

DEEP INSIGHT IN THERMAL SYNTHESIS OF TIN DISULPHIDE(SnS_2) MICROPLATES, STARTING FROM TIN SULPHATE AND SULFUR: GROWTH MECHANISM BASED ON LUX FLOOD'S THEORY OF ACID AND BASE

H. MOSSAK KAMKUI^{a*}, S. LAMINSI^b, D.NJOPWOUO^c, A. TIYA DJOWE^d

^aMineral Chemistry laboratory, Department of Inorganic Chemistry, Faculty of Sciences, University of Yaounde I Cameroon P.O Box: 812 Yaoundé

^bMineral Chemistry laboratory, Department of Inorganic Chemistry, Faculty of Sciences, University of Yaounde I Cameroon P.O Box: 812 Yaoundé

^cLaboratory of Physical Chemistry of Mineral Materials, Department of Inorganic Chemistry, Faculty of Sciences, University of Yaoundé I Cameroon P.O Box 812 Yaoundé

^dCatholic University of Louvain Institute of Condensed Matter and Nanosciences, Belgium

This paper reports new insight in thermal synthesis of tin disulphide microplates, starting from sulfur and tin sulphate, under normal atmosphere and without assistance of template. New reaction mechanism, based on LUX-FLOOD's theory of acid and base, has been proposed to explain the formation of SnS_2 microplates. Temperatures of the reactions are 250°C and 400°C. The mixture of reactants was heated up for forty minutes. The resultant powder has been consequently washed and dried at 100°C until constant mass. XRD, Elemental analysis and MEB reveal that, the product obtained at 250°C consists of microplates of SnS_2 with thickness of about 412nm and length ranging between 573nm and 2.27 μm . At 400°C, the obtained product is a mixture of tin sulphide, tin oxide, sulfur, and unspecified phase. The presence of these phases is revealed by XRD and confirmed by thermal analysis. We have established that, tin disulphide cannot be considered as main product of reaction at 400°C. Molten Sulfur acts as reaction medium and resembles molten salt, that makes possible oxidation of O^{2-} ions and reduction of sulfur, whence the proposed reaction scheme.

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1. Introduction

Tin sulfides have been given in recent years a renewed interest. With the advent of thin films, tin disulfide has more and more applications, such as semiconductor [1] as photo luminescent materials [2], as pigment [3]. CZTS thin films or mono layer grain CZTS in expanding [4-8] make tin disulfides more and more useful.

Given the importance of tin disulfide, many synthesis routes have been explored [2, 9-13]. Although to date, pure SnS_2 with different shapes and sizes is obtained by various methods, the formation of SnO_2 during the synthesis is a parallel and competing reaction [13,14] furthermore, synthesis of nanomaterials or bulk material use as precursors, tin(II) chloride dihydrate or tin(IV) chloride dihydrate and a source of sulfur [12, 13,15]. Synthesis of pure SnS_2 , starting from reactants different to those cited above, remains a challenge. Very few studies report the synthesis of SnS_2 starting from precursors other than $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ under normal atmosphere without template. Photovoltaic diodes expanding require pure SnS_2 , at lower cost, in

*Corresponding author: mossakhilaire@yahoo.fr

large quantities, starting from various reagents. A patent describes the synthesis of pure SnS_2 by solid state reaction, starting from SnSO_4 and sulfur in normal atmosphere in temperatures ranging between 400°C and 500°C [16]. The results seem surprising, indeed, from 450°C SnS_2 divided into SnO_2 and SO_2 [17]. On the other hand it is well known that SnSO_4 decomposes into SnO_2 and SO_2 from 378°C . Therefore, it is unlikely that SnS_2 is the major product of a reaction between sulfur and SnSO_4 at 400°C or above. It has been reported that, crystallinity, morphology, size, shape, crystal defects and surface properties of SnS_2 depend on preparation methods and preparation conditions [2,11,18]. Herein we report the synthesis of SnS_2 microplates, starting from SnSO_4 and sulfur at mild temperatures (250°C) under normal atmosphere and without any template.

2. Materials and method

2.1 Reagents

Hydrochloric acid (37%), sodium hydroxide (99%), sulfur (99%), methanol (99.8%), tin sulphate (98%), and carbon disulphide (99%) were purchased from Riedel-de Haen and used without any treatments.

