydrogène sont faibles.

Cette description est relative au premier phosphite de terre rares mettant en évidence le groupement H_3-$P_2O_6^{3-}$. La décomposition thermique de ce matériau fait apparaître une seule phase anhydre puis un composé mixte phosphite–pyrophosphite. Ces deux phases restant toutefois monocristallines font l'objet d'études cristallographique et structurale.

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Preparation and Structure of $Pb_6O(OH)_6(ReO_4)_4.H_2O$

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Abstract. $M_r = 2380 \cdot 1$, monoclinic, $P2_1/n$, $a = 10 \cdot 489$ (2), $b = 16 \cdot 275$ (3), $c = 14 \cdot 704$ (3) Å, $\beta = 97 \cdot 15$ (3)°, $V = 2490$ Å^3, $Z = 8$, $D_x = 12 \cdot 69$ g cm^{-3}, $\lambda(Mo K\alpha) = 0 \cdot 71069$ Å, $\mu = 233 \cdot 0$ cm^{-1}, $F(000) = 7936$, room temperature, $R = 0 \cdot 032$ for 2361 unique reflections. The structure consists of discrete ReO_4^- tetrahedra and $Pb_6O(OH)_6^{4+}$ units. The crystals were synthesized under hydrothermal conditions at 523 K.

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Introduction. Only two ternary oxides between lead and rhenium have been characterized so far by single-crystal structure determination: $PbRe_2O_6$ (Wentzell, Fuess, Bats & Cheetham, 1985) and $Pb(ReO_4)_2$ (Picard, Baud, Besse & Chevalier, 1984). We are at present investigating the Pb—Re—O system in some detail, and it promises to be as complex as the related Bi—Re—O system (Rae-Smith & Cheetham, 1979; Cheetham & Rae-Smith, 1981, 1985). The objective of the work is to elucidate the ternary phase diagram and to examine the coordination and bonding of rhenium in different oxidation states. We describe here the preparation and crystal structure of a new perrhenate compound that was obtained as a hydrate in a hydrothermal synthesis.

Experimental. An equimolar mixture of ReO_3 (Ventron) and PbO (BDH Chemicals) was ground in an agate mortar and placed in an autoclave with 15 ml distilled H_2O. The reaction mixture was heated at 523 K for 6 d and at 423 K for 1 d. The product was dried in a hot-air cabinet at 373 K. Starting materials and reaction products were monitored by Guinier X-ray powder patterns and energy-dispersive microanalysis on a JEOL 2000FX electron microscope with an Li-drifted Si X-ray detector. The reaction product was composed of an inhomogeneous grey powder and colourless single crystals. Analysis of the grey powder gave an indication of two different phases: $PbRe_3O_x$ and $Pb_3Re_2O_x$, using the ratio method (Cliff & Lorimer, 1975). The Guinier pattern showed lines of metallic rhenium and lead, as well as of ReO_3, ReO_2 and PbO. An examination by energy-dispersive analysis of several of the single crystals obtained in the reaction yielded a Pb:Re ratio of 3:2 which was ultimately confirmed by the structure determination. A colourless needle-shaped crystal with dimensions $0.05 \times 0.05 \times 0.18$ mm was mounted on a glass fibre. Data collection was carried out at room temperature over the range $0 \le \theta \le 23°$ on an Enraf–Nonius CAD-4F diffractometer using a graphite monochromator and $\omega/2\theta$ scan techniques. Unit-cell dimensions were refined from the setting angles of 25 reflections $(8 \le \theta \le 15°)$. 4968 measured reflections were merged to give 2405 unique reflections, of which 2361 reflections with $I > 3\sigma$ were used $(h -11 \rightarrow 11, k -1 \rightarrow 17, l -1 \rightarrow 16)$. The four standard reflections, remeasured every 3600 s, showed no significant intensity variation. Lorentz and polarization corrections were applied, followed by an empirical absorption correction based on the ψ scans of two reflections. Structure solution by direct methods ($MULTAN80$; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) yielded the positions of the metal atoms, and after two cycles of refinement on F the R value was 0.093. Subsequent difference Fourier syntheses revealed the atomic coordinates of the O atoms, and the final cycle of full-matrix least-squares refine-

