Effect of weak Mn doping on optical properties of ZnGeP$_2$ single crystal grown by vertical gradient freezing method

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Abstract
ZnGeP$_2$ single crystals weakly doped by manganese (Mn) were grown by vertical gradient freezing method from polycrystalline batch which was synthesized by the modified two temperature vapor phase transport method. Energy Disperse Spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared Spectrometry (FTIR) were employed to characterize the doping single crystals. The un-doped and Mn doped single crystals show the same color. XRD results manifest that the obtained Mn doped ZnGeP$_2$ has tetragonal structure with slight lattice distortion and has no segregation. The EDS results indicate a good stoichiometry of ZnGeP$_2$ weakly doped with Mn. From the XPS results, the doped single crystal with no impurity phases were successfully obtained by the vertical gradient freezing method. FTIR spectra show a slight decrease in infrared transmittance of Mn doped single crystals.

1. Introduction

Ternary compound semiconductor ZnGeP$_2$ from II–IV–V$_2$ group is one of the most outstanding infrared nonlinear optical materials in Mid-IR region because of its excellent comprehensive performance [1–6]. This material has important application in second-harmonic generation and optical parametric oscillators in military and civil fields [7–12]. In addition, ferromagnetism was detected in Mn doped chalcopyrite ZnGeP$_2$ and the Curie temperature of Mn doped ZnGeP$_2$ is higher than room temperature [13]. Therefore, this magnetic semiconductor is considered to be a prospective important candidate in the spin-electronics field. Medvedkin, G A et al [14] reported the Mn-diffused layer on ZnGeP$_2$ single crystal which shows ferromagnetism at 350 K for the first time. Ishida, Y et al [15] have observed XPS spectra of Mn 3d on surface of Mn-deposited ZnGeP$_2$ crystal and room temperature ferromagnetism was also observed in this case. There are a few reports on Mn doped ZnGeP$_2$ crystals, and almost all of these researches employed heating treatment method of ZnGeP$_2$ single crystal wafer in Mn powder atmosphere to study Mn doping. According to this method, Mn only distributes on the surface of the ZnGeP$_2$ crystal wafer which may result in inhomogeneity of Mn. The fabrication of qualified ternary semiconductors crystals are very difficult [16–19] especially for Mn doped ZnGeP$_2$, because phosphorus is volatile at high temperature and it leads to stoichiometry deviation and composition inhomogeneity. The growth of high quality Mn doped ZnGeP$_2$ crystal is significant important for its further application.

In this study, weakly Mn doped and un-doped ZnGeP$_2$ polycrystalline materials were synthesized by modified two-temperature vapor phase transport method. Then Zn$_{1-x}$Mn$_x$GeP$_2$ single crystal was grown by vertical gradient freezing method. XRD, EDS, XPS and FTIR were employed to characterize the doped crystals quality.

2. Methods

2.1. Synthesis and optimization
ZnGeP$_2$ polycrystalline materials weakly doped by Mn were synthesized using two-temperature vapor phase transport method. High purity (99.999%) zinc, manganese, germanium and phosphorus elements were weighed
according to the atomic mole percentage \( \text{Zn: Mn: Ge: P} = 0.99: 0.01: 1: 2 \) with excess of 0.2% phosphorus, then they were mixed together and put into quartz crucible which would be evacuated to \( 1 \times 10^{-4} \) Pa and sealed. The prepared quartz crucible was loading into a two temperature horizontal furnace with an angle of 15 degrees to the horizontal line, as shown in Figure 1. The heating curves of two sections furnace are shown in Figure 2. Comparing with our previous synthesis process [20], there are some improvements. On the one hand, when the temperature is higher than 850 °C, zone 2 has a much lower heating rate than that in few first hours in order to complete the element reaction, especially by Mn. On the other hand, the zone 2 cooling rate is much lower than that of zone 1 to prevent P and Zn evaporating from the melt. This can provide a good stoichiometry of the synthesis products.

2.2. Single crystal growth

Single crystals were grown by vertical gradient freezing method from polycrystalline materials. The growth was carried out in pyrolytic boron nitride (PBN) crucible which was enclosed in a fused quartz ampoule evacuated to \( 1 \times 10^{-4} \) Pa. The fused quartz ampoule was put into a vertical furnace which can produce three temperature zones. The temperatures of furnace upper zone and bottom zone were 1100 and 980 °C, respectively and temperature gradient for crystallization was 13 °C cm\(^{-1}\). After the whole furnace was heated to the setting temperature and hold for 48 h, the temperature were decreased gradually from seed part to melt zone. Then the whole furnace with the quartz ampoule inside were cooled down to room temperature at the rate of 30 °C h\(^{-1}\) after crystallization was finished. Three wafers cut from the as-grown doped and un-doped single crystal were polished for test use and they are shown in figure 3. As it can be seen from the photograph, weakly Mn doping has not change the image of the as-grown single crystal. The samples were characterized by XRD, EDS and FTIR.
3. Results and discussion

