

## Influence of Time and Temperature on Directional Growth of $\text{MoO}_3$

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**Abstract.** Two-dimensional microstructures of molybdenum trioxide ( $\text{MoO}_3$ ) were synthesized by heptamolybdate tetrahydrate ammonium acidification, followed by calcination. A solution of the precursor compound heptamolybdate tetrahydrate ammonium acidified to pH 3,5 using glacial acetic acid followed by hydrothermal treatment for 150, 180 and 200 °C for 1, 6 and 12 hours. Then, the intermediate was calcined at 300 °C for varying time 6 and 12h to obtain  $\text{MoO}_3$ . X-ray diffraction revealed that the crystals grew with crystalline structure corresponding to the orthorhombic phase of  $\text{MoO}_3$  ( $\alpha\text{-MoO}_3$ ) as major phase, with a preferential growth direction along the planes (0K0). Raman spectroscopy and IR confirmed the formation of the characteristic modes of molybdenum trioxide for stage found. With Scanning Electron Microscopy (SEM) was possible to observe the formation of nanoplates.

## Introduction

Molybdenum trioxide ( $\text{MoO}_3$ ) has encountered numerous applications such as chemical synthesis, sensors, optical or optoelectronic devices, catalysis, smart windows, display, supercapacitor and battery applications [1-4]. The  $\alpha\text{-MoO}_3$  crystalline phase with an orthorhombic structure is the unique thermodynamically stable phase.  $\text{h-MoO}_3$  with an hexagonal structure is the metastable, while  $\beta\text{-MoO}_3$  with a monoclinic symmetry appears to be an unstable phase [5-7].

Structural units in  $\alpha\text{-MoO}_3$  crystal lattice are the distorted octahedra  $[\text{MoO}_6]$  edge-connected along (010) into the chains and corner-linked along (100) directions with resulting in a bilayer. The bilayers are parallel to the (010) lattice plane and bonded into a bulk with strong Van der Waals forces [8]. These specific structure makes  $\alpha\text{-MoO}_3$  as a sensing material for different gases, cathode material in batteries, catalyst and many others [8]. Wide range applications led to numerous efforts in preparation of crystalline  $\alpha\text{-MoO}_3$  by different methods like sputtering, thermal evaporation, template synthesis, chemical synthesis and hydrothermal method [7]. Compared to the above mentioned methods, the hydrothermal method is the solution phase route, has been proven to be an effective and convenient process to fabricate new meta(stable) structures.

In this paper, Molybdenum trioxide ( $\alpha\text{-MoO}_3 \rightarrow \beta\text{-MoO}_3/\text{h-MoO}_3 \rightarrow \alpha\text{-MoO}_3$ ) were synthesized using hydrothermal method followed by calcination. The reaction (and calcination) temperature and time were varied and their effect on the crystal structure, shape, size and preferential growth was investigated by XRD, FTIR, Raman and SEM to know the structural, functional and morphology of the resultant products.

## Experimental

Ammonium Heptamolybdate  $[(\text{NH}_4)_6(\text{Mo}_7\text{O}_{24}) \cdot 4\text{H}_2\text{O}]$  – Vetec 99%] was dissolved in deionized water, pH adjusted to 3.5 with glacial acetic acid  $[\text{C}_2\text{H}_4\text{O}_2]$  – Synth 100%. The intermediate precipitate (amorphous  $\text{MoO}_3$ ) was performed hydrothermal treatment for 150, 180 and 200 °C, with time varying by 1, 6 and 12h. Then, the intermediate compound was calcined at 300 °C with time variance of 6 and 12h, obtaining crystals of  $\text{MoO}_3$ . The 18 prepared samples are listed in Table 1.

Table 1. Reaction conditions of  $\text{MoO}_3$  synthesized by hydrothermal method and calcined at 300 °C

| $t_c = 6\text{h}$ |                                |                          | $t_c = 12\text{h}$ |                                |                          |
|-------------------|--------------------------------|--------------------------|--------------------|--------------------------------|--------------------------|
| Sample            | $T_{\text{HP}}/^\circ\text{C}$ | $t_{\text{HP}}/\text{h}$ | Sample             | $T_{\text{HP}}/^\circ\text{C}$ | $t_{\text{HP}}/\text{h}$ |
| HT1               | 150                            | 1                        | HT10               | 150                            | 1                        |
| HT2               |                                | 6                        | HT11               |                                | 6                        |
| HT3               |                                | 12                       | HT12               |                                | 12                       |
| HT4               | 180                            | 1                        | HT13               | 180                            | 1                        |
| HT5               |                                | 6                        | HT14               |                                | 6                        |
| HT6               |                                | 12                       | HT15               |                                | 12                       |
| HT7               | 200                            | 1                        | HT16               | 200                            | 1                        |
| HT8               |                                | 6                        | HT17               |                                | 6                        |
| HT9               |                                | 12                       | HT18               |                                | 12                       |

