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# Hydrothermal Synthesis and Thermal Stability of Natural Mineral Lindgrenite*

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A natural mineral, lindgrenite $Cu_3(MoO_4)_2(OH)_2$, was synthesized from a mixture of sodium molybdate, copper sulfate, and morpholine in water under autogenous pressure at 170 ℃. The crystal structure of the mineral was determined and the final refinement for 791 observed reflections with $I>2\sigma(I)$ gave $R_1=0.0205$ and $wR_2=0.0496$. The thermal stability of the mineral was investigated by using TG-DTA and variable-temperature *in situ* X-ray diffraction(XRD) techniques. The crystalline $Cu_3Mo_2O_9$ was obtained when the mineral underwent thermal dehydration at a temperature ranging from 300 to 400 ℃, and the mixture of $MoO_3$ and CuO was formed through decomposition of $Cu_3Mo_2O_9$ at a temperature ranging from 650 to 700 ℃. Therefore, the structure of the mineral was thermally unstable at above 300 ℃, suggesting that Lindgrenite was likely formed *via* the hydrothermal route occurring in the nature.

**Keywords** Hydrothermal synthesis; Lindgrenite; Structural refinement; Composite metal oxide; Thermal stability
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## Introduction

Synthesis of natural minerals is helpful for tracing the geological origin of mineral formation and for verifying the quality of minerals. The investigations on the conditions for mineral formation, such as pressure, temperature, and starting materials, help mineralogists to explore the minerals in specific zones, where the geological reactions had once occurred under the similar conditions mentioned above.

The structural determination and composition analysis of the synthetic mineral crystals may establish the standards for evaluating the quality and purity of the natural minerals. Also, the synthetic approach may facilitate the large-scale production of low cost, high-quality natural minerals, in particular, those that have high technological and economic interest but are rare or are less pure in nature[1].

Furthermore, the synthesis of natural minerals initiates the search for materials with better properties and wider applications compared with the synthesis of synthetic minerals, such as numerous synthetic zeolites. For the synthesis of minerals, mineralogists extensively use a mild hydrothermal technique for the formation of various minerals, and even today it is of significance in the field of geological sciences[2] and is being used in synthetic chemistry for the synthesis of products ranging from porous materials to inorganic-organic hybrids[3].

Lindgrenite is a hydroxyl copper molybdate, $Cu_3(MoO_4)_2(OH)_2$, which associates with antlerite and iron oxide in massive quartz veins from Chuquicamata, Chile[4] and results from the oxidation of primary molybdenite. Its structure has been determined[5] and refined by the selective crystal of the natural mineral[6].

The hydrothermal synthesis of lindgrenite from an aqueous system of sodium molybdate, copper sulfate, and morpholine under autogenous pressure at 170 ℃ was reported in this study. The crystal structure of the mineral was further refined to give smaller $R$ values than the previous results[5—7]. As the thermal stability

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** To whom correspondence should be addressed. E-mail: yuebin@fudan.edu.cn of the mineral may be related to its natural origin, the schematic thermal transformation from lindgrenite to the metastable $Cu_3Mo_2O_9$ is also described in details.

## Experimental

### 1 Synthesis

Lindgrenite was prepared from a mixture of $Na_2MoO_4 \cdot H_2O$, $CuSO_4 \cdot 5H_2O$, and $C_4H_9NO$ in $H_2O$ with a molar ratio of 1∶1∶1.5∶1389 in an autoclave heated at 170 ℃ for 5 d under autogenous pressure. After the reaction, the autoclave was gradually cooled to room temperature and black strip crystals with *ca.* 10% yield (calculated according to the amount of Cu at charge) were obtained and washed with water.

### 2 Structural Determination

A single crystal with dimensions 0.15 mm × 0.10 mm × 0.10 mm was selected for X-ray diffraction. The structural determination was carried out on a Bruker SMART CCD diffractometer through $\omega$ scans and graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.071073$ mm). The structure was solved by using the direct method and refined *via* full-matrix least-squares on $F^2$ values using SHELXTL and SHELXTL-97[8,9]. All the nonhydrogen atoms were anisotropically refined, and hydrogen atoms were generated and included in the calculations pertaining to the structure using the assigned isotropic thermal parameters; however, they were not refined. For the full-matrix least-squares refinements [$I > 2\sigma(I)$], the unweighted and weighted agreement factors of $R_1 = (|F_o| - |F_c|/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ were used. Crystallographic data (including structure factors) have been deposited at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, and are available on quoting the deposition number CSD No. 415190.

