Layer-Structural $\text{R}_4\text{Mo}_7\text{O}_{27}$ ($R=Ce$ and Pr) Prepared by Thermal Degradation of $R$-Polyoxomolybdate Precursor

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Well-formed single crystals of $\text{R}_2\text{Mo}_5\text{O}_{27}$ ($R=Ce$ and Pr), novel phases in the $\text{R}_2\text{O}_5$-$\text{MoO}_3$ system, have been obtained by thermal degradation of $R$-containing polyoxomolybdate precursor, $[\text{R}_2(\text{H}_2\text{O})_2\text{Mo}_5\text{O}_{27}]_2\cdot n\text{H}_2\text{O}$, in air at 800°C 12 h. Both compounds crystallize in a flux of the dehydrated precursor as a result of loss of excess MoO$_3$. The two species are isomorphous with space group $C2/c$, $Z = 8$, $a = 4.6354(2)$ and $4.6046(2)$ nm, $b = 0.74853(3)$ and $0.74712(2)$ nm, $c = 1.43536(9)$ and $1.42640(5)$ nm, and $\beta = 100.897(2)$ and 101.006(2)°, for $R_4\text{Mo}_7\text{O}_{27}$ ($R=Ce$ and Pr), respectively. The structure is built up with two kinds of $[\text{R}(\text{MoO}_4)_2]$ double-layers and one $[\text{Mo}_3\text{O}_{11}]$ mono-layer, which are stacked alternately parallel to the (110) plane. An arrangement of $[\text{R}(\text{MoO}_4)_2]^+$ unit is different between the two $[\text{R}(\text{MoO}_4)_2]$ double-layers. The $\text{MoO}_3$ group in the mono-layer consists of one $\text{MoO}_3$ trigonal pyramidal corner-shared with two $\text{MoO}_4$ tetrahedra. In comparison with other rare earth molybdates, we found that several materials commonly have similar $[\text{R}(\text{MoO}_4)_2]$ double-layers. Details of their layer structures are discussed.

Key-words: Rare earth, Rare earth molybdate, Polyoxomolybdate, Thermal decomposition, Self-flux method, Crystal structure, Layer structure

1. Introduction

Although the $\text{R}_2\text{O}_5$-$\text{MoO}_3$ systems, where $R$ is rare earth element, have long been investigated, many of the structural studies are concentrated on well-known compositions such as $\text{R}_2(\text{MoO}_4)_3$ and $\text{R}_2\text{MoO}_5$, because of their applicability to optical and catalytic materials. Except for the above compounds whose single crystals can be grown by the Czochralski technique, most other rare earth molybdates are conventionally prepared by solid state reaction of the stoichiometric mixture of $\text{R}_2\text{O}_5$ and $\text{MoO}_3$. However, to avoid a vaporization of $\text{MoO}_3$, the reaction temperature should be selected below ca. 650°C. Such a low-temperature reaction requires long firing time, and the product is usually in a powdered form, which prevents single crystal structure determination. Recently, we established the thermal degradation process of $R$-containing polyoxomolybdates $[\text{R}_2(\text{H}_2\text{O})_2\text{Mo}_5\text{O}_{27}]_n\cdot n\text{H}_2\text{O}$ at high temperatures (750–850°C),$^{8,9}$ and the precursor has a polymeric octamolybdate $[\text{Mo}_8\text{O}_{27}]^{8-}$ attached by hexahydrated $[\text{R}(\text{H}_2\text{O})_6]^+$ cations, being considered as a stoichiometric mixture of $\text{R}_2\text{O}_5$:$\text{MoO}_3$.$^8$ $H_2O = 1:8$ : $(12+n)$ dispersed at a molecular level. The product can be controlled, to a certain extent, by changing the reaction temperature and time which govern the amount of $\text{MoO}_3$ vaporization. Moreover, crystals are well-formed and suitable for single crystal X-ray structure determination. We determined structures of several new and structurally unknown phases, which provide rich crystal chemistry of the $\text{R}_2\text{O}_5$-$\text{MoO}_3$ systems.$^{10,11}$ This paper describes the decomposition behavior of $[\text{R}_2(\text{H}_2\text{O})_2\text{Mo}_5\text{O}_{27}]_n\cdot n\text{H}_2\text{O}$ ($R=Ce$ and Pr) and structural details of the product $\text{R}_4\text{Mo}_7\text{O}_{27}$. Moreover, we demonstrate that the structure of $\text{R}_4\text{Mo}_7\text{O}_{27}$ ($R=Ce$ and Pr) is closely related to several other rare earth molybdates.

