



## Synthesis and characterization of $\text{MnPS}_3$ for hydrogen sorption

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### ABSTRACT

Single phase  $\text{MnPS}_3$  powder was prepared by solid state reaction between Mn, S and P carried out at 650 °C in evacuated silica tube. The structure, morphology and sorption characteristics of the prepared solid were investigated. The results revealed that the obtained  $\text{MnPS}_3$  compound was capable of adsorbing 3.5 wt% hydrogen at –193 °C and a pressure of 30 bar. Little amount of hydrogen (0.07 wt%) was adsorbed at room temperature. The hydrogen adsorption/desorption cycles at various temperatures did not result in irreversible chemical structural changes of the  $\text{MnPS}_3$  compound, but the microstructure after hydrogen cycling diminished and became finer.

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### 1. Introduction

Hydrogen is an ideal energy carrier with dual benefits, being clean for environment and being renewable. Its technical storage is the challenge for the advancement of hydrogen and fuel cell power in transportation, stationary and portable applications [1].

Currently, hydrogen is stored in prototype vehicles as a high-pressure compressed gas or as a cryogenic liquid. The future ultimate use for hydrogen storage technology requires materials to store hydrogen. Materials that are able to adsorb hydrogen by physisorption will be utilized in stationary application, while those capable of absorbing hydrogen by chemical hydride bond formation are good candidates for mobile application [2].

Convenient synthesis method and characterization of the materials properties are crucial issues in the evaluation of materials for their convenience in hydrogen storage. New materials research as potential hydrogen storage media receives continuous interest.

During the last decades the layered compounds of general formula  $\text{MPX}_3$  ( $M$ : transition metal in second oxidation state,  $P$ : phosphorus,  $X$ : S or Se) have attracted considerable attention for their promising applications as cathode materials, catalysts, solid ionic conductors, anisotropic electronic conductors, low-dimensional molecular magnets, nonlinear optical materials and amazing intercalation property for organic compounds [3–6]. The transition metal phosphorous trisulfide,  $\text{MPS}_3$ , has a layered structure related to  $\text{CdCl}_2$  type in the undistorted case; the unit

cell of  $\text{MPS}_3$  can be viewed as monoclinic [7]. The crystalline structure of this compound consists of a succession of sulfur atom planes arranged according to an ABC close-packed hexagonal filling. Within these planes there are octahedral sites that are alternately filled, one third by P–P couples and two thirds by  $\text{Mn}^{2+}$  ions, or empty. Such a cationic filling leads to an alternation of  $\text{S}[\text{Mn}_{2/3}(\text{P}_2)_{1/3}]\text{S}$  sandwiches and the “van der Waals” gaps along the stacking  $c$  direction, where a single  $\text{S}[\text{Mn}_{2/3}(\text{P}_2)_{1/3}]\text{S}$  sandwich constitutes the basic building block. In this minimal sandwich therefore it is possible to distinguish two atomic groups:  $\text{MnS}_6$  and  $\text{P}_2\text{S}_6$  each with near octahedral coordination. The presence of empty and accessible sites in the Van der Waals gaps makes it possible to intercalate different organic and inorganic compounds [8].

The present work reports the result of a study in synthesis and characterization of a new material to be used in hydrogen storage.

### 2. Experimental

#### 2.1. Synthesis

Green  $\text{MnPS}_3$  powder compound was prepared by solid state reaction between stoichiometric amounts of elemental Mn, P and S powders of purity 99.8%. These elements were mixed thoroughly. The mixed brown powders were sealed in a silica ampoule under vacuum of  $10^{-2}$  bar. The ampoule was put in a programmable furnace heated with controlled heating rate of 1 °C/min to 650 °C for 6 days. Then the silica ampoule was left to cool inside the furnace till room temperature.

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## 2.2. Techniques

Powder X-ray diffractograms (XRDs) were recorded in the range  $5^\circ < 2\theta > 70^\circ$ , with Philips X' pert instrument of  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ).

