

Direct hydrothermal synthesis of metal intercalated hexagonal molybdates, $M_x^+ Mo_{6-x/3} O_{18-x} (OH)_x \cdot yH_2O$ ($M = Li, Rb, Cs, NH_4$)[†]

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Abstract. Here we report direct hydrothermal synthesis of a few hexagonal molybdates with composition, $M_x^+ Mo_{6-x/3} O_{18-x} (OH)_x \cdot yH_2O$ ($M = Li, Rb, Cs, NH_4$). The molybdates crystallize in the space group $P6_3/m$ with $a \sim 10.5$ and $c \sim 3.7 \text{ \AA}$. Unlike previous studies, our work suggests that hexagonal molybdates could be stabilized in the presence of monovalent cations with varying ionic size (smaller lithium to larger cesium) under hydrothermal condition. The phases showed exceptional thermal stability till 550°C .

Keywords. Hexagonal molybdates; intercalation; hydrothermal synthesis.

1. Introduction

Metal molybdates are attractive materials for possible applications as sensors, catalysts, ion-exchangers etc.^{1,2} Mild hydrothermal condition is a convenient soft-chemical route for stabilizing porous metastable metal molybdates.^{3,6} Due to high solubility of alkali molybdates, these are commonly employed as starting materials for the formation of porous organic/inorganic hybrid molybdates or transition metal molybdates. In many reactions, hexagonal molybdates appear as a competing phase during hydrothermal treatment. The first hexagonal polyoxomolybdate was reported by Sotani *et al.*⁴ Krebs and Paulat–Boschen⁵ were the first to solve the single crystal structure of this phase. They described the structure to be constructed from zigzag chains of molybdenum octahedra as observed in layered molybdenum oxide, $\alpha\text{-MoO}_3$ and the chains are connected to each other through corners. The alkali cations occupy the hexagonal tunnels along with water molecules. The structure was found to be slightly molybdenum deficient and the charge compensation was through hydroxyl groups. McCarron⁶ synthesised sodium hexagonal molybdate through precipitation at the boiling of acidified molybdate solution and demonstrated its ion-exchange behaviour with other monovalent cations (K, Rb, Cs, NH_4 and Ag). However, he could not stabilise the structure with lithium ions. Whittingham⁷ and his group explored hydrothermal medium of acidified molybdates for crystallizing hexagonal molybdates, $M_y Mo_{6-x} O_{18-x} H_{4x-y} \cdot zH_2O$ where $M = Na, NH_4$ and Ag. In addition, they also obtained a new hexagonal hydrate, $MoO_3 \cdot 0.6H_2O$ using acid ion-exchange. There are a few other reports on the synthesis of mixed-valent hexagonal phase with the composition $M_x Mo_6 O_{18}$.^{8,9} While $(NH_4)_6 Mo_6 O_{18}$ was prepared from a hydrothermal route

[†]Dedicated to Professor C N R Rao on his 70th birthday

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using hydroxylamine hydrochloride as a reducing agent, a cesium analogue was obtained from a solid state reaction around 600°C. In addition, vanadium stabilised hexagonal molybdates are also reported in the literature.^{10–12}

In this paper, we describe our results on the formation of hexagonal molybdates in the presence of monovalent cations without using any acid. We could directly precipitate highly crystalline single phasic lithium, rubidium, cesium and ammonium analogues under hydrothermal condition. Under our reaction condition, sodium and potassium analogues were invariably obtained with unreacted $\mathbf{a}\text{MoO}_3$.

2. Experimental

A mixture of MoO_3 and MCl ($\text{M} = \text{Li, Na, K, Rb, Cs, Tl}$ and NH_4) taken in 1:3 molar ratio was suspended into 7 ml water and was sealed in an 11 ml acid digestion reactor. The reactor was heated at 180°C for 36 h under autogeneous pressure. In the case of silver, silver nitrate was used. In all the cases, the pH of the initial mixture was around 6.0 and pH of the solution after hydrothermal precipitation was around 1–2. The colourless or creamish precipitates were washed off with water, acetone and dried under vacuum. In a few cases, reactions were also carried out in the presence of other alkali salts (bromide, iodide, and nitrate). Our results show the formation of only fully oxidised hexagonal molybdates and the anions has no influence on the nature of the phase or crystallinity of the materials. When we treated $\mathbf{a}\text{MoO}_3$ suspended in water hydrothermally at 180°C for 36 h, no new phase was formed.