2. Experimental

2.1 Synthesis

The $R$-polyoxomolybdate, $[\text{R}_2(\text{H}_2\text{O})_2\text{Mo}_5\text{O}_{27}]_n\cdot n\text{H}_2\text{O}$ ($n = 6$ for $R=Ce; n = 8$ for Pr), was prepared by acidification (pH 3.0) of a stoichiometric mixture of $\text{R}_2\text{O}_5$ and $[\text{MoO}_4]^2-$ in a diluted aqueous solution. This was described in greater detail in our previous paper.$^{13,15}$ Found: Ce, 16.3; Mo, 41.0; $\text{H}_2\text{O}$, 17.2 wt%, and Pr, 16.0; Mo, 42.9; $\text{H}_2\text{O}$, 20.5 wt%. Calcd for $\text{Ce}_2\text{Mo}_5\text{O}_{27}(\text{H}_2\text{O})_6$: Ce, 15.53; Mo, 42.55; $\text{H}_2\text{O}$, 17.96 wt%, and $\text{Pr}_2\text{Mo}_5\text{O}_{27}(\text{H}_2\text{O})_8$: Pr, 15.30; Mo, 41.68; $\text{H}_2\text{O}$, 20.56 wt%.

A powder sample of $[\text{R}_2(\text{H}_2\text{O})_2\text{Mo}_5\text{O}_{27}]_n\cdot n\text{H}_2\text{O}$ (100 mg) was placed in a boat-shaped alumina container, fired rapidly at 800°C for 12 h in a furnace, and then quenched by exposure to ambient temperature (ca. 20–25°C). The detailed set up of the furnace, reaction container, and other firing conditions are described in our paper.$^8$

2.2 Thermogravimetric and differential thermal analyses (TG-DTA)

A TG-DTA of $[\text{R}_2(\text{H}_2\text{O})_2\text{Mo}_5\text{O}_{27}]_n\cdot n\text{H}_2\text{O}$ was performed on the ULVAC MTS9000 + TGD9600 system. Sample (40–50 mg) and reference ($\text{Al}_2\text{O}_3$) were placed in Pt-cells (diameter, 3 mm; depth, 3 mm), heated in air to 800°C at a rate of 10°C min$^{-1}$, and maintained for 1 h.

2.3 Single crystal X-ray crystallography

Single crystals of $\text{R}_4\text{Mo}_7\text{O}_{27}$ ($R=Ce$ and Pr) were fixed on glass fibers and mounted on a Rigaku RAXIS-RAPID imaging-plate X-ray diffractometer with graphite-monochromatized MoKα radiation (0.071069 nm). Structures were solved by SIR92$^{13}$ and refined with full-matrix least-squares techniques. All atoms were refined anisotropically. Numerical absorption correction was done using SHAPE$^{14}$ and NUMABS.$^{15}$ All calculations were carried out using the software package, CrystalStructure.$^{16}$ The complete crystallographic data and results of the refinements are summarized in Table 1. Further details of the crystal structures can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247–808–666; email: crysdata@fiz-karlsruhe.de; URL: http://www.fiz-karlsruhe.de) on quoting the depository numbers CSD-413477 ($\text{Ce}_4\text{Mo}_7\text{O}_{27}$) and CSD-413478 ($\text{Pr}_4\text{Mo}_7\text{O}_{27}$).

