1. Introduction

The pnictide and chalcogenide semiconductors have attracted considerable attentions in recent years for their wide applications in the area of photo-voltaic detectors, solar cells, light emitting diodes, and nonlinear optics [1–9]. The nonlinear optical (NLO) crystals, such as ZnGeP$_2$, CdSiP$_2$, CdGeAs$_2$, AgGaS$_2$, and AgGaSe$_2$, are urgently demanded in the directed infrared countermeasures of these materials require the high-purity and high-volume required in the real-world applications is hard to be synthesized due to the high vapor pressure of phosphorus and sulfur components at high temperature. A new high-pressure-resisted method was used to investigate the synthesis of the nonlinear-optical semiconductor ZnGeP$_2$. The high-purity ZnGeP$_2$ polycrystalline material of approximately 500 g was synthesized in one run, which enables the preparation of nominally stoichiometric material. Since increasing internal pressure resistance of quartz crucible and reducing the reaction space, the high-pressure-resisted method can be used to rapidly synthesize other pnictide and chalcogenide semiconductors and control the components ratio.
2. Pre-experiment

Fig. 1 displays the saturated vapor pressure (SVP) of phosphorus, sulfur, selenium, and arsenic as a function of temperature [15,16]. As seen, the SVP of P can reach 43 atm at the temperature of 590 °C. The exothermic reactions can increase the temperature and further increase the vapor pressure in the reactor. The vapor pressure far exceeds the pressure-resistant capacity of quartz crucible in the process of synthesis of ZnGeP₂. Using a single-temperature process can only synthesize no more than 25 g of ZnGeP₂ [17]. To synthesize high-volume and stoichiometric ZnGeP₂ polycrystalline, both avoiding the reactor explosion and reducing reaction space are necessary.

In order to solve this problem, the quartz crucible is placed in a high-pressure furnace (Fig. 2), whose purpose is to counteract the high pressure in the crucible and avoid the explosion in the process of reactions. Our pre-experiments indicated that a vacuum quartz crucible with an inner diameter of 40 mm and a thickness of 3 mm can resist an external pressure of 130 atm over the temperature range of 20–950 °C, which is ten times more than its internal pressure resistance (10–12 atm). This may be due to the circular structure and the large difference between the compression modulus and the tension modulus of quartz tube. Moreover, the mechanical properties of quartz increase slightly with the temperature over the temperature range of 20–950 °C. It is noted that the external pressure of 130 atm still cannot crush the quartz crucible. We did not continue to raise the pressure in the high-pressure furnace because of the safety concerns. Applying high pressure from the external of the quartz ampoule can largely increase its internal pressure resistance.

A schematic of high-pressure synthesis furnace is shown in Fig. 2. The 1-furnace body is made of nickel alloy (GH747), which can be used long-term under the temperature of 1100 °C. The loaded crucible is packed into the furnace through the 2-flange fixed by bolts. The furnace is pressurized by a high-pressure argon tank. 3-two-heater is used to maintain a uniform temperature field. The pressure control system is composed by 4-pressure transmitter, 5-solenoid valve, and 6-control instrument. The furnace can be used long-term under the pressure of 150 atm over the temperature range of 20–950 °C. Normally, the 6-control instrument displays the pressure value in the furnace, which has the same function with the 7-pressure gauge. When the pressure exceed preset limit, 3-solenoid valve opens and reliefs pressure. The pressure control system is necessary for safety purpose. The decompression of the furnace can also be done by the 8-manual valve.

3. Synthesis techniques

High-purity (6N) zinc (Zn), germanium (Ge) and phosphorus (P) elements according to the stoichiometry of ZnGeP₂ were used to prepare the polycrystalline. The raw materials were filled into a carbon-coated quartz crucible with an inner diameter of 40 mm, a thickness of 3 mm and a length of 350 mm. The crucible was evacuated to 10⁻⁴ Pa and was then sealed using hydrogen-oxygen flame. The crucible was placed at the bottom of the furnace, as shown in Fig. 2.