The IR spectrum of the powder was recorded in KBr disks containing a small amount of the compound, with a JASCO FT/IR 6300.

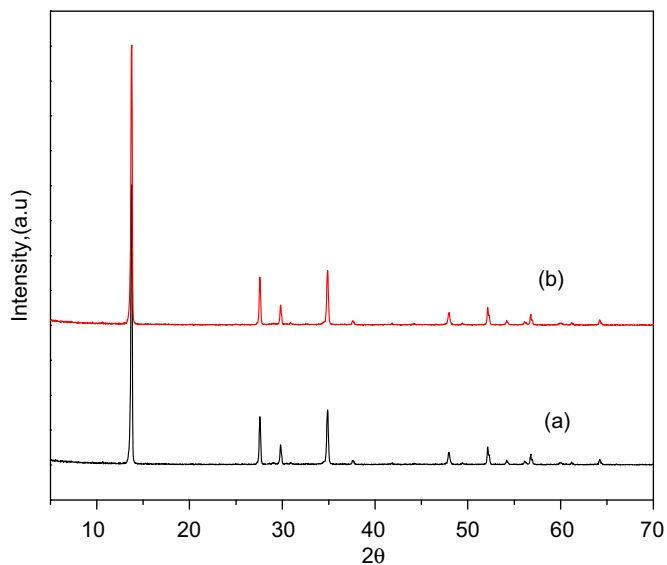
Surface morphology of  $\text{MnPS}_3$  powder was studied by scanning electron microscopy (SEM) JEOL JXA-840A. The powder was spread over double face scotch tapes attached to the holder and sputtered with gold. The voltage used was 30 kV and the magnification was  $3500\times$ .

The transmission electron microscopy (TEM) experiments were carried out at room temperature, on JEOL-1230 microscope running at 120 kV with a tungsten cathode. The sample was prepared by adding minute amount of the powder to de-ionized water. Then ultra-sonication was performed to obtain a suspension of thin particles. One droplet of this dispersion was deposited on a holey carbon grid and after evaporation of water, the particles stuck to the carbon film.

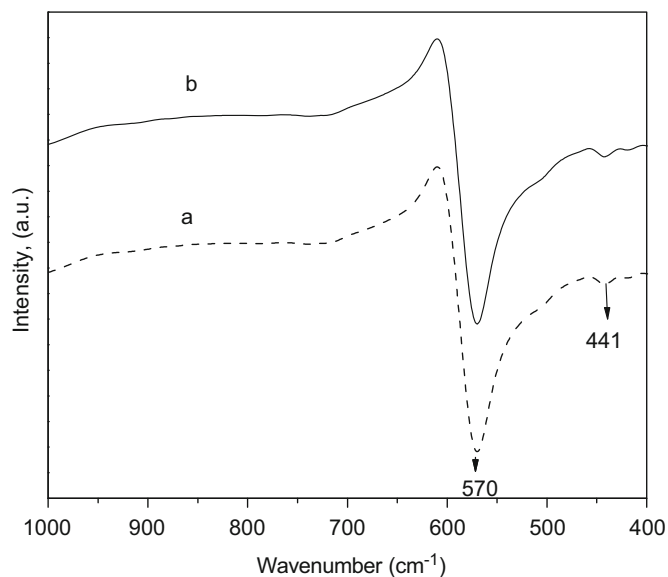
The determination of hydrogen content was carried out by measurement of pressure–composition isotherms (PCI) by a gravimetric method (direct uptake of gas by the material) using an AMC PCI-HP 1200 equipment. The sorption measurements were carried out up to 20 and 30 bar applied hydrogen pressure at room temperature,  $-100$  and at  $-193^\circ\text{C}$ . Temperature was controlled with a precision of  $\pm 0.1^\circ\text{C}$ . The accuracy of hydrogen content measurements was  $\pm 0.04 \text{ wt\%}$ . In order to minimize contamination from air the compound powder was degassed at  $200^\circ\text{C}$  for 1 h under dynamic vacuum before test. Pressure–composition isothermal (PCI) plots were traced under the above mentioned conditions. In addition the sorption kinetics at  $-193^\circ\text{C}$  was evaluated.