2.2 Synthesis

In a porcelain mortar, mix intimately 0.042 mol of tin sulfate and 0.093 mol of sulfur. Transfer the mixture to a porcelain crucible, heat the crucible to 250°C for forty minutes and then stop heating and cool the crucible at room temperature. The resulting powder was successively washed with concentrated hydrochloric acid, carbon disulfide, methanol and then sodium hydroxide ($\text{pH} > 11$) for twenty four hours. The resulting product is consequently rinsed with distilled water, dried in an oven at 100°C to constant weight and the resulting yellow powder is named P_1 . The product obtained at 400°C is called P_2 .

2.3 Characterization

X-ray powder diffraction (XRD) data were collected at room temperature with a diffractometer operating with the focusing Bragg–Brentano geometry, using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The diffraction patterns were collected at 40 kV and 40 mA (D8, Bruker), over the angular range of 5° – 70° (2θ) with a counting time of 10 s/step and a step length of 0.02° (2θ). Elemental analyses were carried out using a WDX-Ray fluorescence spectrometer (S4 Pioneer, Bruker). The morphology of particle was studied by Scanning Electron Microscopy (SEM) (mod. XL40, Philips, Netherlands). The TGA-DTA measurements of the samples were performed on a thermal analyzer (TA Instruments, Model STD 2960, simultaneous DTA-TGA) at a heating rate of $10^\circ\text{C}.\text{min}^{-1}$ in an air atmosphere.

3. Results and discussion

3.1. Results

P_1 is a yellow powder, well-known tin disulfide color [13]. Elemental analysis for sulfur and tin was carried out and revealed that $\text{Sn}:\text{S} = 32.48:65.23$ and the ratio was 1:2.01 confirming the formation of compound SnS_2 . The Sample is slightly rich in sulfur; this may be explain by the fact that reaction medium is sulfur-rich or by relatively low temperature of reaction.

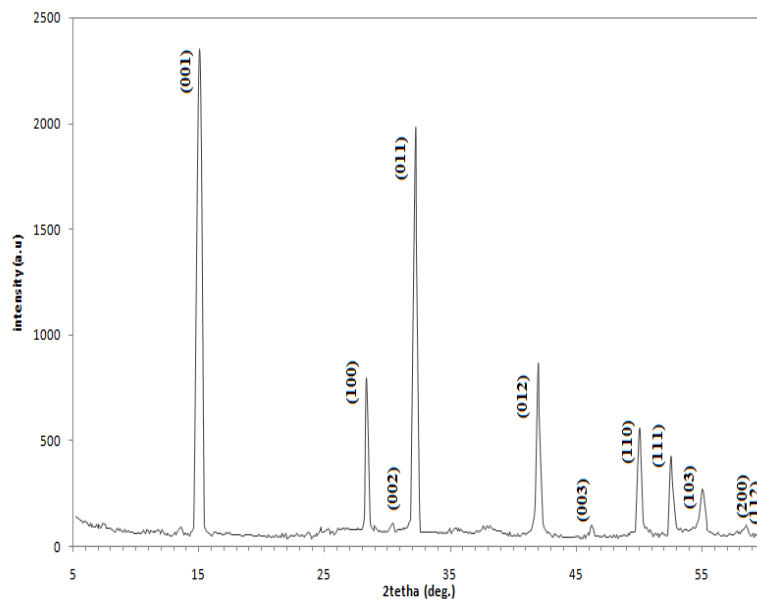


Fig.1. XRD of P_1

XRD patterns of Fig.1 show diffraction peaks that index the hexagonal phase of pure SnS_2 [12,13]. According to prominent Bragg reflection occurring at $2\theta=15.091^\circ$, the preferential orientation growth of as-obtained SnS_2 is along C -direction. The lattice constants, determined in this case are $a=3.6370\text{\AA}$ and $c=5.8661\text{\AA}$, we found $c/a=1.613$. These values are close to standard values¹. No XRD peaks indexing possible impurities such as SnO_2 and S have been detected in Fig.1, also indicating that pure hexagonal SnS_2 was successfully obtained via reaction between tin sulphate and sulfur at 250°C , coupled with a subsequent washing treatment.