After mounting the flange, the furnace was pressurized to approximately 70 atm, and then the manual valve was closed. The preset limit of the pressure was set to 130 atm. The temperature and pressure profiles of the synthesis process are shown in Fig. 3. The reaction products at different stages are also displayed in Fig. 3, which have been determined by Verozubova et al. [17]. During the first stage of the reactions, the temperature was raised up to 560 °C in an hour, in which process the pressure in the furnace gradually increased to 130 atm. Such temperature was held for two hours. During this stage, the reaction of phosphorus and zinc created ZnP₂ and Zn₃P₂. To ensure sufficient reactions, the temperature was raised up to 670 °C in half an hour and held for two hours. During the second stage of the reaction, the temperature was raised up to 950 °C in four hours and held for four hours, in which process the pressure was held (approximately 130 atm).

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![Fig. 1. Schematic diagrams of the saturated vapor pressure (SVP) of phosphorus, sulfur, selenium, and arsenic as a function of temperature [15,16]. The SVP of phosphorus far exceeds the pressure-resistant capacity of quartz crucible in the process of synthesis of ZnGeP₂.](image1)

![Fig. 2. Schematic of the high-pressure synthesis furnace device.](image2)

![Fig. 3. Temperature and pressure VS time program for ZnGeP₂ synthesis. The reaction products at different stages are determined according to Ref. [17].](image3)
During this stage, the main products were zinc phosphide, germanium phosphide, and ZnGeP$_2$, and there is little element phosphorus left in the crucible. After maintaining the temperature of 950 °C for approximately four hours, the pressure in the furnace decreased directly to 70 atm. On the third step, the temperature was raised up to 1060 °C and the pressure was gradually decreased to approximately 4 atm. After that, the temperature of 1060 °C was held for 10 h. During this stage, a furnace rocking in the angle range of 0–30° was carried out several times to ensure sufficient reaction and reduce the enclosure of the Zn$_3$P$_2$ compound. At the last step, the temperature was cooled to room temperature at a rate of 30 °C/h.

4. Characterizations

Using the high-pressure-assisted synthesis method with the described procedure, approximately 500 g ZnGeP$_2$ polycrystalline can be obtained in one run. Fig. 4(a) shows the 300 g and 500 g ZnGeP$_2$ polycrystalline. Crystal growth was performed using the Bridgman method combined with the seed direction technique. At the bottom of the crucible, a [0 0 1] single crystal was put into its seed pocket. The crystal growth was performed according to Ref. [18]. Fig. 4(b) and (c) shows the as-grown ZnGeP$_2$ crystal and single crystal components respectively.

4.1. XRD

The phase composition and crystallography of the polycrystalline were characterized using X-ray diffraction (XRD) analysis. The XRD patterns were recorded using a Shimadzu XRD-6000 X-ray diffractometer equipped with Cu K$_α$ radiation (λ = 0.15406 nm). A scanning rate of 0.02 s$^{-1}$ was used to record the pattern over a 2θ range of 10–90°. Fig. 5 displays the XRD patterns measured from ZnGeP$_2$ synthesized using the high-pressure assisted method. Both the diffraction peaks and the lattice constants, which were calculated to be a = 5.661 Å and c = 10.729 Å, are in good agreement with the Powder Diffraction Files (PDF no. 50-1201). It is indicated that the synthesized polycrystalline is single phase of ZnGeP$_2$. Since the XRD is sensitive to composition changes of 1–2%, we did not compare the XRD patterns of ZnGeP$_2$ polycrystalline synthesized using the high-pressure assisted method to that of TTVTM.

4.2. XRF

The elemental contents were measured using wavelength dispersive X-ray fluorescence spectroscopy (WD-XFS). These measurements were performed using an XFS-1800 (SHIMADZU) with a 4 kW Rh anode X-ray generator. Three samples from different portions of the as-synthesis ZnGeP$_2$ polycrystalline were used to measure the elemental contents. The WD-XRF spectrum of a prepared sample is shown in Fig. 6. It is noted that all of the samples contain trace amounts (<0.0091 wt%, being ignored in present work) of Si and Al element. This may be due to the contamination of quartz crucible. The result shows the average weight percentages of Zn, Ge and P is 32.6759%, 36.1753% and 31.1365% and the calculated atomic percentage is 24.95%, 24.87% and 50.18%, which is close to the ideal stoichiometric. It is indicated that the synthesized polycrystalline have a good stoichiometry and homogeneity. Since reducing the reaction space, high-pressure-resisted method can significantly suppress the volatilization of P and Zn components compared to the TTVTM. The TTVTM usually leads to the phenomenon of poor-P even if adding excessive P when preparing the raw material, as seen in Refs. [31–33]. Moreover, the residual P can burn in the air and lead to the oxidation of the surface of ZnGeP$_2$ polycrystalline [32].

