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The Crystal Structure of $Na_7Mg_{4.5}(P_2O_7)_4$

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The crystal structure of $Na_7Mg_{4.5}(P_2O_7)_4$ has been solved by direct methods from the three-dimensional X-ray data. The space group is $P\bar{1}$. The crystal structure consists of Mg^{2+}, Na^+, and $P_2O_7^{4-}$ ions. One magnesium atom at symmetry center (0,0,0) and two sodium atoms at ±(–0.0421, –0.0596, 0.2230) display occupation factors 0.5 each. A short interatomic distance between these Na^+ and Mg^{2+} ions (1.80 ± 0.01 Å) excludes the occupation of both sites in the same unit cell. The crystal structure of $Na_7Mg_{4.5}(P_2O_7)_4$ consists of unit cells containing $Na_8Mg_4(P_2O_7)_4$ or $Na_6Mg_5(P_2O_7)_4$ with a statistical occurrence 1:1.

Each Mg^{2+} ion is octahedrally coordinated by six O^{2-} ions at distances 1.979–2.270 Å. The coordination polyhedra around the Na^+ ions are ill-defined. The bond angles P–O–P in the $P_2O_7^{4-}$ groups are 126.6 and 133.6° (±0.3°). The final reliability factor R is 7.1 %.

Introduction

In the system $Na_4P_2O_7$–$Mg_2P_2O_7$, only one intermediate phase of chemical composition $Na_7Mg_{4.5}(P_2O_7)_4$ exists which melts congruently at 832°C (*1*). The compound is triclinic with the lattice constants $a = 10.882(1)$, $b = 9.734(1)$, $c = 6.372(1)$ Å, $\alpha = 112.49(1)$, $\beta = 99.63(1)$, $\gamma = 107.40(1)°$. The number of formula units ($Z = 1$) calculated from the unit-cell volume ($V = 563.9$ Å^3) and the observed density ($\rho_m = 2.83$ gcm^{-3}) indicated a nonintegral number of atoms in the primitive parallelepiped. This anomaly may be related to various types of defects (formation of solid solution, presence of vacancies, framework structures). The purpose of this work was the explanation of the nature of the defect structure.

Experimental

Single crystals of $Na_7Mg_{4.5}(P_2O_7)_4$ were grown from a melt of $Na_4P_2O_7$ and $Mg_2P_2O_7$ containing 50 mole% of $Mg_2P_2O_7$ (*1*). The crystals form poorly developed parallelepipeds displaying the (100), (010), and (0$\bar{1}$1) faces. Approximate dimensions of the selected crystals were 0.25 × 0.26 × 1.00 mm. The reciprocal levels *hk*0–*hk*5 were recorded by integrating equi-inclination techniques using Cu*Kα* radiation. The intensities were measured photometrically on a ZEISS–JENA microdensitometer. The intensities of weak reflections were estimated visually. The 89 unobserved reflections were substituted by the statistical values according to Hamilton (*2*). A total of 2111 intensity data were collected. Lorentz-polarization and absorption correc-

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tions for an approximately cylindrical shape of crystal were applied ($\mu = 93.9$ cm^{-1}). The intensity data were brought to an absolute scale and a first estimation of the overall temperature factor was obtained by means of the Wilson plot (*3*). The space group symmetry, $P\bar{1}$, was established from the statistical distribution of the normalized structure amplitudes E_{hkl}. A GIER computer program (*4*) was used to determine 279 phases from $\sum_1$ and $\sum_2$ relationships involving the 289 normalized structure factors with $|E_{hkl}|>1.5$. The structure was found in an E-map calculated using these phases. 8 P, 6 Na, 4 Mg, and 28 O could be localized in 49 electron density maxima. The remaining three maxima render positions for 1 Mg (at symmetry center) and 2 Na with an occupation factor 0.5. Such an arrangement of atoms corresponds to the composition $Na_7Mg_{4.5}(P_2O_7)_4$. Provided that only one of the two equivalent positions would be fully occupied, the possible chemical compositions were $Na_6Mg_5(P_2O_7)_4$ (occupation of the position at symmetry center) or $Na_8Mg_4(P_2O_7)_4$ (occupation of the two general positions). All three models were refined isotropically. The least-squares refinement was performed with a set of programs written in the Chemical Institute of the Aarhus University by Drs. R. Hazzel, J. Nyborg, J. Danielsen, and S. Lauesen. Calculations were carried out on a GIER computer in the Computing Center of the Slovak Academy of Sciences. The least-squares program employed a block-diagonal approximation and weighting scheme proposed by Hughes (*5*). For both $Na_8Mg_4(P_2O_7)_4$ and $Na_6Mg_5(P_2O_7)_4$ arrangements, the reliability factor $R = \sum||F_0| - |F_c||/\sum|F_0|$ decreased to 0.220 during five cycles of refinement. The $Na_7Mg_{4.5}(P_2O_7)_4$ model converged

