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Refinement of some $Na_{0.5-x}M'_{0.5+x/3}\square_{2x/3}MoO_4$, M = Bi, Ce, La, Scheelite Structures with Powder Neutron and X-ray Diffraction Data

By Raymond G. Teller

BP Research International, 4440 *Warrensville Center Road, Cleveland, Ohio* 44128, *USA*

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Abstract. Bismuth sodium molybdate, $Na_{0.5}Bi_{0.5}MoO_4$ (I), $M_r = 275.92$, tetragonal, $I4_1/a$, $a = 5.2717\,(1)$, $c = 11.5801\,(2)$ Å, $V = 321.824\,(5)$ Å^3, $Z = 4$, $D_n = 5.69$ g cm^{-3}, $R_p = 4.06\%$ (263 reflections, neutron data). Bismuth sodium molybdate, $Na_{0.32}Bi_{0.56}MoO_4$ (II), $M_r = 284.33$, tetragonal, $I4_1/a$, $a = 5.2785\,(1)$, $c = 11.6410\,(2)$ Å, $V = 324.342\,(5)$ Å^3, $Z = 4$, $D_n = 5.82$ g cm^{-3}, $R_p = 4.82\%$ (293 reflections, neutron data). Cerium sodium molybdate, $Na_{0.5}Ce_{0.5}MoO_4$ (III), $M_r = 241.64$, tetragonal, $I4_1/a$, $a = 5.3167\,(4)$, $c = 11.6600\,(11)$ Å, $V = 329.58\,(3)$ Å^3, $Z = 4$, $D_x = 4.87$ g cm^{-3}, $R_p = 12.34\%$ [105 reflections, X-ray data, Cu $K\alpha$ (1.5415 Å) radiation]. Lanthanum sodium molybdate, $Na_{0.5}La_{0.5}MoO_4$ (IV), $M_r = 241.03$, tetragonal, $I4_1/a$, $a = 5.3424\,(4)$, $c = 11.7376\,(11)$ Å, $V = 335.01\,(3)$ Å^3, $Z = 4$, $D_x = 4.78$ g cm^{-3}, $R_p = 10.82\%$ [107 reflections, X-ray data, Cu $K\alpha$ (1.5415 Å) radiation]. The structures have been refined with room-temperature time-of-flight powder neutron diffraction data or X-ray diffraction data as indicated. Results of Rietveld refinements indicate that all of the materials adopt the scheelite ($CaWO_4$) structure, with Na, vacancies and Bi, La or Ce cations randomly distributed on the Ca site, and Mo occupying the W site.

Introduction. There is a large family of molybdate materials that form scheelite (ABO_4) or scheelite-related structures and also are selective alkene oxidation catalysts. In addition to $M^{2+}Mo^{6+}O_4$ compounds [*e.g.* $PbMoO_4$ (Leciejewicz, 1965; Mentzen, Latrach, Bouix & Hewat, 1984) or $CaMoO_4$ (Hazen, Finger & Maraithason, 1985)], a series of $M_{2/3}\square_{1/3}MoO_4$ (M: 3+) materials have been structurally characterized [M^{3+} = Bi, La, Ce (Brazdil, Teller, Grasselli & Kostiner, 1985; Jeitschko, 1973)]. While lead molybdate adopts the scheelite structure, the latter three compounds adopt scheelite-related super cells in which the defects, $\square$, are ordered. Interestingly, while $Bi_{2/3}MoO_4$ and $BiVO_4$ (Cox, Moodenbaugh, Sleight & Chen, 1980) adopt defect and reduced symmetry scheelite-related unit cells respectively, they form a solid solution, $Bi_{1-x/3}\square_{x/3}V_{1-x}Mo_xO_4$, that is isostructural with $CaWO_4$.

