

Fabrication and Characterization Single Crystal of FePS₃ Layered Material

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Abstract: Single crystal sheet of layered material, FePS₃, grows inside sealed and evacuated silica tube. The FePS₃ forms at 650°C under a controlled heating rate. X-ray diffraction (XRD), Scanning electron microscope (SEM) and transmission electron microscope (TEM) have been used to study the crystal structure and morphology. The XRD pattern exhibits sharp 001 reflections of the single crystal alloy sheet. The prepared samples exhibit high thermal stability with a decomposition temperature of 780 °C. The SEM images show smoothness of the single crystal sheets. Corrosion behavior was investigated by using open circuit potential, Tafel polarization and cyclic voltametry in presence of 10% hydrochloric acid. The crystal open circuit potential shifts to the nobler direction. There is a passive region in the anodic branch of the polarization curve. The presence of the passive region reflects high corrosion resistance. This behavior of high corrosion resistance can be rationalized on the basis that single crystals are free from grain boundaries.

Keywords: Layered materials, FePS₃; Single Crystal; XRD; Electrochemical Behaviour.

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1. INTRODUCTION

Single crystal is the perfect structure of crystalline materials. It is free of grain boundaries. This behavior increases its corrosion resistance. However, there are few methods for preparing bulk single crystals. MnPS₃ single crystals were grown from a powder mixture of Mn, P and S [1, 2]. Transition metal chalcogenophosphates or layered materials, MPX₃ (M ≡ transition metals; X ≡ S or Se) show fascinating structure, electric and magnetic properties [3-6]. The structure of these materials is closely related to that of the well-known transition metal dichalcogenide, MX₂ [7-9]. They have been applied in many fields such as nonlinear optical materials, magnetic materials, photomagnetic materials, catalytic materials, medical and biomedical materials and cathode materials in the rechargeable batteries [10-14]. The layered materials, especially, FePS₃, MnPS₃ and MgPS₃, were investigated for hydrogen storage application and the results were promising [15-17]. Physical properties and characterization of such materials were extensively studied [18-23]. The electrochemical characteristics of the MPS₃ and NiPS₃ as cathodic materials in room temperature lithium batteries were investigated [24]. The theoretical specific capacities of a family of layered compounds MPX₃ (M = Fe, Co, Ni; X = S, Se) involving 1.5, 2, 6 and 9 lithium atoms per MPX₃ molecule have been estimated [25]. The data show that FePS₃ and NiPS₃ are good electroactive materials for primary lithium cells [26]. This work aims at studying growth of single crystal of the FePS₃ layer material under vacuum conditions. The single

crystal growth was noticed during fabrication of the FePS₃ and aging the material in the sealed evacuated ampoule. Electrochemical behavior was tested in an acidic solution to investigate corrosion resistance of the single crystal sheet of FePS₃.

2. RESEARCH METHODOLOGY

Stoichiometric weights of starting materials (iron (Fe), phosphorus (P) and sulfur (S) powders) were thoroughly mixed together. They were sealed in an evacuated silica tube under vacuum of 10⁻² bar. The sample was heated to 650 °C under fast heating rate of 40 °C/min.. Single crystal sheets with different sizes (up to 1 cm length) grow inside the tube during reaction in the furnace and after taking the tube out of the furnace. The structure was detected by X-ray diffraction pattern using a Philips X' pert instrument of CuK_α radiation (λ=1.5418 Å). Infrared spectra were obtained in the range 400 – 1000 cm⁻¹ on samples pressed into KBr pellets, using a JASCO FT/IR 6300 Fourier transformations infrared spectrometer. The thermal stability of the prepared materials and its decomposition temperature were determined by measuring its thermo gravimetric analysis (TGA) curve by a "DSC Q 600"-V 20.5 under nitrogen flow atmosphere with a heating rate 10 °C/min. Surface morphology was studied by scanning electron microscopy using a SEM-EDEX JEOL JXA-840 A. An electrochemical classic three-electrode cell was used for corrosion experiments, open circuit potential, Tafel polarization and cyclic voltametry measurements. The saturated calomel electrode (SCE) was used as a reference, and all potentials are given with respect to this

reference. The counter electrode was a platinum grid. The working electrode is made of the single crystal sheet of an area of size 1 cm². Electrochemical measurements were made using a Volta-Lab, Potentiostat-PGZ 301.