## 3. Results and discussion

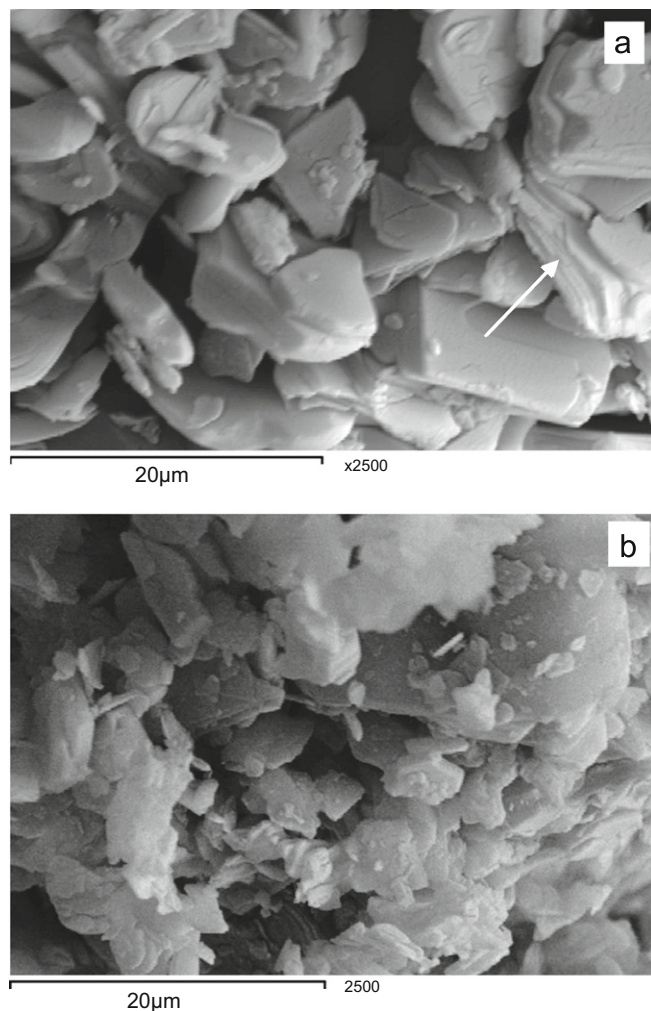
The XRD diffractogram of prepared  $\text{MnPS}_3$  is shown in Fig. 1(a). All characteristic diffraction lines of the  $\text{MnPS}_3$  phase were observed, indicating the formation of a single compound. The sharpness of the peaks suggests the formation of well crystallized



**Fig. 1.** X-ray diffractograms of  $\text{MnPS}_3$  (a) as-prepared and (b) after hydrogen adsorption/desorption cycles.



**Fig. 2.** IR spectra of  $\text{MnPS}_3$  powder (a) as-prepared and (b) after hydrogen adsorption/desorption cycles.



**Fig. 3.** SEM images of  $\text{MnPS}_3$  powder (a) show the agglomeration of the platelets as pointed by the arrow and (b) display the agglomeration in vertical arrangement.

[001]  $\text{MnPS}_3$ . The parameters of the monoclinic unit cell are  $a=6.076 \text{ \AA}$ ,  $b=10.524 \text{ \AA}$ ,  $c=6.796 \text{ \AA}$  and  $\beta=107.35^\circ$  in agreement with JCPDS card 33-0903.

The IR spectrum of pure  $\text{MnPS}_3$  in Fig. 2(a) shows the presence of the characteristic degenerate stretching band  $\nu(\text{PS}_3)$  at  $570 \text{ cm}^{-1}$ . This band is an evidence for the formation of phosphorous trisulfide transition metal compound. Additionally, in the medium infra red band at  $441 \text{ cm}^{-1}$  a peak appears that corresponds to the  $\nu(\text{P-P})$  bands or  $T_2(\text{PS}_3)$  [9]. These studies confirm the formation of the desired species.

