

Preparation of $\text{MnMoO}_4 \cdot X\text{H}_2\text{O}$ ($X=0.9, 1.5$) by a Microemulsion Method under Different Manganese Precursors and Analysis of Their Band-gap Energy

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Abstract: Manganese molybdates $\text{MnMoO}_4 \cdot X\text{H}_2\text{O}$ ($X=0.9, 1.5$) were obtained by a microemulsion method based on a quaternary system (CTAB/ water/pentane/isoamyl alcohol) under different manganese precursors. According to XRD, DSC and TG analyses, it is proved that $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ can be prepared under the precursor of manganese of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, while under the precursor of manganese of $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ the product is $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$. $\omega([\text{CTAB}]/[\text{H}_2\text{O}])$ (the molar ratio) and the different manganese precursors have great influence on the microstructures of the final products. It can be calculated from the solid ultraviolet spectra that the band-gap energy of $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ could reach 3.08 eV, and that of $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ is 3.04 eV.

Key words: manganese molybdates; quaternary system; CTAB; band-gap energy

Molybdate is an important family of inorganic functional materials. And its formula is ABO_4 with a tetragonal structure. In this structure, molybdenum ions are located in tetrahedral symmetry center, four O^{2-} ions surround the center of molybdenum, so it has good stability. Molybdates, owing to their special structure, are recommended as functional materials, and the properties of other materials cannot be superior to theirs, such as significant electrical^[1], optical^[2], magnetic^[3,4], catalytic properties^[5].

Manganese molybdates have widely used in various fields, such as catalysis^[6,7], magnetic properties^[8], supercapacitor^[9], and photoluminescence^[10]. Manganese ion with ionic radius of the bivalent cations (0.066~0.09 nm), is compounded with molybdate ion to form scheelite structure. There are three kinds of MnMoO_4 morphology structures. One is $\alpha\text{-MnMoO}_4$ which can be obtained by solid phase reaction in high temperature kettle and this kind of structure is stable at room temperature^[11]. Another phase of MnMoO_4 is wolframite structure^[12], which can be prepared through the interaction between MoO_3 and MnO or MnCO_3 at high temperature (900 °C) and pressure (6 GPa), and it will be transformed into $\alpha\text{-MnMoO}_4$ structure when

the MnMoO_4 is heated for more than 2 d at 60 °C in air. The manganese molybdate with crystallization water is the last structure^[13], which is hexahedral shape morphology structure. In recent years, more and more novel methods for the synthesis of the molybdates have received considerable attention, such as a hydrothermal method^[14], a microwave method^[15], a template method^[16], a microemulsion method^[17], and some other liquid phase methods^[18]. Manganese molybdate can be prepared under the different sources of manganese. A few reports on the preparation of $\text{MnMoO}_4 \cdot \text{H}_2\text{O}$ ^[19] under the reaction of MnSO_4 solution and Na_2MoO_4 ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$) solution, and $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ ^[20] under the reaction of MnCl_2 solution and Na_2MoO_4 solution showed that the different manganese precursors had a certain influence on the final products.

In the present paper, we took an effective way to systematically synthesize $\text{MnMoO}_4 \cdot X\text{H}_2\text{O}$ ($X=0.9, 1.5$) with well defined nano/microstructures. The results showed that the factors of the different manganese precursors and $\omega([\text{ratio of CTAB}]/[\text{H}_2\text{O}])$ had an important influence on the final products. From DSC and TG curves, it was found that the $\text{MnMoO}_4 \cdot X\text{H}_2\text{O}$ ($X=0.9, 1.5$) could be dehydrated in the air at

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a certain temperature. Moreover, we worked out the band-gap energies of $\text{MnMoO}_4 \cdot X\text{H}_2\text{O}$ ($X=0.9, 1.5$) from the solid ultraviolet spectra.

1 Experiment

$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were analytical grade and used as starting materials without further purification purchased from Sinopharm Chemical Reagent Co., Ltd.

A quaternary microemulsion system, CTAB (hexadecyl trimethyl ammonium bromide)/water/pentane/isoamyl alcohol, was selected for synthesis of the variety of manganese molybdates with different morphology structures.

The concentration of surfactant (CTAB)=0.4 mol/L, Amyl alcohol/CTAB=7.3 (molar ratio), the volume of solution was computed to be 20 mL, so $m(\text{CTAB})=2.945$ g, and $\omega([\text{CTAB}]/[\text{H}_2\text{O}])$ was 15, 20, 25, 30, 35, and 40.