### 3 Thermal Stability

The TG-DTA measurement was carried out by using a Perkin-Elmer TGA 7 thermogravimetric analyzer at a nitrogen flow of 100 mL/min at 25—800 ℃ at the rate of 0.2 ℃/s.

XRD patterns were recorded on a Bruker D8 Advanced X-ray diffractometer with Cu $K\alpha$ radiation at a voltage of 40 kV and a current of 40 mA. The variable temperature *in situ* XRD experiment was carried out from room temperature to 700 ℃ at a rate of 0.2 ℃/s under nitrogen atmosphere.

## Results and Discussion

At present, hydrothermal method using organic amine is being extensively used to establish a general approach for the preparation of inorganic-organic hybrids, where amine serves not only as the template but also as the structural unit, which is crucial for maintaining the integrity of the frameworks[10—13]. Interestingly, in this study the product was found to be free of organic component in its framework although it cannot be obtained from the system without morpholine under hydrothermal condition[7].

Experimental details of the X-ray data collection of the synthesized lindgrenite are summarized in Table 1, and the atomic coordinates and equivalent isotropic thermal parameters for nonhydrogen atoms are listed in Table 2.

**Table 1 Crystallographic data collection and structure refinement**

| | |
|---|---|
| Empirical formula | $H_4Cu_6Mo_4O_{20}$ |
| Molecular weight | 1089.03 |
| Temperature/K | 298(2) |
| Wavelength/nm | 0.071073 |
| Crystal system, space group | Monoclinic, $P2(1)/n$ |
| $a$/nm | 0.53867(10) |
| $b$/nm | 1.4001(3) |
| $c$/nm | 0.56010(11) |
| $\beta$/(°) | 98.535(2) |
| $V$/nm$^3$ | 0.41773(14) |
| $Z$ | 2 |
| $D_{calc}$/(Mg · m$^{-3}$) | 4.329 |
| Absorption coefficient/mm$^{-1}$ | 10.469 |
| $F(000)$ | 506 |
| Crystal size | 0.15 mm × 0.10 mm × 0.10 mm |
| $\theta$ Range for data collection | 3.96°—26.00° |
| Limiting indices | $-6 \leqslant h \leqslant 6$, $-15 \leqslant k \leqslant 17$,<br>$-6 \leqslant l \leqslant 4$ |
| Reflections collected/unique | 1861/812 |
| Absorption correction | Multiscan |
| Max and min transmission | 0.4208 and 0.3027 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameter | 812/0/75 |
| Goodness-of-fit on $F^2$ | 1.115 |
| Final $R$ indices[$I > 2\sigma(I)$] | $R_1 = 0.0212$, $wR_2 = 0.0496$ |
| $R$ indices(all data) | $R_1 = 0.0205$, $wR_2 = 0.0493$ |

**Table 2 Atomic parameters for $Cu_3(MoO_4)_2(OH)_2$**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Mo | 0.04373(6) | 0.34544(2) | 0.12285(6) | 0.0088(1) |
| Cu1 | 1/2 | 1/2 | 0 | 0.0100(2) |
| Cu2 | 0.13614(8) | 0.09392(3) | 0.01287(8) | 0.0108(2) |
| O1 | 0.3548(5) | 0.3870(2) | 0.1254(5) | 0.0129(5) |
| O2 | 0.0213(5) | 0.2233(2) | 0.0630(5) | 0.0196(6) |
| O3 | 0.1509(5) | 0.4079(2) | 0.0998(5) | 0.0168(6) |
| O4 | 0.0524(5) | 0.3701(2) | 0.4065(5) | 0.0151(6) |
| O5 | 0.1316(6) | 0.0306(2) | 0.1600(5) | 0.0113(6) |

Its single crystal structure is not significantly different from those of the natural mineral and the synthetic sample that have been obtained previously; smaller $R$ values ($R_1 = 0.0205$ and $wR_2 = 0.0496$) were observed in the present study[5—7]. The unsymmetrical unit contained two symmetrically distinct $Cu^{2+}$ positions, one symmetrically distinct $Mo^{6+}$ position, and five $O^{2-}$ positions [Fig. 1(A)]. Each $Cu^{2+}$ was coordinated by four $O^{2-}$ and two $OH^-$ in a distorted octahedral arrangement (Table 3) because of the well-known Jahn-Teller effect associated with a $d^9$ metal cation in an octahedral ligand-field[14]. The octahedral $Cu^{2+}\Phi_6$ ($\Phi$: unspecified ligand) share edges to form strips that are parallel to [001] and these strips are cross-linked by tetrahedral $MoO_4$ through corner-sharing octahedral $Cu^{2+}\Phi_6$, resulting in a three-dimensional tetrahedral-octahedral framework [Fig. 1(B)].