3. RESULTS AND DISCUSSION

3.1 Synthesis of FePS₃ Single Crystal

The structure of the FePS₃ single crystal was identified by XRD diffraction patterns, as shown in Fig. (1). The d-spacing value of the FePS₃ is nearly 6.4 Å (Bragg angle, 2θ = 13.8°). The XRD patterns were indexed in the monoclinic unit cell space group C2/m in which the parameters calculated by a least-squares refinement of the observed reflections, are a = 5.946 Å, b = 10.300 Å, c = 6.7222 Å, and β = 107.16° [27, 28]. IR spectra shows stretching peak at about 604 cm⁻¹, as in Fig. (2). The IR spectrum of the FePS₃ was identified by the presence of the ν(PS₃)²⁻ asymmetric stretching peak at 570 cm⁻¹ of FePS₃ powder and other layered materials [18, 28, 29]. As observed in Fig. 2, there is a shift in the stretching band. This shift may be due to the formation of single crystal of the FePS₃, which is free of grain boundaries.

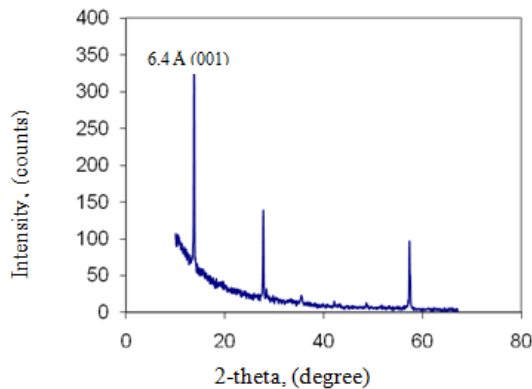


Fig. 1. XRD patterns of FePS₃ single crystal formed inside evacuated ampoule at RT.

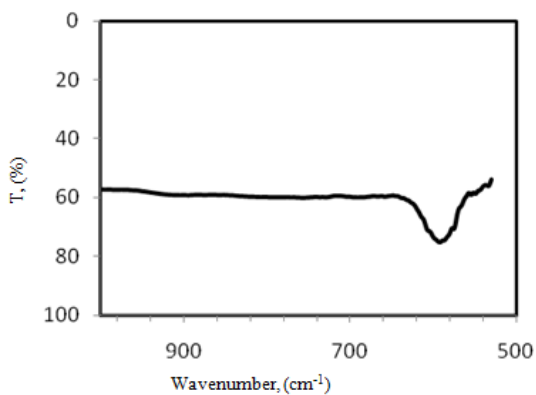


Fig. 2. IR Spectra of FePS₃, single crystal sheet.

3.2 TGA of FePS₃ Single Crystal

Thermogravimetric analysis (TGA) investigates thermal properties of FePS₃ single crystal, as shown in Fig. (3). The FePS₃ single crystal shows two steps of weight loss, the first is from 20 to 200 °C, and the second is from 200 to 760 °C, where the total weight loss is about 40 % of the FePS₃. It can be seen that the trend of the TGA measurements changes from 20 °C to about 200 °C. This behavior may be due to dehydration of the FePS₃ over this range of temperatures. It was stated that silicate showed the same behavior due to gradual and differential dehydration over a wide temperature range up to 800 °C [30]. In fact, water inserts in the interlayer gap of FePS₃, 6.4 Å, [13]. The DSC measurements indicated that decomposition temperature of FePS₃ was within the range of 720 to 740 °C [16]. As observed in Fig. 3, the decomposition temperature increases to about 780 °C due to the formation of single crystal sheet.