At first, 250 mL 2 mol/L Mn^{2+} solution, and 250 mL 2 mol/L $(\text{MoO}_4)^{2-}$ solution were configured, and then 10 mL Mn^{2+} solution was taken out to pour into the quaternary microemulsion system, which formed manganese ion reverse micelle; similarly, molybdate ion reverse micelle were formed. Then equal volumes of the above two microemulsions were mixed quickly. The resulting solutions were stood here for 24 h without stirring at room temperature. Then the white products were centrifuged many times by deionized water and ethanol, and at last dried in vacuum at 80 °C for 24 h.

The products were characterized by X-ray diffraction pattern (XRD), recorded on a MAC Science Co. Ltd MXP 8 AHF X-ray diffractometer with monochromatized $\text{Cu-K}\alpha$ radiation ($\lambda=0.1541874$ nm). The field-emission scanning electron microscope (FE-SEM) examination were carried out with a field-emission microscope (JEOL, 7500B) operated at an acceleration voltage of 10 kV. Thermogravimetric analysis (TG) was carried out on a STA409PC thermal analyzer (Naichi Corporation) with a heating rate of 10 °C min^{-1} in flowing air. Solid UV-Vis spectroscopy test was carried out on a SP-752 type spectrophotometer.

2 Results and Discussion

When the precursor manganese is $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, the obtained product is $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ with good crystallinity as shown in Fig.1. All the diffraction peaks of the obtained product could be easily indexed as $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ (JCPDS Card No.50-1286). The results demonstrate that the products obtained under different $\omega([\text{CTAB}]/[\text{H}_2\text{O}])$ are $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$.

$\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ ^[21] could be obtained under the precursor manganese of $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$. Fig.2 shows XRD patterns of the products obtained under different $\omega([\text{CTAB}]/[\text{H}_2\text{O}])$.

In this experiment, it is found that the $\omega([\text{CTAB}]/[\text{H}_2\text{O}])$ has an important effect on the morphology and size distribution of the final products. Obviously, the varying of

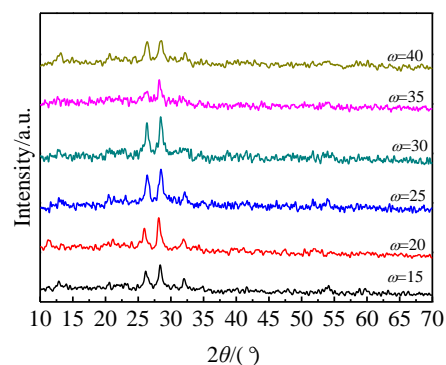


Fig.1 XRD patterns of $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ under different $\omega([\text{CTAB}]/[\text{H}_2\text{O}])$

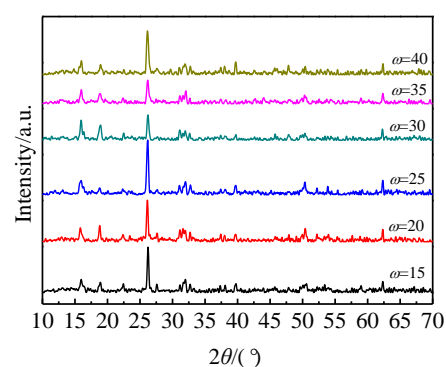


Fig.2 XRD patterns of $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ under different $\omega([\text{CTAB}]/[\text{H}_2\text{O}])$

$\omega([\text{CTAB}]/[\text{H}_2\text{O}])$ can produce a series of $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ microstructure with controlled sizes and morphologies. As illustrated from Fig.3, it is clearly seen that the $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ microstructure is composed of a lot of lamellae crystals with different controlled sizes. Fig.3a shows that the $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ is in form of nanosheets with an average thickness of 200 nm and the length of about 5 μm . Comparing Fig.3a ($\omega=15$) with Fig.3c ($\omega=25$), it is found that the structure of the final product in Fig.3c ($\omega=25$) is tighter than that in Fig.3a ($\omega=15$). Moreover, its size of thickness is thinner than that of the product in Fig.3a ($\omega=15$). And the length is also longer than that in Fig.3a ($\omega=15$). When the $\omega([\text{CTAB}]/[\text{H}_2\text{O}])$ is increased to 35, the lamellae crystals are tightly aligned radially and intercrossed with each other to form $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ microstructure. It is more tighter compared with the final product in Fig.3c ($\omega=25$). From SEM images, it is clear to see that the final product in Fig.3c ($\omega=25$) has the best distribution with a uniform and tight structure.