3.1. XRD analysis

The small pieces of Mn doped and un-doped ZnGeP₂ samples that cut from the as-grown single crystal were ground into powder and characterized by XRD measurements. The operating parameters of the XRD are 45 kV, 15 mA of x-ray generator with $\lambda$ (Cu $K\alpha$) = 0.154184 nm, 10° to 90° of scan 2$\theta$ range, and 0.05° s$^{-1}$ of scan speed. The acquired XRD patterns are shown in figure 4. It can be seen that no other phases were detected except ZnGeP₂ and the acquired patterns of Mn doped and un-doped ZnGeP₂ single crystals are both well consistent with the standard XRD pattern (PDF No. 73–0398). Meanwhile, it indicates that the Mn doped and un-doped ZnGeP₂ single crystals have tetragonal structure and both samples have no composition segregation. Besides, foreign phases that containing Mn were not detected by XRD analysis that may owing to the fairly low content of Mn.

The lattice constants obtained from XRD patterns are given in table 1. To obtained reliable lattice constants, powder XRD test were carried out twice for Mn-doped and un-doped samples respectively, and then the average lattice constants were obtained. It can be note that the lattice constant of Mn doped ZnGeP₂ single crystal is slightly larger than that of un-doped ZnGeP₂ single crystal, but two samples are both in agreement with

![Figure 3. Photograph of polished wafers cut from as-grown Mn doped and un-doped single crystals. I and II are Mn-doped samples, III is un-doped sample.](image)

![Figure 4. Comparison of XRD patterns on Mn doped and un-doped ZnGeP₂.](image)
PDF (73-0398). Besides, c/a ratio of Mn doped ZnGeP2 single crystal is larger than that of un-doped ZnGeP2 single crystal. The reason for the difference between Mn doped and un-doped ZnGeP2 single crystals may be due to the substitution of larger-radius bivalent manganese ions for smaller-radius bivalent zinc ions. Krivosheeva A V et al [21] have reported that the energy of Mn in Zn sites is lower than that of Mn in Ge sites and Mn in Zn and Ge sites. Baranov, P G et al [22] have studied EPR spectra to characterize substitution of bivalent Mn ions on bivalent Zn ions sites. Meanwhile, the P-Mn bond length is larger than those of that of P-Zn and P-Ge, as discussed by Bacewicz, R et al [23]. Therefore, the larger lattice constants of Mn-doped ZnGeP2 may be attributed to substitution of Mn in Zn sites and a larger P-Mn bond length.

### 3.2. Composition analysis

The elemental compositions in Mn-doped and un-doped ZnGeP2 single crystals were measured by EDS. The results are shown in table 2. According to the obtained results, it can be seen that Mn has not been detected in Mn-doped ZnGeP2 single crystal because of its fairly low content. Both Mn doped and un-doped ZnGeP2 single crystal have good stoichiometric ratio which are close to the ideal stoichiometric ratio (1:1:2). However, comparing with un-doped sample, the Mn-doped ZnGeP2 single crystal has a slight deviation from stoichiometric ratio. One of the reasons may be that at high temperature during synthesis process, volatile Zn and P elements from the melt will transport from zone 2 to zone 1 as shown in figure 1. Meanwhile, intermediates such as zinc phosphide, manganese phosphate and germanium phosphate might be produced during synthesis process [24]. Although there is a slight deviation from stoichiometric ratio, the obtained Mn-doped ZnGeP2 single crystal has little composition segregation.

### 3.3. XPS analysis

The Mn-doped and un-doped ZnGeP2 single crystals were cut into 10 × 10 mm² squares and polished for XPS measurements. The XPS test was operated with an ESCALAB 250Xi spectrometer using Al-Kα source. The test vacuum was lower than 6 × 10⁻¹⁰ mbar and C 1s line assigned at 284.8 eV was applied to the binding energy scale calibration.

The survey XPS spectra obtained on the surfaces of Mn-doped and un-doped ZnGeP2 single crystal samples are given in figure 5. In figure 6, the Ge 3d (a), P 2p (b), Zn 2p(c) and Mn 2p (d) XPS spectra of the two samples are respectively shown. According to the analysis of the spectra, the XPS spectra of Mn-doped ZnGeP2 single crystal show a little difference with those of un-doped sample. Comparing with un-doped sample, the binding energies of Ge 3d, P 2p of Mn-doped ZnGeP2 single crystal samples are shifted from 29.6 eVto 29.8 eV and 128.9 eVto 129.2 eV, respectively, as shown in figures 6(a) and (b) which may attribute to the substitution of Mn in Zn sites. Meanwhile, Mn has been detected at 641.4 eV in Mn-doped ZnGeP2 sample, as shown in figures 5 and 6(d). The reason may be that the content of Mn elements is extremely low which is under EDS test allowed error. The content of ZnGeP2 containing manganese phases are fairly low which cannot be detected by XRD either. However, the lattice constant variation was detected by XRD measurements.