In at least one material, ferrous cations can substitute for Mo resulting in $Bi(Fe_{1/3}Mo_{2/3}O_4)$ (Jeitschko, Sleight, McClellan & Weiher, 1976). This material has both high- and low-temperature forms. The low-temperature structure is thought to be isostructural with scheelite with ferrous and Mo^{6+} ions randomly distributed at the tetrahedral '*B*' site. At temperatures above 873 K, or at lower temperatures in the presence of alkene and oxygen, the low-temperature form undergoes a transition wherein the tetrahedral cations display long-range ordering and a super cell is observed.

A report in the literature (Sleight, Aykan & Rogers, 1975) of the formation of bismuth sodium molybdate phases ($Na_{0.5-x}Bi_{0.5+x/3}\square_{2x/3}MoO_4$) apparently isostructural with scheelite prompted the synthesis and structural characterization of two of the title compounds (x = 0, 0.18). Since small deviations of O-atom positions from the ideal scheelite structure may not be readily apparent from analysis of X-ray diffraction data, time-of-flight (TOF) neutron diffraction data were collected for these materials to determine if they were isostructural with $CaWO_4$. Additionally, Ce and La analogs of the x = 0 phase, $Na_{0.5}Ce_{0.5}MoO_4$ and $Na_{0.5}La_{0.5}MoO_4$ were synthesized to determine if these materials also adopted the scheelite structure. These last two compounds were analyzed with powder X-ray diffraction data. Synthesis and cell constants for the La compound have been reported (Shugal, Britan & Shklover, 1969).

Experimental. Synthesis of $Na_{0.5}Bi_{0.5}MoO_4$ (I) was accomplished by the co-precipitation method. Bismuth nitrate pentahydrate (21.825 g, 0.045 mol) was dissolved in 150 ml of 10% nitric acid solution. Similarly, 1.800 g (0.045 mol) of sodium hydroxide and 15.891 g (0.01286 mol) of ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$] were dissolved in 150–200 ml of distilled water. The sodium hydroxide and then bismuth nitrate solutions were added to the molybdate solution in a 1 l beaker while the latter was rapidly stirred. At this point a fine white precipitate was observed. The mixture was stirred and

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Table 1. *Results of Rietveld refinements for* $Na_{0.5-x}M'_{0.5+x/3}\square_{2x/3}MoO_4$

	(I) ($x = 0$, $M' =$ Bi) Neutron	(II) ($x = 0.18$, $M' =$ Bi) Neutron		(III) ($x = 0$, $M' =$ Ce) X-ray	(IV) ($x = 0$, $M' =$ La) X-ray
Unit cell ($I4_1/a$, No. 88, $Z = 4$)					
a (Å)	5.2717 (1)	5.2785 (1)		5.3167 (3)	5.3424 (3)
b (Å)	11.5801 (2)	11.6410 (3)		11.6600 (9)	11.7376 (9)
V (Å^3)	321.824 (5)	324.342 (8)		329.60 (2)	335.01 (2)
Range* of data used in refinement					
T_{min} (μs)	6000	7000	$2\theta_{min}$ (°)	10	10
T_{max} (μs)	31 000	31 000	$2\theta_{max}$ (°)	110	110
No. of data points	3126	4801		2501	2501
No. of variables†	25	25		17	17
Agreement factors (%)					
R_p	3.25	4.82		12.3	10.8
R_{wp}	4.59	7.87		16.3	15.3
R_{Bragg}	5.39	8.76		5.16	2.54
R_{exp}	1.50	3.24		7.00	6.80
No. of reflections	263	293		105	107
Profile shape parameters‡					
Sig0	29 (7)	−5 (5)	U	0.003 (1)	0.016 (1)
Sig1	130 (5)	61 (6)	K	0.077 (1)	0.071 (1)
Sig2	6 (1)	0 (1)			

* For the neutron data, convert times-of-flight (TOF) to d values according to $\mathrm{TOF} = \mathrm{DIFA} \times d^2 + \mathrm{DIFC} \times d + \mathrm{ZERO}$, where DIFC = 10453.49, DIFA = −2.59, ZERO = −13.50. X-ray data were collected with Cu $K\alpha$ radiation.

† The number of parameters allowed to vary in the least-squares process.