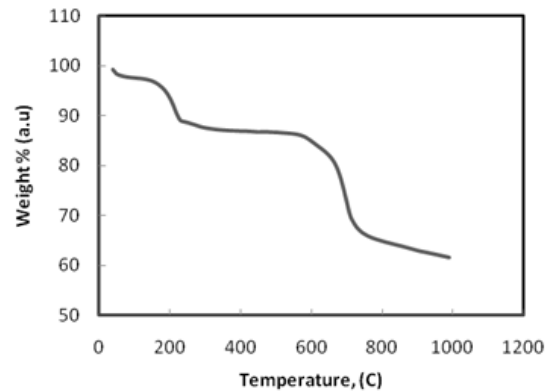


Fig. 3. TGA plots of single crystal sheet of FePS₃.

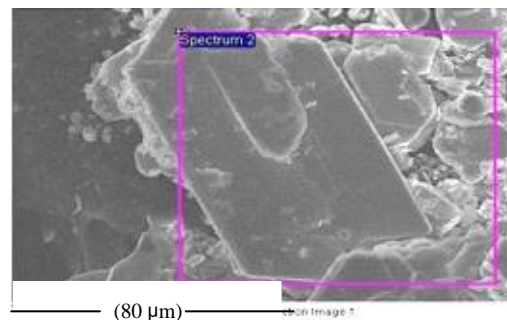


Fig. 4. SEM of FePS₃ single crystal alloy.

3.3 Structure Morphology

SEM-EDEX analyses the structure morphology and chemical composition of the FePS₃ single crystal, as shown in Fig. 4. The SEM images show a homogeneous aspect composed of a flat and smooth crystal surface. The sheets have different widths (up to 0.5 cm) and lengths (up to 1.5 cm).

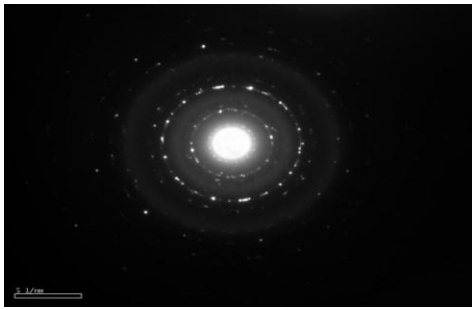


Fig. 5. The SAED of single phase (001) of FePS₃.

The EDX analysis indicates the presence of S, P and Fe elements in the crystal sheet. The analysis of an area corresponding to the image on Fig. 4 shows that the material essentially contains Fe, P and S in respective proportion of atomic percent, 18.38 % Fe, 20.72 % P and 60.92 % S. This result confirms that the chemical structure of the single crystal is FePS₃. The selected area electron diffraction patterns (SAED) uses to measure the single crystal of the FePS₃ [16], as shown in Fig. 5. The pattern shows perfectly crystalline structure of the FePS₃.

3.4 Electrochemical Measurements

Open circuit potential measurement of FePS₃ single crystal was recorded in an acidic solution (10 % HCl) and shown in Fig. 6. The potential varies within a potential of -150 mV and there is a little shift towards the cathodic direction. This means that the presence of 10% HCl affects the corrosion resistance of the FePS₃ single crystal. Fig. 7 shows a potentiodynamic polarization curve of the FePS₃ single crystal in 10% HCl solution at RT. The corrosion potential was -530 mV with a passive region with its average current density of ~1.2 mAcm⁻², extending from -420 to -30 mV, where a passive layer breakdown takes place due to the aggressiveness of the HCl. Fig. 8 shows a cyclic voltamograms (CV) obtained of FePS₃ single crystal in presence of 10 % HCl at RT. A number of cycles have been run under the same conditions. Whatever the cycles, the CVs seem to keep the same shape with two peaks [31]: the FePS₃ reduction and oxidation peaks. The comparison of the shapes of the anodic and cathodic peaks on the CV, as a function of acidic solution, shows the influence of the chloride ions on the FePS₃ reduction and oxidation mechanisms. On the anodic part, the rise of the oxidation peak is in accordance with the presence of Cl⁻. The more Fe²⁺ ions reduce in the cathodic part, the more FePS₃ oxidizes in the anodic region [31, 32]. It was noticed some slight changes of the CV shape. There are some humps on both sides of the CV voltamogram due to presence of Cl⁻ [31].