TABLE I

FINAL FRACTIONAL ATOMIC COORDINATES IN $Na_7Mg_{4.5}(P_2O_7)_4$ AND THE CORRESPONDING ANISOTROPIC THERMAL VIBRATION MATRIX ELEMENTS, WITH STANDARD DEVIATIONS. A TEMPERATURE FACTOR OF THE FORM $\exp(-b_{11}h^2 + b_{12}hk + \ldots)$ WAS EMPLOYED

Atom	P(1)	P(2)	P(3)	P(4)
Occupation factor	1.0	1.0	1.0	1.0
x	0.4535(1)	0.6835(1)	0.2168(1)	0.9626(1)
y	0.6567(1)	0.6392(2)	0.8947(2)	0.2704(2)
z	0.7333(3)	0.0180(3)	0.3247(3)	0.4783(3)
b_{11}	0.0001(1)	0.0005(1)	0.0010(1)	0.0003(1)
b_{22}	0.0004(2)	0.0014(2)	0.0024(2)	0.0008(2)
b_{33}	0.0036(5)	0.0031(5)	0.0093(5)	0.0056(5)
b_{12}	−0.0007(2)	0.0003(2)	0.0015(2)	0.0002(2)
b_{13}	−0.0046(2)	−0.0041(3)	−0.0007(4)	−0.0027(3)
b_{23}	−0.0043(4)	−0.0035(4)	0.0020(5)	−0.0026(4)

Atom	Mg(1)	Mg(2)	Mg(3)	Na(1)
Occupation factor	1.0	1.0	0.5	1.0
x	0.2155(2)	0.2638(2)	0.0000	0.5239(2)
y	0.6086(2)	0.2624(2)	0.0000	0.2100(3)
z	0.8370(3)	0.4054(3)	0.0000	0.6806(5)
b_{11}	0.0004(2)	0.0005(2)	0.0113(12)	0.0028(2)
b_{22}	0.0009(2)	0.0012(2)	0.0266(25)	0.0041(3)
b_{33}	0.0063(7)	0.0025(6)	0.0515(51)	0.0079(9)
b_{12}	0.0007(3)	0.0001(3)	0.0304(32)	0.0012(4)
b_{13}	−0.0026(5)	−0.0030(5)	−0.0471(43)	−0.0051(6)
b_{23}	−0.0032(6)	−0.0037(6)	−0.0735(62)	0.0018(8)

TABLE I (continued)

Atom	Na(2)	Na(3)	Na(4)	O(11)
Occupation factor	1.0	1.0	0.5	1.0
x	0.8841(5)	0.6608(3)	0.9579(7)	0.5392(4)
y	0.5359(5)	0.0161(3)	0.9404(7)	0.7231(5)
z	0.8140(9)	0.0931(6)	0.2230(22)	0.6086(8)
b_{11}	0.0152(6)	0.0049(3)	0.0055(7)	0.0010(3)
b_{22}	0.0206(8)	0.0043(4)	0.0018(8)	0.0047(6)
b_{33}	0.0621(22)	0.0247(12)	0.1090(65)	0.0106(16)
b_{12}	0.0322(12)	−0.0032(5)	0.0031(12)	0.0013(7)
b_{13}	0.0505(19)	−0.0079(9)	−0.0483(36)	−0.0020(11)
b_{23}	0.0514(22)	0.0043(10)	−0.0234(34)	0.0024(14)

