# $\varepsilon$-NaMo$_2$P$_3$O$_{13}$, a New Structural Form of the Mo (V) Phosphates Series $A$Mo$_2^{\text{V}}$P$_3$O$_{13}$

A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU

*Laboratoire de cristallographie et Sciences des matériaux (CRISMAT), CNRS, ISMRa, University of Caen, Boulevard du Maréchal Juin, 14032 Caen Cedex, France*

Single crystals of a new form of Mo (V) phosphates, $\varepsilon$-NaMo$_2$P$_3$O$_{13}$, have been isolated and its structure has been determined. It crystallizes in the space group $P\bar{1}$ with $a = 6.352$ Å, $b = 7.448$ Å, $c = 10.991$ Å, $\alpha = 75.08°$, $\beta = 85.33°$, and $\gamma = 79.10°$. The [Mo$_2$P$_3$O$_{13}$]$_x$ host lattice is formed of corner-sharing PO$_4$ tetrahedra, P$_2$O$_7$ groups, and MoO$_6$ octahedra, forming large cages where the Na$^+$ ions are located. This original structure is compared to those of the other $A$Mo$_2$P$_3$O$_{13}$ phosphates and especially to that of $\gamma$-Cs Mo$_2$P$_3$O$_{13}$. © 1990 Academic Press, Inc.

## Introduction

The investigation of the systems $A$–Mo–P–O, in which $A$ is an alkaline cation, has shown that it is possible to synthesize a tremendous number of new phosphates of molybdenum. In those oxides, Mo is in octahedral coordination and presents various oxidation states Mo (VI), Mo (V), Mo (IV), and Mo (III) as well as mixed valent states such as Mo (III)–Mo (IV). Among those compounds, phosphates of pentavalent molybdenum with the general formulation $A$Mo$_2$P$_3$O$_{13}$ represent a very rich series. Four different structural types corresponding to this composition have indeed been isolated up to now. The discovery of those phases started with that of the $\alpha$-form of potassium-formulated K$_4$Mo$_8$P$_{12}$O$_{52}$ *(1)* which was later synthesized also in the case of cesium *(2)*. Then the second form, $\beta$, was discovered for cesium *(2)* and extended to rubidium *(3)* and potassium *(4)*.

Recently, two other forms $\gamma$-Cs Mo$_2$P$_3$O$_{13}$ *(5)* and $\delta$-KMo$_2$P$_3$O$_{13}$ *(6)* were isolated. The determination of the structure of those phases has shown the extraordinary number of possibilities to accomodate MoO$_6$ octahedra and PO$_4$ tetrahedra keeping the same formulation $A$Mo$_2$P$_3$O$_{13}$. This led us to investigate the sodium molybdenum phosphate system in detail. The present paper reports on a new form $\varepsilon$-NaMo$_2$P$_3$O$_{13}$ which was isolated during this investigation.

## Synthesis

The synthesis of single crystals of the molybdenum phosphate NaMo$_2$P$_3$O$_{13}$ was performed in two steps. First, H(NH$_4$)$_2$PO$_4$, Na$_2$CO$_3$, and MoO$_3$ were mixed in an agate mortar in the adequate molecular ratio to obtain the composition "NaMo$_{1.66}$P$_3$O$_{13}$." The mixture was heated at 600 K in air in order to decompose the carbonate and the ammonium phosphate. The resulting prod-

uct was then added to the required amount of molybdenum and placed in an evacuated silica ampoule. This mixture was heated for 5 days at 1073 K. The final product corresponding to this thermal treatment did not allow a pure phase to be synthesized. However, yellow green single crystals of a new phase were isolated and revealed to correspond to NaMo₂P₃O₁₃. Their composition was determined both by chemical analysis and by the structure determination.

## Structure Determination

A yellowish green crystal with dimension 0.24 × 0.096 × 0.072 mm was selected for the structure determination. The cell parameters reported in Table I were determined and refined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections with $18 < \theta < 22°$.