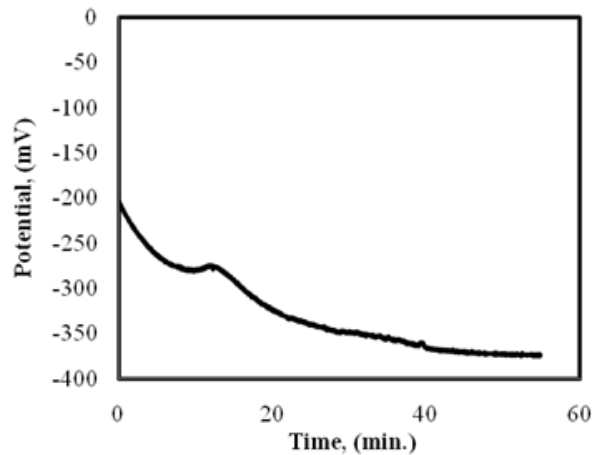


Fig. 6. Open circuit potential of FePS₃ single crystal sheet in 10% HCl at RT.

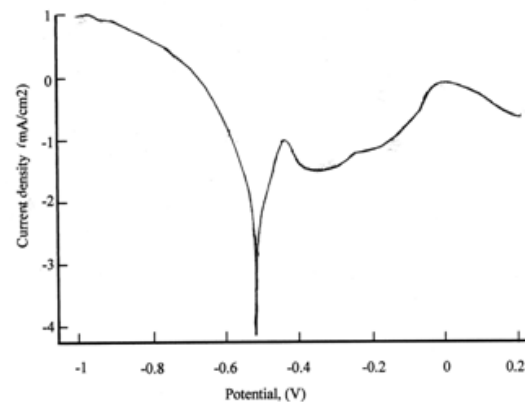


Fig.7. Tafel polarisation of FePS₃ single crystal in 10% HCl at RT.

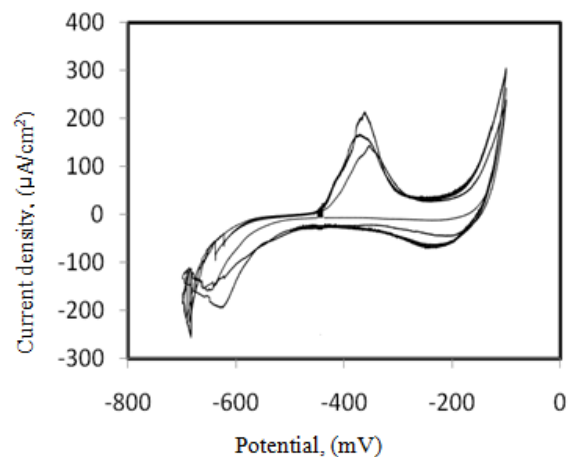


Fig. 8. Cyclic voltamograms of the FePS₃ single crystal in 10% HCl at RT.

4. CONCLUSION

A single crystal of FePS₃ grows in evacuated silica tube. XRD identifies crystalline structure of the FePS₃ single crystal. SEM images show perfect platelet layers of the FePS₃ material and the EDX analysis indicates presence of the FePS₃ elements, Fe, P and S. The most important outcome of this work is the formation of the single crystal sheet of the FePS₃. The electrochemical measurements indicate high corrosion resistance of the FePS₃ single crystal due to presence of the passive region, low current density and anodic trends of open circuit potential.

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