Surface morphology of  $\text{MnPS}_3$  was investigated by SEM, as shown in Fig. 3. It shows that its surface is in the form of vertically agglomerated platelets as pointed by the arrow. The particles size varies from 9 to  $18 \mu\text{m}$  while its thickness varies from 0.6 to  $1 \mu\text{m}$ .

TEM micrograph of  $\text{MnPS}_3$  is recorded in Fig. 4. The bright field image (a) displays obviously hexagonal layered plates, which seem to be arranged over one another as pointed by the arrow. The electron diffraction pattern from the selected area is displayed in image (b). It shows diffraction spots superposed on diffused halo rings. The diffraction spots indicate the formation of a single crystalline [001]  $\text{MnPS}_3$  phase and the diffused rings in the background record the presence of a few amorphous phases.

The hydrogen sorption isotherm curves of  $\text{MnPS}_3$  powder at room temperature and at  $-100^\circ\text{C}$  are recorded in Fig. 5. Up to 20 bar, the sample adsorbed low hydrogen content of 0.08 wt% at  $25^\circ\text{C}$  and the adsorption of hydrogen has enhanced at  $-100^\circ\text{C}$  to reach 0.7 wt%.

At  $-193^\circ\text{C}$ , the isotherm shows a linear progression over the investigated pressure range. The hydrogen adsorption content reaches 3.5 wt% at 30 bar as reported in Fig. 6 in the first cycle.

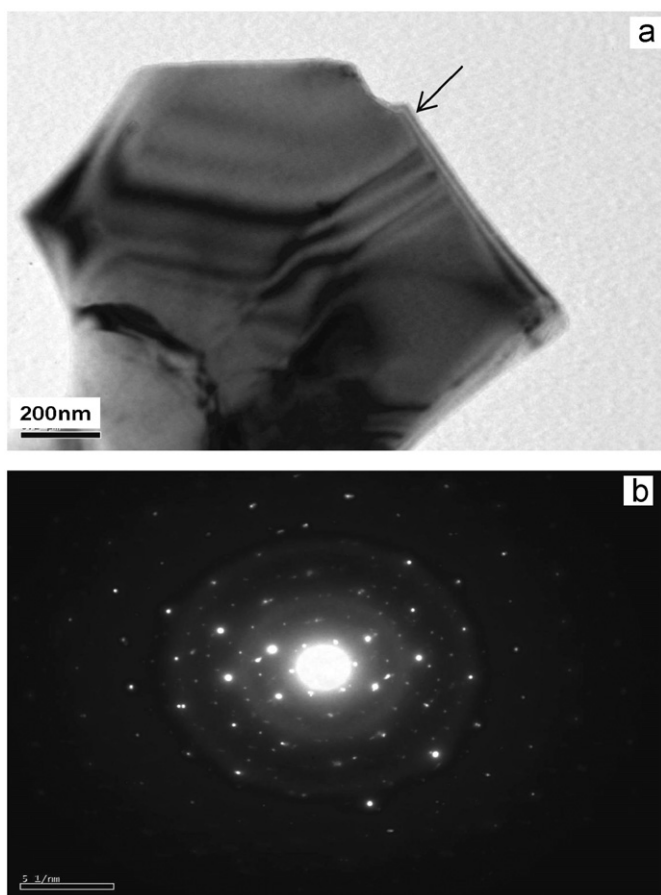


Fig. 4. (a) TEM micrographs recorded on as-prepared  $\text{MnPS}_3$  powder bright field image. (b) Electron diffraction pattern of the studied area.