3. Results and discussion

3.1 Thermal decomposition behavior

Figure 1 displays the TG (middle) and DTA (bottom) curves for $[\text{R}_2(\text{H}_2\text{O})_2\text{Mo}_5\text{O}_{27}]_n\cdot n\text{H}_2\text{O}$ ($R=Ce$ and Pr) under controlled temperatures (top). Dehydration corresponding to
an elimination of all 18–20H₂O is completed twice up to ca. 330°C to form an R₂MoO₅₂ anhydrate, which exhibits amorphous in XRD pattern. The exotherm at ca. 416–417°C with no weight change may be due to recrystallization of the amorphous phase, because some XRD peaks appear above this temperature (data not shown). At ca. 669–689°C, melting of the sample occurs with an accompanying sharp endothermic peak (s). The two endotherms at 669 and 689°C for R = Pr suggest the presence of two crystalline phases formed at 416°C. The continuous endotherm together with a large weight loss at > 650°C is due to vaporization of MoO₃. Similar thermal behavior has been observed for R = Eu and Gd analogs.⁷

R₄MoO₁₇₂ (R = Ce and Pr) was formed as dark red-brown and pale green crystals as shown in Fig. 2. Because the crystal growth occurs gradually in the melting of the precursor at 800°C, the crystallization can be categorized as a self-flux process. After the 800°C-decomposition for 12 h, the flux had almost disappeared, and only a lump of the product remained.

The decomposition can be schematized as follows.

\[ 2[R_2(OH)_3]_2MoO_27 \cdot nH_2O \rightarrow R_2MoO_25 \cdot 9MoO_3 + (24 + 2n)H_2O \]

The released MoO₃ appears at both sides of the cylindrical furnace in the form of pure needle-shaped crystals, which can be collected and reused for preparation of \( [R_2(OH)_3]_2MoO_27 \cdot nH_2O \). Decomposition at a lower temperature (750°C, 2 h) gave crystals of known species, \( R_2MoO_15 \cdot (R = \text{Ce and Pr}) \).⁷⁻¹⁻¹, which has a slightly higher MoO₃ content (\( R_2O_3 : MoO_3 = 1 : 4 + 2 = 8 \)) than \( R_2MoO_27 \). (2 : 7).

3.2 Structural description of \( R_4MoO_{172} \) (R = Ce and Pr)

The \( R_4MoO_{172} \) is a novel phase in the \( R_2O_3-MoO_3 \) (R = Ce and Pr) system, although we have reported \( R_2MoO_{15} \) (R = Eu and Gd) having the same \( R_2O_3 : MoO_3 = 2 : 7 \) composition but different structure (see Sect. 3.3). The crystal structure of \( R_4MoO_{172} \) (R = Ce and Pr) is represented in Fig. 3a. The R = Ce and Pr compounds are isostructural, consisting of an R
Fig. 1. Thermal analysis of [R2(H2O)2(MoO4)2]·nH2O with R = Ce (solid line) and Pr (broken line). Top: temperature variation with time. Middle: TG curves. Bottom: DTA curves. The inserted numbers are temperature ranges at which endo- or exotherms occur.

Fig. 2. Single crystals of R5Mo2O11 (R = Ce and Pr).

Fig. 3. Structures of R5Mo2O11 where R = Ce and Pr (a), and R = Eu and Gd (b). Parallel to the c-axis. Plain and hatched polyhedra are MoO4 and MoO3, respectively. Spheres denote R atoms.