Atom	O(12)	O(13)	O(21)	O(22)
Occupation factor	1.0	1.0	1.0	1.0
x	0.4315(4)	0.3148(3)	0.6931(5)	0.7039(4)
y	0.7855(4)	0.5192(4)	0.7362(5)	0.4853(5)
z	0.9338(8)	0.5761(7)	0.2731(8)	0.9679(8)
b_{11}	0.0019(4)	0.0001(3)	0.0066(5)	0.0043(4)
b_{22}	0.0011(5)	0.0010(5)	0.0045(6)	0.0047(6)
b_{33}	0.0073(15)	0.0091(15)	0.0040(16)	0.0097(16)
b_{12}	0.0003(7)	−0.0013(6)	0.0027(9)	0.0080(8)
b_{13}	−0.0029(11)	−0.0033(10)	0.0001(13)	0.0048(12)
b_{23}	−0.0045(12)	−0.0013(12)	−0.0022(14)	0.0035(15)

Atom	O(23)	O(24)	O(31)	O(32)	O(33)
Occupation factor	1.0	1.0	1.0	1.0	1.0
x	0.5313(4)	0.7744(4)	0.1741(6)	0.2013(4)	0.3508(5)
y	0.5781(5)	0.7426(5)	0.7287(6)	0.0124(4)	0.9543(7)
z	0.8547(8)	0.9295(8)	0.1268(10)	0.2348(8)	0.5072(11)
b_{11}	0.0007(3)	0.0008(3)	0.0132(8)	0.0026(4)	0.0014(4)
b_{22}	0.0028(5)	0.0046(6)	0.0036(6)	0.0013(5)	0.0145(10)
b_{33}	0.0123(16)	0.0065(15)	0.0220(21)	0.0059(14)	0.0329(25)
b_{12}	0.0007(7)	−0.0010(7)	0.0121(11)	0.0002(7)	0.0016(10)
b_{13}	−0.0022(11)	−0.0042(10)	0.0244(21)	−0.0022(11)	−0.0050(15)
b_{23}	0.0032(14)	0.0017(14)	0.0089(18)	−0.0027(12)	0.0304(26)

Atom	O(41)	O(42)	O(43)	O(44)
Occupation factor	1.0	1.0	1.0	1.0
x	0.0365(4)	0.8999(4)	0.8414(4)	0.0569(4)
y	0.4252(5)	0.1252(5)	0.2712(5)	0.2226(5)
z	0.7067(8)	0.5438(8)	0.3292(9)	0.3465(8)
b_{11}	0.0016(4)	0.0026(4)	0.0009(3)	0.0012(4)
b_{22}	0.0016(5)	0.0026(5)	0.0041(6)	0.0036(5)
b_{33}	0.0130(16)	0.0088(15)	0.0201(18)	0.0112(16)
b_{12}	−0.0014(7)	0.0023(7)	0.0015(7)	0.0012(7)
b_{13}	−0.0021(11)	0.0009(11)	−0.0035(12)	0.0005(11)
b_{23}	−0.0060(14)	0.0011(13)	0.0105(16)	−0.0023(14)

to $R = 0.135$. Further anisotropic refinement of this model proceeded to a final R value of 0.071. The refinement was interrupted when all parameter shifts decreased below 1/10th of the standard deviations. The weight analysis showed a satisfactorily uniform distribution of the mean values of $\omega|\Delta F|^2$ according to intervals of F_o values and $\sin\Theta$. The change of the error-square-sum, $\sum\omega|\Delta F|^2$, was less than 1.3%. The residual $R' = \sum\omega|\Delta F|^2/\sum\omega|F_o|^2$ dropped to a value 0.0076. Table 1 shows the final atomic coordinates and corresponding anisotropic thermal parameters of the form: $\exp(-b_{11}h^2 + b_{12}hk + \ldots)$.