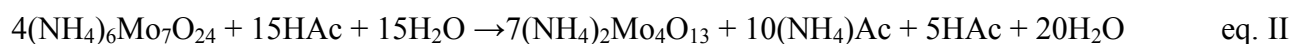
$T_{\text{HP}}$  = Temperature of Hydrothermal process,  $t_{\text{HP}}$  = Time of Hydrothermal process

$t_c$  = Time of calcination

X-ray diffraction (XRD) patterns were measured by a Shimadzu XRD 6000 diffractometer with a copper X-ray tube operated at 40 kV and 30 mA. The samples were also identified by a FT-IR (Bruker, Vertex 70, using KBr pellets) Raman spectrometer (BROKEN, SENTERRA) at an excitation wavelength of 785 nm. SEM micrographs was obtained using FEI, Quanta 200 FEG.

## Results and Discussion

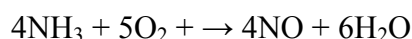
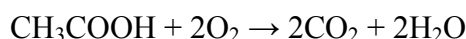
The acidification is carried out with acetic acid and ammonium molybdate in aqueous media. Adding the spectator ions acetate and ammonium we have the like equation I or the simplified equation (eq. II).



This reaction does not require washing, since in addition to the expected molybdate, resulting water and ammonium acetate that decompose easily at low temperatures. Then the general reaction balanced for formation of  $\text{Mo}_4\text{O}_{13}^{2-}$ , from the acidification of  $\text{Mo}_7\text{O}_{24}^{6-}$ :



From the calcination, the molybdate is transformed into molybdenum trioxide,  $\text{MoO}_3$ . The general reaction is as follows:  $2\text{Mo}_4\text{O}_{13}^{2-} \rightarrow 8\text{MoO}_3 + \text{O}_2 + 4\text{e}^-$ . Whereas both the decomposition of ammonium acetate, as the ammonia and acetic acid, we have:



Just after the hydrothermal and calcination treatment, the powders are all of the yellowish color typical of  $\text{MoO}_3$  and the XRD pattern of a pure  $\alpha$ - $\text{MoO}_3$  phase is obtained (Fig. 1 (a, c and e) and 2 (a, c and e)), which indicates that the crystallographic structure of the oxides are

orthorhombic with the (0K0) lines ( $K = 2, 4, 6$ ) typical for an oriented structure of the layered  $\alpha$ - $\text{MoO}_3$  phase (JCPDS 5-0508). The intensified peaks from the (010) plane in the powder XRD pattern suggests that the obtained material has an anisotropic morphology with the (010) face, which is preferentially arranged parallel to the sample holder.

