Zeitschrift für Kristallographie 171, 113–119 (1985)

Crystal data on $Zn_3Rb_2(P_2O_7)_2$ and $Co_3Rb_2(P_2O_7)_2$

Crystal structure of $Zn_3Rb_2(P_2O_7)_2$

M. T. Averbuch-Pouchot

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'U.S.M.G., 166X, 38042 Grenoble Cédex (France)

Received: November 12, 1984

Inorganic diphosphates / $Zn_3Rb_2(P_2O_7)_2$ / $Co_3Rb_2(P_2O_7)_2$ / *Crystal structure*

Abstract. Chemical preparations and crystal data are reported for two new diphosphates: $Zn_3Rb_2(P_2O_7)$ and $Co_3Rb_2(P_2O_7)_2$. These two salts are isotypic, space group $P2_1$, $Z = 2$ and the following unit cell dimensions $a = 13.22(1)$, $b = 7.224(6)$, $c = 7.196(5)$ Å, $\beta = 92.08(2)°$ for the zinc salt and $a = 13.25(1)$, $b = 7.248(7)$, $c = 7.213(6)$ Å, $\beta = 92.00(5)°$ for the cobalt salt.

The crystal structure of this new type of diphosphates has been solved using the zinc salt ($R = 0.043$, 2023 hkl). The main feature of the atomic arrangement is a three dimensional network of ZnO_4 and PO_4 tetrahedra crossed by channels. The rubidium atoms are located inside these channels. The zinc salt is piezoelectric.

Introduction

Very few is known concerning mixed diphosphates of general formula: $M^{II}_3M^{I}_2(P_2O_7)_2 \cdot x\ H_2O$; one can only mention a small number of chemical studies dealing with the following salts:

$Zn_3K_2(P_2O_7)_2 \cdot 3\ H_2O$ (Morozova and Selivanova, 1976)

$Ca_3(NH_4)_2(P_2O_7)_2 \cdot 6\ H_2O$ (Brown et al., 1958)

$Ni_3Na_2(P_2O_7)_2 \cdot 6\ H_2O$ (Bykanova, 1978)

$Ni_3M^{I}_2(P_2O_7)_2 \cdot 10\ H_2O$ (M^{I} = K, NH_4, Rb, Cs) (Bykanova, 1978).

Table 1. Crystal data

$Zn_3Rb_2(P_2O_7)_2$	$Co_3Rb_2(P_2O_7)_2$
a = 13.22(1) Å	a = 13.25(1) Å
b = 7.224(6)	b = 7.248(7)
c = 7.196(5)	c = 7.213(6)
β = 92.08(2)°	β = 92.00(1)°
Z = 2	Z = 2
V = 686.6 Å^3	V = 692.07 Å^3
d_x = 3.458 g cm^{-3}	d_x = 3.338 g cm^{-3}

So far, no attempt for structural investigations of these compounds has been reported. In the present work, we describe the atomic arrangement of $Zn_3Rb_2(P_2O_7)_2$, apparently the first example of an anhydrous diphosphate with such a formula. The crystal data for the isotypic cobalt salt $Co_3Rb_2(P_2O_7)_2$ are also reported.

Chemical preparation

Crystals of $Zn_3Rb_2(P_2O_7)_2$ have been prepared by introducing 1 g of $ZnCO_3$ and 4 g of Rb_2CO_3 into 3.5 cm^3 of H_3PO_4 (85%). This mixture is then heated at 623 K for one day. Crystals of $Zn_3Rb_2(P_2O_7)_2$, not water soluble, are extracted by washing out the excess of the phosphoric flux with hot water. Crystals are stout monoclinic prisms.

In the case of the cobalt salt only polycrystalline samples have been prepared by heating a stoichiometric mixture of $CoCO_3$, Rb_2CO_3 and $(NH_4)_2HPO_4$ at 873 K for several days.

Crystal data

Study of a single crystal of $Zn_3Rb_2(P_3O_7)_2$ by a film technique shows the possible space groups to be $P2_1$ or $P2_1/m$ ($0k0$ with $k = 2n$). The piezoelectricity observed for these crystals leads unambiguously to the non-centrosymmetric $P2_1$ space group.

Unit-cell dimensions of these two salts have been refined by a least-squares method using angular data obtained from low scan speed powder diffractograms (CuK_α); they are reported in Table 1, while a table with the indexed powder diagram of the zinc salt has been deposited[1].