‡ For the neutron data, the peak shape function is a convolution of instrument functions and a sample dependent function Sig, where $\mathrm{Sig} = [\mathrm{sig0} + \mathrm{sig1} \times d^2 + \mathrm{sig2} \times d^4]^{1/2}$. Peak shapes for the X-ray data were fit with a Voigtian function, the FWHM of the Gaussian and Lorentzian portions thereof varying with θ according to $[U\tan^2\theta + V\tan\theta + W]^{1/2}$ and $K\sec\theta$ respectively. Instrumental values of V, W and K are −0.0016, 0.0075 and 0.041, respectively (as determined by refinement of data from an LaB_6 NIST standard reference material No. 660).

Table 2. *Atomic parameters for* $Na_{0.5-x}M'_{0.5+x/3}\square_{2x/3}MoO_4$

Positional parameters*

	x	y	z	
O [(I), $x = 0$, $M' =$ Bi]	0.1488 (2)	0.0094 (2)	0.2090 (1)	Neutron
O [(II), $x = 0.18$, $M' =$ Bi]	0.1483 (2)	0.0083 (2)	0.2074 (1)	Neutron
O [(III), $x = 0$, $M' =$ Ce]	0.1402 (16)	0.0171 (16)	0.2138 (7)	X-ray
O [(IV), $x = 0$, $M' =$ La]	0.1442 (14)	0.0115 (14)	0.2095 (7)	X-ray

Thermal parameters (Å^2)†

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo (I)	0.0052 (6)	$= B_{11}$	0.0012 (2)	0	0	0
Na/Bi (I)	0.0110 (6)	$= B_{11}$	0.0042 (2)	0	0	0
O (I)	0.0094 (4)	0.0139 (5)	0.0026 (1)	0.0008 (6)	0	0
Mo (II)	0.0061 (5)	$= B_{11}$	0.0014 (2)	0	0	0
Na/Bi (II)	0.0100 (6)	$= B_{11}$	0.0038 (2)	0	0	0
O (II)	0.0125 (5)	0.0161 (6)	0.0028 (1)	0.0029 (5)	0	0

* The choice of origin is at the center of symmetry on the glide plane (choice 2 in *International Tables for X-ray Crystallography*). Symmetry constraints require the '*A*' cation (Mo) to be located at $0, \frac{1}{4}, \frac{1}{8}$ (4) and the '*B*' cation Bi/Na, Ce/Na and La/Na to be located at $0, \frac{1}{4}, \frac{5}{8}$ (4).

† The anisotropic thermal correction is $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$. All isotropic thermal parameters were constrained to be identical for models refined based on X-ray data, for (III), $M' =$ Ce, $B_{iso} = 1.24$ (4) Å^2, and for (IV), $M' =$ La, $B_{iso} = 1.30$ (4) Å^2.

Table 3. *Bond distances* (Å) *for* $Na_{0.5-x}M'_{0.5+x/3}MoO_4$ *and* $PbMoO_4$

	(I), $x = 0$, $M' =$ Bi	(II), $x = 0.18$, $M' =$ Bi	(III), $x = 0$, $M' =$ Ce	(IV), $x = 0$, $M' =$ La	$PbMoO_4$
Mo—O	1.781 (1)	1.778 (1)	1.78 (2)	1.79 (2)	1.759
M'—O (type 1)	2.486 (1)	2.495 (1)	2.47 (2)	2.51 (2)	2.595
M'—O (type 2)	2.499 (1)	2.506 (1)	2.60 (2)	2.56 (2)	2.608

heated (353–373 K) until a thick paste formed (4–5 h). This material was dried at 398 K for 72 h, then heated at 563 and 698 K for 16 h each, then finally at 873 K in air for 72 h. In a similar manner samples of $Na_{0.32}Bi_{0.56}MoO_4$ (II), $Na_{0.5}Ce_{0.5}MoO_4$ (III) and $Na_{0.5}La_{0.5}MoO_4$ (IV) were prepared.