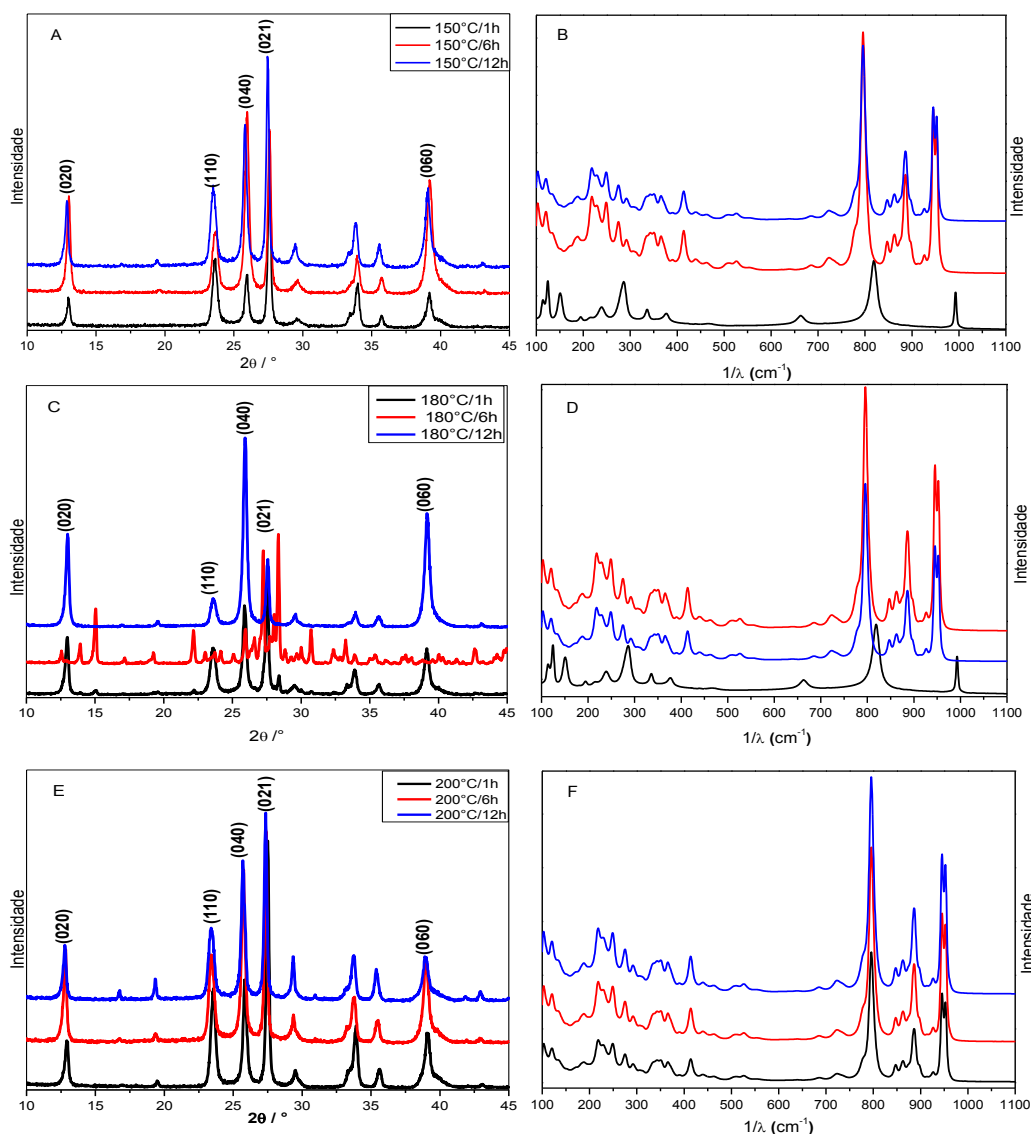


Fig. 1. XRD and Raman of  $\text{MoO}_3$  synthesized by hydrothermal method at 150, 180 and 200 °C from different times (1, 6 and 12h) and calcined at 300 °C by 6h.

Some evolution like color change has been noticed with time of calcination: Some powders become darker and even gray, especially for samples prepared at 200 °C. These changes in color are reduced for samples kept light protected. It is known that the color of  $\text{MoO}_3$  can change when exposed to light as a result of the photochromism phenomenon leading to some reduction to the  $\text{Mo}^{5+}$  state [9].

At 150 °C (HT1, HT2 and HT3) the presence of peaks at 23.6, 23.6 and 23.5°, respectively, suggest the presence of  $\beta$ - $\text{MoO}_3$  (JCPDS 47-1081). At 150 °C (HT3), 180 °C (HT6) and 200 °C (HT7, HT8 and HT9), other peaks were observed at about 9.4°, 16.8°, 19.4°, and 29.4° in addition to  $\alpha$ - $\text{MoO}_3$ . These peaks presumably occurred due to hexagonal  $\text{MoO}_3$  (h- $\text{MoO}_3$ ) (JCPDS 21-0569).