Observed F_o and calculated F_c structure factors obtained from the final parameters in Table I are given in Table II.[1] The bond lengths and angles are given in Table III.

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[1] See NAPS document No. 02210 for 36 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, 305 E. 46th Street, New York, N.Y. 10017. Remit in advance for each NAPS accession number $1.50 for microfiche or $5.00 for photocopies up to 30 pages, 15c for each additional page. Make checks payable to Microfiche Publications.

TABLE III

BOND DISTANCES AND ANGLES IN THE CRYSTAL STRUCTURE OF $Na_7Mg_{4.5}(P_2O_7)_4$, WITH STANDARD DEVIATIONS

MgO_6—octahedra	
Mg(1)–O(12) 2.270(4) Å	O(12)–Mg(1)–O(13) 67.2(0.1)°
Mg(1)–O(13) 2.179(5)	O(12)–Mg(1)–O(22) 86.7(0.2)
Mg(1)–O(22) 2.033(6)	O(12)–Mg(1)–O(31) 98.5(0.2)
Mg(1)–O(31) 1.980(7)	O(12)–Mg(1)–O(41) 169.1(0.2)
Mg(1)–O(41) 1.978(4)	O(12)–Mg(1)–O(43) 86.2(0.2)
Mg(1)–O(43) 2.008(6)	O(13)–Mg(1)–O(22) 89.3(0.2)
	O(13)–Mg(1)–O(31) 165.1(0.2)
	O(13)–Mg(1)–O(41) 102.1(0.2)
	O(13)–Mg(1)–O(43) 90.7(0.2)
	O(22)–Mg(1)–O(31) 85.5(0.3)
	O(22)–Mg(1)–O(41) 91.3(0.2)
	O(22)–Mg(1)–O(43) 172.3(0.2)
	O(31)–Mg(1)–O(41) 91.9(0.2)
	O(31)–Mg(1)–O(43) 92.6(0.3)
	O(41)–Mg(1)–O(43) 96.3(0.2)
Mg(2)–O(11) 2.125(5) Å	O(11)–Mg(2)–O(13) 96.7(0.2)
Mg(2)–O(13) 2.151(4)	O(11)–Mg(2)–O(21) 90.6(0.2)
Mg(2)–O(21) 2.017(6)	O(11)–Mg(2)–O(24) 87.2(0.2)
Mg(2)–O(24) 2.084(6)	O(11)–Mg(2)–O(32) 86.9(0.2)
Mg(2)–O(32) 2.075(4)	O(11)–Mg(2)–O(44) 168.9(0.2)
Mg(2)–O(44) 2.108 (5)	O(13)–Mg(2)–O(21) 90.9(0.2)
	O(13)–Mg(2)–O(24) 90.3(0.2)
	O(13)–Mg(2)–O(32) 176.2(0.2)
	O(13)–Mg(2)–O(44) 88.9(0.2)
	O(21)–Mg(2)–O(24) 177.6(0.2)
	O(21)–Mg(2)–O(32) 90.1(0.2)
	O(21)–Mg(2)–O(44) 98.9(0.2)
	O(24)–Mg(2)–O(32) 88.9(0.2)
	O(24)–Mg(2)–O(44) 83.2(0.2)
	O(32)–Mg(2)–O(44) 87.3(0.2)
Mg(3)–O(24) 2.757(4) Å 2x	O(24)–Mg(3)–O(32) 111.4(0.2)
Mg(3)–O(32) 2.379(5) 2x	O(24)–Mg(3)–O(44) 113.3(0.2)
Mg(3)–O(44) 2.243(4) 2x	O(32)–Mg(3)–O(44) 77.3(0.2)

TABLE III (continued)