The data were collected on a CAD-4 Enraf–Nonius diffractometer with the data

### TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR ε-NaMo₂P₃O₁₃

1. Crystal data

| | | |
|---|---|---|
| Space group | $P\bar{1}$ | |
| Cell dimensions | $a = 6.352(3)$ Å | $\alpha = 75.08(5)$ Å |
| | $b = 7.448(5)$ | $\beta = 85.33(4)$ Å |
| | $c = 10.991(6)$ | $\gamma = 79.10(4)$ Å |
| Volume | $V = 493.0(6)$ Å³ | |
| $z$ | 2 | |

2. Intensity measurement

| | |
|---|---|
| $\lambda$ (Mo $K\alpha$) | 0.71073 Å |
| Scan mode | $\omega$-2/3 $\theta$ |
| Scan width (°) | 1. + 0.35 tan $\theta$ |
| Slit aperture (mm) | 1. + tan $\theta$ |
| Max $\theta$ (°) | 45 |
| Standard reflections | 3 measured every 3000 sec (no decay) |
| Reflections with $I > 3\sigma$ | 6347 |
| $\mu$ (mm⁻¹) | 3.08 |

3. Structure solution and refinement

| | |
|---|---|
| Parameters refined | 172 |
| Agreement factors | $R = 0.033, R_w = 0.038$ |
| Weighting scheme | $W = f(\sin \theta/\lambda)$ |
| $\Delta/\sigma$ max | 0.1 |

### TABLE II

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

| Atom | x | y | z | B(A2) |
|---|---|---|---|---|
| Mo(1) | 0.21573(3) | 0.21226(2) | 0.08508(2) | 0.496(2) |
| Mo(2) | 0.24357(3) | 0.19432(2) | 0.59317(2) | 0.532(2) |
| P(1) | 0.74282(8) | 0.19750(8) | 0.66237(5) | 0.562(6) |
| P(2) | 0.11903(8) | 0.47629(7) | 0.30773(5) | 0.570(6) |
| P(3) | 0.73572(8) | 0.07237(7) | 0.10861(5) | 0.530(6) |
| Na | 0.6551(5) | 0.4024(4) | 0.2543(4) | 4.46(5) |
| O(1) | 0.2362(4) | 0.3698(3) | −0.0520(2) | 1.28(3) |
| O(2) | 0.5241(3) | 0.2008(2) | 0.1314(2) | 0.86(2) |
| O(3) | 0.2706(3) | −0.0145(2) | 0.0139(2) | 0.97(2) |
| O(4) | 0.2421(3) | −0.0047(3) | 0.2545(2) | 1.03(2) |
| O(5) | −0.0956(3) | 0.1978(3) | 0.1008(2) | 1.09(2) |
| O(6) | 0.1279(3) | 0.3923(3) | 0.1969(2) | 1.06(2) |
| O(7) | 0.3176(4) | −0.0254(3) | 0.5786(2) | 1.35(3) |
| O(8) | −0.0722(3) | 0.2142(3) | 0.5643(2) | 0.81(2) |
| O(9) | 0.2194(3) | 0.1049(3) | 0.7831(2) | 1.03(2) |
| O(10) | 0.5274(3) | 0.2743(3) | 0.6003(2) | 1.03(2) |
| O(11) | 0.2603(3) | 0.3473(3) | 0.4128(2) | 0.95(2) |
| O(12) | 0.1088(3) | 0.4585(2) | 0.6498(2) | 0.80(2) |
| O(13) | 0.2375(3) | 0.6553(2) | 0.2558(2) | 0.85(2) |

collection parameters reported in Table I. The reflections were corrected for Lorentz and polarization effects; no absorption corrections were performed.