Fig. 1 (b, d and f) shows the frequency of the Raman for  $\text{MoO}_3$ . The Raman spectra suggests that the molybdenum trioxide exists as more one phase:

(I) at 150 °C and 180 °C (samples HT1 and HT4, respectively) the profile of Raman spectra suggests existence of  $\alpha$ - $\text{MoO}_3$  or  $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$  as polycrystalline powders [3,4,10]. In the wave

number range 600–1100  $\text{cm}^{-1}$ , the Raman spectra displays the typical features of Molybdenum trioxide polycrystalline material (peaks at about 662, 818 and 995  $\text{cm}^{-1}$ ). The profile of Raman spectra in the region of low frequency confirms the existence of  $\alpha$ - $\text{MoO}_3$  hydrated

(II) at 150 °C (samples HT2 and HT3), 180 °C (samples HT5 and HT6) and 200 °C (samples HT7, HT8 and HT9), the profile of Raman spectra suggests existence of Molybdenum trioxide partially hydrated ( $\text{MoO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{MoO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  or  $\text{MoO}_3 \cdot \frac{1}{3}\text{H}_2\text{O}$ ) as polycrystalline powders. In the wave number range 600–1100  $\text{cm}^{-1}$ , the Raman spectra displays the typical features of  $\text{MoO}_3 \cdot \text{H}_2\text{O}$  (or  $\text{MoO}_3 \cdot \frac{1}{3}\text{H}_2\text{O}$ ) polycrystalline material (bands at about 685, 723, 796, 847, 862, 886, 925, 945 and 952  $\text{cm}^{-1}$ ). The profile of Raman spectra in the region of low frequency confirms the existence of  $\text{MoO}_3$  partially hydrated.

The FT-IR spectra for orthorhombic  $\alpha$ - $\text{MoO}_3$  (or  $\text{MoO}_3$  hydrated) (not shown), shows sharp and broad peak in the region 1000–900  $\text{cm}^{-1}$  attributed to stretching vibration of molybenyl bond  $\nu_s(\text{M}=\text{O})$ . Another broad vibration band at about 590  $\text{cm}^{-1}$  is due to interaction of oxygen atom with three metal atoms ( $\text{O}-3\text{Mo}$ ). FT-IR spectra gives similar spectral band as h- $\text{MoO}_3$  and a small peak appears at about 990  $\text{cm}^{-1}$ , indicating the presence of secondary phase [7].

At 150 °C (HT10 and HT11), 180 ° (HT13 and HT14) and 200 °C (HT17 and HT18), using calcination time of 12h (Fig. 2a, 2c and 2e, respectively) the products comprises of hexagonal (h- $\text{MoO}_3$ ) and orthorhombic ( $\alpha$ - $\text{MoO}_3$ ) phases [4]. On the other hand, at 150 °C (Fig. 2a) and 12h of hydrothermal process (HT12), 180 °C (Fig. 2c) and 1h of hydrothermal process (HT15) and 200 °C (Fig. 2e) and 6h of hydrothermal process (HT17), the profile of XRD pattern suggests existence of  $\alpha$ - $\text{MoO}_3$  pure phase as polycrystalline powders [3,4,10].

Fig. 2 (b, d and f) shows the frequency of the Raman for  $\text{MoO}_3$ . The Raman spectra suggests that the molybdenum trioxide can exist as more one phase:

(I) at 150 °C (samples HT10, HT11 and HT12, respectively), the profile of Raman spectra suggests existence of Molybdenum trioxide partially hydrated ( $\text{MoO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{MoO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  or  $\text{MoO}_3 \cdot \frac{1}{3}\text{H}_2\text{O}$ ) as polycrystalline powders [4, 10]. In the wave number range 600–1100  $\text{cm}^{-1}$ , the Raman spectra displays the typical features of  $\text{MoO}_3 \cdot \text{H}_2\text{O}$  (or  $\text{MoO}_3 \cdot \frac{1}{3}\text{H}_2\text{O}$ ) polycrystalline material (bands at about 685, 723, 796, 847, 862, 886, 925, 945 and 952  $\text{cm}^{-1}$ ). The profile of Raman spectra in the region of low frequency confirms the existence of  $\alpha$ - $\text{MoO}_3$  hydrated.

(II) at 180 °C (HT13, HT14 and HT15) and 200 °C (samples HT16, HT1 and HT18), the profile of Raman spectra suggests existence of Molybdenum trioxide partially hydrated ( $\text{MoO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{MoO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  or  $\text{MoO}_3 \cdot \frac{1}{3}\text{H}_2\text{O}$ ) as polycrystalline powders. In the wave number range 600–1100  $\text{cm}^{-1}$ , the Raman spectra displays the typical features of  $\text{MoO}_3 \cdot \text{H}_2\text{O}$  (or  $\text{MoO}_3 \cdot \frac{1}{3}\text{H}_2\text{O}$ ) polycrystalline material (bands at about 685, 723, 796, 847, 862, 886, 925, 945 and 952  $\text{cm}^{-1}$ ). The profile of Raman spectra in the region of low frequency confirms the existence of  $\text{MoO}_3$  partially hydrated.