NaO$_x$—polyhedra	
Na(1)-O(11) 2.248(7) Å	Na(2)-O(13) 2.763(7) Å
Na(1)-O(12) 2.404(6)	Na(2)-O(22) 2.342(8)
Na(1)-O(21) 2.606(7)	Na(2)-O(24) 2.571(7)
Na(1)-O(22) 2.505(4)	Na(2)-O(31) 2.650(9)
Na(1)-O(33) 2.315(4)	Na(2)-O(41) 2.295(7)
Na(1)-O(33)′ 2.498(7)	Na(2)-O(41)′ 2.873(8)
Na(1)-O(23) 3.169(5)	Na(2)-O(44) 2.853(8)
Na(1)-O(31) 3.095(7)	Na(2)-O(31) 2.992(7)
	Na(2)-O(43) 3.019(6)
Na(3)-O(12) 2.522(4)	
Na(3)-O(12)′ 2.475(6)	Na(4)-O(24) 2.210(7)
Na(3)-O(32) 2.747(6)	Na(4)-O(32) 2.509(9)
Na(3)-O(33) 2.482(9)	Na(4)-O(42) 2.472(11)
Na(3)-O(43) 2.350(4)	Na(4)-O(42)′ 2.360(12)
Na(3)-O(11) 3.009(5)	Na(4)-O(44) 2.370(8)
Na(3)-O(24) 3.159(6)	Na(4)-O(21) 3.119(11)
Na(3)-O(42) 3.108(5)	

Contacts of the oxygen atoms	
O(11)-P(1) 1.483(6) Å	O(31)-P(3) 1.487(5) Å
O(11)-Mg(2) 2.125(5)	O(31)-Na(2) 2.650(9)
O(11)-Na(1) 2.248(7)	
	O(32)-P(3) 1.501(6)
O(12)-P(1) 1.523(4)	O(32)-Mg(2) 2.075(4)
O(12)-Mg(1) 2.270(4)	O(32)-Mg(3) 2.379(5)
O(12)-Na(1) 2.400(6)	O(32)-Na(3) 2.747(6)
O(12)-Na(3) 2.522(4)	O(32)-Na(4) 2.509(9)
O(12)-Na(3)′ 2.475(6)	
	O(33)-P(3) 1.492(5)
O(13)-P(1) 1.528(3)	O(33)-Na(1) 2.315(5)
O(13)-Mg(1) 2.179(5)	O(33)-Na(1)′ 2.498(7)
O(13)-Na(2) 2.763(7)	O(33)-Na(3) 2.482(9)
O(21)-P(2) 1.502(5)	O(41)-P(4) 1.498(4)
O(21)-Mg(2) 2.017(6)	O(41)-Mg(1) 1.978(4)
O(21)-Na(1) 2.606(7)	O(41)-Na(2) 2.295(7)
O(22)-P(2) 1.501(5)	O(42)-P(3) 1.639(5)
O(22)-Mg(1) 2.033(6)	O(42)-P(4) 1.615(5)
O(22)-Na(1) 2.505(4)	O(42)-Na(4) 2.472(11)
O(22)-Na(2) 2.342(8)	O(42)-Na(4)′ 2.360(12)
O(23)-P(1) 1.588(6)	O(43)-P(4) 1.495(5)
O(23)-P(2) 1.594(4)	O(43)-Na(3) 2.350(4)
O(24)-P(2) 1.528(5)	O(44)-P(4) 1.501(5)
O(24)-Mg(2) 2.084(6)	O(44)-Mg(2) 2.108(5)
O(24)-Na(2) 2.571(7)	O(44)-Mg(3) 2.243(4)
O(24)-Na(4) 2.210(7)	O(44)-Na(4) 2.370(8)
O(24)-Mg(3) 2.757(4)	O(44)-Na(2) 2.853(8)

The number of electrons at the positions of atoms was evaluated from the electron density function $\rho(xyz)$ calculated at intervals 1/100, 1/100, and 1/40 along the a, b, and c axes, respectively. The fluctuation of the density function in the different Fourier series was ±0.3 electrons. The integration of electron density at the positions of atoms was extended to the range of $\rho(xyz)$ values larger than 0.3.

