https://doi.org/10.30544/MMESEE100

SYNTHESIS OF TIN SULFIDE USING HIGH EXOTHERMIC REACTION

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Abstract

Because of very important compounds such as tin sulfide, tin is critical metal for green economy. SnS applications are mostly used in optoelectronic devices (photovoltaics), lithium- and sodium-ion batteries, and sensors among others with a significant potential for a variety of future uses. Thermochemical analysis of synthesis of SnS and SnS_2 was used for an analysis of possibility for formation of the aimed product. This study explores pyrometallurgical method for synthesis of SnS using pure elements of tin and Sulphur through one strong exothermic reaction in laboratory conditions. The goal is to offer new synthesis method in one closed reactor at temperatures between 220° and 440°C. The mass loss during synthesis was followed in the static conditions. We concluded that this synthesis of SnS can be controlled via an exothermic reaction in very short time. The better results can be reached using the synthesis process in dynamic conditions via an intensive mixing through the synthesis reaction

Keywords: synthesis, tin sulfide, exothermic reaction, thermochemistry

Introduction

Tin(II) sulfide has emerged as an alternative solar absorber material to conventional thin film absorbers such as cadmium telluride (CdTe) and copper indium gallium selenide (CIGS), due to several properties including biological non-toxicity (Norton et al. 2021). Tin and sulfur are also environmentally benign elements that are inexpensive and abundant in nature.

A range of methods have been developed for the creation of nanoscale SnS, ranging from liquid-phase chemical synthesis methods using a variety of different chemicals and reaction conditions including hydrothermal, solvothermal, aqueous solution and hot injection methods. Bottom-up approaches involve the direct synthesis of nanomaterials, and includes methods such as chemical and physical vapour deposition as well as wet chemical synthesis methods. Tin(II) chloride ($SnCl_2$) and tin(IV) chloride ($SnCl_4$) are commonly used as reagents for the synthesis of nanoscale SnS, and have appeared several published methods (Zhu et al. 2005).

Other methods of SnS synthesis include mechanochemical synthesis by high energy milling which involves the tribological reaction between stoichiometric amounts of elemental Sn and S in a ball mill. The resulting SnS in nanocrystalline and forms aggregates with typical length scales of 30–50 µm (Balaz et al. 1999)

This paper will study the synthesis of tin sulfide using elemental sulfur and tin in a closed reaction in temperature between 220°C and 440°C using high exothermic reaction in laboratory conditions and thermochemical prediction.

Thermochemical prediction of the synthesis of SnS and SnS_2

Using thermochemical modelling of this software was performed using HSC Software, Finland for the following reactions:

$$Sn\ (s) + S\ (s) = SnS\ (s) \quad (1)$$

$$Sn\ (s) + 2\ S\ (s) = SnS_2 \quad (2)$$

The analysis presented at Figure 1 confirms high probability for the formation of SnS and SnS_2 via solid state reaction in both cases. An increase of temperature increases the probability for the formation of SnS between room temperature and 600°C in contrast to formation of SnS_2. Generally, the formation of SnS has shown more negative Gibbs energy compared to that formation of SnS_2 what confirms high probability for this synthesis.