(\text{MoO}_4^2-)−containing double-layer \((\text{MoO}_3\text{Pr})_2\) and MoO4-containing mono-layer \((\text{MoO}_3\text{Ce})_2\) which are stacked alternately parallel to the (011) plane with an interlayer distance of 0.565\((a\sin\beta)/8\) nm. There are two kinds of double-layers: described as \((\text{MoO}_3\text{Pr})_2\) and \((\text{MoO}_3\text{Ce})_2\) in Fig. 3a, in which the arrangement of R and MoO4 tetrahedra is different (details will be discussed in 3.3). The layer sequence in \(R_5\text{Mo}_2\text{O}_{11}\) \((R = \text{Ce}, \text{Pr})\) is described to be \(\cdots (\text{MoO}_3\text{Pr})_2(\text{MoO}_3\text{Ce})_2(\text{MoO}_3\text{Pr})_2(\text{MoO}_3\text{Ce})_2\cdots\). Selected interatomic distances are listed in Table 2. The MoO41 group comprises a distorted Mo(1)O3 trigonal bipyramid (defined by equatorial O(1,2,4) and polar O(3,6) atoms) and Mo(2,3)O4 tetrahedra sharing the corer−O(6,4) atoms, respectively (Fig. 4a). Because the apical Mo(1)−O(6) bond distance (0.2690(7) nm for Ce, 0.2660(6) nm for Pr) is much longer than other Mo−O bonds (mean 0.1772−0.1773 nm for Ce and Pr), the geometry of the Mo(1)O3 polyhedron can also be regarded as a O(6)−capped Mo(1)O4 tetrahedron. In both \((\text{MoO}_3\text{Pr})_2\) and \((\text{MoO}_3\text{Ce})_2\), the MoO4 tetrahedra are isolated and bonded only to R atoms. Figures 4b and 4c show R and surrounding O−ligands with R−O distances shorter than 0.29 nm. Each of the R(1) and R(2) atoms achieves 9−fold coordination by O atoms (Fig. 4b). The resulting \(R_1\text{O}(\text{Pr})_4\) polyhedra are connected by sharing \([\text{O}(\text{Pr})_4(\text{O})_2(\text{O})_2]\)−face and \([\text{O}(\text{Pr})_2(\text{O})_2]\)−edge, forming an infinite zigzag \(R_5\text{Mo}_{11}\) chain running along the b-axis with \(R(1)\cdots R(2)\) separations of 0.41315(7) and 0.41889(7) nm for \(R = \text{Ce}\), and 0.41175(4) and 0.41752 nm for \(R = \text{Pr}\). This chain structure bears a resemblance to that of \([\text{La}_3\text{O}_{19}]^\infty\) observed in \(\beta\)-La3Mo10O42,12 in this case \(\cdots \text{La}−\cdots \text{La}−\cdots \text{La}−\cdots\) framework is almost linear. On the other hand, both the R(2) and R(3) centers are 8−coordinate with distorted square-antiprismic conformation (Fig. 4c). The \(R(2,3)\text{O}_4\) polyhedra share their \([\text{O}(\text{Pr})_4(\text{O})_2(\text{O})_2]\)−face to form a dimeric \(R_5\text{Mo}_{11}\) group with \(R(3)\cdots R(4)\) separations of 0.38836(6) and 0.38457(4) nm for \(R = \text{Ce}\) and \(\text{Pr}\), respectively. In the \(R_5\text{Mo}_{11}\) (R = Eu and Gd) compounds (Fig. 3b), all of the R atoms are 7− and 8−coordinate by O atoms, and dimerized to \(R_5\text{O}_{12}\) and \(R_5\text{O}_{13}\) groups, forming no chain structure. We tentatively conclude that the \(R^3+\) cation with larger ionic size (viz. lower atomic number) prefers the \(R_5\text{Mo}_{12}\) (R = Ce and Pr) structure because of a tendency to take higher coordination numbers.

3.3 Comparison with other layered rare earth molybdates
It is noteworthy that other rare earth molybdates, \(R_5\text{Mo}_{12}\) (R = Eu and Gd), \(R_5\text{Mo}_{15}\) (R = Ce and Pr), 17,18 and \(\beta-R_5\text{Mo}_{12}\) \((R = \text{Pr−Ho})\), 19 commonly have \((\text{MoO}_3\text{O}_4)_2\) double-layer blocks with slightly different structures depending on the compounds. We note that any \((\text{MoO}_3\text{O}_4)_2\) layer is composed of a basis structural unit \((\text{MoO}_3\text{O}_4)_2\)− an R atom attached by one apex of a MoO4 tetrahedron (see scheme in Fig. 5).