[1] Additional material to this paper can be ordered referring to the no. CSD 51250, name(s) of the author(s) and citation of the paper at the Fachinformationszentrum Energie – Physik – Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG

Table 2. Experimental conditions used for the X-ray data collection

Apparatus: Philips PW 1100	Scan with: 1.20°
Monochomator: Graphite plate	Scan speed: 0.02°/s
Wavelength: Ag $K\alpha$ (0.5608 Å)	Total background measurement: 20 s
Crystal size: 0.13 × 0.11 × 0.11 mm^3	Number of independent collected reflexions: 2082
Scan mode: Ω	Intensity reference reflexions: 10.0.0 and $\bar{1}0.0.0$
θ range: 3–25°	
μ: 70.98 cm^{-1}	

Table 3. Atomic coordinates for $Zn_3Rb_2(P_2O_7)_2$. Beq. is defined as Beq = $\frac{4}{3}\sum_i\sum_j \vec{a}_i\vec{a}_j\beta_{ij}$

Atoms	x (σ)	y (σ)	z (σ)	Beq.
Rb(1)	0.09409(8)	0.4927(2)	0.3890(2)	1.83(3)
Rb(2)	0.41692(9)	0.2508(2)	0.9468(2)	1.78(3)
Zn(1)	0.09781(8)	0.0000(0)	0.2090(2)	0.90(2)
Zn(2)	0.26327(9)	0.6200(2)	0.7920(2)	0.92(3)
Zn(3)	0.38737(10)	0.0898(2)	0.4518(2)	1.13(3)
P(1)	0.3882(2)	0.5129(4)	0.4328(3)	0.87(5)
P(2)	0.3103(2)	0.7885(4)	0.1647(3)	0.93(6)
P(3)	0.1834(2)	0.9842(4)	0.6350(3)	0.85(5)
P(4)	0.1075(2)	0.2753(4)	0.8883(3)	0.84(6)
O(E11)	0.3656(7)	0.508(2)	0.636(1)	1.8(2)
O(E12)	0.4909(7)	0.590(2)	0.391(1)	2.9(3)
O(E13)	0.3661(13)	0.331(2)	0.338(2)	3.2(4)
O(L12)	0.3050(7)	0.651(1)	0.337(1)	1.4(2)
O(E21)	0.2009(8)	0.837(2)	0.126(1)	2.1(3)
O(E22)	0.3776(9)	0.946(1)	0.225(1)	1.9(3)
O(E23)	0.3541(7)	0.684(1)	0.005(1)	1.2(2)
O(E31)	0.1679(6)	0.778(1)	0.658(1)	1.2(2)
O(E32)	0.1259(7)	0.068(1)	0.471(1)	1.4(2)
O(E33)	0.2947(7)	0.040(2)	0.647(1)	1.7(2)
O(L34)	0.1304(7)	0.072(1)	0.816(1)	1.2(2)
O(E41)	0.0213(8)	0.347(2)	0.767(1)	1.8(2)
O(E42)	0.0801(8)	0.236(1)	0.087(1)	1.7(2)
O(E43)	0.2008(9)	0.392(1)	0.877(2)	2.3(3)

Crystal structure determination

The structure of this new kind of diphosphates has been determined with the help of a crystal of the zinc salt.

All the experimental conditions used during the intensity data collection are reported in Table 2. The intensities have been corrected for Lorentz

Table 4. Main interatomic distances and bond angles in the P_2O_7 anions

$P(1)P(2)O_7$ group				
P(1)	O(E11)	O(E12)	O(E13)	O(L12)
O(E11)	1.510(5)	2.540(9)	2.51(1)	2.503(9)
O(E12)	114.5(4)	1.511(7)	2.52(1)	2.52(1)
O(E13)	112.3(5)	113.2(6)	1.510(8)	2.45(1)
O(L12)	105.9(4)	106.8(4)	102.9(5)	1.624(7)
P(2)	O(L12)	O(E21)	O(E22)	O(E23)
O(L12)	1.595(6)	2.42(1)	2.49(1)	2.516(7)
O(E21)	102.7(4)	1.508(7)	2.55(1)	2.50(1)
O(E22)	106.9(4)	115.7(5)	1.500(7)	2.485(8)
O(E23)	108.1(4)	111.5(4)	111.1(4)	1.513(6)

P(1)–P(2) 2.939(3) P(1)–O(L12)–P(2) 131.9(4)

