Micromorphology and energy spectrum analysis of AsSe prepared by high-pressure and high-temperature

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Abstract. Polycrystal compound AsSe was prepared rapidly by high pressure and high temperature (HPHT) method under the condition of 2.5GPa and 950K. The phase analysis, SEM and EDS of the samples were carried out. The results show that AsSe compound samples with fine crystallinity can be prepared rapidly by HPHT method, and the grain diameter of the samples is about 20 μm. The results of AsSe EDS analysis show that the atomic ratio of the compound is close to 1:1.

1. Introduction
Arsenic and selenium compounds AsₓSeᵧ (x=1,2,4; y=1,3,4,9) in sulfur semiconducting materials are often used in infrared permeable optical materials, thin film optical storage materials and photonic crystal fiber materials in the form of glass-ceramics[1-3]. As₄Se₃ glass has a wide wavelength range in the infrared region, and also has the characteristics of transparency and good chemical stability. Compared with single crystal germanium, which is commonly used in infrared night vision instrument, it has the advantages of low cost and easy processing. It is an ideal infrared transmission optical material[2]. In addition, it has been reported that microstructure optical fibers based on As₄Se₃ system can be used as background materials because of their high refractive index characteristics. At the same time, the core microstructures are introduced to fabricate high birefringence photonic crystal fibers[3,4].

As an optical material, arsenic-selenium compound AsₓSeᵧ has been widely used. However, due to its low melting point, the melting point of Se is only 221°C and the boiling point is 685°C, which is very easy to volatilize. The elemental arsenic will sublimate at 616°C, and the solid state will directly change into gaseous state. Therefore, the preparation of arsenic-selenium compounds is usually sealed in quartz tube, heated to 750°C after vacuum extraction, and the reaction time is about 20 hours, then take out the quenching and annealing. Or the amorphous semiconductor film material can be prepared as evaporation material after quenching. Because of the complicated preparation process of AsₓSeᵧ, the grain size and structure are often uncontrollable, and the preparation technology is complex.

Compared with the conventional methods, the HPHT method has prominent advantages. Pressure (~GPa) during high temperature preparation can modulate the electronic structure of the material by the distance between atoms in the variable material, thus effectively changing the physical and
chemical properties of the material. In this study, when the stoichiometric ratio of arsenic to selenium is 1, a new way to prepare arsenic and selenium compounds by high temperature and high pressure was studied, and the phase and microstructure of the prepared samples were tested and analyzed.

2. Experiment

In the experiment, as powder with purity of 99.99% and Se powder with purity of 99.999% were used as initial raw materials. According to the stoichiometric ratio of chemical formula AsSe, the powder was weighed on the analytical balance, and then uniformly mixed in agate mortar under argon protection. The powder is formed into a cylinder with a diameter of 10 mm, and a height of 4mm. The experimental equipment of high-pressure synthesis is domestic hexahedral top high-pressure equipment (SPD 6 × 1200). The pressure of the sample is 2.5 GPa, the formation temperature is about 950 K, and the synthesis time is 0.5 h.

The synthetic pressure in this experiment is calibrated by measuring the phase-change point calibration curve of the metal Bi, Ba and Tl at normal temperature. The temperature is measured by a K-type thermocouple. The X-ray diffraction (XRD) test is based on the TD-2500 type X-ray diffractometer (Cu-K radiation, and the diffraction angle is 20-80 °). The electron microscopy analysis and the EDS element analysis employ a FEI Nova Nano SEM 450 ultra-high-resolution scanning electron microscope.

3. Result and discussion

3.1. Phase analysis

Figure 1 shows the XRD phase analysis of AsSe samples prepared by high temperature and high pressure method. It can be seen from the diagram that the samples have obtained obvious characteristic peaks under the preparation conditions of 2.5GPA and 950K, and have a certain degree of crystallization from the strength of the characteristic peaks. However, compared with the standard PDF2-2004 card, it is found that there is no corresponding As,Se map to correspond to it, which may be due to the effect of high pressure on the compound AsSe to produce a new phase.

3.2. Microscopic morphology analysis

The SEM photograph of AsSe compounds prepared by HPHT method show in Figure 2. The Figureure a is 300 times magnification and Figureure b is 1000 times magnification. It can be seen
from the electron micrograph that the grain of AsSe compound prepared by high temperature and high pressure is broken and the crystallinity is not very good as a whole. The grains of AsSe compound are closely arranged, and the average grain diameter is about 20μm. This phenomenon is mainly due to the high temperature and high pressure preparation method, the heating rate is faster, the reaction time is shorter under the huge pressure and a certain temperature, after the preparation reaction due to the role of circulating water to produce quenching effect on the sample.

Figure 2. The SEM image of section plane inner of AsSe

3.3. EDS analysis of samples. Phase analysis
The EDS of AsSe compounds prepared by HPHT method is shown in Figure 3. On different crystal surfaces, 3 points are randomly taken for testing. The test results are shown in Figure 4. According to the EDS results, the atomic ratio statistics of arsenic and selenium are shown in Table 1. From the test results, it can be seen that the surface arsenic and selenium atoms of AsSe compound prepared by high temperature and high pressure method are about 47.88:52.12, and its true value is close to 1:1, which is not much different from the original raw materials.
Figure 4. The EDS analysis of the different points of AsSe

| Serial number | As  | Se  |
|---------------|-----|-----|
| 1             | 47.1| 52.9|
| 2             | 47.1| 52.9|
| 3             | 49.44| 50.56|
| Average value | 47.88| 52.12|
4. Conclusion
Polycrystalline compound AsSe was prepared by high temperature and high pressure reaction at 2.5 GPa and 950 K. XRD phase analysis and energy spectrum analysis show that AsSe compound with certain crystallinity can be prepared rapidly by high temperature and high pressure solid state reaction method. The grain diameter of AsSe compound is about 20 um, and the atomic ratio of As to Se is close to 1:1.

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