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$Na_xMoP_2O_7$, a mixed valence molybdenum diphosphate with a tunnel structure

A. Leclaire, M. M. Borel, A. Grandin and B. Raveau

Laboratoire de Cristallographie et Sciences des Matériaux,
CRISMAT – Institut des Sciences de la Matière et du Rayonnement,
Université de Caen, Campus 2, Boulevard du Maréchal Juin, 14032 Caen, Cedex, France

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Abstract. The crystal structure of $Na_{0.3}MoP_2O_7$ has been solved by three-dimensional single crystal X-ray analysis. The refinement in the cell of symmetry $P\bar{1}$ with $a = 4.8813(6)$ Å, $b = 7.0110(5)$ Å, $c = 8.2563(4)$ Å, $\alpha = 91.400(5)$ Å, $\beta = 92.466(8)°$, $\gamma = 106.551(9)°$, $Z = 2$ has led to $R = 0.030$ and $R_w = 0.031$ for 3327 reflections with $I \geq 3\sigma(I)$. The framework of the structure, built up from corner-sharing MoO_6 octahedra and diphosphate groups, delimits large octogonal tunnels where the Na^+ ions are located. This structure is closely related to that of $NaMoP_2O_7$ which differs only by the stacking of similar layers.

Introduction

The investigation of phosphates and silicophosphates of molybdenum has allowed several compounds to be isolated whose mixed frameworks are built up from PO_4 tetrahedra and MoO_6 octahedra. In these different oxides, molybdenum can take various oxidation states. One of them, Mo(III), which was thought to be very rare, has been observed for the first time in the mixed valence oxides of type $AMo_2^{IV}Mo^{III}P_6Si_2O_{25}$ (A = K, Rb, Tl, Cs) (Leclaire et al., 1984, 1985a, b). The great stability of Mo(III) in these silicophosphates was then confirmed with the synthesis of the oxide $Mo^{III}P_3SiO_{11}$ (Leclaire and Raveau, 1987). Recently, a new sodium molybdenodiphosphate, $NaMo^{III}P_2O_7$, has been isolated (Leclaire et al., 1988). The structure of this latter phase which belongs to the $NaFeP_2O_7$ type (Gabelica-Robert et al., 1982), shows a similar behaviour of Mo(III) and Fe(III). In order to understand this particular ability of molybdenum to form Mo(III) phosphates, the system "$MoO_2-Mo_2O_3-P_2O_5-Na_2O$" was studied. The present work deals with the structural study of a novel mixed-valence molybdenum oxide $Na_xMoP_2O_7$, whose tunnel structure allows a rather wide homogeneity range ($0.25 \leq x \leq 0.50$) to be realized.

Synthesis

Some crystals of the title compound were first obtained in a mixture of nominal composition $NaMoP_2O_7$. Most of them were twinned. A single one was used for this X-ray study in order to identify its chemical formula. After this we obtained crystals and microcrystalline powder from mixtures of nominal composition $Na_xMoP_2O_7$ ($0.25 \leq x \leq 0.50$). Powder diffraction patterns show that within this range we obtained pure phases.

The preparation was performed in two steps. First $(NH_4)_2HPO_4$, MoO_3 and Na_2CO_3 were mixed in an agate mortar in the molecular ratio to obtain the stoichiometry $Na_xMo^{VI}_{0.667-x/6}P_2O_7$ and heated at 600 K to decompose the sodium carbonate and the ammoniumphosphate. The resulting mixture was then added to the required amount of molybdenum ($0.333+x/6$) and heated in evacuated silica ampoules for several days at 1373 K.

Structure determination

A dark purple crystal of 0.120 × 0.096 × 0.048 mm has been chosen for the structure determination. The Laue patterns showed triclinic symmetry ($P\bar{1}$). The cell parameters, determined by diffractometric techniques, at 294 K, with a least-squares refinement based on 25 reflections, are given in the Abstract. The data were collected on a CAD4 Enraf-Nonius diffractometer using graphite-monochromatized MoK_α radiation ($\lambda = 0.71069$ Å). The intensities were measured up to $\theta = 45°$ with a $w-\theta$ scan of $(1.2+0.35\ \mathrm{tg}\theta)°$ and a counter slit aperture of $(1.0+\mathrm{tg}\theta)$ mm, all determined after a study of some reflections in the $w\theta$ plane. The background intensity was measured on both sides of each reflection. A periodic control of three standard reflections verified the stability of the sample. The 3327 reflections with $I > 3\sigma(I)$ were corrected for Lorentz and polarisation effect; no absorption corrections were performed.