$P(3)P(4)O_7$ group				
P(3)	O(E31)	O(E32)	O(E33)	O(L34)
O(E31)	1.513(7)	2.544(9)	2.534(9)	2.473(9)
O(E32)	114.4(4)	1.513(6)	2.539(9)	2.492(7)
O(E33)	112.8(4)	113.2(4)	1.528(6)	2.546(8)
O(L34)	103.4(3)	104.6(3)	107.1(3)	1.636(6)
P(4)	O(L34)	O(E41)	O(E42)	O(E43)
O(L34)	1.590(6)	2.48(1)	2.397(7)	2.53(1)
O(E41)	106.1(4)	1.507(7)	2.540(9)	2.50(1)
O(E42)	101.0(4)	114.3(4)	1.516(6)	2.51(1)
O(E43)	109.6(4)	112.5(5)	112.4(5)	1.502(8)

P(3) – P(4) 2.986(3) P(3)–O(L34)–P(4) 135.5(4)

and polarization effects but being given the short wavelength used and the crystal size, no absorption correction has been applied.

The crystal structure has been solved using classical methods: three-dimensional Patterson function for the localization of some heavy atoms and successive Fourier syntheses giving all the remaining atomic positions.

All calculations have been done using the SDP system (1977). Atomic scattering factors were taken from International Tables for X-Ray Crystallography, Table 2.2 B (Cromer and Waber, 1974). Anomalous dispersion has been taken into account. Full-matrix refinements have been run using a unitary weighting scheme. The final refinement cycles lead to a R value of 0.043 for a set of 2023 reflexions corresponding to the following criterion: $|F_{obs} - F_{cal}| < 60$ in a F scale ranging from 0 to 1853.

For the complete set of 2082 reflexions the R value is 0.050.

Table 3 reports the final atomic coordinates. The lists of hkl, F_{obs}, F_{cal} and of the anisotropic thermal parameters have been deposited. The

Table 5. Main interatomic distances and bond angles in cation coordinations

Zn(1)	O(E21)	O(E32)	O(E41)	O(E42)
O(E21)	1.917(7)	3.18(1)	3.07(1)	3.31(1)
O(E32)	109.9(3)	1.972(6)	3.01(1)	3.06(1)
O(E41)	105.6(4)	100.5(3)	1.940(7)	3.31(1)
O(E42)	118.5(3)	103.4(3)	117.4(3)	1.933(7)
Zn(2)	O(E11)	O(E23)	O(E31)	O(E43)
O(E11)	1.967(7)	2.956(8)	3.28(1)	2.96(1)
O(E23)	97.3(3)	1.970(6)	3.51(1)	3.05(1)
O(E31)	114.2(2)	128.1(3)	1.938(6)	3.23(1)
O(E43)	98.0(3)	102.0(3)	112.3(3)	1.955(7)
Zn(3)	O(E12)	O(E13)	O(E22)	O(E33)
O(E12)	1.937(7)	3.19(1)	3.38(1)	2.89(1)
O(E13)	110.5(5)	1.945(9)	2.91(1)	3.23(1)
O(E22)	121.5(3)	96.9(3)	1.940(6)	3.34(1)
O(E33)	96.5(3)	112.9(4)	119.2(3)	1.934(5)

Zn(1)–P(2)	3.231(2)	Zn(2)–P(1)	3.220(2)	Zn(3)–P(1)	3.065(2)
Zn(1)–P(3)	3.238(2)	Zn(2)–P(2)	2.997(2)	Zn(3)–P(1)	3.109(2)
Zn(1)–P(4)	3.059(2)	Zn(2)–P(3)	3.043(2)	Zn(3)–P(2)	3.151(2)
Zn(1)–P(4)	3.225(2)	Zn(2)–P(4)	3.327(2)	Zn(3)–P(3)	3.146(2)

Rb(1)–O(L12)	3.055(6)	Rb(2)–O(E11)	2.971(7)
–O(E31)	2.977(6)	–O(E12)	3.000(7)
–O(E32)	3.156(7)	O(E13)	2.978(8)
–O(E32)	3.168(7)	O(E22)	3.042(7)
–O(E41)	3.107(7)	O(E23)	3.276(7)
O(E41)	3.170(8)	O(E23)	3.080(6)
O(E42)	2.865(6)	O(E33)	3.063(6)
		O(E43)	3.065(9)

interatomic distances and the bond angles reported in structure description are calculated from the cell parameters refined from 17 high angle data measured during the intensity data collection. These last parameters:

$$a = 13.25(1), \quad b = 7.237(5), \quad c = 7.213(5)\ \text{Å}, \quad \beta = 92.09(1)^\circ$$

are slightly different from these calculated from the powder data.