Fig.2 shows SEM images of as-obtained SnS_2 at different magnifications. P_1 is formed of microplates that are either bonded to one another or isolated. The microplates have a thickness of about 412 nm and a length ranging between 573nm and 2.27 microns. Formation of plate-like SnS_2 may be explained by anisotropic nature of SnS_2 which has a CdI_2 - Related crystal structure [19].

¹ X-ray powder diffraction file JCPDS File reference number 23-677

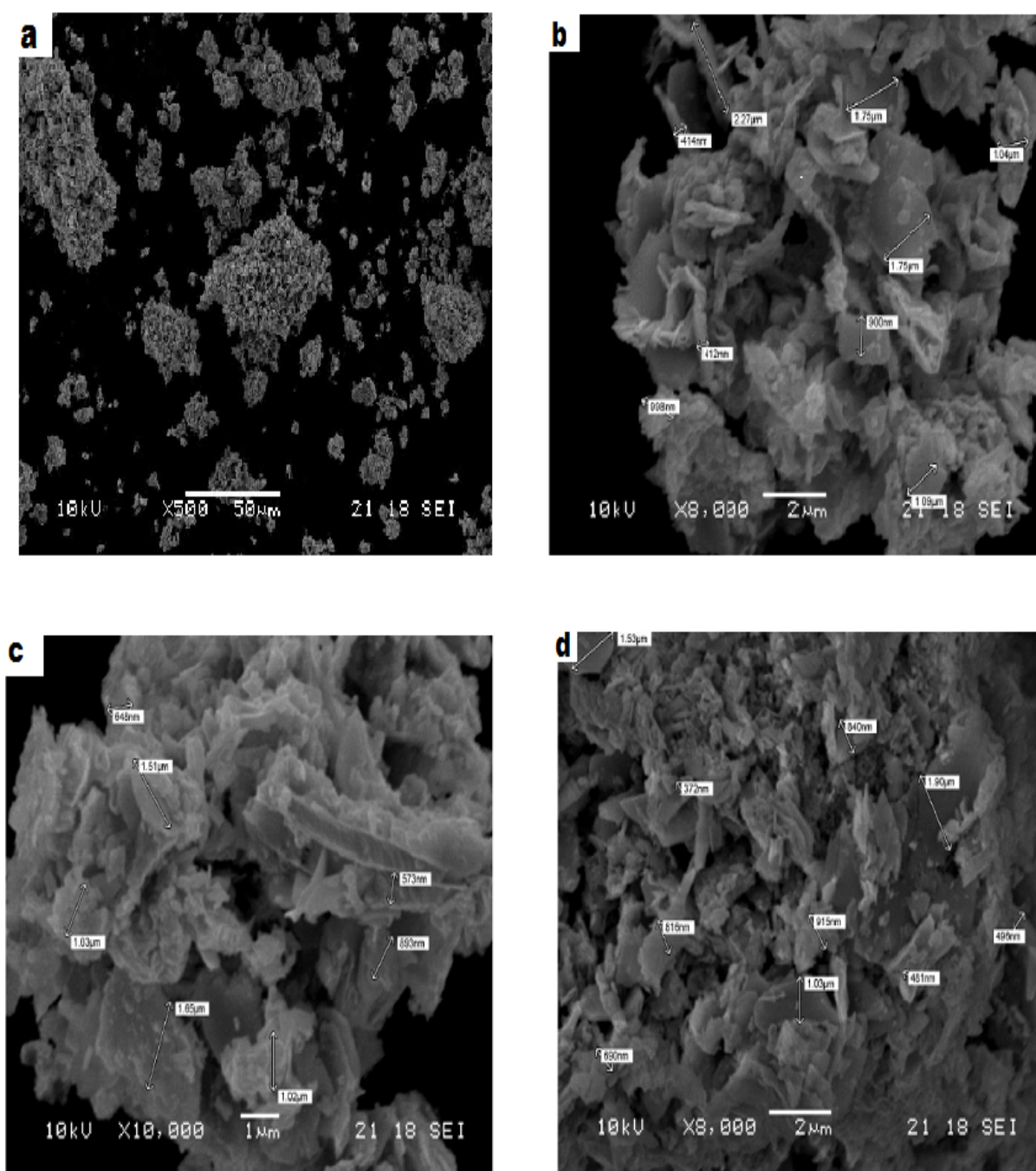
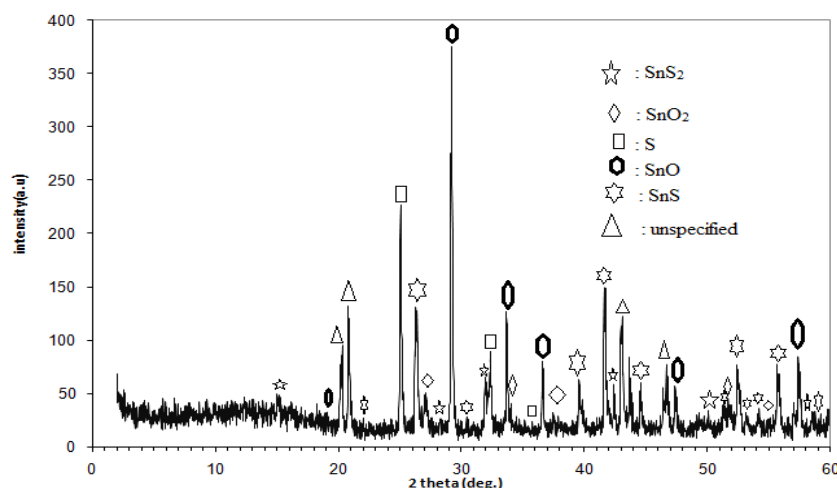
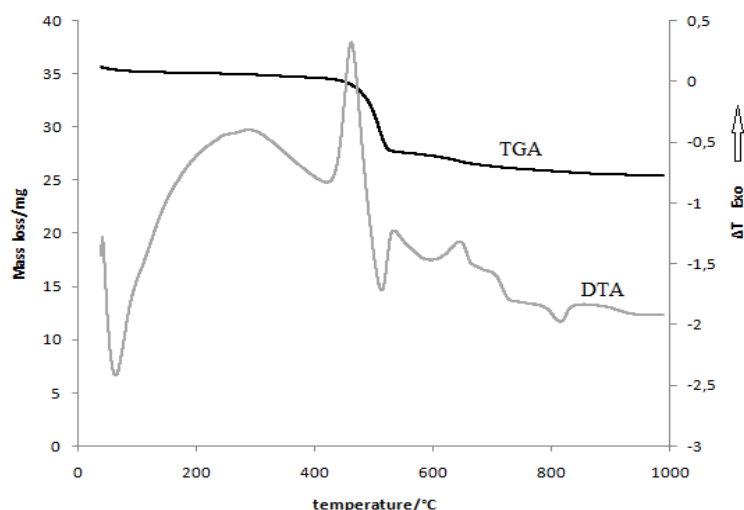


