ZnGeP₂ synthesis and growth from melt

G.A. Verozubova a, A.I. Gribenyukov a,*, V.V. Korotkova a, M.P. Ruzaikin b

a Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences, Tomsk 634021, Russia
b Tomsk State University, Tomsk 634050, Russia

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Abstract

The two-temperature technique has been examined for ZnGeP₂ synthesis. The effect of the cold zone temperature on the Zn diffusion and the ZnP₂ formation outside the ternary compound reaction zone has been studied. A qualitative analysis of the Zn diffusion equation taking into account the P mass transport has allowed us to identify conditions where no Zn diffusion is observed. The effect of the ampoule surroundings on the ZnGeP₂ crystal growth has been investigated for the vertical Bridgman and vertical gradient freezing methods. The steady-state thermal conductivity equation has been solved for different ampoule surroundings. The proposed numerical model has established the reasons for the polycrystalline structure and physical properties heterogeneity of ZnGeP₂ crystals, viz. the isotherm concavity and variable growth rate with respect to the ampoule translation speed. © 1997 Elsevier Science S.A.

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1. Introduction

ZnGeP₂ is known to be a most interesting nonlinear optical crystal in the IR region. According to the literature data the melting point of ZnGeP₂ is between 1025 and 1028°C [1]. Due to dissociation its synthesis and growth are carried out in evacuated quartz ampoules.

The problem of high-yield ZnGeP₂ synthesis is related to the presence of two volatile components (Zn and P) that can form thermally stable binary phases Zn₃P₂ (Tₘ = 1193°C) and ZnP₂ (Tₘ = 1040°C). A number of synthesis techniques have been described in the literature for A²B₄C₈ [1-8]. Our studies deal with a high-yield two-temperature technique for ZnGeP₂ synthesis.

Solid ZnGeP₂ is inferior to its liquid counterpart as a heat conductor. This makes the crystallization heat removal through the crystal difficult. As a consequence, the temperature gradient near the interface must be lower in the liquid phase than in the solid one. For similar reasons high growth rates are thus unattainable.

* Corresponding author.

The most popular ZnGeP₂ growth methods are the Bridgman technique [4-8] and the gradient freezing technique [1,2,6]. We used the vertical Bridgman (VB) and gradient freezing techniques (GF).

In this work we discuss some effects that can cause the polycrystallinity and physical properties heterogeneity in ZnGeP₂.

2. Synthesis

With the one-temperature method for ZnGeP₂ synthesis high pressure of P limits the charge amount and takes a long time for synthesis.

The conventional two-temperature method is not suitable for A²B₄C₈. Vohl [3] points to the fact that if the cold zone temperature remains fixed throughout the run, the volatile binary phosphides would be condensed in the cold zone and no ternary compound would be produced. Therefore, the method was modified by adding a final step in which the cold zone temperature was raised. Vohl placed the nonvolatile Ge in a hot zone, while the volatile Cd and P were placed in the cold zone.

We have chosen a different arrangement of species for ZnGeP₂. An equiatomic Zn−Ge mixture was placed...
in the hot zone and P in the cold zone. We have assumed that this arrangement was justified because the saturated Zn vapor pressure is lower than the P pressure (Fig. 1, [9]). It has turned out, however, that sufficiently rigid time-temperature conditions have to be satisfied for successful ZnGeP₂ synthesis.

In our earlier experiments the cold zone temperature was 485°C, which corresponded to a P pressure of 4.5 atm. The hot zone temperature was 1030°C, the pure Zn vapor pressure being 4 atm. According to Raoult’s law we believed that the Zn pressure decreased by a factor of about two because of its mixing with Ge. Under these conditions the Zn vapor was transported to the colder part of the reactor and ZnP₂ was formed on the reactor walls. The latter prevented the P transport toward the hot zone and free P remained in the reactor. Hence, an increase in the cold zone temperature caused an explosion. To reduce the Zn pressure we have decreased the hot zone temperature down to 1010°C. Yet two oppositely directed processes (Zn diffusion and P transport) occurred in the vapor phase as previously and ZnP₂ was formed.