Table 1. *List of atomic parameters* ($\times 10^4$) *and thermal parameters with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

Oxygen atoms of the hydroxyl groups are indicated as O_H and the water molecule as O_w.

	x	y	z	U_{eq}/U_{iso} ($Å^2 \times 10^4$)
Pb(1)	7855 (1)	201 (1)	1646 (1)	177
Pb(2)	5629 (1)	1252 (1)	3054 (1)	174
Pb(3)	1539 (1)	518 (1)	2440 (1)	187
Pb(4)	9150 (1)	808 (1)	4077 (1)	212
Pb(5)	2701 (1)	-2852 (1)	783 (1)	207
Pb(6)	8946 (1)	2301 (1)	2430 (1)	258
Re(1)	5703 (1)	1031 (1)	5856 (1)	231
Re(2)	86 (1)	1325 (1)	9855 (1)	200
Re(3)	9136 (1)	5566 (1)	6160 (1)	223
Re(4)	10489 (1)	1615 (1)	6779 (1)	243
O_H(1)	7138 (18)	176 (12)	3106 (13)	218 (45)
O_H(2)	7584 (18)	1869 (12)	3564 (13)	203 (44)
O_H(3)	1749 (19)	794 (13)	4037 (14)	261 (49)
O_H(4)	131 (17)	2228 (11)	3938 (12)	171 (42)
O(5)	173 (22)	2253 (15)	9312 (15)	388 (58)
O(6)	-76 (24)	526 (16)	9052 (17)	466 (64)
O_H(7)	6746 (19)	1414 (12)	1804 (13)	243 (47)
O(8)	9443 (21)	2382 (14)	7053 (15)	374 (55)
O(9)	3984 (23)	449 (15)	1483 (16)	417 (60)
O(10)	9385 (17)	943 (11)	2569 (12)	175 (43)
O(11)	8823 (22)	1360 (14)	467 (16)	395 (59)
O(12)	7034 (23)	1177 (15)	8431 (16)	431 (61)
O(13)	6049 (23)	649 (15)	16 (16)	415 (61)
O(14)	1460 (24)	1141 (16)	611 (17)	472 (65)
O(15)	9729 (28)	676 (18)	6579 (19)	611 (77)
O(16)	4086 (35)	1175 (23)	5635 (25)	929 (112)
O_w(17)	3591 (29)	2039 (20)	79 (21)	710 (88)
O(18)	1193 (24)	1867 (16)	5816 (17)	468 (65)
O(19)	6277 (34)	1914 (22)	6292 (24)	869 (105)
O(20)	1692 (23)	1487 (15)	7678 (16)	424 (62)
O_H(21)	1968 (27)	1846 (18)	2704 (19)	603 (77)
O(22)	6015 (22)	252 (14)	6632 (15)	376 (57)
O(23)	4384 (24)	914 (15)	8402 (17)	453 (63)
O(24)	6331 (29)	766 (19)	4853 (21)	696 (86)

ment, including anisotropic temperature factors for Pb and Re and isotropic ones for the oxygens, yielded $R = 0.032$ with unit weights. $\Delta\rho < 0.5$ e Å^{-3}. All calculations were performed with the Oxford $CRYSTALS$ package (Betteridge, Carruthers & Watkin, 1985) on a VAX11/750 computer. Atomic scattering factors and anomalous-dispersion values f' and f'' were obtained from *International Tables for X-ray Crystallography* (1974). For the structure plots the program $MODEL$ was used ($CHEMGRAF$, 1984). Positional and thermal parameters are presented in Table 1; distances and angles in Table 2.*

The location of the OH groups was determined by bond-strength calculations (Brown & Wu, 1976). The valence sums for the oxide ions range from 1.90 to 2.15, whilst the oxygen atoms of the hydroxide groups give values in the range 1.17 to 1.29. Infrared spectra were recorded on a Perkin–Elmer spectrophotometer.

