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Synthesizing sulphides by a temperature gradient method

Tao Liu *, Jingkun Yu *, Min Chen

Institute for Ferrous Metallurgy, School of Materials & Metallurgy, PO Box 313, Northeastern University, Wenhua Road 3-11, Liaoning, Shenyang 110004, PR China

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Abstract

Metal sulphides were synthesized with a temperature gradient method by using metal and S as starting materials. The relationship among the amount of evaporating sulphur, volume of quartz tube, synthesis temperature and pressure in the quartz tube was studied. The results showed that the maximum amount of evaporating sulphur is 1.15 g in the quartz tube under the experimental conditions, this confirming that the temperature gradient and heating-rate in the synthesis system were controlled. MgS, TiS_2, ZrS_2 and WS_2 were synthesized safely and in large amount: 56.37, 112.00, 155.36 and 247.97 g, respectively.

Keywords: Evaporating sulphur; Temperature gradient method; Sulphide

1. Introduction

Sulphide is one of the important starting materials for synthesizing solid electrolyte sensors [1,2]. The amount and purity of synthesized sulphide are the key factors in the synthesis of solid electrolyte. At present, although there are many ways to synthesize sulphide [3–9], the amount of sulphide synthesized is very limited, ranging from several grams to about 10 g. In addition, the purity of sulphide synthesized does not fit the demands of solid electrolyte sensors. Sulphide synthesized by using metal and sublimed sulphur as the starting materials has been considered as one of the best approaches to obtaining high-purity sulphide [6–9]. With the one-temperature method for sulphide synthesized, the pressure of S increases rapidly and explosion frequently occurs in the synthesis. This method limits the amount of sulphide synthesized and takes a long time for synthesis. To solve this problem, metal is placed in the hot zone (1000 °C) and sublimed sulphur in the zone with temperature gradient. Under these conditions the S vapor is transported to the colder part of the quartz tube gradually and sulphide is formed in the synthesis system. With the process of the reaction and the decreasing of the sulphide, the cold zone temperature is raised gradually. Finally, the temperature gradient disappeared and a large quantity of sulphide is synthesized safely and rapidly by using metal and sublimed sulphur as the starting materials in this experiment.

2. Experimental procedure

2.1. Starting materials

The starting materials used in the present study were Mg (99% purity, ≤75 μm), Ti (99.0% purity, ≤75 μm), Zr (99% purity, ≤20 μm), W (99% purity) and S (sublimed sulphur, 99.0% purity).

3. Experimental

The metal and sublimed sulphur were prepared in a molar ratio of Mg:S = 1:1, Ti:S = 1:2, Zr:S = 1:2 and W:S = 1:2 and then placed on two end of quartz tube ($\Phi = 50$ mm and $h = 50$ mm), respectively. The quartz tube was evacuated using a vacuum pump, then argon at 0.1 MPa pressure was introduced and the quartz tube was evacuated again. This cleaning procedure was repeated thrice to remove any oxygen in the quartz tube. At last the quartz tube was sealed under vacuum of 1.3×10^{-3} Pa. These powders were then subjected to the combustion synthesis.

* Corresponding authors. Fax: +86 24 83681576.
E-mail addresses: liutle@eyou.com (T. Liu), jingkunyu@yahoo.com (J. Yu).

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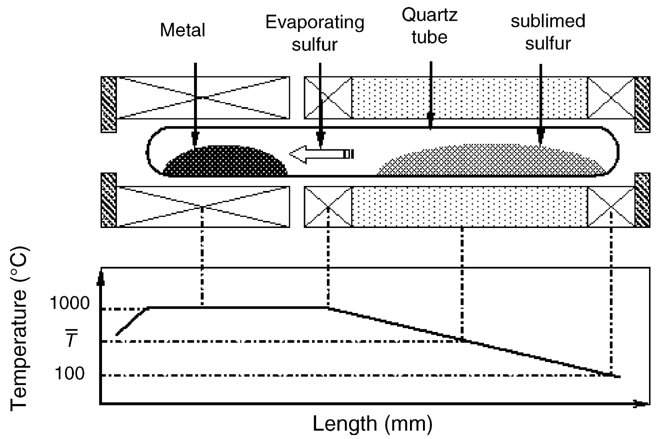

Fig. 1. Schematic diagram of electric furnace and quartz tube reactor used for sulphide synthesis and temperature profiles.