To analyze the problem at hand we have considered the diffusion equation for Zn vapor [10]:

\[ J_{Zn} = \frac{D}{RT} \nabla P_{Zn} + \frac{V}{RT} P_{Zn}, \tag{1} \]

Here \( D \) is the diffusion coefficient, \( P_{Zn} \) is the partial Zn pressure, \( R \) is the gas constant, \( T \) is the temperature, and \( V \) is the molar rate of flow for the mixture:

\[ V = x_p V_p + x_{Zn} V_{Zn}, \tag{2} \]

where \( x_{Zn} \) and \( x_p \) are the mole fractions and \( V_{Zn} \) and \( V_p \) are the rates of the ordered motion for Zn and P.

Assuming that the first term in Eq. (2) is larger than the second one, Eq. (1) will have the form:

\[ J_{Zn} = \frac{D}{RT} \frac{dP_{Zn}}{dx} - \frac{V_{Zn}}{RT}. \tag{3} \]

Since the first term in Eq. (3) is larger than zero the Zn diffusion will not occur if the second term associated with the mass transport of P is equal to, or larger, than the first term. If the P flow rate is sufficiently high, it will cause Zn vapor to flow back toward the hot reaction zone. Another factor hindering the Zn diffusion is a decrease in the diffusion coefficient as the total pressure is increased:

\[ D \sim P^{-1} T^{3/2}, \tag{4} \]

where \( P \) is the total pressure and \( T \) is the temperature.

Thus, to prevent the Zn diffusion the cold zone temperature had to be increased, the total pressure and the P flow rate therewith being increased.

We have identified experimental conditions where the Zn gas diffusion does not occur. Under these conditions the hot zone temperature is 1010°C (the pure Zn pressure is 2.58 atm) and the cold zone temperature is 510–520°C (the P pressure is 8.3–10.5 atm). Phosphorus is found to react completely within 2–3 h with the total charge weighing 500 g.

Thus, Zn diffusion analysis and experimental data available have allowed us to create a valid temperature-time sequence for ZnGeP₂ synthesis.

By way of example let us consider the sequence shown in Fig. 2:

1. Simultaneous heating of the hot zone up to 1010°C and of the cold zone up to 520°C.
2. Soaking for 2 h.
3. The cold zone heating up to 1010°C.
4. Simultaneous heating of the hot zone up to 1050°C and of the cold zone up to 1060°C. It takes 8–9 h to heat the reactor from room temperature to 1050–1060°C.
5. Soaking for 6–8 h.
6. ZnGeP₂ melt crystallization at a rate of 1–2 °h⁻¹.

Fig. 2. Schematic of furnace and fused-silica reactor used for ZnGeP₂ synthesis (a) and temperature profiles (b).
3. Crystal growth

A 40 mm diameter nine-section furnace has been used for VB (Fig. 3(a)). The temperature profile consists of a hot zone at 1050–1060°C, a gradient part and a cold zone at 900–980°C. The T-gradient is 10–25°C cm⁻¹. The ampoule translation speed is 0.5–4 mm h⁻¹.

A 100 mm diameter two-section furnace has been used for GF (Fig. 3(b)). After the charge fusion a linear T-gradient is established as high as 3–5 ° cm⁻¹. The cooling rate is 1° h⁻¹.

In terms of the crystallization front stability the VB method seems to be more preferable both for spontaneous nucleation and for seeded growth because of a higher T-gradient. Furthermore, the higher T-gradient appears to provide nucleation before a wide melt area gets supercooled [11].

Our statistical data, however, have shown a different picture. The yield with the VB technique was 10%, while with GF it was 60% using spontaneous nucleation.

With the VB technique the fine crystalline structure was often observed in the first crystallized portions of the material. We ascribed this effect to high initial supercooling (lower than Tₘ) and fast crystallization of the supercooled area at certain temperatures.

We have attempted to prevent the initial supercooling by means of heat-removing rods attached to the bottom of the ampoule. However, this has reduced the probability of successful nucleation.