Table 2. *Selected interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses*

Within the $Pb_6O(OH)_6^{4+}$ cluster

Pb(1)–Pb(2)	3·724 (1)	Pb(4)–Pb(5)	3·942 (2)
Pb(1)–Pb(3)	3·929 (2)	Pb(4)–Pb(6)	3·418 (2)
Pb(1)–Pb(4)	3·793 (2)	Pb(4)–O$_{11}$(1)	2·55 (2)
Pb(1)–Pb(6)	3·741 (2)	Pb(4)–O$_{11}$(2)	2·44 (2)
Pb(1)–O$_{11}$(1)	2·36 (2)	Pb(4)–O$_{11}$(3)	2·73 (2)
Pb(1)–O$_{11}$(7)	2·32 (2)	Pb(4)–O$_{11}$(4)	2·61 (2)
Pb(1)–O(10)	2·31 (2)	Pb(4)–O(10)	2·27 (2)
Pb(2)–Pb(4)	3·878 (2)	Pb(5)–O$_{11}$(3)	2·28 (2)
Pb(2)–Pb(6)	4·081 (2)	Pb(5)–O$_{11}$(4)	2·26 (2)
Pb(2)–O$_{11}$(1)	2·36 (2)	Pb(5)–O$_{11}$(21)	2·26 (3)
Pb(2)–O$_{11}$(2)	2·32 (2)	Pb(6)–O$_{11}$(2)	2·43 (2)
Pb(2)–O$_{11}$(7)	2·31 (2)	Pb(6)–O$_{11}$(4)	2·41 (2)
Pb(3)–Pb(4)	3·715 (2)	Pb(6)–O$_{11}$(7)	2·78 (2)
Pb(3)–Pb(5)	3·740 (2)	Pb(6)–O(10)	2·26 (2)
Pb(3)–Pb(6)	3·976 (2)		
Pb(3)–O$_{11}$(3)	2·37 (2)		
Pb(3)–O(10)	2·39 (2)		
Pb(3)–O$_{11}$(21)	2·23 (3)		