First, we compare the structures of \((\text{MoO}_3\text{O}_4)_2\) and \((\text{MoO}_3\text{O}_4)_2\) layers in \(R_5\text{Mo}_{12}\) (R = Ce and Pr) (Fig. 5). In both layers, the R−bonded apex of the MoO4 tetrahedron points to two opposite directions (upward and downward of the layers). However, the \((\text{MoO}_3\text{O}_4)_2\)− units are differently arrayed in two layers. When we notice the linkage of R atoms by bridging O atoms (black circles) in Fig. 5, it is clearly shown how the structure of \((\text{MoO}_3\text{O}_4)_2\) enables R(3) and...
Table 2. Selected Interatomic Distances (nm) in $R_2\text{Mo}_7\text{O}_{27}$ ($R = \text{Ce}$ and Pr)

<table>
<thead>
<tr>
<th>$R$</th>
<th>$R_1$-O21#1</th>
<th>$R_2$-O6</th>
<th>$R_3$-O12</th>
<th>$R_4$-O16#3</th>
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<tr>
<td>Ce</td>
<td>0.2383(4)</td>
<td>0.2354(4)</td>
<td>0.2382(5)</td>
<td>0.2394(6)</td>
</tr>
<tr>
<td>Pr</td>
<td>0.2408(6)</td>
<td>0.2392(4)</td>
<td>0.2384(5)</td>
<td>0.2367(6)</td>
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<td>0.2408(6)</td>
<td>0.2392(4)</td>
<td>0.2384(5)</td>
<td>0.2367(6)</td>
</tr>
</tbody>
</table>

Symmetry operations: (1#): 3/2-x, 1/2-y, -z (2#): x, -y, -1/2+z (3#): 1+x, -1+y, 1+z (4#): x, 1-y, 1/2+z

(5#): 3/2-x, 1/2+y, 1/2-z (6#): x, 1+y, z (7#): x, -y, 1/2+z (8#): 2-x, -y, -z

$R(4)$ to be paired, while that of $\{R(\text{MoO}_4)^{2-}\}_2$ induces the zigzag polymerization of $R(1)$ and $R(2)$. The structure of $R_2\text{Mo}_7\text{O}_{27}$ ($R = \text{Eu}$ and Gd)$^{17}$ (Fig. 3b) is similar to that of the $R(= \text{Ce and Pr})$ compounds except for the absence of a $\{R(\text{MoO}_4)^{2-}\}_2$ layer, resulting in formation of $\cdots\{R(\text{MoO}_4)^{2-}\}_2\{\text{MoO}_4\}_2\cdots$ layer repetition. Hence, as mentioned previously, $R_2\text{Mo}_7\text{O}_{27}$ ($R = \text{Eu}$ and Gd) does not have the zigzag $\{R(\text{O})_8\}_4$ chain unlike the $R(= \text{Ce and Pr})$ analogs. On the other hand, $R_2\text{Mo}_7\text{O}_{27}$ ($R = \text{Ce}$ and Pr)$^{17,18}$ (Fig. 6) consists of $\{R(\text{MoO}_4)^{2-}\}_2$ and $\{\text{MoO}_4\}_2$ layers piled up alternately along the $a$-axis, to give a repetition of $\cdots\{R(\text{MoO}_4)^{2-}\}_2\{\text{MoO}_4\}_2\cdots$. The $\{\text{MoO}_4\}_2$ layer contains a $\{\text{MoO}_4\}_2$ polymeric chain, which is composed of Mo$,\text{O}_2$ tetrahedra and Mo$\text{O}_4$ octahedra, along the $c$-axis. The structure of $\{R(\text{MoO}_4)^{2-}\}_2$ (Fig. 6 bottom) is derived from $\{R(\text{MoO}_4)^{2-}\}_2$ (Fig. 4 left) by gliding two rows of the $\{R(\text{MoO}_4)^{2-}\}_2$ unit toward opposite directions (indicated by arrows in Fig. 5 left), thereby all $R$-$R$ pairs become parallel. The last example, $\beta-R_2(\text{MoO}_4)_3$,$^{19}$ which is obtained for a wider range in the rare earth series ($R = \text{Pr-Ho}$), exhibits a $\cdots\{R(\text{MoO}_4)^{2-}\}_2\{R(\text{MoO}_4)^{2-}\}_2\cdots$ layer structure as shown in Fig. 7 top. The structure of $\{R(\text{MoO}_4)^{2-}\}_2$ (Fig. 7 bottom) also induces the pairing of $R$ atoms with parallel $R$-$R$ direction. It should be noted that small rotation of each $\{R(\text{MoO}_4)^{2-}\}_2$ unit in $R_2(\text{MoO}_4)_3$ gives rise to formation of low temperature form, $\beta-R_2(\text{MoO}_4)_3$, which exhibits interesting ferroelectric/ferroelastic properties.$^{1,19}$