2.1 Characterisation

FTIR spectra were recorded on KBr pellets using Nicolet 5DX spectrophotometer. TGA and DTA analyses were carried out using Perkin-Elmer TGA7 and DTA7 systems on well ground samples in nitrogen atmosphere with a heating rate of 5 or 10°C/min. Powder X-ray diffraction patterns were recorded on a Bruker D8 Advance diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{\AA}$). SEM photographs were recorded on a Cambridge Streoscan 360 microscope. EDAX analysis was carried out using Leica 4401.

3. Results and discussion

Powder X-ray diffraction (XRD) analysis revealed the formation of single phasic hexagonal molybdates in the case of Li, Rb, Cs and NH_4 (figure 1 and table 1). XRD patterns could be unambiguously indexed on a hexagonal cell with $a \sim 10.5$ and $c \sim 3.7\text{\AA}$ with space group $P6_3/m$. In all the cases, a few very weak unidentified reflections were observed. The cell parameters indicate that the size of the cations have little influence on the c parameter but the a parameter shift significantly. However there is no correlation between the size of the cations and the cell volume as the amount of water molecules vary. Under our reaction condition, sodium and potassium analogues invariably precipitated along with unreacted $\mathbf{a}\text{MoO}_3$. Increasing reaction time, temperature or decreasing pH of the initial solution with concentrated HCl or HNO_3 or change in molar ratio of the reactants did not result in a single phase. The reaction of $\mathbf{a}\text{MoO}_3$ with thallium chloride under hydrothermal condition yielded a new unidentified phase. In the case of silver we ended up with a poorly crystalline unidentified phase.

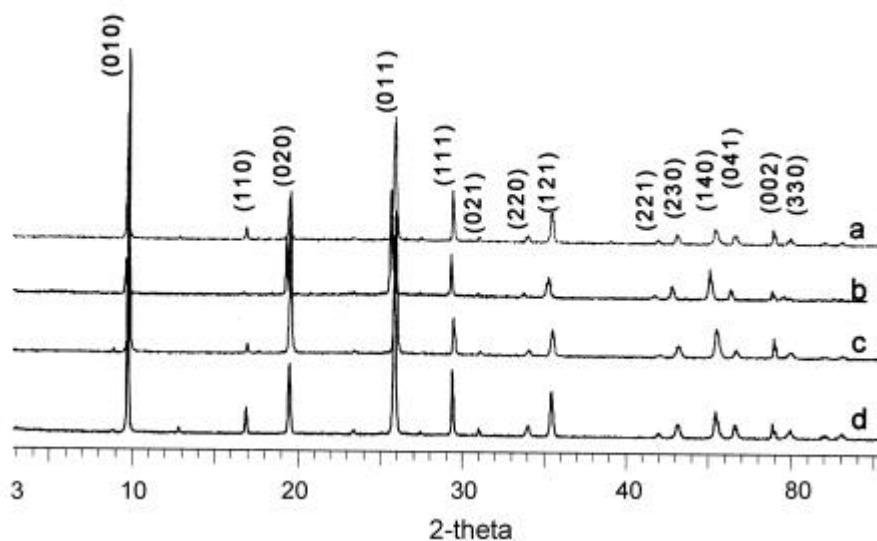


Figure 1. Powder XRD patterns of hexagonal molybdates, $M_x^+M_o_{6-x/3}^{6+}O_{18-x}(OH)_x \cdot yH_2O$: (a) $M = Li$, (b) $M = Rb$, (c) $M = Cs$ and (d) $M = NH_4$.

Table 1. Refined cell parameters and chemical analysis for $M_xM_o_{6-x/3}O_{18-x}(OH)_x \cdot yH_2O$.