When the manganese precursor is $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$, the obtained product is $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ under different $\omega([\text{CTAB}]/[\text{H}_2\text{O}])$. The $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ product consists of many lamella-like particles and flakes with an average thickness of about 500 nm and the length of 1~1.5 μm , as shown in Fig.4. And comparing these images, it is obviously

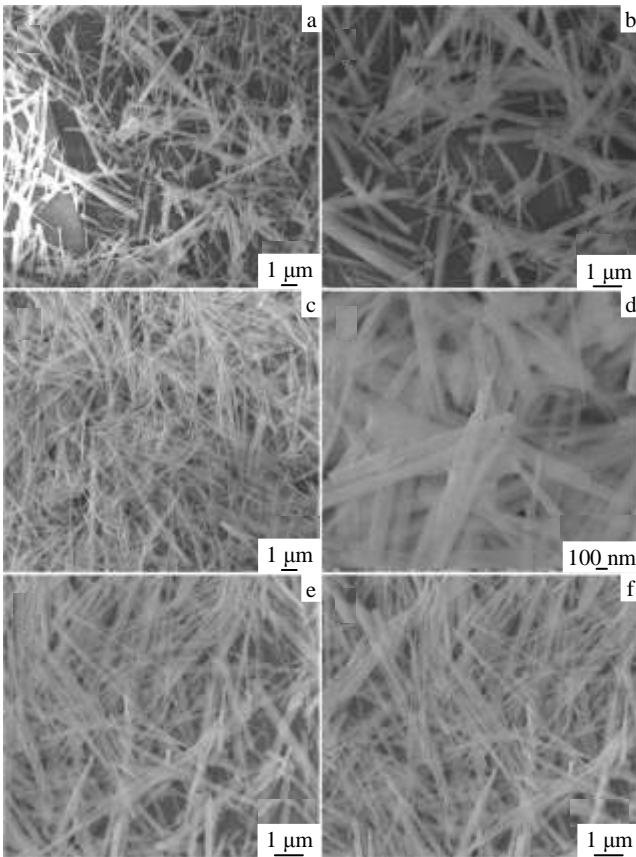


Fig.3 SEM images of the MnMoO₄·0.9H₂O under different ω ([CTAB]/[H₂O]): (a, b) 15, (c, d) 25, and (e, f) 35

seen that the shape of the MnMoO₄·1.5H₂O product has a certain transformation upon increasing of ω ([CTAB]/[H₂O]). Fig.4c shows that the MnMoO₄·1.5H₂O exhibits a lot of nanofibers with average diameter of 100 nm and very long length. Moreover, these nanofibers are orderly arranged together. When ω ([CTAB]/[H₂O]) is increased to 35 (Fig.4e, 4f), the MnMoO₄·1.5H₂O product almost consists of innumerable fiber-like microwires; however, their diameters are bigger than those of the nanofibers in Fig.4d, while the lengths are less than those of the nanofibers in the Fig.4c. So the product obtained under the condition of ω =25 achieves the best morphology and size distribution of MnMoO₄·1.5H₂O.

The DSC and TG curves for the synthesized compound (Fig.5) show mass losses, indicating that the products contain some crystallization water. This measurement was conducted at a heating rate of 10 K/min. The DSC and TG curves of the MnMoO₄·0.9H₂O (Fig.5a) and MnMoO₄·1.5H₂O (Fig.5b) specimens in the temperature range from 30 °C to 800 °C under the condition of nitrogen show that the whole mass loss for MnMoO₄·0.9H₂O is 7.4% and that for MnMoO₄·1.5H₂O is 11.4%. It is obvious that the mass loss is greatly ascribed to the loss of crystallization water. From DSC and TG curves (Fig.5b), it is noted that the dehydration process of MnMoO₄·1.5H₂O occurs in three temperature ranges, i. e.,