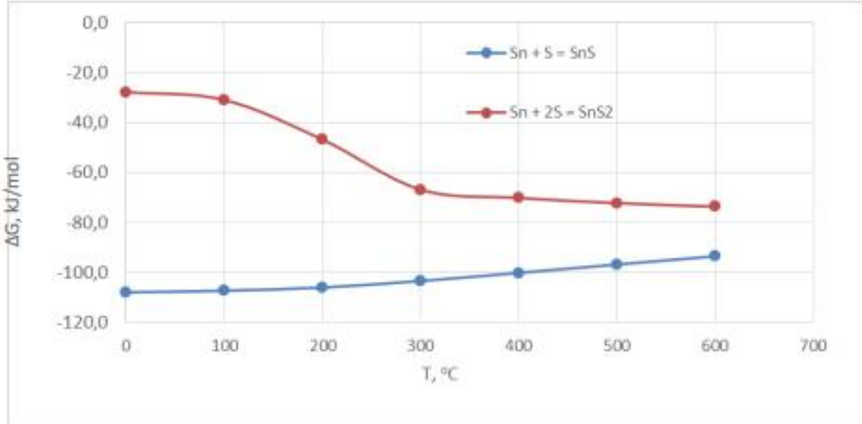

Figure 1: Thermochemical analysis of synthesis of SnS and SnS_2

Materials and methods

Pure sulfur and tin powders were used for the synthesis. The reactor produced in Germany has a small volume, of approximately 1 liter, and has a lid that screws onto the reactor body, where there are pressure connections and other things, as shown at Figure 2.

Figure 100: Reactor for the synthesis of tin sulfide

In this study, the synthesis of tin sulfide (SnS_2) was carried out using an electric heating system with the temperature serving as the primary initiator for the synthesis reaction. A stoichiometric mixture of tin (Sn) and sulfur (S) powders was prepared according to their atomic mass ratio with 65 % Sn and 35 % S to weight, taking in account the atomic masses of Sn (118.7 g/mol) and S (32 g/mol).

The mixing procedure involved homogenizing the powders in a closed plastic container by agitating the mixture for several minutes to ensure uniform distribution of the reactants. Following homogenization, the prepared mixture was introduced into a closed reactor capsule designed for the synthesis reaction. This reactor was equipped with several essential features, including a robust lid, multiple valves, a temperature probe, a pressure gauge, and a valve for pressure regulation, as well as the capability to introduce protective gases as shown in Figure 2.

The duration of the heating process, from the initiation of heating to the completion of the reaction, was 75 minutes.

We did not turn on the reactor to oscillate because we were concerned that the openings leading to the pressure gauge and the opening for pressure release would not be blocked, however this also happened because most likely S sublimated and blocked the opening. Due to technical issues, real-time pressure monitoring during the exothermic reaction was not possible.

A total of 727 gram of tin powder and 391.5 gram of sulfur were loaded into the reactor container. The heating proceeded slowly until at one point the temperature started to rise rapidly, around 220 °C, and in the next 3.5 min it reached 440 °C. Then it started to fall because the heaters did not keep up with the rise in temperature. The reactor capsule was removed and allowed to cool. After an overnight cooling period the product of the reaction was analyzed to access whether it exhibited a crystalline structure with a hexagonal lattice.

The synthesized product was subsequently sent to a laboratory for further chemical analysis. This method of SnS_2 synthesis effectively mitigates the release of excess sulfur into the atmosphere as SO_2 or H_2S, as well as the sublimation of elemental sulfur. Additionally, the effect of metal additives, such as copper (Cu), iron (Fe), or nickel (Ni) powders, was tested to assess potential improvements in the mechanical properties of the synthesized product.

Results and discussion

After the completion of the experiment, a mass loss of 0.86 g was observed from the initial 1118.5 g of reactants. This minimal mass loss confirms the successful completion of the reaction, supporting the formation of the expected tin sulfide (SnS_2) product.

The obtained powder is shown in Figure 3.

After the crystallization of the powder, the resulting structure was obtained, as depicted in Figure 4.

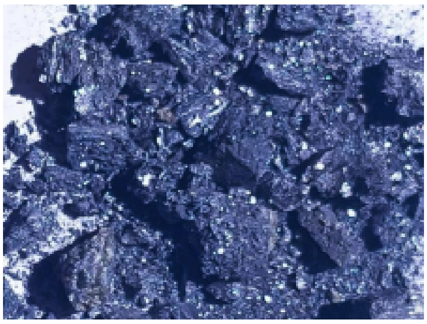

Figure 3: The obtained powder of tin sulfide

Figure 4: The obtained crystalline structure of tin sulfide

Conclusion

Successful synthesis of SnS was performed between 220°C and 440°C using pure tin and sulfur via a high exothermic process. The thermochemical analysis of synthesis has confirmed high probability for the formation of SnS and SnS_2, with a greater probability of SnS formation. The prepared powder of SnS synthetized via solid-state reaction can be alloyed with copper and nickel to improve its mechanical properties

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