Fig.2. SEM images of the product called P_1 . (a)-Distribution of agglomerates and isolated SnS_2 plates, (b)-measurement of the thickness of SnS_2 chips, (c and d)-dimensions of SnS_2 microplates.

Fig.3. XRD of P_2

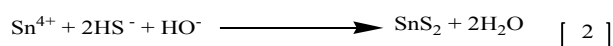
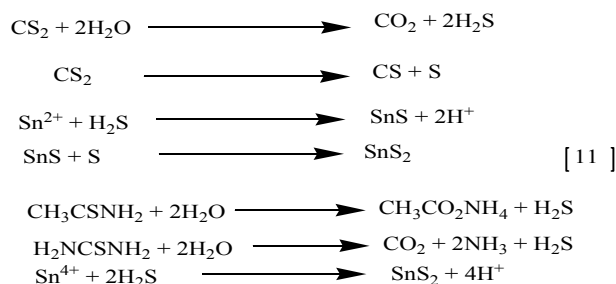
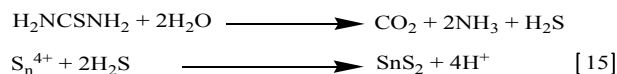
XRD of P_2 has diffraction peaks attributable to several crystalline phases. Those indexing SnS_2 are low in intensity, reflecting either a low presence of SnS_2 or the presence of poorly crystalline SnS_2 . As other crystalline phases we have found sulfur [20], tin oxide (IV) [21], tin oxide (II) [22], tin sulfide (II) [23] and unidentified phase.