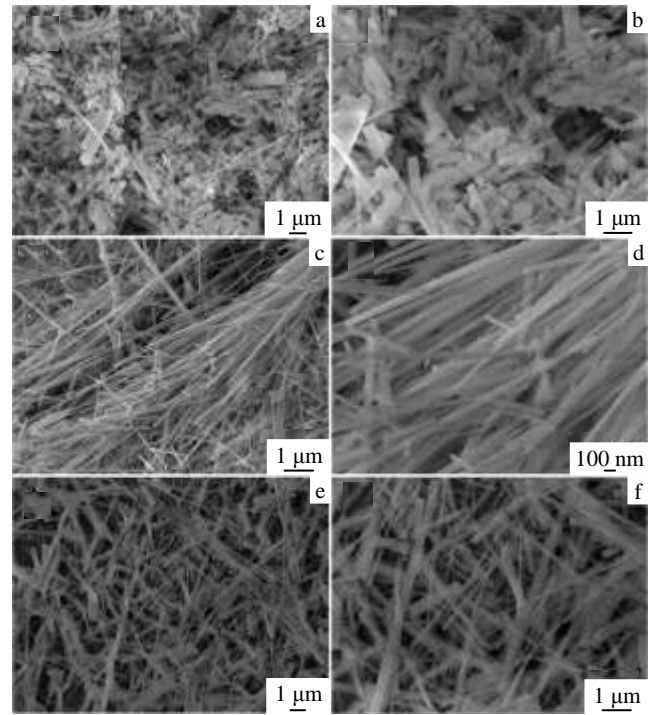


Fig.4 SEM images of the MnMoO₄·1.5H₂O under different ω ([CTAB]/[H₂O]): (a, b) 15, (c, d) 25, and (e, f) 35

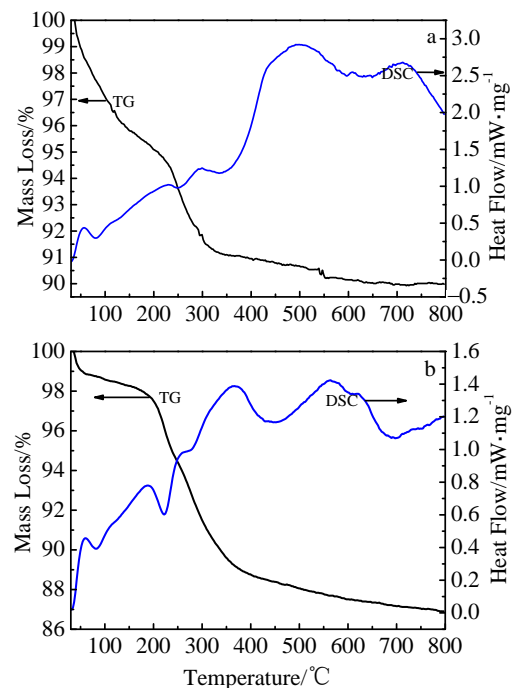


Fig.5 DSC and TG curves of MnMoO₄·0.9H₂O (a) and MnMoO₄·1.5H₂O (b)

from room temperature to 220 °C, from 220 °C to 450 °C and from 450 °C to 700 °C. The three steps mean the different products. The product is MnMoO₄·1.1H₂O when the temperature is up to 220 °C, and MnMoO₄·0.2H₂O for 450 °C.

The whole mass loss can be seen from the DSC and TG curves, e. g. mass loss (wt%)=98.6%–87.2%=11.4%. The calculation of theory is as follows: mass loss=11.2%. Obviously, the mass losses obtained by the theoretical calculation and the experiment are very close, which just verifies that the product is $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$.

There are two steps of the mass loss for $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$. One occurs at 250 °C, the product is $\text{MnMoO}_4 \cdot 0.4\text{H}_2\text{O}$, and the mass loss is about 0.5 crystallization water. The other is the final product of $\alpha\text{-MnMoO}_4$. Comparing the two curves, the mass is no longer reduced when the temperature is increased to 750 °C. The mass loss obtained by the experiment is 97.6%–90.2%=7.4%. And the theoretical calculation is as follows: mass loss=7.0%. It is well verified that the product is $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$.

The solid ultraviolet spectra were applied in the analysis of calculating the band-gap energy of $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$. It is clearly seen that there are two absorption peaks A (272 nm) and B (295 nm) in the ultraviolet range of the light (Fig.6a), corresponding to band-gap energy $E_A=4.56$ eV, $E_B=4.20$ eV, respectively. Mn would be heated from the ground state to excited state when a beam of light irradiates to the product ($\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$). It implies that Mn requires energy ($E_1=E_B=4.20$ eV) when it loses an electron. The energy required for loss of another electron is $E_2=E_A=4.56$ eV.

The solid ultraviolet spectrum of the $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ is shown in Fig.6a. From this figure, $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ shows an absorption edge around 442 nm, corresponding to band-gap energy of about 2.81 eV. By plotting $(ah\nu)^2$ versus $h\nu$ (Fig.7a),

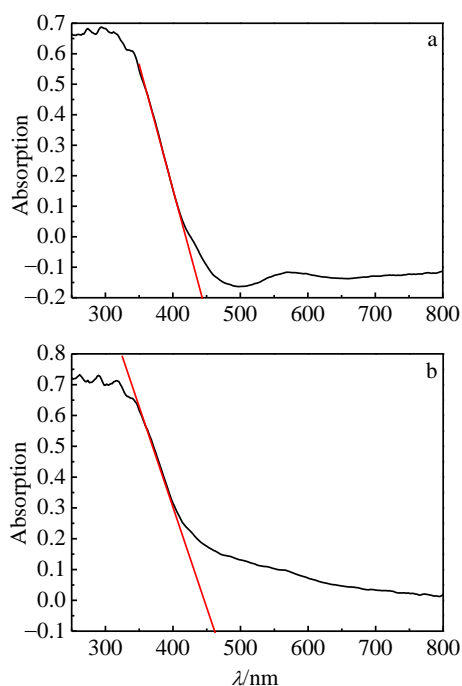


Fig.6 Solid ultraviolet spectra of $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ (a) and $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ (b)