Description of the Structure and Discussion

The crystal structure of $Na_7Mg_{4.5}(P_2O_7)_4$ consists of Mg^{2+}, Na^+, and $P_2O_7^{4-}$ ions (Fig. 1). One magnesium atom at symmetry center (0,0,0) and two sodium atoms at ±(−0.0421, −0.0596, 0.2230) display occupation factor 0.5. The number of electrons at these positions found by summation of the $\rho(xyz)$ function is one-half of those at the fully occupied Na and Mg positions. The average numbers of electrons found for the magnesium, sodium, phosphorus, and oxygen atoms are 10.8, 10.0, 14.0, and 8.0, respectively. A short interatomic distance between the Na^+ and Mg^{2+} ions (1.80 ± 0.01 Å) at positions with the statistical occurrence excludes the presence of atoms at both sites simultaneously. This conception is made clear in Fig. 2 representing the arrangement and linkage of MgO_6 polyhedra in the unit cells. The phosphorus and sodium atoms at the fully occupied positions are omitted. Two sodium atoms around the empty magnesium position at (1,1,0) are indicated.

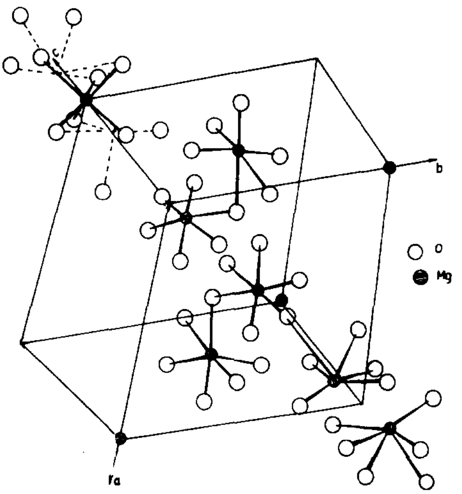

FIG. 2. The arrangement and linkage of MgO_6 polyhedra in the unit cells of $Na_7Mg_{4.5}(P_2O_7)_4$. The phosphorus and sodium atoms at the fully occupied positions are omitted. Two sodium atoms around the empty magnesium position at (1,1,0) are indicated (perspective view).

Each Mg^{2+} ion is octahedrally coordinated by six O^{2-} ions (Fig. 2). The oxygen atoms

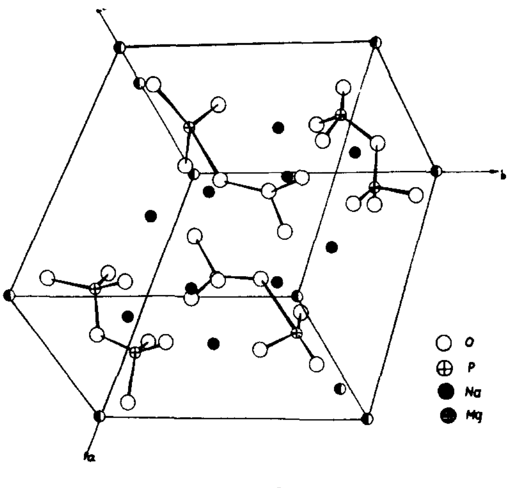

FIG. 1. Perspective view of the crystal structure of $Na_7Mg_{4.5}(P_2O_7)_4$.

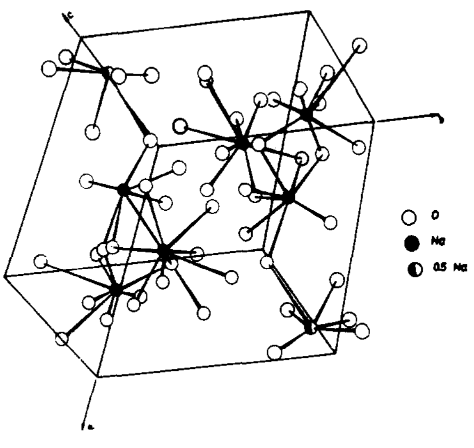

FIG. 3. The arrangement and linkage of NaO_x polyhedra in the unit cells of $Na_7Mg_{4.5}(P_2O_7)_4$. The phosphorus and magnesium atoms are omitted (perspective view).