Fig. 1 shows the apparatus of electric furnace and quartz tube reactor used for sulphide synthesis and temperature profiles. The equipment consists of two electric furnaces (constant temperature furnace and temperature gradient furnace) and temperature controller. The quartz tube reactor was placed on the electric furnaces. The one end of quartz tube reactor with the metal was placed on the constant temperature furnace and the other end was placed on the temperature gradient furnace. The metal was heated from room temperature to 1000 °C at the rate of 6 K min^{-1} and held for 8 h. At the same time the sublimed sulphur near the metal was heated from room temperature to 1000 °C at the rate of 6 K min^{-1} and held for 8 h and the sublimed sulphur far away from the metal was heated from room temperature to 100 °C at the rate of 0.46 K min^{-1}. Then the sublimed sulphur far away from the metal was heated from 100 to 1000 °C at the rate of 1.875 K min^{-1}. And the synthesis reaction occurred in the quartz tube.

XRD patterns were used to identify the crystal structure of the samples synthesized. The synthesized samples morphology was studied by SEM and their semiquantitative composition was obtained by energy-dispersive analysis of EDAX.

Table 1
Boiling and melting points of reactants

Temperature	Mg	Ti	Zr	W	S
Melting point (°C)	649	1670	1852	3400	115
Boiling point (°C)	1090	3290	4410	5550	445

Table 2
Effect of temperature on the reaction formation of metal with sublimed sulphur

Temperature (°C)	Mg	Ti	Zr	W
~115	Solid–solid	Solid–solid	Solid–solid	Solid–solid
115–445	Solid–liquid	Solid–liquid	Solid–liquid	Solid–liquid
445–649	Solid–gas	Solid–gas	Solid–gas	Solid–gas
649–1090	Liquid–gas	Solid–gas	Solid–gas	Solid–gas
1090–1670	Gas–gas	Solid–gas	Solid–gas	Solid–gas

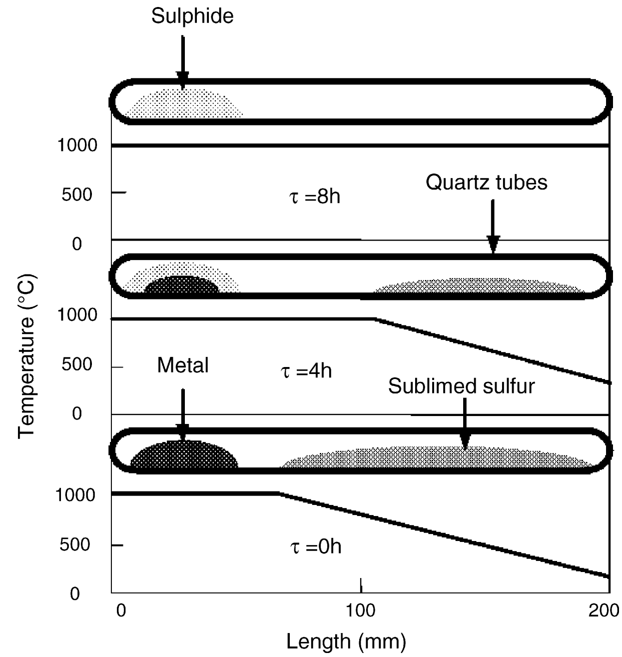

Fig. 2. Temperature distribution along the length direction of quartz tube at different heating time.