A Patterson map and subsequent Fourier syntheses allowed us to determine the "MoP_2O_7" framework which forms large tunnels running along $\vec{a}$. A full-matrix least-squares refinement, with a weighting scheme $w = f(\sin\theta/\lambda)$ adjusted using the program POND (Leclaire, unpublished), of the coordinates and the anisotropic thermal factors of the atoms belonging to the framework lead to $R = 0.041$, $R_w = 0.036$ and $s = 0.6$. Then a difference synthesis shows sodium atoms in the tunnels.

Table 1. Atomic parameters of $Na_{0.30}MoP_2O_7$.

Atom	x	y	z	B_{eq}
Mo(1)	0.00000(0)	0.00000(0)	0.00000(0)	0.39(1)
Mo(2)	0.50000(0)	0.50000(0)	0.50000(0)	0.42(1)
P(1)	−0.38075(9)	0.24019(6)	0.19526(5)	0.51(1)
P(2)	0.02281(9)	−0.36972(6)	0.25600(5)	0.48(1)
O(1)	−0.18760(33)	0.10297(22)	0.18306(18)	0.86(2)
O(2)	0.10535(34)	−0.19509(22)	0.14722(20)	0.96(2)
O(3)	0.37337(30)	0.18907(22)	0.06736(19)	0.87(2)
O(4)	0.12703(33)	0.32130(23)	0.59689(19)	0.95(2)
O(5)	0.27468(35)	0.55597(26)	0.29875(19)	1.03(2)
O(6)	0.52932(35)	0.24450(22)	0.36858(17)	0.88(2)
O(7)	−0.20427(31)	0.45792(20)	0.14898(17)	0.82(2)
Na	−0.0956(28)	0.0080(7)	0.4766(9)	4.36(2)

To know the amount of sodium we evaluated the sum of bond strengths received by the molybdenum atoms using the Zachariasen (1978) curves. This sum is about 3.70 instead of 4. To balance the bond strengths one must have 0.30 Na^+ ions in the tunnels leading to the formula $Na_{0.30}MoP_2O_7$. The refinement of all the parameters leads then to $R = 0.03$, $R_w = 0.03$, $s = 1.2$ and the coordinates listed in Table 1[1].

Description of the structure and discussion

The host-lattice of $Na_{0.3}MoP_2O_7$ is built up from corner-sharing MoO_6 octahedra and diphosphate groups in such a way that each MoO_6 octahedron is surrounded by six PO_4 tetrahedra and reciprocally each PO_4 tetrahedron is linked to three MoO_6 octahedra and one PO_4 tetrahedron. This framework delimits large octogonal tunnels where the Na^+ ions are located (Fig. 1). Besides these tunnels, much smaller tunnels characterized by a distorted hexagonal section, which are empty, can also be observed.

The geometry of the PO_4 tetrahedra (Table 2) is very similar to that previously observed on other molybdenum phosphates or silicophosphates involving diphosphate groups. They are indeed characterized by three short P−O distances ranging from 1.498 to 1.531 Å, which correspond to Mo−P−O bonds, and one longer P−O distance ranging from 1.589 to 1.603 Å, which corresponds to the bridging oxygen of the P_2O_7 group. The configuration of the diphosphate groups is almost eclipsed (Fig. 2).

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[1] Lists of structure factors and anisotropic thermal parameters are available from the authors on request.

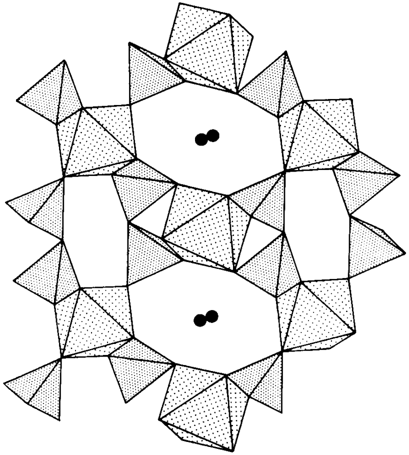

Fig. 1. Projection of the structure along [100] showing the tunnels.

Table 2. Distances (Å) and angles (°) in the PO_4 tetrahedra.