TOF neutron diffraction data were collected at ambient temperature and pressure at Argonne National Laboratory with the IPNS (Intense Pulsed Neutron Source) on the GPPD (General Purpose Powder Diffractometer). Data summed from the right-angle detector banks ($2\theta = \pm 90°$) or backscattering banks ($2\theta = 150°$) were used in the refinements. In the TOF technique, the sample, detector and source are fixed and neutrons of differing wavelengths are detected. The sample was contained within a 12.7 mm diameter seamless vanadium tube, capped at one end with an aluminium plug. Details of the instrument and the data collection and data analysis software package have been previously published (Hauman, Daley, Worlton & Crawford, 1982; Von Dreele, Jorgensen & Windsor, 1982; Jorgensen & Faber, 1982). Analysis of the neutron data was performed with a Rietveld profile least-squares program adapted for time-of-flight neutron data and multiphase samples.

Step-scan X-ray powder-diffraction data were collected with a Rigaku DMAXB diffractometer utilizing Bragg–Brentano parafocusing geometry and a post-sample curved graphite monochromator. Cu $K\alpha$ radiation was used for data collection. Rietveld refinement of the data was accomplished with the use of a locally modified version of *LHPM* (Wiles & Young, 1981; Howard & Hill, 1986).

Starting structural parameters for the least-squares process were taken to be identical with $CaWO_4$. All reasonable parameters were allowed to vary including background, peak shape, scale factor(s), cell constants, thermal, and positional (for the O atom) parameters for the scheelite phase. Thermal parameters were allowed to vary anisotropically for the neutron data, while a single isotropic thermal parameter was utilized for the X-ray data. In refining the neutron data the occupancy of a single atom with a scattering length equal to a weighted sum of scattering lengths of Na and Bi located at $(0, \frac{1}{4}, \frac{5}{8})$ was refined. For (I) the scattering length was $(0.5b_{Na} + 0.5b_{Bi})$ and for (II), $(0.32b_{Na} + 0.56b_{Bi})$. This occupancy did not differ significantly from the expected (*i.e.* '100%') occupancy. Occupancies were not varied during refinements of the models for (III) and (IV). In three of the samples [(I), (III) and (IV)] traces of MoO_3 were noted in the diffraction patterns. This phase was included in the refinement as well (Kihlborg, 1963), although the small amount present precluded a structural refinement of MoO_3. Results of the refinement are given in Tables 1 and 2. Atomic distances are given in Table 3. Figs. 1, 2, 3 and 4 show raw, calculated and difference diffraction data.*

At the conclusion of the refinement processes there were no Bragg peaks in the diffraction patterns that were not accounted for by the majority (>99%, scheelite) or minority (<1%, MoO_3) phases. This, coupled with the low profile and Bragg agreement factors for the neutron data, provides strong evidence for (I) and (II) adopting the scheelite structure. It is also very likely that (III) and (IV) are isostructural with $CaWO_4$. Scattering factors (for the X-ray data, neutral atoms) and lengths (for the neutron data) were taken from *International Tables for X-ray Crystallography* (1962, Vol. III and 1974, Vol. IV, respectively).

Discussion. The scheelite structure [prototype mineral scheelite: $CaWO_4$ (Burbank, 1965)] is commonly adopted by ABO_4 compositions and is composed of BO_4 tetrahedra and eight coordinate A ions (see Fig. 2). Typically the B cation is rather small (*ca* 0.6 Å) and the A cation large (*ca* 1.0 Å). $CaWO_4$ crystallizes in the $I4_1/a$ space group with four ABO_4 units per unit cell. In the work presented herein, analysis of neutron diffraction data demonstrates