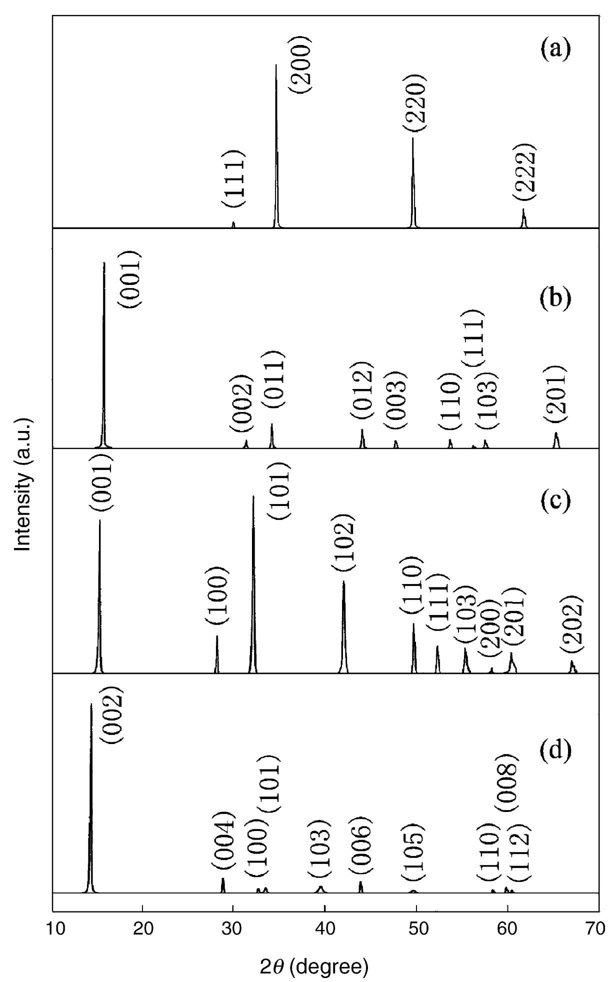

Fig. 3. XRD patterns of the different synthesized samples: (a) MgS; (b) TiS_2; (c) ZrS_2; (d) WS_2.

4. Results and discussion

Table 1 lists melting and boiling points of Mg, Ti, Zr, W and S [10]. The metal reacts with sublimed sulphur according to reaction (1).

$$2xM + yS_2 = 2M_xS_y \quad (1)$$

Reaction (1) proceeds in the different reaction formation based on the different synthesis temperatures. Table 2 shows the effect of the synthesis temperature on the reaction formation.

In the above reaction formation, the solid–gas, liquid–gas and gas–gas reaction play an important role in the synthesis of sulphide, which make the reaction more rapid and complete. But when the gas–gas reaction formation is adopted, much gas is generated in the reaction system, which might cause the quartz tube explosion if the amount of synthesis sulphide is large. Therefore, the solid–gas and liquid–gas reaction formations are considered as important means of synthesizing sulphide safely and in large amount.

In the solid–gas and liquid–gas reaction formations, the metal is heated and controlled as condensed phases (solid or liquid), and sublimed sulphur is controlled as gas state. Reaction (1) can proceed when gas sulphur diffuses toward solid or liquid metal. When the amount of synthetic sulphide is large and the sublimed sulphur in the synthesis material turns to gas sulphur at the same time, explosion danger occurs during the synthesis process. So the key technique to synthesize sulphide safely and largely is to control the maximal amount of evaporating sulphur.