P(1)	O(1)	O(3$^{\rm iii}$)	O(6$^{\rm iii}$)	O(7)
O(1)	1.531(8)	2.541(3)	2.476(3)	2.535(3)
O(3$^{\rm iii}$)	112.77(8)	1.520(2)	2.55(3)	2.421(3)
O(6$^{\rm iii}$)	108.62(9)	114.66(9)	1.517(2)	2.538(3)
O(7)	108.64(8)	102.24(8)	109.60(8)	1.589(2)
P(2)	**O(2)**	**O(4$^{\rm i}$)**	**O(5$^{\rm v}$)**	**O(7$^{\rm v}$)**
O(2)	1.507(2)	2.501(2)	2.476(3)	2.472(3)
O(4$^{\rm iv}$)	111.23(9)	1.524(2)	2.530(3)	2.526(3)
O(5$^{\rm v}$)	111.00(9)	113.64(9)	1.498(2)	2.502(3)
O(7$^{\rm v}$)	105.23(8)	107.73(8)	107.54(9)	1.603(2)

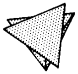

Fig. 2. Configuration of P_2O_7 projected along P–P.

Table 3. Distances (Å) and angles (°) in the MoO_6 octahedra.

Mo(1)	O(1)	O(1$^{\rm i}$)	O(2)	O(2$^{\rm i}$)	O(3)	O(3$^{\rm i}$)
O(1)	2.022(2)	4.043(3)	2.865(3)	2.837(3)	2.844(3)	2.804(3)
O(1$^{\rm i}$)	180.00(8)	2.022(2)	2.837(3)	2.865(3)	2.804(3)	2.844(3)
O(2)	90.57(8)	89.43(8)	2.010(2)	4.020(3)	2.748(3)	2.882(3)
O(2$^{\rm i}$)	89.43(8)	90.57(8)	180.00(8)	2.010(2)	2.882(3)	2.748(3)
O(3)	90.80(7)	89.20(7)	87.29(7)	92.71(7)	1.972(2)	3.944(3)
O(3$^{\rm i}$)	89.20(7)	90.80(7)	92.71(7)	87.29(7)	180.00(3)	1.972(2)
Mo(2)	**O(4)**	**O(4$^{\rm ii}$)**	**O(5)**	**O(5$^{\rm ii}$)**	**O(6)**	**O(6$^{\rm ii}$)**
O(4)	2.097(2)	4.195(3)	2.993(3)	2.886(3)	2.928(3)	3.028(3)
O(4$^{\rm ii}$)	180.00(8)	2.097(2)	2.886(3)	2.993(3)	3.028(3)	2.928(3)
O(5)	92.10(7)	87.90(7)	2.060(2)	4.121(3)	2.862(3)	3.040(3)
O(5$^{\rm ii}$)	87.90(7)	92.10(7)	180.00(8)	2.060(2)	3.040(3)	2.862(3)
O(6)	88.07(7)	91.93(7)	86.55(8)	93.45(8)	2.115(2)	4.229(3)
O(6$^{\rm ii}$)	91.93(7)	88.07(7)	93.45(8)	86.55(8)	180.00(8)	2.115(2)

Table 4. Distances (Å) and angles (°) in the NaO_6 polyhedron.

Na	O(1)	O(4$^{\rm iv}$)	O(4)	O(6$^{\rm iv}$)	O(6$^{\rm iii}$)	O(6)
O(1)	2.583(8)	3.599(3)	3.785(3)	4.591(3)	2.476(2)	3.614(3)
O(4$^{\rm iv}$)	94.0(1)	2.333(6)	4.549(3)	2.928(2)	4.737(3)	4.356(3)
O(4)	100.6(2)	154.5(6)	2.331(6)	4.356(3)	3.307(3)	2.928(2)
O(6$^{\rm iv}$)	119.5(4)	70.1(2)	118.6(3)	2.731(10)	4.050(3)	5.865(3)
O(6$^{\rm iii}$)	53.0(2)	128.2(4)	77.1(2)	91.4(4)	2.925(12)	4.881(3)
O(6)	76.4(2)	102.6(4)	61.5(2)	162.2(4)	105.5(2)	3.205(12)

Symmetry code: $^{\rm i}$: $-x, -y, -z$; $^{\rm ii}$: $1-x, 1-y, 1-z$; $^{\rm iii}$: $x-1, y, z$; $^{\rm iv}$: $-x, -y, 1-z$; $^{\rm v}$: $x, y-1, z$.