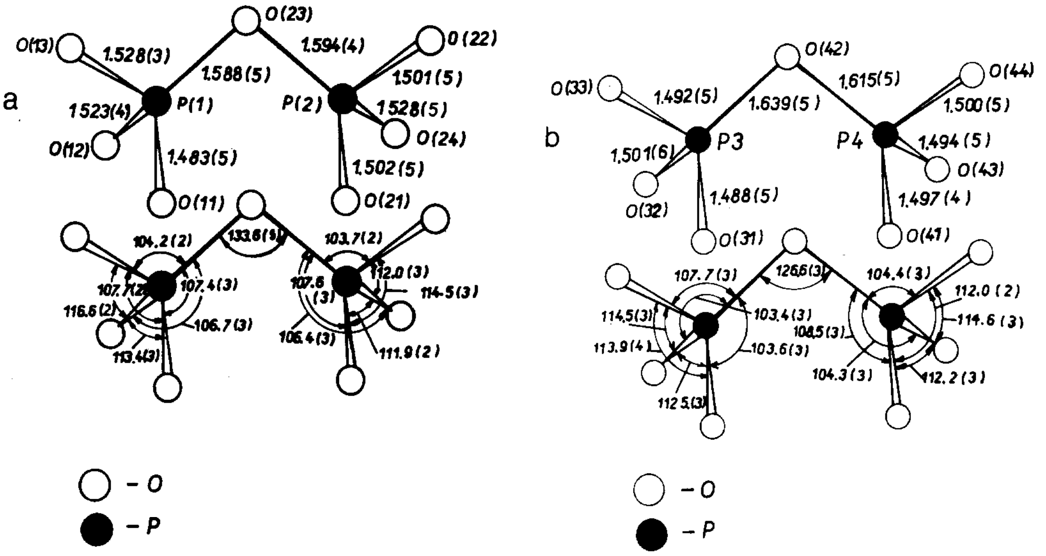

FIG. 4. The bond lengths and bond angles in two independent P_2O_7 groups.

around the fully occupied magnesium sites Mg(1) and Mg(2) are at distances 1.979–2.270 Å (Table III). The mean Mg–O distance around Mg(1) and Mg(2), 2.08 Å, approximately equals the sum of ionic radii 2.05 Å ($r_{Mg^{2+}} = 0.65$ Å, $r_{O^{2-}} = 1.40$ Å (*6*)). The Mg–O distances 2.243, 2.378, 2.756 Å (2*x*) around the Mg(3) site at the symmetry center exceed the sum of ionic radii. Coefficients b_{ij} of the thermal ellipsoid of Mg(3) (Table I) indicate strongly anisotropic vibrations. In fact, they represent statistical displacements of the Mg(3) atoms from the (0,0,0) position.

The Na^+ ions are surrounded by 5–7 nearest O^{2-} neighbors (Table III). The distances range from 2.25 to 2.87 Å. In addition, two or three further oxygen atoms occur at distances 2.99–3.17 Å ($r_{Na^+} = 0.95$ Å). Figure 3 shows the arrangement and linkage of NaO_x polyhedra in the unit cells. The phosphorus and magnesium atoms are omitted. The shape of the coordination polyhedra NaO_x is ill-defined.

The P–O distances of the nonbridging atoms in the P_2O_7 groups are 1.483–1.528 (±0.005) Å, those for the bridging atoms in the P–O–P linkage are 1.588–1.639 Å. The bond angles P–O–P are 126.6 and 133.6 (±0.3)°, respectively. The lowest electrostatic potential energy U_c for an ionic arrangement $X_3M\text{–}X\text{–}MX_3$ in which two tetrahedra share a common corner occurs at the angle M–X–M of 180° for both eclipsed and staggered formations. At angles smaller than 180°, the electrostatic potential energy becomes more positive for all charges (z+) and (z–) of ions M^{z+} and M^{z-}, respectively (*7*). This fact indicates the predominantly covalent character of the P–O–P bonds. Figure 4 represents the bond lengths and bond angles in the pyrophosphate groups.

Table III shows the participation of the oxygen atoms in the linkage of different MgO_6 and NaO_x polyhedra.

Acknowledgments

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