The FT-IR spectra for orthorhombic  $\alpha$ - $\text{MoO}_3$  (or  $\text{MoO}_3$  hydrated) (not shown), shows sharp and broad peak in the region 1000–900  $\text{cm}^{-1}$  attributed to stretching vibration of molybenyl bond  $\nu_s(\text{M}=\text{O})$ . Another broad vibration band at about 590  $\text{cm}^{-1}$  is due to interaction of oxygen atom with three metal atoms ( $\text{O}-3\text{Mo}$ ). FT-IR spectra gives similar spectral band as h- $\text{MoO}_3$  and a small peak appears at about 990  $\text{cm}^{-1}$ , indicating the presence of secondary phase [7].

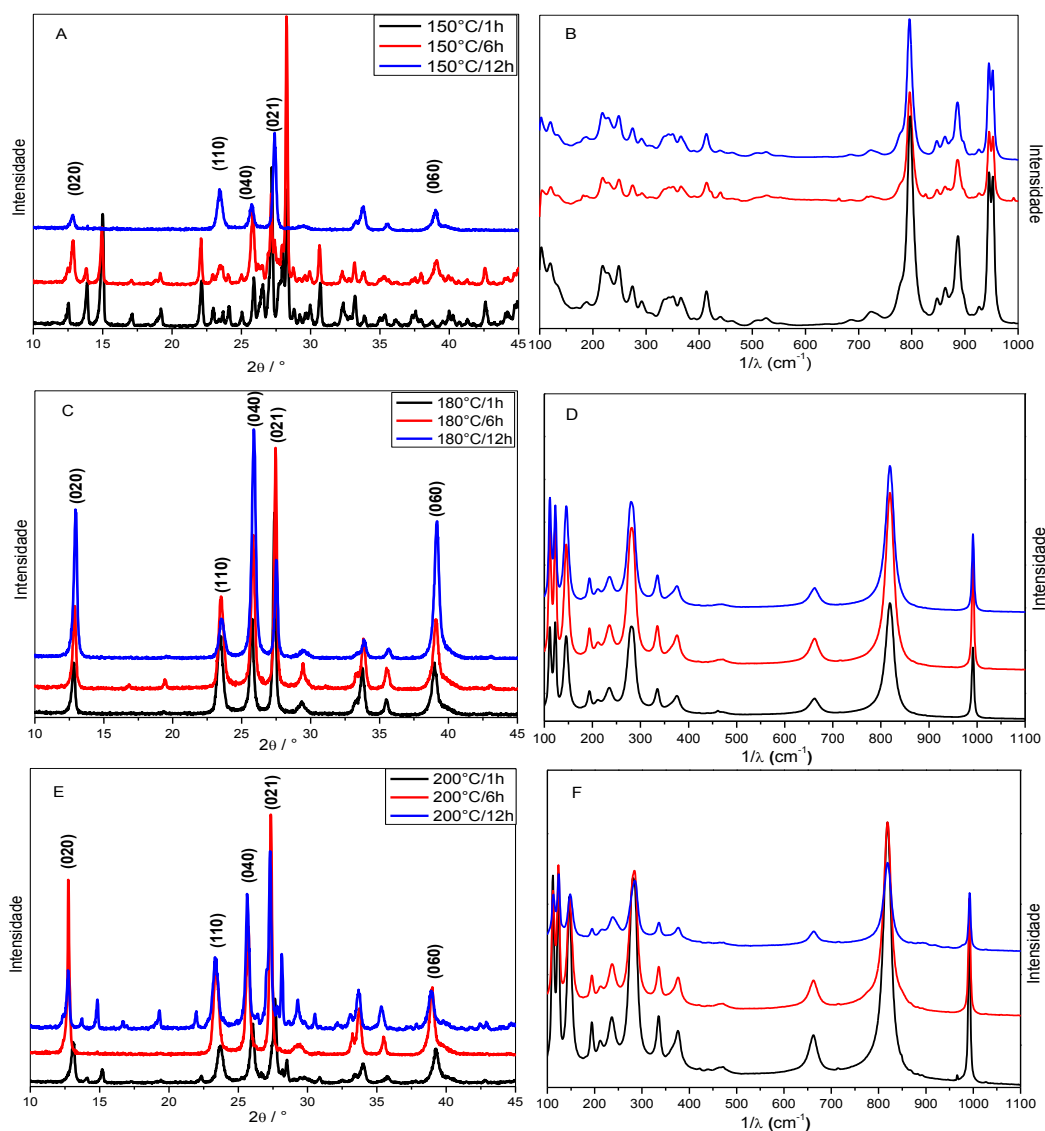


Fig. 2. XRD and Raman of  $\text{MoO}_3$  synthesized by hydrothermal method at 150, 180 and 200 °C from different times (1, 6 and 12h) and calcined at 300 °C by 12h.

Fig. 1 (a, c and e) presents the intensity of (0K0), (110) and (021) peaks from  $\text{MoO}_3$ . It is possible to observe that the variation intensity of peaks are not regular, but for all temperature of synthesis the (0K0) peaks shows more intensity at 180 °C (HT6). With 6h of calcination at 300 °C, Fig. 2 (a, c and e), the (110) and (021) peaks are more intense on hydrothermal conditions at 150 °C/12h (HT3). On the other hand, on hydrothermal conditions at 200 °C the (0K0) peaks shows more intensity with 1h of calcination (HT7). With calcination time of 12h at 300 °C it is observe that the variation intensity of peaks are not regular, such as HT1 to HT9. For all temperature of synthesis the (0K0) peaks shows more intensity at 180 °C (HT14). In this calcination conditions, the (110) and (021) peaks are more intense on hydrothermal conditions at 180 °C (HT14). On hydrothermal conditions at 200 °C the (0K0) peaks shows more intensity with 6h of calcination (HT17).