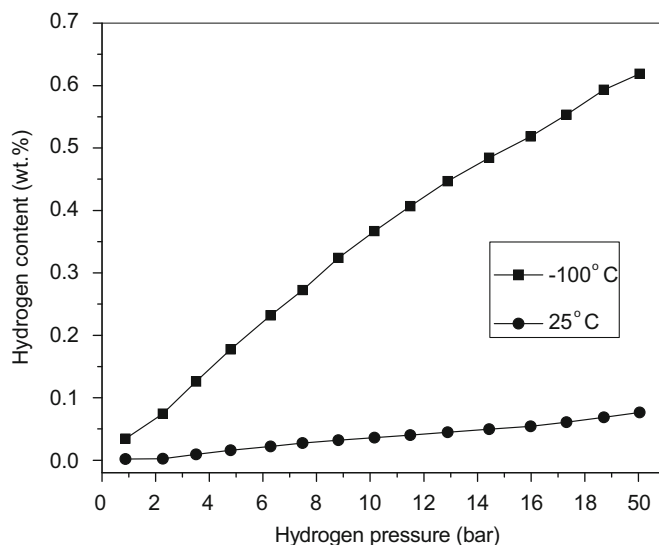


Fig. 5. Pressure-composition isotherm (PCI) curve of  $\text{MnPS}_3$  at room temperature and  $-100^\circ\text{C}$ .

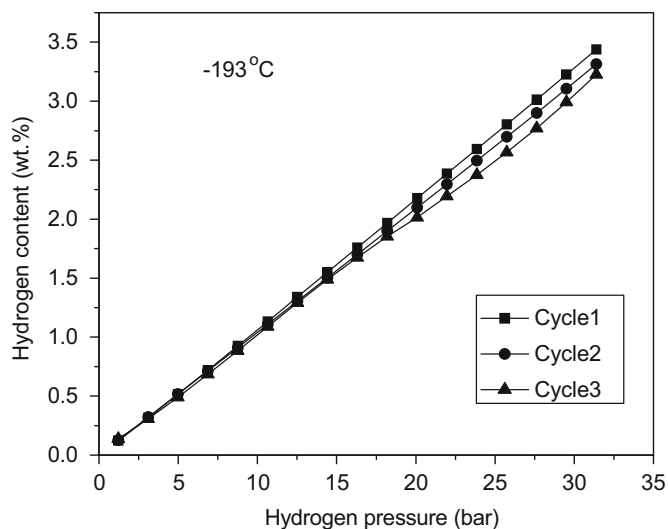


Fig. 6. Pressure-composition isotherm (PCI) cycles of  $\text{MnPS}_3$  powder at  $-193^\circ\text{C}$ .

Cycling the hydrogen revealed that the amount of hydrogen adsorption before 15 bar is almost identical in the three cycles. After 15 bar, the adsorption slightly decreases on increasing the cycle number.

The adsorption/desorption kinetics of the powder is studied under different conditions as shown in Fig. 7. At  $-100^\circ\text{C}$  and 30 bar, the  $\text{MnPS}_3$  powder adsorbs 0.7 wt% hydrogen within 100 min and it takes the same duration to desorb it completely. When the applied hydrogen pressure increases to 20 and 30 bar, the powder is capable of adsorbing 2 and 2.9 wt% hydrogen, respectively, within 30 min. Yet, the kinetics of the hydrogen desorption is slow so that full desorption of 2.9 and 2 wt% hydrogen takes 100 and 200 min, respectively.

The corresponding specific surface area and apparent micropore volume have been calculated from the physisorption isotherm data of  $\text{N}_2$  at 77 K on the basis of Brunauer-Emmett-Teller (BET) theory [10]. From the linear regression of the BET plot the value of  $16 \text{ m}^2/\text{g}$  was obtained from the surface area. The apparent micropore volume obtained was  $5 \times 10^{-3} \text{ cm}^3/\text{g}$ . BET

