High-pressure preparation and structural analysis of Se-S-As ternary system compounds

Bingke Qin, Yonghua Ji, Zhiling Bai

School of Chemistry and Materials Engineering, Liupanshui Normal University, Liupanshui, Guizhou 553004, PR China

Guizhou Provincial Key Laboratory of Coal Clean Utilization, Liupanshui, Guizhou, 553004, PR China

qinbingke@lpssy.edu.cn

Abstract. Se-S-As ternary polycrystalline compounds were prepared at a synthesis temperature of 900 K under a pressure of 4 GPa. The samples were analyzed by XRD, SEM and EDS. The experimental results showed that the high-pressure conditions promoted the reaction between the ternary compound Se-S-As, and the prepared samples had fairly crystallinity with the sample grain diameter around 50 μm. The results of Se-S-As elemental composition analysis showed that the atomic ratio Se:S:As was close to 8:5:8.

1. Introduction

Chalcogenides, as semiconducting materials, are often in the form of glass ceramics, which are widely used in infrared optical materials, thin film optical storage materials and photonic crystal fiber materials [1-3]. As₂Se₃ glass has a wide wavelength range in the infrared region, and also has the characteristics of transparency and excellent chemical stability. Compared with single crystal germanium, which is commonly used in infrared night vision devices, it has the advantages of low cost, easy forming and processing, and is an ideal infrared optical material [2]. In addition, it has been reported that the As₂Se₃ based microstructural fiber can be used as the background material because of its high refractive index, and the microstructure can be used to prepare high birefringence photonic crystal fiber [3,4].

Se-S-As ternary compound can be used as an optical material has a wide range of applications, but due to the low melting point of Se, its melting point is only 221 °C, the boiling point is 685 °C, very easy to volatile. Elemental arsenic will sublime after 616°C, there is a solid state directly into a gaseous state, and arsenic oxidation has a strong toxicity. Therefore, the preparation of the ternary compound Se-S-As is often done by sealing the raw material in a quartz tube, evacuating it and then heating it to 750 °C and holding it for a uniform reaction time of about 20 h [5,6]. After the reaction synthesis, the sample is quenched and cooled, followed by annealing, or quenched and cooled and used as a raw material for vapour deposition to prepare amorphous semiconductor thin film materials [7].

As the conventional preparation process is tedious and the preparation technology is complicated, the high-temperature and high-pressure (HTHP) preparation technology has outstanding advantages compared with the conventional preparation methods, such as the effect of pressure (4GPa) in the synthesis process, which can change the distance between the atoms inside the material and modulate the electronic structure of the material during the synthesis reaction, and can effectively prepare the
physicochemical properties of the material. In this study, a high-pressure synthesis method with a preparation pressure of 4 GPa at a stoichiometric ratio of 1:1:1 for arsenic-sulfur-selenium was used to explore a new route for the preparation of the ternary compound Se-S-As and its microstructural characteristics.

2. Experiment

In the experiment, the initial raw materials were As powder, S powder and Se powder of 99.99% purity, accurately weighed according to the atomic ratio of chemical formula SeSAs, then mixed well under the protection of inert atmosphere and powder pressed and molded into cylinders of 10 mm in diameter and 4 mm in thickness. After experimental assembly, the experiments were carried out on the HTHP synthesis equipment. The experimental equipment for high-pressure synthesis was a domestic six-sided top press (SPD 6×1200), and the pressure during sample preparation was 4 GPa, the temperature during synthesis was about 900 K, and the synthesis time was about 30 min. The structure analysis of the prepared samples was carried out using a TD-2500 X-ray diffractometer (Cu-K radiation, diffraction angle of 10-90°), and the microstructure and EDS of the samples were tested and analyzed using a FEI Nova NanoSEM 450 scanning electron microscope.

3. Results and discussion

3.1. Phase analysis of the ternary compounds Se-S-As

Figure 1 shows the XRD diffraction pattern of Se-S-As sample prepared by high temperature and high pressure method. From the figure, it can be seen that under the preparation condition of 4 GPa and temperature 900 K, the sample obtained obvious characteristic peak near 32.8°, and from the width and intensity of the characteristic peak, although the crystallization is incomplete but still has a certain degree of crystallinity. For the arsenic sulfur and selenium ternary compounds, the current standard PDF2-2004 card only has a standard PDF card for one compound As2(SeS)3, and the characteristic peaks of the compound As2(SeS)3 could not correspond to the XRD pattern of this sample by comparison, which may be due to the difference in the stoichiometric ratio of the starting materials and the effect of high pressure, which led to a new phase of the ternary compound Se-S-As structure.
3.2. Microstructural analysis of the ternary compounds Se-S-As