M in $M_xM_o_{6-x/3}O_{18-x}(OH)_x \cdot yH_2O$	Ionic radius of M (\AA)	Cell parameters		Cell volume (\AA^3)	Value of y (from TGA)	Value of x (from EDAX)
		a (\AA)	c (\AA)			
Li^+	0.92	10.5852 (4)	3.7288 (2)	361.8	1.17	—
Rb^+	1.52	10.6245 (6)	3.7280 (6)	359.5	0.81	0.75
Cs^+	1.67	10.6243 (6)	3.7247 (5)	364.1	1.00	1.25
NH_4^+	1.48	10.5760 (4)	3.7280 (2)	361.1	0.55	0.81

*See reference 14

FTIR spectra of the hexagonal molybdates showed a sharp band at 975 cm^{-1} owing to the characteristic Mo=O double bond stretch as observed for $aMoO_3$. The peaks around 1610 and 3550 cm^{-1} respectively are assigned to the bending modes of coordinated water molecules and OH stretching of hydroxyl group. The bending modes of Mo—O—H appear around 910 cm^{-1} . In addition to these peaks, ammonium analogue showed peaks around 3200 and 1400 cm^{-1} characteristic of N—H vibrations. SEM photographs of the phases with Li, Rb, Cs and NH_4 showed well-defined hexagonal habits (figure 2) as observed in the literature.^{7,10} All the samples contain varying amounts of water depending on the nature of the cation (figure 3). The light colour of the solids, suggest that molybdenum is present in the highest oxidation state (+6). On the basis of chemical analysis (flame photometry, TGA and EDAX), the composition of the phases are found to be closer to the composition, $M_xM_o_{6-x/3}O_{18-x}(OH)_x \cdot yH_2O$ (refer table 1).

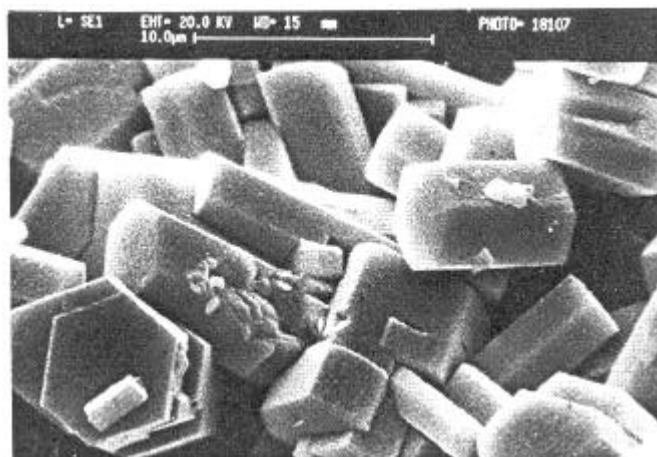


Figure 2. SEM photograph of lithium hexagonal molybdate.

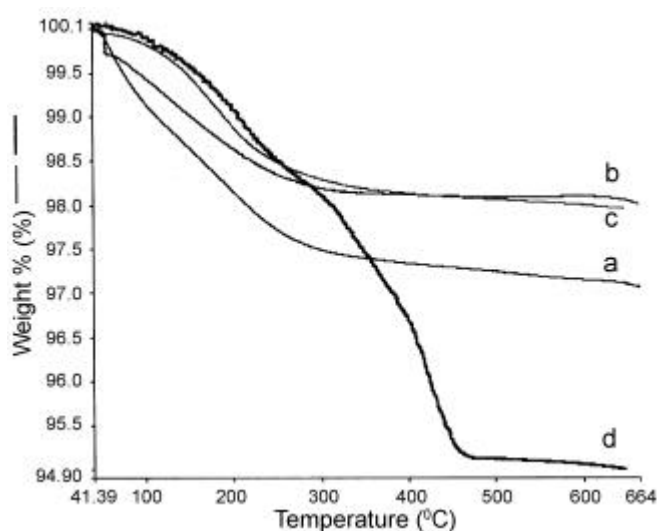


Figure 3. TGA of hexagonal molybdates, $M_x^+Mo_{6-x/3}^{6+}O_{18-x}(OH)_x \cdot yH_2O$: (a) $M = Li$, (b) $M = Rb$, (c) $M = Cs$ and (d) $M = NH_4$.

TGA analysis of the alkali intercalated hexagonal molybdates (figure 3) showed a continuous weight loss till 300°C due to coordinated water molecules. We have discounted the possibility of physically adsorbed water molecules by drying the samples under vacuum. DTA showed a sharp endothermic peak around 600°C for Rb and Cs analogues (figure 4). We recorded powder XRD of Li, Rb and Cs samples heated at different temperatures in the furnace. The data for cesium (figure 5) clearly show that the hexagonal phase is stable till 580°C. This is in contrast to the observations made in the literature.¹⁰ XRD patterns recorded at different temperatures showed the conversion of hexagonal phase into more stable αMoO_3 above this temperature (figure 5). The broad

DTA curves for lithium and ammonium is due to loss of water and decomposition of ammonia over a wide temperature range. We have confirmed the presence of lithium, but could not estimate it quantitatively due to solubility problems. We have discounted the possibility of $(\text{H}_3\text{O})^+$ instead of lithium on the basis of TGA and powder XRD. Compositions of the other phases given in table 2 were based on EDAX and TGA. The amount of cesium estimated from EDAX appears to be higher though the amount of alkali in the framework cannot exceed one per Mo_6O_{18} .