### Table 1. Lattice parameter values.

| Sample | Lattice constant (Å) | Mn-doped ZnGeP2 | Un-doped ZnGeP2 | Reference (PDF: 73-0398) |
|--------|----------------------|-----------------|-----------------|--------------------------|
| a (Å)  | 5.482 (2)            | 5.459 (2)       | 5.465           |                          |
| c (Å)  | 10.952 (4)           | 10.703 (4)      | 10.711          |                          |
| c/a    | 1.9978               | 1.9606          | 1.9599          |                          |

### Table 2. Composition of Mn-doped and un-doped ZnGeP2 polycrystalline samples.

| Element | Mn-doped ZnGeP2 | Un-doped ZnGeP2 |
|---------|-----------------|-----------------|
| Mn (at%)| —               | —               |
| Zn (at%)| 24.49           | 24.94           |
| Ge (at%)| 25.53           | 25.27           |
| P (at%) | 49.98           | 49.79           |
| Average| 0.96:1:1.96     | 0.97:1:1.97     |
However, Mn presence can be detected by XPS because the sensitivity of XPS is higher than that of XRD or EDS. In addition, when the surrounding atoms is not the same for the same kind of element with the same valence state, the binding energy will be different which can be tested by this method [25–27]. The high resolution Mn 2p XPS spectra obtained on the outer surface of Mn-doped ZnGeP₂ single crystal are displayed in figure 7. The Mn 2p₁/₂ and Mn 2p₃/₂ components are situated at 653.3 and 640.9 eV, which have not been reported in the NIST database may owing to the existence of Zn₁₋ₓMnxGeP₂.

3.4. FTIR analysis
Two 4.5 mm thick samples cut from the as-grown Mn-doped and un-doped crystals were polished. Then, the samples were annealed in atmosphere of ZnGeP₂ powders at 650 °C for 130 h. The FTIR transmission test of the
two samples was conducted by a Fourier transform infrared spectrophotometer at room temperature. The obtained transmittance spectra are shown in figure 8.

It is found that both the Mn-doped and un-doped crystals have intensive absorption near 2 μm. In the range of 2.5–8.2 μm, the average infrared transmittance of weakly Mn-doped sample are about 53% which is 5% lower than that of un-doped annealed sample (58%). The curve of un-doped annealed sample is shown in red color. The results indicate that weakly Mn-doping of ZnGeP2 crystals may have a negative effect on its optical properties. At 1.8 μm, the infrared transmittance of weakly Mn-doped sample (42%) has a sharp decrease comparing to un-doped sample (57%). It has been reported that the transmittance in the region of 0.65–2.5 μm was affected by Zn vacancy [28] and deficiency of P [29]. The formation of zinc phosphate during polycrystalline synthesis and volatilization of P and Zn at high temperature will lead to deficiency of P and Zn. After Mn doping, zinc phosphate and manganese phosphate are more easily formed according to our many times experiments, the higher the content of Mn doping, the higher the content of binary compound.

Therefore, Mn doping might result in aggravation of Zn and P deficiency, and meanwhile, it might lead to a non-stoichiometry of single crystal which are harmful to the crystals optical properties.

4. Conclusions

The ZnGeP2 single crystals weakly doped by Mn were successful grown by vertical gradient freezing method. The XRD results indicate that Mn-doped ZnGeP2 samples have tetragonal structure with no composition
segregation. Meanwhile, it shows slightly heavier lattice distortion of Mn-doped than un-doped ZnGeP2 single crystal which may owing to the substitution of Mn in Zn sites and a larger P-Mn bond length. The composition analysis manifests that Mn-doped ZnGeP2 single crystal has good stoichiometry. According to study of XPS spectra, Zn1−xMnxGeP2 have been detected on Mn doping single crystal sample which indicate a successful growth of ZnGeP2 single crystal with weakly Mn doping by vertical gradient freezing method. The FTIR results manifest a decrease in infrared transmittance of the weakly Mn-doping sample which may result from heavier loss of Zn and P in Mn-doped sample. The results provide important reference for further growth of Mn doping ZnGeP2 single crystal and in-dept study in the spin-electronics field on semiconductor nonlinear optical crystal materials.

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