Structure description

All the zinc atoms are in a tetrahedral coordination and their distances to the phosphorus atoms are quite comparable to the phosphorus–phosphorus distances in the P_2O_7 groups. Each ZnO_4 tetrahedron is linked to four different P_2O_7 groups, so building a three-dimensional network of corner sharing tetrahedra as suggested by the ratio $\frac{Zn + P}{O} = 1/2$ in the framework global formula.

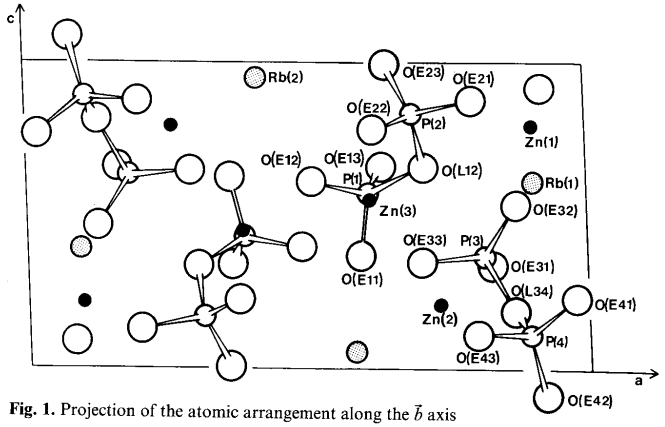

Fig. 1. Projection of the atomic arrangement along the $\vec{b}$ axis

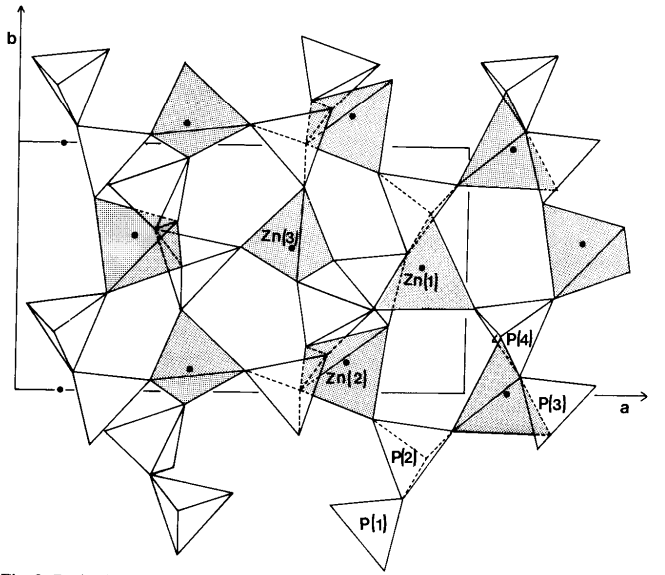

Fig. 2. Projection along the $\vec{c}$ axis of the linkage of P_2O_7 groups and ZnO_4 tetrahedra (hatched)

The main geometric features of the respective P_2O_7 and ZnO_4 groups are reported in Tables 4 and 5.

Rb(1) atoms have a seven-fold coordination with Rb–O distances ranging from 2.865 to 3.170 Å while Rb(2) atoms have eight oxygen neighbours with Rb–O distances varying from 2.971 to 3.276 Å (Table 5). Rb(1) atoms are located in channels parallel to the $\vec{c}$ axis and Rb(2) atoms in channels parallel to the $\vec{b}$ axis.

Figures 1 and 2 give projections of this atomic arrangement respectively along the $\vec{b}$ and $\vec{c}$ axis.

All attempts to relate the M_7O_{14} (M = Zn,P) tetrahedral atomic arrangement to other ones already known, in various silica forms for instance, have failed.

References

Brown, E. H., Brown, W. E., Lehr, J. R., Smith, J. P., Frazier, A. W.: Calcium ammonium pyrophosphates. J. Phys. Chem. **62**, 366 (1958)

Bykanova, T. A., Lavrov, A. V.: Thermal dehydration of double pyrophosphates of nickel and alkali metals. Izv. Akad. Nauk SSSR. Neorg. Mater. **14**, 2044–2048 (1978)

Cromer, D. T., Waber, J. T.: *International Tables for X-Ray Crystallography*, Vol. IV, Table 2–2B. Birmingham: The Kynoch Press, 1974

Morozova, N. Yu., Selivanova, N. M.: The $K_4P_2O_7-Zn_2P_2O_7-H_2O$ system at 25°C. Russ. J. Inorg. Chem. **21**, 878–879 (1976)

Structure Determination Package, version RSX 11M, September 1977; Enraf-Nonius