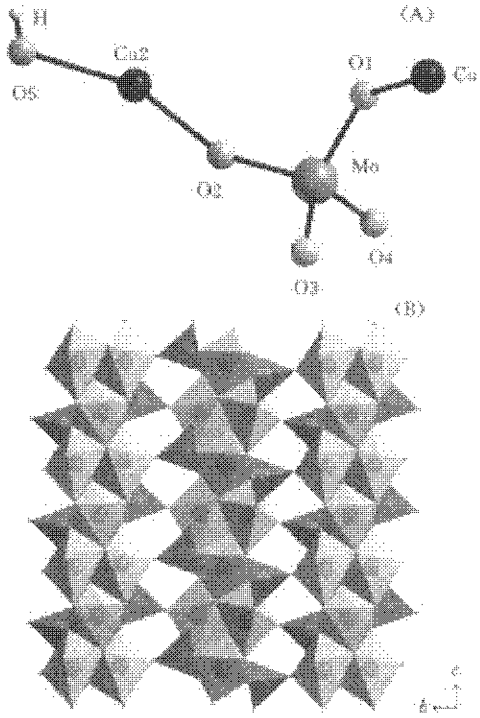


**Fig. 1 The unsymmetrical unit(A) and the crystal structure of lindgrenite projected onto (100)(B).**

The investigation on the thermal stability of lindgrenite may be related to the causative factor leading to the formation and the deposition of the mineral in the nature. TG-DTA curves obtained under nitrogen atmosphere are shown in Fig. 2. The TG curve displays a sharp weight loss of 3.26% in the region of 300—400 ℃, which can be assigned to dehydration (3.31% theoretical mass loss). The mass becomes constant in the region of 400—700 ℃. The sublimation of $MoO_3$ accounts for the further weight loss above 700 ℃. The DTA curve exhibits two distinct endothermic peaks centered at 386 and 668 ℃, corresponding to the dehydration of lindgrenite and phase transition of the remainder, respectively.

**Table 3 Comparison of selected bond lengths(nm) of $Cu_3(MoO_4)_2(OH)_2$ with $Cu_3Mo_2O_9$ ***

| $Cu_3(MoO_4)_2(OH)_2$ | | | |
|---|---|---|---|
| Mo—O1 | 0.1772(3) | Cu1—O5#10 | 0.1978(3) |
| Mo—O2 | 0.1743(3) | Cu1—O5#11 | 0.1978(3) |
| Mo—O3 | 0.1741(3) | Cu2—O1 | 0.2470(3) |
| Mo—O4 | 0.1777(3) | Cu2—O3#9 | 0.2299(3) |
| Cu1—O1 | 0.1942(3) | Cu2—O2 | 0.1948(3) |
| Cu1—O1#6 | 0.1942(3) | Cu2—O4#10 | 0.1929(3) |
| Cu1—O3#7 | 0.2413(3) | Cu2—O5#3 | 0.1993(3) |
| Cu1—O3#8 | 0.2413(3) | Cu2—O5 | 0.1974(3) |
| $Cu_3Mo_2O_9$ [15] | | | |
| Mo1—O7 | 0.179(2) | Mo2—O2 | 0.174(2) |
| Mo1—O6 | 0.169(2) | Mo2—O3 | 0.172(3) |
| Mo1—O8 | 0.174(3) | Mo2—O4 | 0.173(3) |
| Mo1—O5 | 0.186(3) | Mo2—O9 | 0.183(5) |
| Cu1—O5 | 0.221(3) | Cu2—O5 | 0.212(3) |
| Cu1—O8 | 0.227(3) | Cu2—O2 | 0.190(2) |
| Cu1—O9 | 0.211(5) | Cu3—O4 | 0.196(3) |
| Cu1—O4 | 0.224(3) | Cu3—O7 | 0.192(2) |
| Cu1—O1 | 0.179(9) | Cu3—O9 | 0.210(5) |
| Cu1—O1′ | 0.193(9) | Cu3—O6 | 0.239(2) |
| Cu2—O8 | 0.190(3) | Cu3—O3 | 0.253(2) |
| Cu2—O3 | 0.218(3) | Cu3—O1 | 0.195(2) |
| Cu2—O1 | 0.192(2) | | |