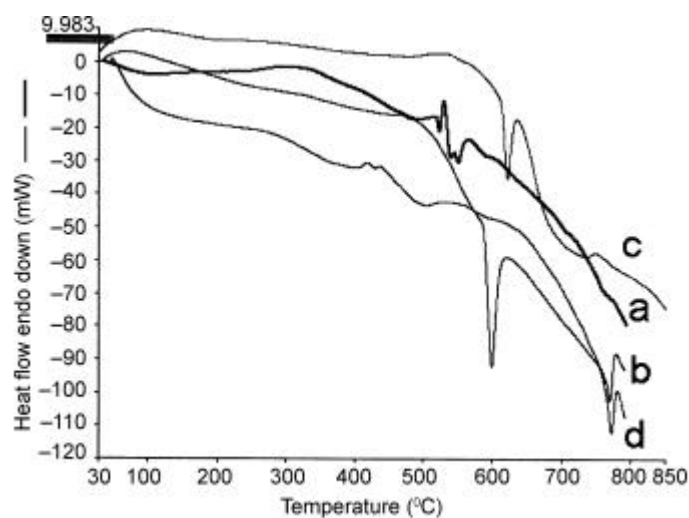


Figure 4. DTA of hexagonal molybdates, $\text{M}_x^+\text{Mo}_{6-x/3}^{6+}\text{O}_{18-x}(\text{OH})_x\cdot y\text{H}_2\text{O}$: (a) $\text{M} = \text{Li}$, (b) $\text{M} = \text{Rb}$, (c) $\text{M} = \text{Cs}$ and (d) $\text{M} = \text{NH}_4$.

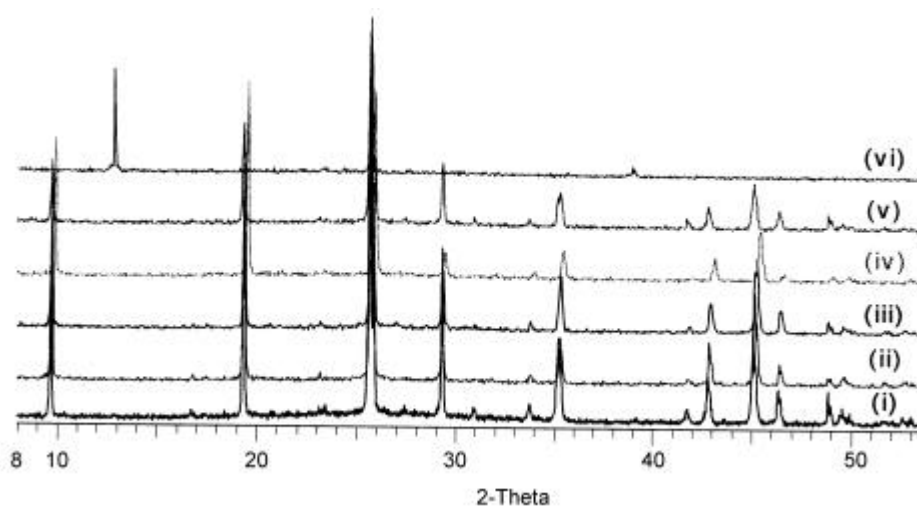
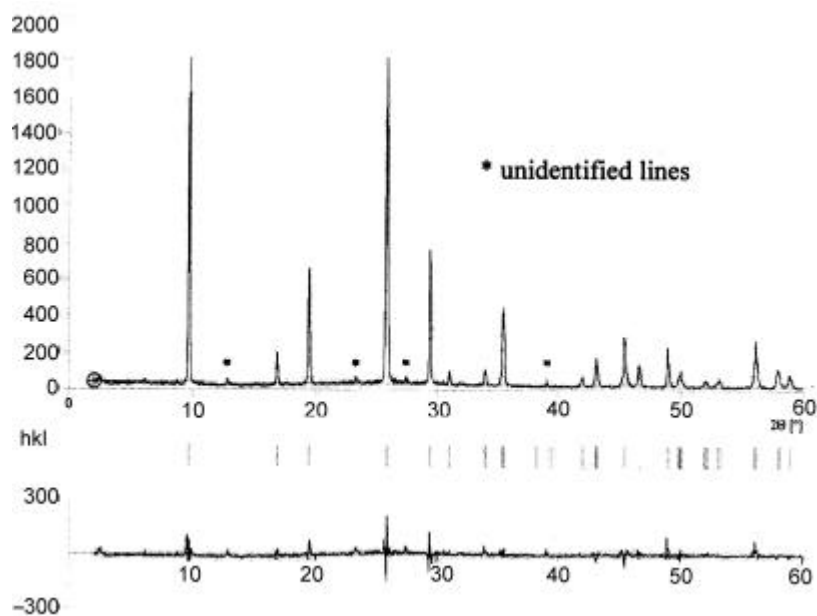
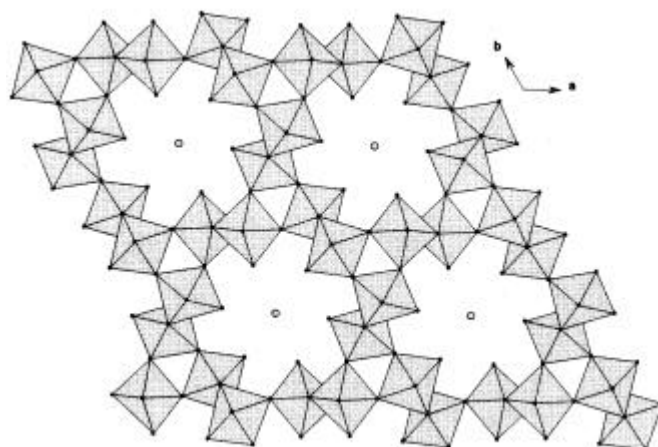