Atomic coordinates of the molybdenum atom were deduced from the Patterson function and the other atoms were located by subsequent Fourier series. Refinement of the atomic coordinates and their anisotropic thermal parameters led to $R = 0.033$ and $R_w = 0.038$ and to the atomic parameters of Table II.[1]

## Description of the Structure and Discussion

The [ε-NaMo₂P₃O₁₃]∞ framework is, like the four other [Mo₂P₃O₁₃]∞ host lattices, built up from corner-sharing MoO₆, single PO₄ tetrahedra, and diphosphate P₂O₇ groups (Fig. 1).

[1] Lists of structure factors and anisotropic thermal motion parameters are available on request to the authors.
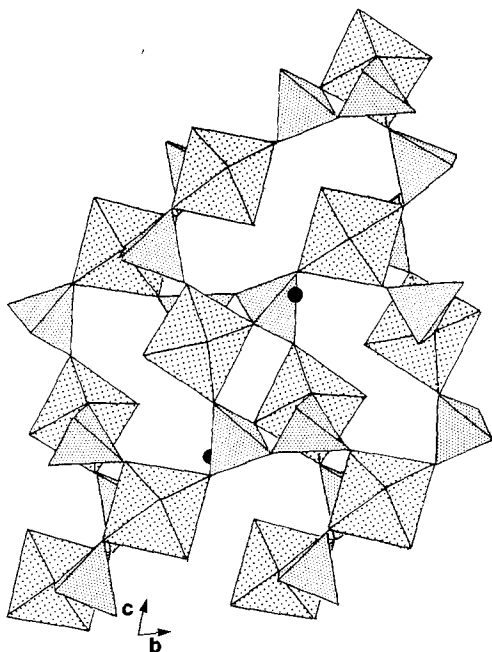
FIG. 1. Projection of $\varepsilon$-NaMo$_2$P$_3$O$_{13}$ along $\vec{a}$.

All of these five host lattices have in common the geometry of their MoO$_6$ octahedra, which appears as a characteristic of Mo (V). One indeed observes, like for other Mo

(V) phosphates (*1–8*), one every short Mo–O bond (1.60–1.667 Å) and one abnormally long Mo–O distance (2.123–2.213 Å), whereas the four other Mo–O distances are normal (1.992–2.044 Å) (Table III). The sum of the electrostatic valences calculated with the Zachariasen curves (*9*) confirms that molybdenum is present in the pentavalent state. It is worth pointing out that, in all these Mo (V) phosphates, the Mo$^V$O$_6$ octahedron has one free corner and the abnormally short Mo–O distance corresponds to this oxygen atom which is not shared with other polyhedra of the host lattice. This particular feature of Mo (V) which imposes one oxygen atom to be "free" with respect to the PO$_4$ tetrahedra allows a great flexibility of the structure and is certainly at the origin of the various [Mo$_2$P$_3$O$_{13}$]$_\infty$ frameworks observed for the same $A$Mo$_2$P$_3$O$_{13}$ composition.

The geometry of the PO$_4$ tetrahedra is similar to that commonly observed in other phosphates. The P–O distances in the monophosphate groups are almost equal, whereas the diphosphate groups which exhibit an eclipsed configuration are characterized by one long P–O bond corresponding

TABLE III

DISTANCES (Å) AND ANGLES (°) IN THE MoO$_6$ OCTAHEDRA

| Mo(1) | O(1) | O(2) | O(3) | O(4) | O(5) | O(6) |
|---|---|---|---|---|---|---|
| O(1) | 1.667(2) | 2.723(3) | 2.735(3) | 3.778(3) | 2.871(3) | 2.806(3) |
| O(2) | 93.8 (1) | 2.044(2) | 3.035(3) | 2.638(3) | 3.982(3) | 2.786(3) |
| O(3) | 96.1 (1) | 97.3 (1) | 2.000(2) | 2.655(3) | 2.802(3) | 3.981(3) |
| O(4) | 170.9 (1) | 78.5 (1) | 80.1 (1) | 2.123(2) | 2.790(3) | 2.823(3) |
| O(5) | 103.0 (1) | 161.3 (1) | 89.2 (1) | 85.3 (1) | 1.992(2) | 2.654(3) |
| O(6) | 98.7 (1) | 86.6 (1) | 164.4 (1) | 85.9 (1) | 82.9 (1) | 2.019(2) |