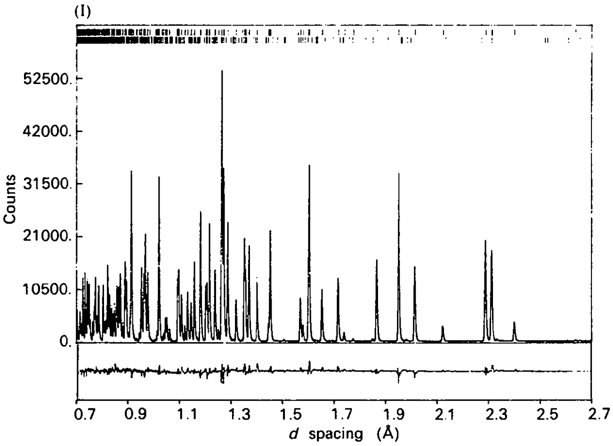

Fig. 1. Neutron TOF diffraction data for $Na_{0.5}Bi_{0.5}MoO_4$. Raw data are represented by points, and the calculated pattern from the Rietveld fit by a continuous line. A difference plot is presented at the bottom of the figure. The fitted background has been subtracted from the observed data and calculated curve. A small amount of a secondary phase (MoO_3) is present in the sample.

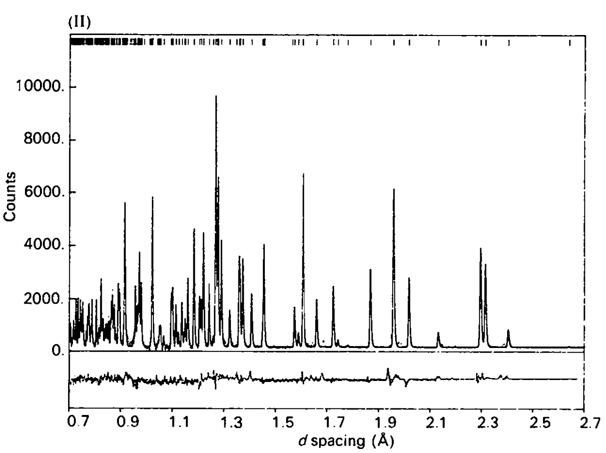

Fig. 2. Neutron TOF diffraction data for $Na_{0.32}Bi_{0.56}MoO_4$. β-$Bi_2Mo_2O_9$ is present as an impurity.

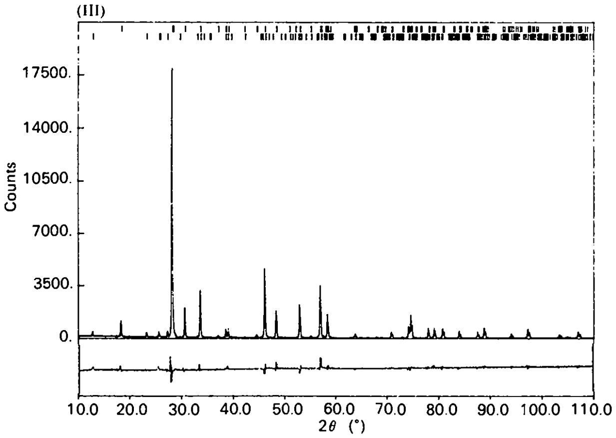

Fig. 3. X-ray diffraction data for $Na_{0.5}Ce_{0.5}MoO_4$.

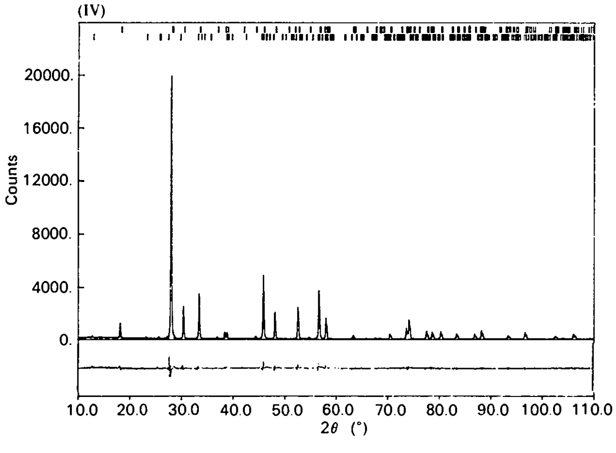

Fig. 4. X-ray diffraction data for $Na_{0.5}La_{0.5}MoO_4$.