Figure 5. Powder XRD patterns of cesium hexagonal molybdate at different temperatures: (i) 200°C, (ii) 350°C, (iii) 400°C, (iv) 500°C, (v) 600°C and (vi) 650°C.

Table 2. Refined atomic coordinates for lithium molybdate.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Mo	-0.1035 (6)	-0.4588(6)	0.25
O1	-0.2110 (37)	-0.7003(43)	0.25
O2	0.0669 (30)	-0.5058(29)	0.25
O3	-0.0204 (33)	-0.2288(28)	0.25
Li	0	0	0.25

**Figure 6.** Rietveld profile of lithium molybdate showing the observed and difference plots ($R_p = 18.0$ and $R_{wp} = 25.4$).**Figure 7.** Structure of lithium hexagonal molybdate viewed along [001].

For further structural detail of synthesised samples, we carried out Rietveld treatment of the powder XRD data. Atomic coordinates of sodium molybdate⁷ were taken as a starting model in the space group $P6_3/m$. Preliminary structural analysis revealed the structure to be closer to other hexagonal molybdates (figure 6). While the cell parameters, profile parameters and the molybdenum and framework oxygen positions refine closer to the initial model (table 2), we were unable to refine the alkali metal position and oxygen of water molecules satisfactorily. The crystal structure of hexagonal molybdate is shown in figure 7. The framework $\text{Mo}_{6-x/3}\text{O}_{18-x}(\text{OH})_x$ is built of corner-shared as well as edge-shared molybdenum octahedra. In the structure zigzag chains of edge-shared MoO_6 units propagate along the c -axis of the crystal; these chains are then corner-shared in such a way as to create a 1D hexagonal tunnel structure. The alkali atoms and the water molecules occupy the hexagonal tunnels. Single crystal X-ray and powder neutron diffraction studies are being carried out to determine its full structure.

4. Conclusions

The paper reports direct synthesis of four hexagonal molybdates, $\text{M}_x^+\text{Mo}_{6-x/3}^{6+}\text{O}_{18-x}(\text{OH})_{x,y}\text{H}_2\text{O}$ ($\text{M} = \text{Li}, \text{Rb}, \text{Cs}$ and NH_4) from the hydrothermal treatment of aMoO_3 in the presence of monovalent cation salts. The solids thus obtained showed exceptional thermal stability.

Acknowledgements

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