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A new phase in the Mn^{II}–Se^{IV}–Mo^{VI}–O system, $Mn(MoO_3)(SeO_3)(H_2O)$: Hydrothermal synthesis, crystal structure and properties

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A B S T R A C T

A new phase in the Mn^{II}–Se^{IV}–Mo^{VI}–O system, $Mn(MoO_3)(SeO_3)(H_2O)$ (**1**), has been hydrothermally synthesized with a high yield (82%), and characterized by IR, TG-DSC, magnetism measurement and single crystal X-ray diffraction. The structure of $Mn(MoO_3)(SeO_3)(H_2O)$ features a complicated 3D network composed of the 1D molybdenum(VI) oxide chains and the 1D manganese(II) selenite chains interconnected via Se–O–Mo and Mn–O–Mo bridges. It is stable up to approximately 340 °C, and losses water molecule at 340 °C, then release SeO_2 at about 420 °C. The result of magnetic property measurements has indicated that there exist antiferromagnetic interactions between Mn(II) centers. Photocatalysis experimental result illustrates that the compound exhibits good photocatalytic performance for degradation of RhB under visible light irradiation.

1. Introduction

Mixed metal selenites and tellurites are of special interest because of their structural variety and potential properties, such as, second-harmonic generation (SHG), ferroelectricity, piezoelectricity, semiconductor, optical and magnetic properties, etc. [1–5]. For the class of containing Mo^{VI} mixed metal selenites, dozens of them have been reported and structurally characterized so far, such as, alkali, alkaline earth, NH_4^+ as well as main group cation compounds, $A_2(MoO_3)_2(SeO_3)$ (A = NH_4, Rb, Tl, and Cs) [6–8], $BaMoO_3SeO_3$ [9], $A(Mo_2O_5)(SeO_3)_2$ (A = Sr, Pb, Ba) [9,10], A_2MoSeO_6 (A = Na, K, and Rb) [11], $Li_6(Mo_2O_5)_3(SeO_3)_6$ [12], $Bi_2MoSe_3O_{12}$ [13]; lanthanide molybdenum selenites, $Gd_2MoSe_3O_{12}$ [14], $A_2MoSe_2O_{10}$ (A = Nd or Ga) [14,15], $In_2Mo_2Se_2O_{13}(H_2O)$ [15]; molybdenum-rich quaternary lanthanide selenites, $H_3Ln_4Mo_{9.5}O_{32}(SeO_3)_4(H_2O)_2$ (Ln = La, Nd) and $Ln_2Mo_3O_{10}(SeO_3)_2(H_2O)$ (Ln = Eu, Dy, Er) [16]; and transition metal molybdenum selenites, $Ag_4(Mo_2O_5)(SeO_4)_2(SeO_3)$ [17], $Ag_2(MoO_3)_3SeO_3$ [16], $Ni_3(Mo_2O_8)(SeO_3)$ [18], $TM(MoO_3)(SeO_3)(H_2O)$ (TM = Mn, Co) [19], $Fe_2(Mo_2O_7)(SeO_3)_2(H_2O)$ [19], $Cu_2(MoO_4)(SeO_3)$ [19], $Zn_2(MoO_4)(SeO_3)$ [20]. Herein we reported hydrothermal syntheses, crystal structure, photocatalytic activity, as well as magnetic properties of a new phase in the Mn^{II}–Se^{IV}–Mo^{VI}–O system, $Mn(MoO_3)(SeO_3)(H_2O)$ (**1**). Although compound **1** has the same chemical composition as that of compound **2** reported in ref. [19], the two compounds exhibit different types of 3D structures. Photocatalysis experimental result illustrated that compound **1** exhibits good photocatalytic performance for degradation of rhodamine B (RhB) under visible light irradiation.

2. Experimental

2.1. General procedures

All reagents for the synthesis were purchased from commercial without further purification. IR (KBr pellet) spectrum was recorded on a Nicolet Magna 750 FT-IR spectrometer. Magnetic measurements were carried out using a Quantum Design MPMS-XL SQUID magnetometer. Powder X-ray diffraction (XRD) was carried out with a Shimadzu XRD-7000 X-ray diffractometer using Cu-K_α radiation ($\lambda = 0.15418$ nm) at a scanning rate of 2° min^{-1} in the 2θ range from 5° to 80°. The simulated XRD patterns were calculated using single crystal X-ray diffraction data and processed by the free Mercury 3.0 program provided by the Cambridge Crystallographic

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Data Centre. The thermal analysis was performed on a STA449C integration thermogravimetric (TG) analysis under air with a heating rate of 10 °C min^{-1}.