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* Lists of raw time-of-flight neutron diffraction data and raw X-ray diffraction data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55114 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0345]

that $Na_{0.5}Bi_{0.5}MoO_4$ and $Na_{0.32}Bi_{0.56}\square_{0.18}MoO_4$ both adopt the scheelite structure with Na^+, Bi^{3+} and vacancies randomly occupying the eight coordinate '*A*' site. Similarly, on the basis of powder X-ray diffraction data, $Na_{0.5}M'_{0.5}MoO_4$ (M' = Ce, La) have been shown to be isostructural with scheelite. Presumably, a deficiency of Na in these structures can also be compensated for by excess Ce or La and vacancies in a manner similar to the Bi-containing compound.

An examination of Table 3 shows the similarity of the structures examined herein. All four structures have very similar '*B*' (MoO_4) and '*A*' coordination environments. This is not surprising in light of the similarities in cation size [Na^+ 1.16, Bi^{3+} 1.11, Ce^{3+} 1.14, La^{3+} 1.18 Å (Huheey, 1972)]. For comparison, *A*—O and *B*—O distances for $PbMoO_4$ are given in Table 3.

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Structure Refinement of $Co_3(OH)_2(PO_3OH)_2$ and $Co[PO_2(OH)_2]_2.2H_2O$

By H. Effenberger

Institut für Mineralogie und Kristallographie der Universität Wien, Dr Karl Lueger-Ring 1, *A*-1010 *Wien, Austria*

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Abstract. Tricobalt dihydroxide bis(hydrogenphosphate), $Co_3(OH)_2(PO_3OH)_2$, $M_r = 402.77$, monoclinic, $P2_1/c$, $a = 7.524$ (2), $b = 7.512$ (2), $c = 7.395$ (2) Å, $\beta = 117.88$ (2)°, $V = 369.5$ (1) Å^3, $Z = 2$, $D_x = 3.621$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 6.9$ mm^{-1}, $F(000) = 390$, room temperature, $wR(F) = 0.027$ for 2049 reflections. The structure is closely related to that of lazulite, $MgAl_2(OH)_2(PO_4)_2$. Cobalt bis(dihydrogenphosphate) dihydrate, $Co[PO_2(OH)_2]_2.2H_2O$, $M_r = 288.94$, monoclinic, $P2_1/n$, $a = 7.268$ (2), $b = 9.886$ (3), $c = 5.331$ (1) Å, $\beta = 94.86$ (2)°, $V = 381.7$ (1) Å^3, $Z = 2$, $D_x = 2.514$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 2.56$ mm^{-1}, $F(000) = 290$, room temperature, $wR(F) = 0.028$ for 1678 reflections. A member of the $M[PO_2(OH)_2]_2.2H_2O$-type structures with M = Mg, Mn, Fe, Co or Cd.

Introduction. In connection with investigations of the coordination chemistry of transition-metal atoms towards O atoms, syntheses in parts of the system $CoO–P_2O_5–H_2O$ were performed. As a result, the crystal structure of $Co(PO_3OH).H_2O$ was recently determined (Effenberger, Parik, Pertlik & Rieck, 1991); the crystal structures of $Co_3(OH)_2(PO_3OH)_2$ and $Co[PO_2(OH)_2]_2.2H_2O$ were presented at the common meeting of the 'Arbeitsgemeinschaft Kristallographie' and the 'Vereinigung für Kristallographie' in Münich, Germany (Effenberger, 1991). In the meantime a paper about the structural investigation and magnetic characterization of $Co_3(OH)_2(PO_3OH)_2$ was published by Pizarro, Villeneuve, Hagenmuller & Le Bail (1991). Because their structure determination was based only on powder X-ray (X_p) and powder neutron (N_p) diffraction data a comparison with single-crystal X-ray diffraction data (X_s) seemed to be worthwhile. The lattice parameters of $Co[PO_2(OH)_2]_2.2H_2O$ have been given by Vasić, Prelesnik, Ćurić & Herak (1985); in addition they mentioned the isotypism with $M[PO_2(OH)_2]_2.2H_2O$,

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