The MoO_6 octahedra are almost regular (Table 3) but two sets of octahedra must be distinguished according to their size and to their surrounding. The Mo(1) octahedra which share their corners with six different P_2O_7 groups exhibit smaller M–O distances ranging from 1.972 to 2.022 Å. The Mo(2) octahedra, which exhibit larger distances, ranging from 2.060 to 2.115 Å form original structural units with the surrounding diphosphate groups each Mo(2) octahedron shares four corners of one of its basal planes with two P_2O_7 groups, forming $[MoP_4O_{16}]$ units (Fig. 3) in which the diphosphate groups are in trans position; the two other opposite apices of the Mo(2) octahedron are linked to two different diphosphate groups. The structure of $Na_{0.30}MoP_2O_7$ can be described in a very simple way by taking into consideration the existence of the $[MoP_4O_{16}]$ units; each unit shares the opposite corners of its Mo(2) octahedra with the next one along $\vec{a}$ forming infinite columns $[MoP_4O_{16}]_\infty$ running along

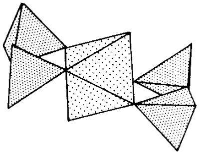

Fig. 3. $[MoP_4O_{16}]$ unit.

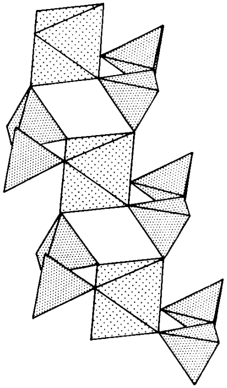

Fig. 4. $[MoP_4O_{14}]_\infty$ columns running along [100].

this direction (Fig. 4); laterally in the (010) plane, these columns are linked through the Mo(1) octahedra which form themselves columns along $\vec{a}$ (Fig. 1) leading to the structural formulation $[Mo(2)P_4O_{11}]$ $[Mo(1)O_3]$.

The examination of the sodium distribution in the structure shows its non-stoichiometric character. The sodium ions are not located at the center of the tunnel, but close to the walls. Two sites are available, which cannot be fully occupied simultaneously owing to the too short distance between two neighbouring sites (1.03 Å).

This leads to a maximum occupancy coefficient of 0.5, corresponding to the limiting formula $Na_{0.5}MoP_2O_7$. Thus $Na_{0.30}MoP_2O_7$ corresponds to an intermediate composition in which the Na^+ ions and cationic vacancies are statistically distributed over the two types of sites. The possibility of deviation from stoichiometry for sodium has been effectively observed; a pure phase has indeed been isolated for $0.25 \leq x \leq 0.50$, whereas the X-ray diffraction patterns show up a mixture of this phase and of MoP_2O_7 (Kinomura et al., 1985) for $0 < x < 0.25$, and the formation of another unidentified oxide for $x > 0.5$. The coordination of sodium, which is surrounding by six close oxygen neighbours, with distances ranging from 2.333 to 3.205 Å is rather similar to that observed in many oxides. The anisotropic thermal agitation of this cation along the tunnel axis is also remarkable.

The mixed valence of molybdenum in this phosphate is closely related to the sodium non-stoichiometry. The smaller values of the Mo(1)–O distances suggest that the Mo(1) sites are occupied by molybdenum(IV), whereas the Mo(2) sites are occupied by molybdenum(III) leading for the limiting phosphate to the formulation $NaMo^{IV}Mo^{III}P_4O_{14}$. The calculation of the sum of the electrostatic bond strengths for $Na_{0.30}MoP_2O_7$ according to the theory developped by Zachariasen (1978) is in agreement with this hypothesis; one obtains 4.22 and 3.18 Å for Mo(1) and Mo(2) respectively. This result is also supported by the examination of the coordination polyhedron of sodium which shares one oxygen atom with each Mo(1) octahedron and five oxygen atoms with each Mo(2) octahedron. The oxygen atoms surrounding Mo(2) receive less bond strengths from it than those surrounding Mo(1), the difference being provided by sodium.