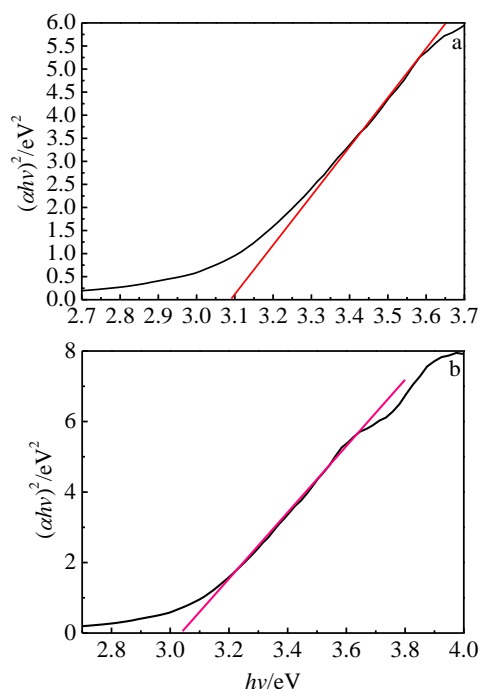


Fig.7 Curves by plotting $(ah\nu)^2$ versus $h\nu$ of $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ (a) and $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ (b)

where α is the absorption coefficient, h is planck constant, ν is the frequency of ray, the band-gap energy is the intersection point of tangent and the X axis (3.08 eV).

The band-gap energy of $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ could be worked out in the same way above. There are two absorption peaks A (261 nm) and B (289 nm) (Fig.6b), thus corresponding to band-gap energy $E_A=4.75$ eV and $E_B=4.29$ eV, respectively. Mn would be heated from the ground state to excited state when a beam of light irradiates to the product ($\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$). It is implied that Mn requires energy ($E_1=E_B=4.29$ eV) when it loses an electron. The energy required for loss of another electron is ($E_2=E_A=4.75$ eV).

It is shown that $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ has an absorption edge at about 462 nm, corresponding to band-gap energy of about 2.68 eV. By plotting $(ah\nu)^2$ versus $h\nu$ (Fig.7b), in which α is the absorption coefficient, h is Planck constant, ν is the frequency of ray, the band-gap energy is the intersection point of tangent and the X axis (3.04 eV).

3 Conclusions

1) $\text{MnMoO}_4 \cdot X\text{H}_2\text{O}$ ($X=0.9, 1.5$) can be synthesized by a simple microemulsion method under different precursors of manganese. When the precursor of manganese is $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, the obtained product is $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$; when the precursor of manganese is $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$, the obtained product is $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$. $\omega([\text{CTAB}]/[\text{H}_2\text{O}])$ has an important effect on the morphology and the size distribution of the final products.

2) The band-gap energy of $\text{MnMoO}_4 \cdot X\text{H}_2\text{O}$ ($X=0.9, 1.5$) can

be calculated from the solid ultraviolet spectra. The band-gap energy of $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ could reach 3.08 eV, and that of $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ is 3.04 eV. The band-gap energies of the two different products are almost the same.

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基于不同锰源微乳液法合成 $\text{MnMoO}_4 \cdot x\text{H}_2\text{O}$ ($x=0.9, 1.5$)及相应的带隙能研究

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摘 要: 在不同锰源条件下, 通过一个四元体系 (CTAB/水/戊烷/戊醇) 微乳液法合成了 $\text{MnMoO}_4 \cdot x\text{H}_2\text{O}$ ($x=0.9, 1.5$)。XRD 和热重分析证明: 当锰源是 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 时, 能够合成出 $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$, 当锰源为 $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ 时, 产物为 $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ 。 $\omega(\text{CTAB}/\text{水})$ 和不同锰源对最终产物结构有很大影响。通过固体紫外吸收光谱图可以计算出 $\text{MnMoO}_4 \cdot 0.9\text{H}_2\text{O}$ 的带隙能达到 3.08 eV, $\text{MnMoO}_4 \cdot 1.5\text{H}_2\text{O}$ 的带隙能是 3.04 eV。

关键词: 钼酸锰; 四元体系; CTAB; 能带

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