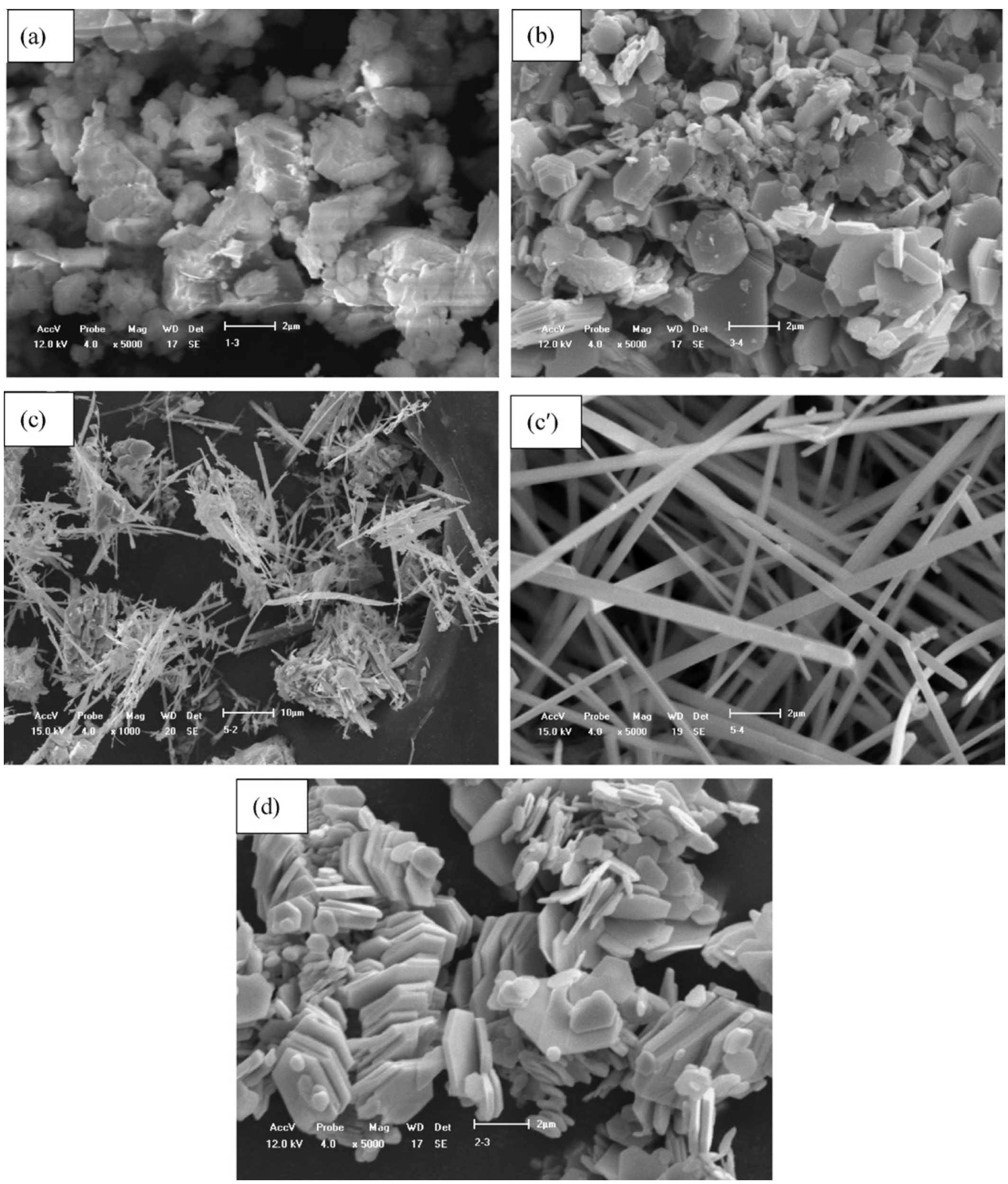

Fig. 4. SEM morphologies of the different samples synthesized: (a) MgS; (b) TiS_2; (c), (c′) ZrS_2; (d) WS_2.

As is shown in Table 2, the sublimed sulphur turns to liquid phase at 115–445 °C, and turn to gas phase when the temperature is higher than 445 °C. Therefore, if the liquid sulphur is transformed into gas sulphur gradually by forming temperature gradient technique, the formation rate of sulphide can be controlled effectively.

M_xS_y is synthesized by the reaction of metal and sublimed sulphur under this experimental condition according to the following reaction.

$$2x\mathrm{M}\,(\mathrm{s\,or\,l}) + yS_2\,(\mathrm{g}) = 2\mathrm{M}_x\mathrm{S}_y\,(\mathrm{s}) \quad (2)$$

To avoid explosion during the synthesis of M_xS_y, the maximal amount of evaporating sulphur is controlled in the quartz tube with temperature gradient. Assuming that mean temperature is $\bar{T}$, volume of quartz tube is V and pressure in the quartz tube is p, the maximum amount of evaporating sulphur m can be expressed by equation (3),

$$m = \frac{MpV}{R\bar{T}} \quad (3)$$

where $M = 64.12$, $p = 0.4$ MPa, $V = (\Phi^2 h/4) \approx 4 \times 10^{-4}\ \mathrm{m}^3$, $R = 8.31\ \mathrm{J\,mol^{-1}\,K^{-1}}$, $\bar{T} = 1073$ K. Then the maximal amount of evaporating sulphur m is 1.15 g, that is, the instantaneous amount of evaporating sulphur m in the quartz tube is limited to 1.15 g by controlling the temperature gradient and heating-rate in this synthesis system.

Fig. 2 shows temperature distribution along the length direction of the quartz tube at different heating time. The variations of reactant and product with the heating time are also showed in the quartz tube during the synthesis process. With reaction time increased, temperature of synthesis system increased, high temperature region extended, low temperature region shortened, the metal and the sublimed sulphur decrease and the sulphide increase. When reaction time is about 11 h, the temperature of the reaction system reaches 1000 °C. Temperature gradient disappears, and metal and sublimed sulphur are converted to sulphide almost entirely.

Fig. 3 shows the XRD patterns of the samples. All these samples were synthesized with a temperature gradient technique by using metal and sublimed sulphur as the starting materials. The XRD patterns showed that MgS, TiS_2, ZrS_2 and WS_2 were the single phases in the compositions. Meanwhile, the amount of MgS, TiS_2, ZrS_2 and WS_2 were 56.37, 112.00, 155.36 and 247.97 g, respectively, by using the method. The important thing is the amount of these sulphides is much more than that by using the other methods.