| Mo(2) | O(7) | O(8) | O(9) | O(10) | O(11) | O(12) |
|---|---|---|---|---|---|---|
| O(7) | 1.660(2) | 2.755(3) | 2.655(3) | 2.875(3) | 2.877(3) | 2.851(3) |
| O(8) | 96.1 (1) | 2.028(2) | 3.005(3) | 3.981(3) | 2.754(3) | 2.713(3) |
| O(9) | 91.7 (1) | 95.7 (1) | 2.024(2) | 2.906(3) | 4.015(3) | 2.656(3) |
| O(10) | 102.5 (1) | 159.6 (1) | 92.0 (1) | 2.016(2) | 2.658(3) | 2.831(3) |
| O(11) | 102.3 (1) | 85.7 (1) | 165.7 (1) | 82.3 (1) | 2.022(2) | 2.966(3) |
| O(12) | 167.7 (1) | 79.4 (1) | 77.5 (1) | 83.9 (1) | 88.8 (1) | 2.213(2) |

TABLE IV

Distances (Å) and Angles (°) in the PO₄ Tetrahedra

| P(1) | O(4$^i$) | O(8$^{ii}$) | O(10) | O(13$^{iii}$) |
|------|----------|-------------|-------|---------------|
| O(4$^i$) | 1.481(2) | 2.501(2) | 2.518(2) | 2.534(3) |
| O(8$^{ii}$) | 112.4 (1) | 1.529(2) | 2.514(2) | 2.494(3) |
| O(10) | 113.9 (1) | 110.9 (1) | 1.523(2) | 2.473(3) |
| O(13$^{iii}$) | 109.9 (1) | 105.0 (1) | 104.0 (1) | 1.614(2) |

| P(2) | O(6) | O(11) | O(12$^{iv}$) | O(13) |
|------|------|-------|--------------|-------|
| O(6) | 1.498(2) | 2.501(3) | 2.501(3) | 2.446(3) |
| O(11) | 111.5 (1) | 1.527(2) | 2.555(2) | 2.477(2) |
| O(12$^{iv}$) | 112.3 (1) | 114.4 (1) | 1.513(2) | 2.552(2) |
| O(13) | 103.8 (1) | 104.3 (1) | 109.7 (1) | 1.608(2) |

| P(3) | O(2) | O(3$^v$) | O(5$^{ii}$) | O(9$^i$) |
|------|------|----------|-------------|----------|
| O(2) | 1.538(2) | 2.508(3) | 2.408(2) | 2.543(2) |
| O(3$^v$) | 110.1 (1) | 1.521(2) | 2.525(3) | 2.488(2) |
| O(5$^{ii}$) | 103.3 (1) | 111.6 (1) | 1.533(2) | 2.521(3) |
| O(9$^i$) | 111.9 (1) | 109.2 (1) | 110.7 (1) | 1.531(2) |

*Note.* P(1) and P(2) belong to the P₂O₇ group and P(3) corresponds to the monophosphate.

*Note.* Symmetry codes. (i): $1 - x$, $-y$, $1 - z$. (ii): $1 + x$, $y$, $z$. (iii): $1 - x$, $1 - y$, $1 - z$. (iv): $-x$, $1 - y$, $1 - z$. (v): $1 - x$, $-y$, $-z$. (vi): $1 - x$, $1 - y$, $-z$.

to the bridging oxygen and three shorter P–O distances (Table IV).