Pb(3)–Pb(1)–Pb(2)	115·83 (4)	Pb(2)–O$_{11}$(1)–Pb(1)	104·3 (7)
Pb(4)–Pb(1)–Pb(2)	62·13 (3)	Pb(4)–O$_{11}$(1)–Pb(1)	99·4 (7)
Pb(4)–Pb(1)–Pb(3)	57·22 (3)	Pb(4)–O$_{11}$(1)–Pb(2)	102·7 (7)
Pb(6)–Pb(1)–Pb(2)	66·19 (3)	Pb(4)–O$_{11}$(2)–Pb(2)	109·1 (8)
Pb(6)–Pb(1)–Pb(3)	62·30 (3)	Pb(6)–O$_{11}$(2)–Pb(2)	118·3 (8)
Pb(6)–Pb(1)–Pb(4)	53·92 (3)	Pb(6)–O$_{11}$(2)–Pb(4)	89·2 (6)
Pb(4)–Pb(2)–Pb(1)	59·81 (4)	Pb(4)–O$_{11}$(3)–Pb(3)	93·0 (6)
Pb(6)–Pb(2)–Pb(1)	57·01 (4)	Pb(5)–O$_{11}$(3)–Pb(3)	106·7 (8)
Pb(6)–Pb(2)–Pb(4)	50·75 (3)	Pb(5)–O$_{11}$(3)–Pb(4)	103·1 (7)
Pb(4)–Pb(3)–Pb(1)	59·42 (3)	Pb(5)–O$_{11}$(4)–Pb(4)	109·9 (7)
Pb(5)–Pb(3)–Pb(1)	114·57 (4)	Pb(6)–O$_{11}$(4)–Pb(4)	87·2 (6)
Pb(5)–Pb(3)–Pb(4)	63·78 (3)	Pb(6)–O$_{11}$(4)–Pb(5)	124·2 (8)
Pb(6)–Pb(3)–Pb(1)	56·43 (4)	Pb(2)–O$_{11}$(7)–Pb(1)	107·0 (8)
Pb(6)–Pb(3)–Pb(4)	52·60 (4)	Pb(6)–O$_{11}$(7)–Pb(1)	94·0 (7)
Pb(6)–Pb(3)–Pb(5)	64·46 (3)	Pb(6)–O$_{11}$(7)–Pb(2)	106·1 (7)
Pb(2)–Pb(4)–Pb(1)	58·01 (4)	Pb(3)–O(10)–Pb(1)	113·3 (7)
Pb(3)–Pb(4)–Pb(1)	63·11 (4)	Pb(4)–O(10)–Pb(1)	111·8 (8)
Pb(3)–Pb(4)–Pb(2)	117·27 (3)	Pb(4)–O(10)–Pb(3)	105·5 (7)
Pb(4)–Pb(4)–Pb(1)	122·70 (4)	Pb(6)–O(10)–Pb(1)	109·9 (7)
Pb(4)–Pb(4)–Pb(2)	134·63 (4)	Pb(6)–O(10)–Pb(3)	117·3 (8)
Pb(4)–Pb(4)–Pb(3)	94·32 (4)	Pb(6)–O(10)–Pb(4)	97·9 (7)
Pb(5)–Pb(4)–Pb(1)	113·10 (4)	Pb(5)–O$_{11}$(21)–Pb(3)	112·6 (12)
Pb(5)–Pb(4)–Pb(2)	131·88 (3)	Pb(6)–O$_{11}$(21)–Pb(3)	91·5 (9)
Pb(5)–Pb(4)–Pb(3)	58·30 (4)	Pb(6)–O$_{11}$(21)–Pb(5)	95·8 (9)
Pb(5)–Pb(4)–Pb(4)	91·62 (4)		
Pb(6)–Pb(4)–Pb(1)	62·16 (4)		
Pb(6)–Pb(4)–Pb(2)	67·64 (4)		
Pb(6)–Pb(4)–Pb(3)	67·61 (4)		
Pb(6)–Pb(4)–Pb(4)	157·47 (3)		
Pb(6)–Pb(4)–Pb(5)	67·72 (4)		
Pb(4)–Pb(5)–Pb(3)	57·66 (4)		
Pb(2)–Pb(6)–Pb(1)	56·61 (3)		
Pb(3)–Pb(6)–Pb(1)	61·07 (4)		
Pb(3)–Pb(6)–Pb(2)	107·20 (4)		
Pb(4)–Pb(6)–Pb(1)	63·81 (4)		
Pb(4)–Pb(6)–Pb(2)	61·48 (3)		
Pb(4)–Pb(6)–Pb(3)	59·69 (4)		

Additional Pb—O distances

Pb(1)–O(6)	2·91 (2)	Pb(3)–O(9)	3·03 (2)
Pb(1)–O(11)	2·83 (2)	Pb(3)–O(14)	2·87 (2)
Pb(1)–O(13)	2·96 (2)	Pb(3)–O(15)	2·85 (2)
Pb(1)–O(20)	2·94 (2)	Pb(3)–O(22)	3·02 (3)
Pb(1)–O(23)	2·96 (2)	Pb(4)–O(15)	2·90 (2)
Pb(2)–O(5)	3·13 (2)	Pb(5)–O(5)	3·16 (2)
Pb(2)–O(8)	2·86 (2)	Pb(5)–O(12)	2·96 (2)
Pb(2)–O(9)	3·01 (2)	Pb(5)–O(16)	3·07 (3)
Pb(2)–O(22)	3·06 (2)	Pb(5)–O(18)	2·79 (2)
Pb(2)–O(24)	2·77 (3)	Pb(6)–O(20)	3·14 (2)
Pb(3)–O(6)	3·04 (2)		