Fig.4. TGA and DTA of product P_2

3.2. Discussion

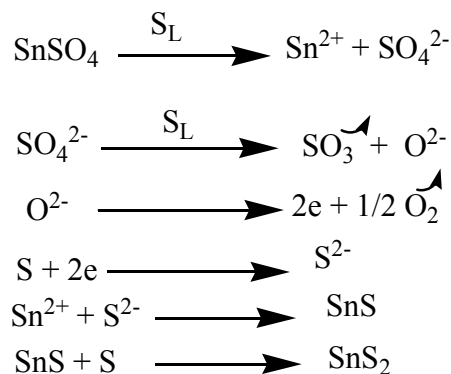
3.2.1 Synthesis of tin disulfide

The role of sulfur during the formation of SnS_2 has already been discussed. Yon Cai Zhang & Al [13] suggest that melted sulfur as vector increases the interface and contact surface areas between reactants, which increase the rate of reaction. Melted sulfur prevents oxidation in air of synthesized SnS_2 . The role of sulfur as reactant remains unclear. The same authors have synthesized SnS_2 from thiourea and tin dichloride dihydrate [12] without proposing reaction scheme. To date, proposed reaction mechanisms are the following:



These reaction schemes are based on the formation of H_2S or HS^- whose species make the reaction medium strongly oxidizing. Reaction between melted sulfur and tin sulphate does not offer favourable conditions for the formation of H_2S or HS^- . Tin sulphate is supplier of sulphate ions; the temperature of reaction, above the melting point of sulfur and below its boiling point allows to consider the reaction in the molten sulfur. The reaction medium being liquid, SnSO_4 can dissolve, hence the mechanism:

- SnSO_4 dissolves in the molten sulfur and dissolved SO_4^{2-} is as LUX-FLOOD's base, whence the following assumptions:



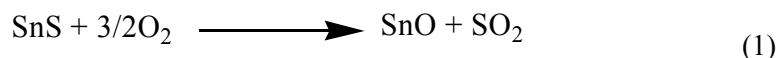
This mechanism involves SnS which is a stable sulfide but not found in the final product. SnS as intermediate species during the formation of SnS_2 has already been mentioned [11]. Oxidation of O^{2-} and reduction of sulfur are the key steps in the formation of SnS_2 . These steps could be explained by the reaction conditions; in fact, the reaction medium is comparable to molten salt medium, which allows oxidation states and attend redox reactions that are not possible in aqueous medium. [24]

3.2.2 Synthesis of P_2

P_2 is a mixture of stannous sulfide, stannic sulfide, stannous and stannic oxide, sulfur and unidentified phase.

Apart from sulfur, all other crystalline phases identified contain tin. Based on the intensity of the diffraction peaks, the most abundant phase is SnO in sequence S and SnS . At 250°C SnS is completely formed and is the predominant product in the reaction medium. The temperature

gradient allows the formation of small amount of SnS_2 according to proposed reaction scheme. A part of SnS_2 is oxidized into SnO_2 . Between 250°C and 400°C we have the following reaction:



Reaction (1) does not consume sulfur; this explains an abundance of sulfur in the mixture although the temperature of reaction is close to the boiling point of sulfur. The presence of liquid sulfur could limit the oxidation of sulfides formed [13], hence the persistence of sulfides in the reaction mixture at 400°C.

The TGA curve shows a mass loss between 37°C and 200°C corresponding to the evolving of water molecules. Between 450°C and 500°C we observe a loss of mass corresponding to the oxidation of tin disulfide (% mass loss calculated / theoretical mass loss: 18.6 / 17.6) into tin oxide. The mass loss observed between 500°C and 900°C corresponds to the passage of sulfur in the vapor state and oxidation of tin sulfide. Tin oxides are stable between 500°C and 900°C. The variations observed in the DTA curve are attributed to transformations of the unidentified phase. Only the exothermic peak with T_{max} at 466°C and the endothermic peak, which rises to 514°C, correspond to the thermal behavior of pure SnS_2 [16].

4. Conclusion

We have synthesized pure SnS_2 at mild temperature. As reagents, we used sulfur, and tin sulfate. The product obtained at 250°C formed by microplates. By the same method but at 400°C we get a mixture of tin sulphide, tin oxide, sulfur, and unidentified phase. The reactions leading to the formation of SnS_2 probably go through the oxidation of O^{2-} ions and sulfur reduction. These reactions are plausible in molten sulfur that apparent the reaction medium to molten salt. SO_4^{2-} dissolved in molten sulfur behaving as LUX-FLOOD's base.

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