Fig. 4 (a), (b) and (d) show SEM images of the MgS, TiS_2 and WS_2 powders synthesized. From these figures it is revealed that their particles shapes of the samples synthesized were spherical, stratiform and stratiform, respectively. The MgS, TiS_2 and WS_2 powders consist mainly of agglomerates and aggregates of a few microns particle size. Fig. 4 (c) and (c′) are the SEM images of the ZrS_2 powders. The particles were

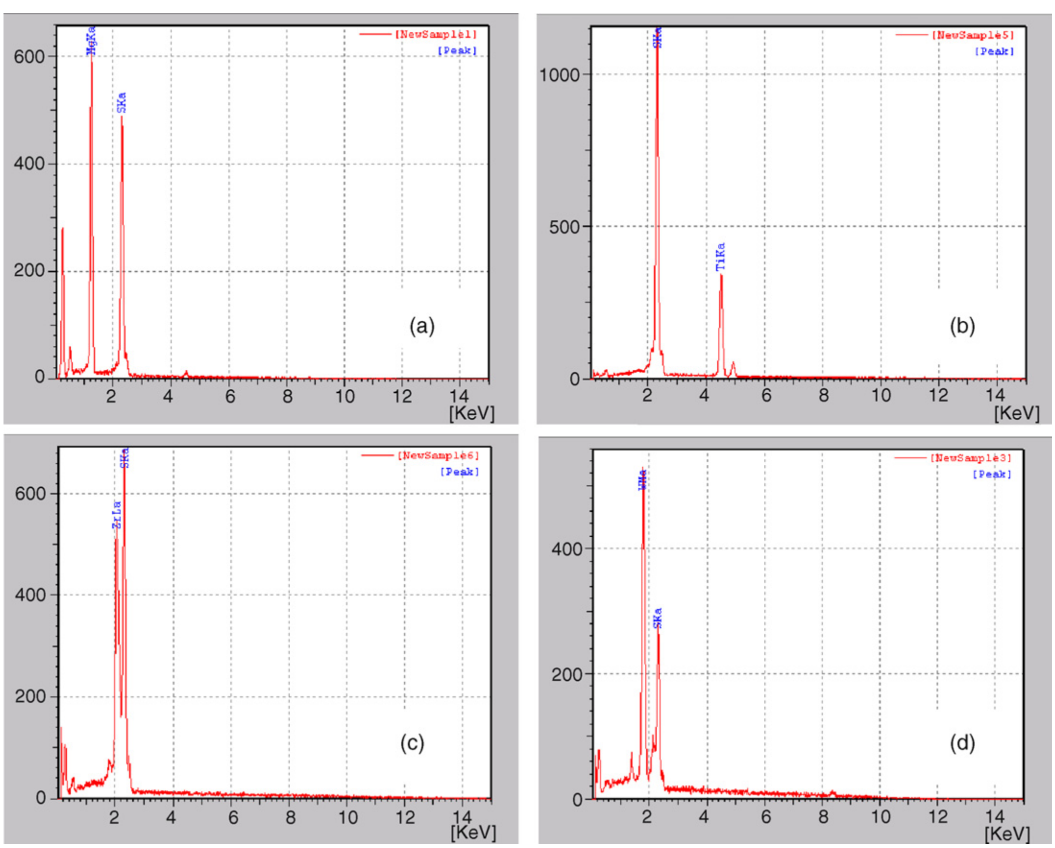

Fig. 5. EDAX spectra of the different samples synthesized: (a) MgS; (b) TiS_2; (c) ZrS_2; (d) WS_2.

acicular in shape and particles display lengths of 20–30 μm and diameters of 0.2–0.8 μm, with aspect ratios ranging from 25 to 150. A typical EDAX spectrums are shown in Fig. 5. The EDAX analysis (by the standard less quantification ZAF) done on agglomerates and several randomly chosen grains of this powder, shows the grain composition to be MgS, TiS_2, ZrS_2 and WS_2, respectively.

5. Conclusions

Metal sulphide has been synthesized with a temperature gradient technique by using metal and sublimed sulphur as the starting materials. The relationship among the amount of evaporating sulphur, volume of quartz tube, synthesis temperature and pressure in the quartz tube is studied. The results have shown that the maximum amount of evaporating sulphur is 1.15 g in the quartz tube under the experimental conditions. Based on the amount of evaporating sulphur, the temperature gradient and heating-rate in the synthesis system were controlled. MgS, TiS_2, ZrS_2 and WS_2 were synthesized safely and in large amount: 56.37, 112.00, 155.36 and 247.97 g, respectively.

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