In the ReO_4^- tetrahedra

Re(1)–O(16)	1·70 (4)	Re(3)–O(9)	1·73 (2)
Re(1)–O(19)	1·66 (4)	Re(3)–O(12)	1·74 (2)
Re(1)–O(22)	1·71 (2)	Re(3)–O(13)	1·72 (2)
Re(1)–O(24)	1·74 (3)	Re(3)–O(23)	1·70 (2)
Re(2)–O(5)	1·72 (2)	Re(4)–O(8)	1·74 (2)
Re(2)–O(6)	1·75 (3)	Re(4)–O(15)	1·73 (2)
Re(2)–O(11)	1·69 (2)	Re(4)–O(18)	1·72 (2)
Re(2)–O(14)	1·73 (2)	Re(4)–O(20)	1·72 (2)

O(19)–Re(1)–O(16)	105 (2)	O(12)–Re(3)–O(9)	111 (1)
O(22)–Re(1)–O(16)	109 (1)	O(13)–Re(3)–O(9)	110 (1)
O(22)–Re(1)–O(19)	111 (1)	O(13)–Re(3)–O(12)	108 (1)
O(24)–Re(1)–O(16)	110 (2)	O(23)–Re(3)–O(9)	109 (1)

Table 2 (*cont.*)

O(24)–Re(1)–O(19)	113 (2)	O(23)–Re(3)–O(12)	109 (1)
O(24)–Re(1)–O(22)	109 (1)	O(23)–Re(3)–O(13)	110 (1)
O(6)–Re(2)–O(5)	110 (1)	O(15)–Re(4)–O(8)	112 (1)
O(11)–Re(2)–O(5)	108 (1)	O(18)–Re(4)–O(8)	112 (1)
O(11)–Re(2)–O(6)	112 (1)	O(18)–Re(4)–O(15)	108 (1)
O(14)–Re(2)–O(5)	111 (1)	O(20)–Re(4)–O(8)	109 (1)
O(14)–Re(2)–O(6)	108 (1)	O(20)–Re(4)–O(15)	108 (1)
O(14)–Re(2)–O(11)	108 (1)	O(20)–Re(4)–O(18)	108 (1)
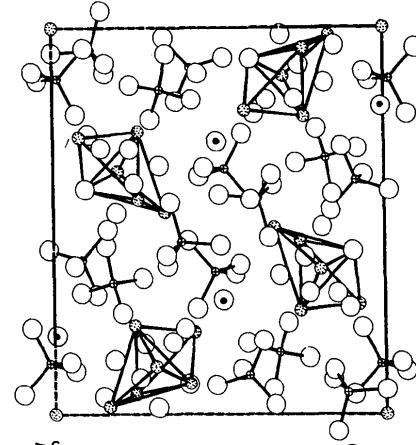
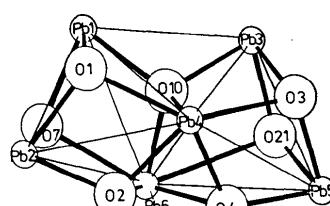Fig. 1. The unit cell of $Pb_6O(OH)_6(ReO_4)_4.H_2O$ viewed down the *a* axis.

Fig. 2. A view of the $Pb_6O(OH)_6^{4+}$ unit. The faint lines define the lead polyhedra. O(10) in the centre is the oxide ion.

Discussion. The structure of $Pb_6O(OH)_6(ReO_4)_4.H_2O$ (see Fig. 1) consists of discrete ReO_4^- tetrahedra and $Pb_6O(OH)_6^{4+}$ units which can be considered as three face-sharing Pb_4 tetrahedra. Six OH groups are associated with each cluster (see Fig. 2), plus a central oxide ion, O(10). The distances from O(10) to its four Pb neighbours range from 2·26 (2) to 2·39 (2) Å, in good agreement with the Pb—O distance in tetragonal PbO (Moore & Pauling, 1941). Each Pb has a small number of nearest-neighbour oxygens at approximately 2·3 Å, giving pyramidal coordination in the cases of Pb(1), Pb(2), Pb(3) and Pb(5). If the more distant oxygens associated with the perrhenate ions are included, the coordination numbers are, of course, higher.