* Symmetry transformations used to generate equivalent atoms: #1 $x-1, y, z$; #2 $-x+1/2, y-1/2, -z+1/2$; #3 $-x, -y, -z$; #4 $x-1/2, -y+1/2, z-1/2$; #5 $x-1/2, -y+1/2, z+1/2$; #6 $-x+1, -y+1, -z$; #7 $x+1, y, z$; #8 $-x, -y+1, -z$; #9 $x+1/2, -y+1/2, z+1/2$; #10 $x+1/2, -y+1/2, z-1/2$; #11 $-x+1/2, y+1/2, -z+1/2$.

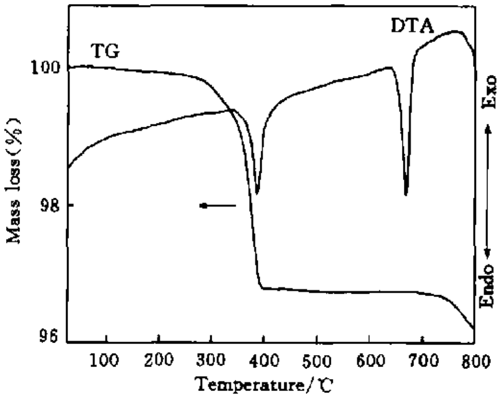


**Fig. 2 TG-DTA curves of lindgrenite.**

To further study the intermediates, metastable phases, or products during the thermal decomposition of lindgrenite and the structural relationship among them, variable-temperature *in situ* XRD was carried out at a temperature ranging from room temperature to 700 ℃ under nitrogen atmosphere. As shown in Fig. 3, the pattern exhibited at room temperature shows the characteristic diffractions, which can be indexed according to the crystal parameters of lindgrenite. At 300 ℃, the pattern shows no significant changes, indicating the stability of lindgrenite at this temperature.

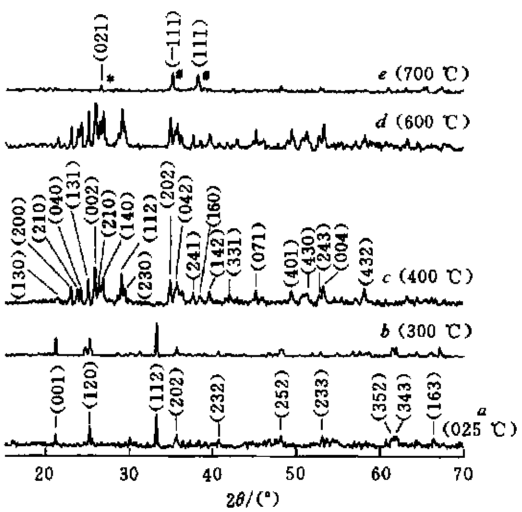


**Fig. 3 Variable-temperature *in situ* XRD patterns of lindgrenite.**

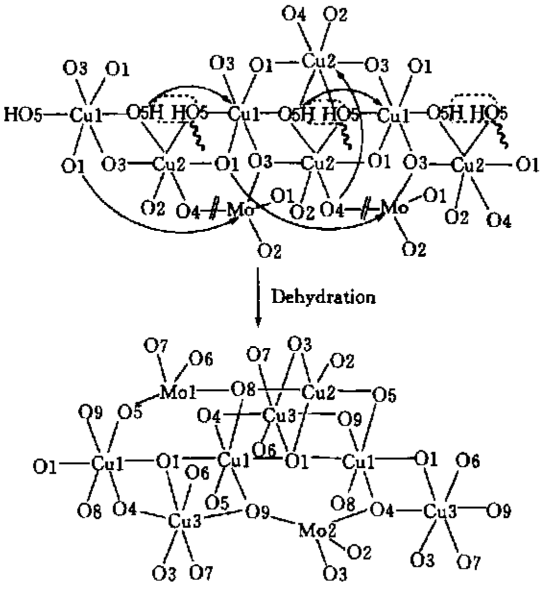
The peaks in curve *a* are attributed to lindgrenite and those in curve *c* to orthorhombic phase of $Cu_3Mo_2O_9$ with lattice constants of $a = 0.7659$ nm, $b = 1.4613$ nm, and $c = 0.6875$ nm (JCPDS 24-55). The * peak corresponds to orthorhombic phase of $MoO_3$ (JCPDS 5-508, $a = 0.3962$ nm, $b = 1.386$ nm, $c = 0.3697$ nm) and the # peaks to monoclinic phase of CuO (JCPDS 45-937, $a = 0.4685$ nm, $b = 0.3426$ nm, $c = 0.5130$ nm, $\beta = 99.55°$).