Although they are very different from each other, the [Mo₂P₃O₁₃]∞ frameworks of the five AMo₂P₃O₁₃ phosphates have a common feature, which deals with the existence of MoP₂O₁₁ units built up from one P₂O₇
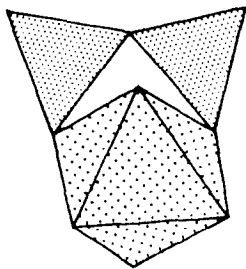


Fig. 2. MoP₂O₁₁ units in the [Mo₂P₃O₁₃]∞ frameworks in AMo₂P₃O₁₃.
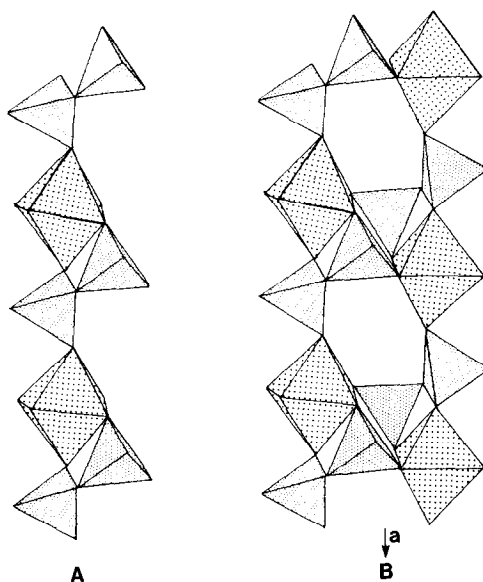


Fig. 3. (A) Infinite chains [MoP₂O₁₀]∞ running along $\vec{a}$. (B) Double chain [Mo₂P₄O₁₈]∞ running along $\vec{a}$.

groups sharing two of its corners with the same MoO₆ octahedron (Fig. 2). In ε-Na-Mo₂P₃O₁₃, these MoP₂O₁₁ units share their corners along $\vec{a}$ exactly in the same way as in β-AMo₂P₃O₁₃ (2–4) and in γ-CsMo₂P₃O₁₃ (5) forming infinite [MoP₂O₁₀]∞ chains (Fig. 3A). Two single [MoP₂O₁₀]∞ chains share the corners of their polyhedra in such a way that one tetrahedron of one chain be linked to one MoO₆ octahedron of the other chain. It results in double infinite ribbons [Mo₂P₄O₁₈]∞ running along $\vec{a}$ (Fig. 3B), which are similar to those observed for γ-CsMo₂P₃O₁₃ (5). Another interesting feature concerns the existence of infinite [MoPO₈]∞ chains running along $\vec{a}$ (Fig. 4A), in which one single PO₄ tetrahedron alternates with one MoO₆ octahedron. Those single chains share the corners of their polyhedra forming double ribbons [Mo₂P₂O₁₄]∞ (Fig. 4B) similar to those observed in β-AMo₂P₃O₁₃, (2–4), in γ-CsMo₂ P₃O₁₃ (5), and in MoPO₅ (10). Thus ε-NaMo₂P₃O₁₃ appears as more closely re-

| | |
|---|---|
| Na–O(12$^{iii}$) | = 2.417(4) Å |
| Na–O(2) | = 2.544(4) Å |
| Na–O(1$^{vi}$) | = 2.559(4) Å |
| Na–O(5$^{ii}$) | = 2.766(4) Å |
| Na–O(7$^{i}$) | = 2.916(3) Å |
| Na–O(13) | = 2.950(3) Å |
| Na–O(11) | = 2.967(4) Å |
| Na–O(6$^{ii}$) | = 3.009(4) Å |

*Note.* See symmetry codes in foot-note to Table IV.
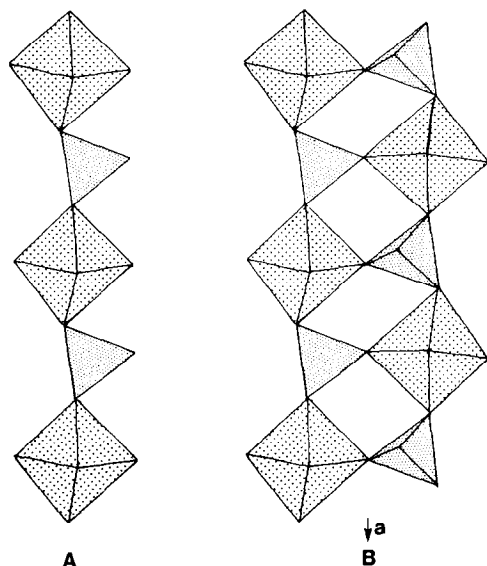
FIG. 4. (A) Infinite chains [MoPO$_8$]$_\infty$ running along $\vec{a}$. (B) Double chain [Mo$_2$P$_2$O$_{14}$]$_\infty$ running along $\vec{a}$.