2.2. Synthesis of $Mn(MoO_3)(SeO_3)(H_2O)$

$Mn(MoO_3)(SeO_3)(H_2O)$ was synthesized by hydrothermal reaction. A mixture of $Na_2MoO_4 \cdot 2H_2O$ (0.484 g, 2.0 mmol), SeO_2 (0.2200 g, 2.0 mmol), $MnSO_4 \cdot H_2O$ (0.3380 g, 2.0 mmol) in 10 mL of distilled water was sealed in an autoclave equipped with a Teflon liner (25 mL), and then heated at 160 °C for 4 days. Then the temperature was recovered to room temperature for 2 days. The pH values before and after the reaction were 3.87 and 4.0, respectively. Brown, block-shaped crystals were collected in about 82% yield (0.565 g) (based on Mo). Its purity was confirmed by XRD studies (Supporting Information). The elemental analyses found: Mo, 27.6%; Mn, 15.6%; Se, 22.9%; Calc. for $H_2MnSeMoO_6$: Mo, 27.90%; Mn, 15.98%; Se, 22.96%. The thermal analyses found: H_2O, 5.6%; Calc. H_2O, 5.24%. IR data (KBr, cm^{-1}): 917 (m), 854 (s), 812 (m), 710 (w), 605 (s), 491 (m), 441 (m).

2.3. X-ray crystallography

A brown single crystal with dimensions of 0.772 × 0.186 × 0.129 mm^3 was glued on a glass fiber. The diffraction data were collected on a Bruker-Smart 1000/CCD diffractometer with graphite monochromated radiation Mo-$K\alpha$ ($\lambda = 0.71073$ Å). The structure was solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares methods on F^2 using the SHELXL-97 program package. All of the non-hydrogen atoms were refined anisotropically. Crystal data are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. Atomic coordinates and anisotropic displacement parameters are deposited in Table S1. Further details of the crystal details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 417847 Eggenstein-Leopoldshafen.

2.4. Photocatalytic activity

The evaluation of photocatalytic performance of samples for photocatalytic decolorization of RhB aqueous solution was performed as follows: A 500 W Xe-arc lamp was used as the visible light source with a cutoff filter to cut off the light below 420 nm. The suspensions containing 200 mg of photocatalyst and 250 mL fresh aqueous solution of RhB (10 mg L^{-1}) were continuously magnetically stirred in the dark for 30 min to establish an adsorption/desorption equilibrium of RhB solution. After this period of time, the light source was turned on. During the reaction, samples of 5 mL were taken at given time intervals and then separated photocatalysts through centrifugation. The absorbance of RhB in the supernatant solution was monitored by a Shimadzu 2550 UV–vis spectrophotometer at the maximum absorption of 553 nm.

Table 1
Crystallographic parameters of compound 1.

Formula	$Mn(MoO_3)(SeO_3)(H_2O)$
Formula weight	343.86
Crystal size	0.772 × 0.186 × 0.129
Crystal color	Brown
Crystal system	Triclinic
Space group	p_{-1}
a (Å)	5.094(4)
b (Å)	6.867(5)
c (Å)	9.193(7)
α (°)	91.797(9)
β (°)	97.562(9)
γ (°)	110.535(8)
V (Å^3)	297.5(4)Z
D_{calc} (mg m^{-3})	3.839
μ (mm^{-1})	10.325
F(000)	318
Goodness-of-fit on F^2	1.037
Max. shift (Δ/σ) in final cycle	0.000
Largest diff. peak and hole (e Å^{-3})	1.085, −0.853
Data/restraints/parameters	969/2/101
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0317$, $wR_2 = 0.0989$
R indices (all data)	$R_1 = 0.0335$, $wR_2 = 0.1012$

$R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $wR_2 = \sum w\{(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for compound 1.