4. Summary

Firing of $[R_2(\text{H}_2\text{O})_2\text{MoO}_{27}]\cdot n\text{H}_2\text{O}$ ($R = \text{Ce and Pr}$) at 800°C in air causes dehydration (RT–300°C), crystallization (416–417°C), and melting (669–689°C) with accompanying intense vaporization of MoO$_3$. Two new layered compounds $R_2\text{Mo}_7\text{O}_{27}$ ($R = \text{Ce and Pr}$) are crystallized in the flux of the dehydrated precursor. The structure can be character-
Fig. 4. Structures of (a) MoO$_3$, (b) [R$_2$O$_{13}$]$_n$ chain, and (c) R$_2$O$_3$ groups in CeMoO$_3$. All symmetry operations have been omitted.

Fig. 5. Idealized structures of $\langle R$ (MoO$_4$) $\rangle_2$ (left) and $\langle R$ (MoO$_4$) $\rangle_6$ (right) double-layers observed in R$_2$MoO$_3$ ($R$ = Ce and Pr). Filled large circles: R atoms. Small black circles: O atoms linking R. Gray triangles represent basal planes in the MoO$_3$ groups. R–R connections in the [R$_2$O$_{13}$]$_n$ chains and R$_2$O$_3$ groups are denoted with thick broken lines. Glide directions for producing $\langle R$ (MoO$_4$) $\rangle_2$ double-layer of R$_3$MoO$_3$ ($R$ = Ce and Pr) are denoted with arrows (see text).

Fig. 6. Structures of R$_2$MoO$_3$ ($R$ = Ce and Pr) (top) and $\langle R$ (MoO$_4$) $\rangle_6$ double-layer (bottom).$^{17,18}$

Fig. 7. Structures of $\beta$-R$_2$ (MoO$_4$)$_3$ ($R$ = Pr–Ho) (top) and $\langle R$ (MoO$_4$) $\rangle_6$ double-layer (bottom).$^{19}$

ized by two kinds of $\langle R$ (MoO$_4$) $\rangle_2$ double-layer and $\langle MoO$_3$ $\rangle$ mono-layer which are piled up alternately. We found that the $\langle R$ (MoO$_4$) $\rangle_2$ double-layer is commonly observed in several rare earth molybdates: R$_2$MoO$_3$ ($R$ = Ce and Pr), R$_2$MoO$_3$ ($R$ = Eu and Gd), R$_2$MoO$_3$ ($R$ = Ce and Pr), and $\beta$-R$_2$ (MoO$_4$)$_3$ ($R$ = Pr–Ho) can be re-formulated as $\langle R$ (MoO$_4$) $\rangle_2$ $\langle R$ (MoO$_4$) $\rangle_2$ (MoO$_3$)$_n$, $\langle R$ (MoO$_4$) $\rangle_2$ (MoO$_3$)$_n$, $\langle R$ (MoO$_4$) $\rangle_2$ (MoO$_3$)$_n$, $\langle R$ (MoO$_4$) $\rangle_2$ (MoO$_3$)$_n$, and $\langle R$ (MoO$_4$) $\rangle_2$ (MoO$_3$)$_n$, respectively. An arrangement pattern of the $\langle R$ (MoO$_4$) $\rangle_6$ units in the $\langle R$ (MoO$_4$) $\rangle_2$ layers differs among these compounds.

References