The appearance of a new set of diffraction peaks attributed to orthorhombic phase of $Cu_3Mo_2O_9$ (JCPDS 24-55) in Fig. 3*c* indicates that the dehydration of lindgrenite occurred between 300 and 400 ℃. The pattern at 600 ℃ remains unchanged; however, the pattern at 700 ℃ shows the thermal decomposition of $Cu_3Mo_2O_9$ leading to the formation of the mixture of monoclinic phase of CuO (JCPDS 45-937) and orthorhombic phase of $MoO_3$ (JCPDS 5-508). These results are consistent with the TG-DTA analyses. The thermal changes of lindgrenite are summarized as follows:

$$Cu_3(MoO_4)_2(OH)_2 \xrightarrow[-H_2O]{300\text{—}400\ ℃} Cu_3Mo_2O_9$$

$$Cu_3Mo_2O_9 \xrightarrow{650\text{—}700\ ℃} 3CuO + 2MoO_3$$

It is of interest to note that the structural change from lindgrenite to $Cu_3Mo_2O_9$ serves as an example for the dehydration of inorganic compounds with three-dimesional framework. Kihlborg *et al.*[15] has reported previously the preparation and the crystal structure of the copper (Ⅱ) molybdate $Cu_3Mo_2O_9$ by thoroughly heating the ground mixture of 3CuO + $2MoO_3$ in a sealed silica tube over 865 ℃ for 12 days and quenching the tube in water. $Cu_3Mo_2O_9$ contains the zigzag ribbons made up of octahedral copper, and these ribbons are linked by the edge-sharing copper pyramids and the corner-sharing tetrahedral molybdenum. In the present study, the decomposition of $Cu_3Mo_2O_9$ to CuO and $MoO_3$ in the range of 650—700 ℃ in the open system suggests that $Cu_3Mo_2O_9$ is metastable, and therefore, it is necessary that its preparation has to be carried out in a sealed tube at a high temperature with fast quenching[15]. The transformation from lindgrenite to $Cu_3Mo_2O_9$ described in Scheme 1 is based on their structural data shown in Table 3. The dehydration of lindgrenite resulted in a series of changes such as rupture and rearrangement of Cu—O and Mo—O bonds. During the dehydration, the octahedral coordination of Cu1 and the tetrahedral coordination of Mo1 in lindgrenite remained unchanged but Mo1 atoms were divided into two types of molybdenum atoms. A significant change was observed for Cu2 atoms, which included two types of copper atoms with octahedral Cu2 and square pyramidal Cu3 coordinations. From the structural point of view, the transition from lindgrenite to $Cu_3Mo_2O_9$ phase involves the synergic reformation of $Cu_3Mo_2O_9$ with the dehydration of lindgrenite.



**Scheme 1 The possible pathway for dehydration of lindgrenite $Cu_3(MoO_4)_2(OH)_2$ and formation of $Cu_3Mo_2O_9$.**

The postfix numbers to the atoms in lindgrenite are identical to the crystal unit in this study, whereas the postfix numbers to the atoms in $Cu_3Mo_2O_9$ are from ref. [15].

Furthermore, the structural similarity between lindgrenite and szenicsite $Cu_3MoO_4(OH)_4$ may be used to explain the cause of lindgrenite formation. Szenicsite is associated with powellite as fracture fillings and as crystals in vugs in a hydrothermally altered granitic matrix[16], which indicates the similar origin of lindgrenite in nature. Therefore, the present study implies the ubiquity of mineral formation under geological hydrothermal condition in the nature and provides a novel approach to prepare the composite metal oxides free of organic component although the organic template is critical in synthesis.

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