The shortest Pb—Pb distance of 3·418 (2) Å is comparable to 3·5 Å in metallic lead, but the other Pb—Pb distances show considerable variation in the range 3·715 (2)–4·081 (2) Å. The Re atoms are tetrahedrally coordinated with distances between 1·66 (4)

and 1·75 (3) Å, in accord with values found in other Re^{VII} compounds, e.g. Pb(ReO$_4$)$_2$ where the distances range from 1·65 (5) to 1·84 (6) Å (Picard, Baud, Besse & Chevalier, 1984). The IR spectrum shows the characteristic ν_1(ReO$_4^-$) tetrahedral stretching vibrations at 900 and 913 cm^{-1}. It is most probable that the OH groups form hydrogen bonds to neighbouring oxygens of the ReO$_4^-$ groups; the distances of these contacts range from 2·92 (3) to 3·07 (3) Å, and in the IR spectrum the (OH) vibrations occur between 3600 and 3300 cm^{-1}. The water molecule is remote from the metal atoms. Its nearest oxygen neighbours are O(14) at 2·74 Å and O(4) at 2·86 Å, suggesting hydrogen bonding here, too. The other oxygens are at distances of 3·26 Å or more. The lattice parameters of Pb$_6$O(OH)$_6$(ReO$_4$)$_4$.H$_2$O are superficially related to those of α-Pb$_6$O(OH)$_6$-(ClO$_4$)$_4$.H$_2$O [Pbca; $a = 10\cdot814$, $b = 16\cdot706$, $c = 26\cdot273$ Å; Spiro, Templeton & Zalkin (1969)] and the corresponding β-phase [Pbca; $a = 19\cdot953$, $b = 17\cdot624$, $c = 13\cdot383$ Å; Olin & Söderquist (1972)], but the arrangement of the Pb$_6$O(OH)$_6^{4+}$ and XO$_4^-$ units is entirely different in the rhenium compound.

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Structure of High-T_c Superconducting Tetragonal Ba$_2$YCu$_{3-x}$O$_{7-y}$ at 298 and 120 K

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Abstract. A high-T_c superconductor, Ba$_2$YCu$_{3-x}$O$_{7-y}$ [$x = 0\cdot130$ (5), $y = 0\cdot24$ (4)], $M_r = 654\cdot1$, tetragonal, space group P4/mmm, $Z = 1$, Ag $K\alpha$ ($\lambda = 0\cdot56087$ Å), $F(000) = 288\cdot3$. (i) At $T = 298$ K, $a = 3\cdot8683$ (6), $c = 11\cdot688$ (2) Å, $V = 174\cdot89$ (6) Å^3, $D_x = 6\cdot21$ Mg m^{-3}, μ(Ag $K\alpha$) = 14·8 mm^{-1}, $R = 0\cdot029$ (427 unique reflections). (ii) At $T = 120$ K, $a = 3\cdot8609$ (5), $c = 11\cdot645$ (2) Å, $V = 173\cdot60$ (5) Å^3, $D_x = 6\cdot25$ Mg m^{-3}, $\mu = 14\cdot9$ mm^{-1}, $R = 0\cdot032$ (417 unique reflections). The crystal consists of triple layers of oxygen-deficient perovskite-like structure with a linear arrangement of −Ba−Y−Ba− along **c**. In the layer sandwiched between two Ba layers, there are marked deficiencies of Cu and O ions; the valence state of the Cu ion is +3; moreover, the temperature factors of the oxygen ions are very high.

Introduction. Since the discovery of high-T_c superconductivity in a Ba−Y−Cu−O compound system (Wu et al., 1987), many reports characterizing the superconducting properties have been presented (Cava et al., 1987; Batlogg et al., 1987). The crystal is tetragonal at temperatures higher than about 853 K (Sueno, Nakai, Okamura & Ono, 1987). At room temperature

0108-2701/88/010011-04$03.00