Figure 2 is a SEM photograph of the internal section of the ternary compound Se-S-As, with a magnification of 1000 times in the figure. It can be seen from the electron micrographs that the grains of SeSAs compounds prepared by the HTHP method are large, with a diameter of about 50 μm. The overall crystallinity of the samples is not very good, and large local gaps exist. This is mainly due to the HTHP preparation method, where the sample preparation time is short under the high-pressure environment, and the end of the reaction due to the quenching and cooling effect of circulating water. The SEM analysis results of the sample SeSAs compounds are consistent with the test results of the broadening of the characteristic peaks of the XRD diffraction pattern.

3.3. EDS analysis of the ternary compounds Se-S-As

The energy spectrum analysis of the ternary compound SeSAs prepared by high temperature and high pressure method is shown in Figure 3. Three points were randomly taken on different crystal planes for testing, and the results of the tests are shown in Fig. 4. According to the EDS test results, the atomic ratio statistics of arsenic sulfur and selenium are shown in Table 1.

It can be seen that the sample SeSAs compound prepared by high temperature and high pressure method has about 37.13:23.92:38.95 arsenic-sulfur-selenium atoms, and the content of sulfur atoms has a large reduction compared with the initial content, which is mainly caused by the very low melting and boiling points of sulfur and the relatively high preparation temperature. Due to the rapid temperature rise and under conditions such as very high pressure and short preparation time, a considerable amount of sulfur is still retained within the ternary crystal compound. According to the arsenic-sulfur-selenium atomic ratio ratio, the true ratio of each elemental composition of the crystal is close to Se:S:As=8:5:8.
Fig 3. The SEM image of section plane inner of Se-S-As

Fig 4. The SEM image of section plane inner of Se-S-As
Tab 1. The EDS test results of sample Se-S-As

| Number | Element type | Se  | S   | As  |
|--------|--------------|-----|-----|-----|
| 1      |              | 40.49 | 23.38 | 36.13 |
| 2      |              | 37.16 | 23.84 | 39  |
| 3      |              | 39.22 | 24.55 | 36.23 |
| Average value |              | 38.95 | 23.92 | 37.13 |

4. Conclusion
The starting materials were 99.99% pure sulfur, selenium and arsenic powders, and the ternary polycrystalline compounds SeSAs were successfully prepared under the pressure of 4 GPa and the temperature of 900 K. The physical phase, microstructure and elemental analysis of the samples showed that the high-pressure synthesis reaction method could rapidly prepare the ternary compounds SeSAs with a certain degree of crystallinity, and the ternary compounds. The grain diameter of the compound is about 50 μm, and the atomic ratio of Se:S:As is close to 8:5:8.

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References
[1] Chen Weicheng, Ji Jian. Formation and structure of chalcogenide glasses in the As2Se3-AsTe-Cul system[J]. Journal of inorganic materials, 1999, 14(1):23-28.
[2] Wang Hua, Zhao Donghui, Xia Fang, et al. Study on the formation of GeSe2-As2Se3-CdSe infrared glass[J]. Acta silicate Sinica, 2005, 33(8):986-989.
[3] Wang Xiao-Yan, Li Shu-Guang, Liu Shuo et al. Generation of a mid-infrared broadband polarized supercontinuum in As2Se3 photonic crystal fibers [J], Chin. Phys. B .2012, 21(5): 054220-1-7.
[4] Zhao Shun, Cao Yanjun, Cao Ye, et al. A kind of high birefringence photonic crystal fiber with micro-structure core based on As2Se3[J]. Journal of Nankai University (Natural science edition), 2015,48(2):64-68.
[5] Zuzana Zmrhalova, Petr Pilný, Roman Svojbo,et al. Thermal properties and viscous flow behavior of As2Se3 glass [J]. Journal of Alloys and Compounds,2016,655:220-228.
[6] Roman Svojbo, Jiri Malek. Non-isothermal crystallization kinetics of As2Se3glass studied by DSC[J], Thermochimica Acta, 2014,579:56-63.
[7] Liu Qiuming, Hu Ting, Zhao Xuian, et al. Photoinduced effects in amorphous chalcogenide films[J]. Acta silicate Sinica, 2009, 37(6):937-941.