lated to $\gamma$-CsMo$_2$P$_3$O$_{13}$ in that the host lattices of both oxides can be described by the assemblage of the two sorts of ribbons
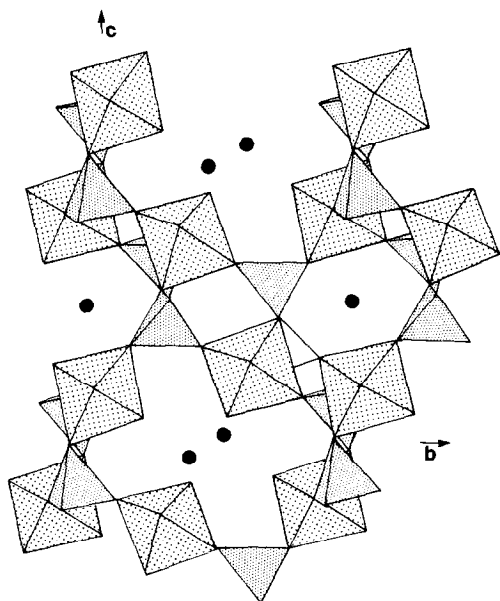


FIG. 5. Projection of $\gamma$-CsMo$_2$P$_3$O$_{13}$ along $\vec{a}$.

[Mo$_2$P$_4$O$_{18}$]$_\infty$ and [Mo$_2$P$_2$O$_{14}$]$_\infty$. In both oxides, those ribbons share the corners of their polyhedra, leaving one oxygen of their MoO$_6$ octahedra free; however, the ribbons are connected in a different manner. Consequently the [$\gamma$-Mo$_2$P$_3$O$_{13}$]$_\infty$ framework delimits cages, containing the Cs$^+$ ions, connected through six-sided or cross-shaped twelve-sided windows (Fig. 5), whereas in the [$\varepsilon$-Mo$_2$P$_3$O$_{13}$]$_\infty$ framework the cages containing the Na$^+$ ions are connected through S-shaped windows (Fig. 1).

The Na–O distances, ranging from 2.41 to 3.2 Å (Table V), are in agreement with the ionic radii of Na$^+$. The rather great size of the windows suggests a good mobility of sodium within the structure. The high thermal factor of this cation is in agreement with this point of view. The investigation of the ionic conductivity of this material will be performed.

## References

1. A. LECLAIRE, J. C. MONIER, AND B. RAVEAU, *J. Solid State Chem.* **48**, 147 (1983).
2. K. H. LII AND R. C. HAUSHALTER, *J. Solid State Chem.* **69**, 320 (1987).
3. D. RIOU AND M. GOREAUD, *J. Solid State Chem.* **79**, 99 (1989).
4. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *Acta Crystallogr.* in press (1990).

5. J. J. CHEN, K. H. LII, AND S. L. WANG, *J. Solid State Chem.* **76,** 204 (1988).

6. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *Z. Kristallogr.* **188,** 77 (1989).

7. K. H. LII, D. C. JOHNSTON, D. P. GOSHORN, AND R. C. HAUSHALTER, *J. Solid State Chem.* **71,** 131 (1987).

8. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *J. Solid State Chem.* **80,** 250 (1989).

9. W. H. ZACHARIASEN, *J. Less-Common Met.* **62,** 1 (1978).

10. P. KIERKEGAARD AND J. M. LANYO, *Acta Chem. Scand.* **24,** 427 (1970).