4.3. FT-IR

The optical spectra of single-crystal samples were measured using a VERTEX70 (Bruker) FT-IR Spectrometer over the wavelength range of 0.83–12 μm. A CaF$_2$ beam splitter and an InGaAs photodiode array detector was used for the wavelength range of 0.83–2.5 μm, while a KBr: Ge beam splitter and thin-film pyroelectric detector was used for the wavelength range of 0.25–12 μm. No annealing or electron irradiation processing was performed on any samples. The optical absorption coefficients (Fig. 7) were calculated using the equation in Ref. [34]. The as-grown ZnGeP$_2$
crystal has a transparency range of approximately 1–1.2 μm. In particular, the absorption coefficient is <0.02 cm⁻¹ at ∼2 μm. The absorption coefficient (∼2 μm) of ZnGeP₂ crystal from the TTVTM synthesis is ∼0.8 cm⁻¹ [33], 0.3–0.5 cm⁻¹ [35], ∼0.47 cm⁻¹ [36], ∼0.3 cm⁻¹ [18], and 0.04–0.1 cm⁻¹ [after annealing] [23]. Compared to Refs. [18,33,35,36], the ZnGeP₂ crystal in this work has lower absorption coefficient at ∼2 μm. However, the crystals in Zawilski’s work [23] had much lower absorption coefficient (0.04–0.1 cm⁻¹). It may be due to that the crystal growth in their work was performed using the horizontal gradient freeze growth, which can produce lower density dislocation and improve the crystal quality.

The wide applications of ZnGeP₂ crystal are hampered seriously due to the absorption at ∼2 μm. The experiment and theoretical studies suggested that the absorption at ∼2 μm was mainly attributed to the Zn vacancy related defects [37–39]. In the process of the synthesis and growth of ZnGeP₂, large free-space in the reactor or crucible can lead to the volatilization and deposit of Zn and P components, which can produce a poor-Zn composition [23]. Moreover, the enclosure of Zn₃P₂ can also lead to the poor-Zn composition. The high concentration of Zn vacancies may lead to the increase of the ∼2 μm absorption. The high-pressure-assisted synthesis method with a furnace rocking can reduce the reaction space and improve the polycrystalline. The vertical Bridgman method with the quartz crucible capsuled technique can also reduce the free space and limit the volatilization of Zn and P components during the process of crystal growth. It is noted that the qualities of crystals can be influenced by other growth parameters. We are not discussed here.

5. Summary and prospects

A new high-pressure-resisted method combined with the quartz crucible capsuled technique was used to investigate the synthesis of the high-volume ZnGeP₂ polycrystalline. Our pre-experiment indicated that a vacuum quartz crucible with an inner diameter of 40 mm and a thickness of 3 mm can resist an external pressure of 130 atm over the temperature range of 20–950 °C, which is ten times more than its internal pressure resistance. Using a designed temperature and pressure program, approximately 500 g ZnGeP₂ polycrystalline can be obtained in one run. The synthesized polycrystalline have good stoichiometry and homogeneity, which is in favour of the growth of high quality ZnGeP₂ single-crystal. The high-pressure-resisted method can also be used to rapidly synthesize other pnictide and chalcogenide semiconductors, such as In₃P, CdSIP₃, AgGaS₂, Cu(In,S)₂GaSe₁₋ₓSₓ, and CdTe. Since reducing the reaction space and increasing internal pressure resistance of quartz crucible, the high-pressure-resisted method can be used to control the component ratio of the pnictide and chalcogenide semiconductors.

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References

[8] S. Lany, A. Zunger, Anion vacancies which can produce lower density dislocation and improve the crystal quality.

Fig. 7. Optical spectra typical for a ZnGeP₂ single-crystal sample over the wavelength range of 0.83–12 μm.