The $[MoP_4O_7]$ framework of $Na_{0.30}MoP_2O_7$ is closely related to that observed for $NaMoP_2O_7$ (Leclaire et al., 1988) i.e. to the $NaFeP_2O_7$ type structure (Gabelica-Robert et al., 1982). Both structures are formed by the staking of layers of MoO_6 octahedra which alternate with layer of diphosphate groups (Fig. 5). Those layers which have the same composition in both oxides can be formulated $[MoO_3]_\infty$ and $[P_2O_4]_\infty$ and are parallel to the (100) plane of $Na_{0.3}MoP_2O_7$, i.e. to the (001) plane of $NaMoP_2O_7$. Moreover the $[MoO_3]_\infty$ octahedral layers are practically identical in both structures; the MoO_6 octahedra exhibit quite similar positions and orientations within the same layer (Fig. 5). In both structures the $[P_2O_4]_\infty$ layers are formed of columns of P_2O_7 groups running along [010] in $Na_{0.3}MoP_2O_7$ and along [100] in $NaMoP_2O_7$. However, only one type of disposition of the P_2O_7 groups is observed in $Na_{0.3}MoP_2O_7$ (Fig. 5a) whereas two sorts of tetrahedral layers are observed in $NaMoP_2O_7$ corresponding to the tetrahedral $Na_{0.3}MoP_2O_7$ type layers and their enanthiomorph (Fig. 5b), respectively. Thus both structures $Na_{0.3}MoP_2O_7$ and $NaMoP_2O_7$ are built up from identical stacking of identical $[MoO_3]_\infty$ octahedral layers (labelled Oc), but differ by the stacking and the geometry of their tetrahedral $[P_2O_4]_\infty$ layers (labelled Te and Te^E, respectively):

Oc – Te – Oc – Te – Oc for $Na_{0.3}MoP_2O_7$ (Fig. 5a)

and

Oc – Te – Oc – Te^E – Oc – Te – Oc for $NaMoP_2O_7$ (Fig. 5b).

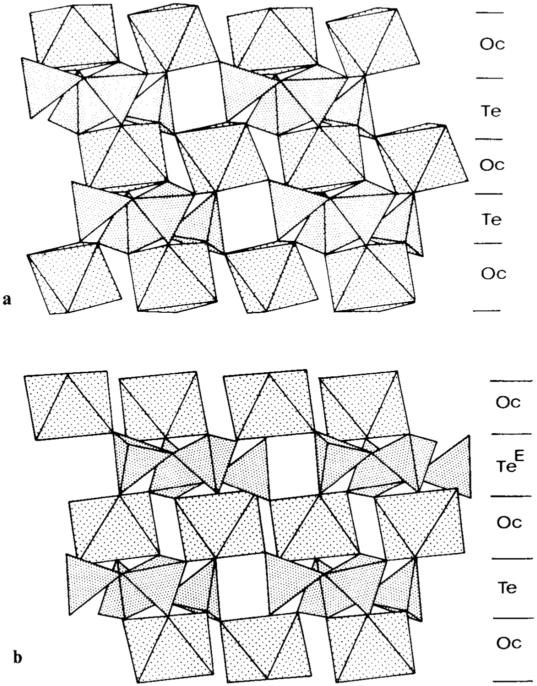

Fig. 5. Stacking of the layers of MoO_6 octahedra and of diphosphate groups: a) in $Na_{0.3}MoP_2O_7$; b) in $NaMoP_2O_7$.

It is worth pointing out that the Te^E layer is shifted by a distance corresponding to an edge of an octahedron with respect to the corresponding Te layer.

These close relationship between the two structures lead to similar strings of corner-sharing MoO_6 octahedra and diphosphate groups running along [010] and [100] in $Na_{0.3}MoP_2O_7$ and $NaMoP_2O_7$, respectively (Fig. 6). On the opposite, the different stacking of the tetrahedral layers and their enantiomorph makes that the $[MoP_4O_{16}]$ units of $Na_{0.3}MoP_2O_7$ (Fig. 3) are replaced by $[MoP_2O_{11}]$ units, built up from one octahedron sharing two apices with the same diphosphate group, in $NaMoP_2O_7$ (Fig. 7).

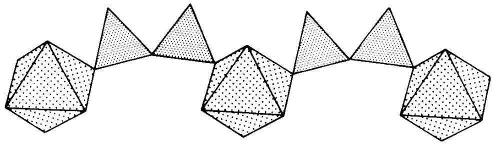

Fig. 6. String of corner-sharing MoO_6 octahedra and P_2O_7 units.

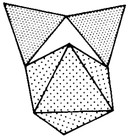

Fig. 7. $[MoP_2O_{11}]$ unit in $NaMoP_2O_7$.

The great similarity between these two structural types suggests that investigations should be carried out in order to isolate intergrowths between the two structures.

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