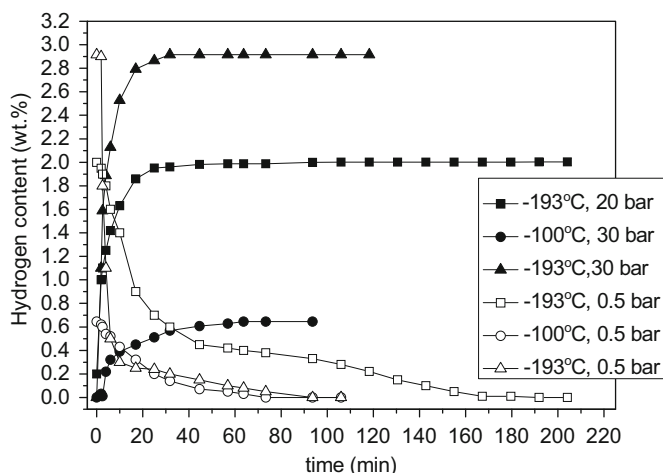


Fig. 7. Kinetic curves of MnPS<sub>3</sub> powder at different conditions.

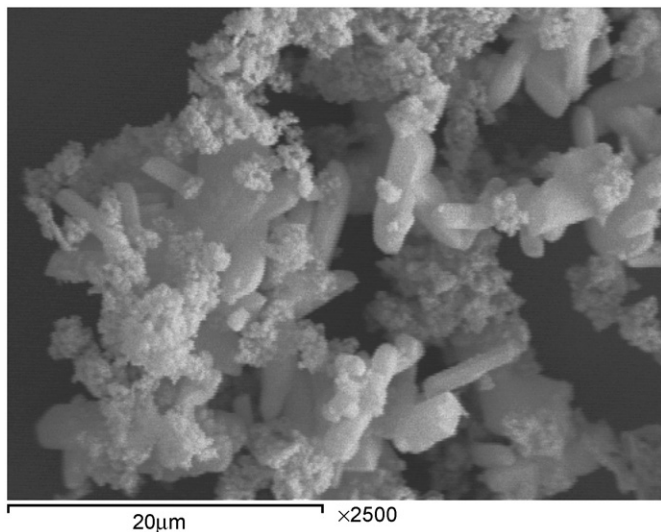


Fig. 8. SEM images of MnPS<sub>3</sub> powder after hydrogenation/dehydrogenation.

analysis yields a small specific surface area and pore volume of the layered MnPS<sub>3</sub>.

It has been proposed that gravimetric adsorption by physisorption on carbon and nanostructured materials is predominantly determined by the surface binding energy at low pressure and by specific surface area at high pressure [11]. Similar mechanism can be assumed for hydrogen adsorption of layered MnPS<sub>3</sub> since it possesses low specific surface area and low pore volume; the capacity to store hydrogen is low. The slow desorption kinetics can be attributed to the presence of Van der Waals forces within the layered structure, which may retard the hydrogen desorption.

After performing adsorption/desorption hydrogen cycles, the structure of MnPS<sub>3</sub> was examined by XRD patterns and IR analysis. Fig. 1(b) clearly shows that MnPS<sub>3</sub> retains its structure when compared to the as prepared sample in Fig. 1(a). In addition, the IR spectrum of MnPS<sub>3</sub> after hydrogenation/dehydrogenation in Fig. 2(b) is similar to that of the as prepared sample in Fig. 2(a).

Nevertheless, the microstructure after dehydrogenation obviously alters as displayed in Fig. 8. The grains appear in rod shape of length 7–10 μm and width 0.6–1 μm, in addition to a fraction of fine microstructure. It is assumed that hydrogenation/dehydrogenation at the above mentioned conditions reduces the microstructure.

#### 4. Conclusions

The MPS<sub>3</sub> atomic structure is based on an ABC close packing of S<sup>2-</sup> anions. Cation (M<sup>2+</sup>) filling of every other layers leads to a succession of [MPS<sub>3</sub>] sandwiches and van der Waals gaps altering along the stacking *c* direction. The elemental composition of MnPS<sub>3</sub> compound reveals no affinity towards hydrogen, i.e. no hydride formation is expected. Hence it is assumed to adsorb hydrogen on the surface, in the micropores and in the interlayer spacing. Similar to other layered and porous materials, MnPS<sub>3</sub> adsorbs little amount of hydrogen at room temperature. But, at cryogenic temperature, the adsorption capacity increases.

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