Compound **1**			
Mo(1)–O(2)	1.755(5)	Mo(1)–O(6)	1.761(4)
Mo(1)–O(7)	1.890(4)	Mo(1)–O(5)#1	2.077(4)
Mo(1)–O(7)#2	2.203(4)	Mo(1)–O(5)	2.340(4)
Se(1)–O(3)	1.694(5)	Se(1)–O(4)	1.694(4)
Se(1)–O(5)	1.824(4)	Mn(1)–O(1)#3	2.121(5)
Mn(1)–O(1)	2.121(5)	Mn(1)–O(3)#3	2.217(4)
Mn(1)–O(3)	2.217(4)	Mn(1)–O(2)#2	2.282(5)
Mn(1)–O(2)#4	2.282(5)	Mn(2)–O(4)#5	2.179(5)
Mn(2)–O(4)	2.179(5)	Mn(2)–O(7)#6	2.240(4)
Mn(2)–O(7)#7	2.240(4)	Mn(2)–O(6)	2.258(5)
Mn(2)–O(6)#5	2.258(5)		
O(2)–Mo(1)–O(6)	105.2(2)	O(7)–Mo(1)–O(7)#2	75.64(16)
O(6)–Mo(1)–O(5)#1	94.37(18)	O(5)#1–Mo(1)–O(5)	70.18(18)
O(6)–Mo(1)–O(7)#2	159.1(2)	O(5)#1–Mo(1)–O(7)#2	82.18(15)
O(3)–Se(1)–O(4)	104.7(2)	O(4)–Se(1)–O(5)	98.4(2)
O(3)#3–Mn(1)–O(3)	180.0(2)	O(1)#3–Mn(1)–O(3)#3	87.7(2)
O(4)#5–Mn(2)–O(4)	180.0(1)	O(4)#5–Mn(2)–O(7)#6	86.68(15)

Symmetry codes: For compound **1**, #1 $-x + 1, -y, -z + 1$, #2 $-x + 2, -y, -z + 1$, #3 $-x + 2, -y, -z + 2$, #4 $x, y, z + 1$, #5 $-x + 1, -y + 1, -z + 1$, #6 $-x + 2, -y + 1, -z + 1$, #7 $x - 1, y, z$, #8 $x + 1, y, z$, #9 $x, y, z - 1$.

3. Results and discussion

3.1. Synthesis and structure

Compound **1** was synthesized by hydrothermal reaction of a mixture of $Na_2MoO_4 \cdot 2H_2O$, SeO_2 and $MnSO_4 \cdot H_2O$ aqueous solution at 160 °C for 4 days. Its isomer (compound **2**) was also synthesized by hydrothermal reaction, but with different starting materials (MoO_3, $MnCO_3$ and SeO_2 aqueous solution) and under higher synthesis temperature (210 °C). Compound **1** crystallizes in triclinic system, space group P-1, which is different from Pmc21 of compound **2**. The asymmetric unit of **1** contains 10 non-hydrogen atoms, one Mo center, one Se center and two Mn centers (the occupancy of Mn1 and Mn2 is 50% in the asymmetric unit) (Fig. 1). Both Mn(1) and Mn(2) atoms are octahedrally coordinated by six oxygen atoms. The coordination geometry around Mn(1) composes of two selenite anions in a unidentate fashion, two oxo anions, and two aqua ligands whereas Mn(2) is surrounded by two selenite anions in a unidentate fashion and four oxo anions. The Mn–O distances in the range of 2.121(5)–2.282(5) Å (Table 2), which are comparable to other reported in manganese(II) molybdenum(VI) selenite(IV) oxides. The Mo(1) atom is octahedrally coordinated by two selenite oxygens, two terminal and two bridging oxo anions. The Se atom is in a ψ-SeO_3 trigonal–pyramidal geometry with the lone pair of Se^{IV} occupying the pyramidal site. The Se–O distances fall in the normal range of 1.694(5)–1.824(4) Å. Valence bond summations for the Mn(1), Mn(2), Mo(1), and Se(1) atoms are 1.94, 1.84, 5.98, and 3.72, respectively, which suggest that the valency of all the atoms remains unchanged.