Observing Fig. 1 and 2, it is possible to conclude that only on calcination time of 6h at 300 and hydrothermal condition of 150 °C/12h (HT3) and in calcination time of 12h at 300 and hydrothermal condition of 150 °C/6h (HT11) reveals the existence of a single crystalline orthorhombic phase and is consistent with the as-synthesized  $\alpha\text{-MoO}_3$  sample

Fig. 3 shows SEM of MoO<sub>3</sub> hydrothermally synthesized at 150 °C for 1h (Fig. 3a) and 150 °C for 6h (Fig. 3b), both calcined at 300 °C for 6h. SEM observation indicates partly cracked elongated nanoplates with ~1.5 μm length, ~350 nm width and up to 50 nm thickness. At higher temperature (180 and 200 °C), the dominant morphology is larger sheets which were formed by the coalescence of individual nanorods

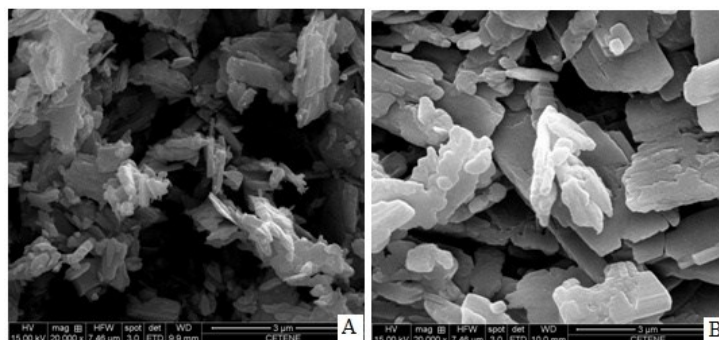


Fig. 3. SEM image of MoO<sub>3</sub> hydrothermally synthesized at 150 °C and calcined at 300 °C for 6h

## Conclusion

We successfully synthesized  $\alpha$ -MoO<sub>3</sub>,  $\beta$ -MoO<sub>3</sub> and h-MoO<sub>3</sub> from commercial [(NH<sub>4</sub>)<sub>6</sub>(Mo<sub>7</sub>O<sub>24</sub>).4H<sub>2</sub>O] in this study. The key to these syntheses were the variation on hydrothermal and calcination conditions (time and temperature) of reaction. It is possible to conclude that only on calcination time of 6h at 300 and hydrothermal condition of 150 °C/12h (HT3) and in calcination time of 12h at 300 and hydrothermal condition of 150 °C/6h (HT11) reveals the existence of a single crystalline orthorhombic phase and is consistent with the as-synthesized  $\alpha$ -MoO<sub>3</sub> sample

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