With the GF-method, monocrystal nucleation has been observed in 90% of events even though the T-gradient was low. In this case the ampoule has been placed on a pedestal made of a heat-insulating material. Yet the growth pattern was occasionally disturbed in the widest part of the ampoule cone and crystalline blocks of different orientation were formed. We have attributed this effect to the problem of latent heat removal through the crystal. To improve the heat sink the heat-removing rods have been attached to the bottom of the ampoule just as we did in VB. However, this has reduced the monocrystal nucleation to zero.

In order to understand why the heat-removing rods play a negative role we have developed a numerical model. In effect, the problem has amounted to elucidation of the role of the thermal conductivity relationship between crystallized ZnGeP₂ and ampoule surroundings.

To this end, the steady-state thermal conductivity equation has been solved by the finite element method with boundary conditions of the first kind:

\[
\frac{\partial}{\partial z} \left( K(z, r) \frac{\partial T}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( rK(z, r) \frac{\partial T}{\partial r} \right) = 0, \quad (5)
\]

where K is the thermal conductivity, r is the radial coordinate, z is the axial coordinate, and T is the temperature.

The fact that solid and liquid ZnGeP₂ have different thermal conductivity has been taken into account. The latent heat release has been neglected. The calculations have simulated the same ampoule surroundings for both methods.

Fig. 4 illustrates ampoule surroundings and temperature distribution within the ampoule. The temperature distribution is the same for both methods. If the thermal conductivity of the surroundings (K = 0.1) is lower than that of ZnGeP₂ the isotherms are convex in the cone, concave in going from the cone to the cylinder and then convex again (Fig. 4(a)). The disturbance of
the growth pattern in the GF method can be explained by the concave isotherms.

If the bottom of the ampoule enters the heat-removing material, the isotherms are convex along the entire ampoule except of the bottom of the ampoule adjacent to the rod (Fig. 4(b)). With concave isotherms monocrystal nucleation is of low probability. If the bottom of the ampoule is in contact with the heat-removing rod only at one point (Fig. 4(c)), the isotherms are convex along the entire ampoule, but the T-gradient is increased substantially in the cone (there is a large number of isolines in Fig. 4(c)), which results in an increase of the growth rate. This is depicted in Fig. 5 where the axial temperature profiles within the ampoule are presented for the VB method at different times.

Fig. 5(a) shows the change in the boundary conditions at uniform motion of the ampoule. As the width of the heat-insulating zone in our problem is 6 cm, three ampoule shifts 2 cm apart are chosen. The nondimensional growth rate is calculated as the ratio of the real growth rate estimated from the shift of the calculated axial temperature profiles to the ampoule translation speed.

Let us examine the dynamics of the axial temperature distribution for three ampoule surroundings mentioned above. Early in the process the crystallization rate is slower than the ampoule translation speed in all three cases. Fig. 5(b) shows an ampoule surrounded by a heat-insulating material. There is a delay in the onset of crystallization and a 3-fold increase in the growth rate from 0.3–1.0 in the first half of the cone. Then the crystal continues to grow but at a slower rate.
When the heat-removing rod is adjacent to the ampoule the growth rate exhibits a smooth rise by a factor of 1.5 (from 0.5–0.85) in the conical part (Fig. 5(c)). As seen in Fig. 5(d) the heat-removing rod gives a 7-fold increase in the growth rate from 0.1–0.75 in the first half of the cone.

As for the heat insulating surroundings of the ampoule for the GF method the real growth rate is doubled as compared to the growth rate in the very bottom of the ampoule, which does not necessarily disturb the growth pattern of the monocrystal. The smaller change in the crystal growth rate is related to a lower $T$-gradient and a large furnace diameter.

Thus the lack of the monocrystal nucleation with heat-removing rods used can be explained by concave isotherms or by the disturbance of the growth pattern because of great changes in the growth rate. The proposed model fails to provide a plausible explanation for
the lack of monocrystal nucleation with the VB method. The nucleation problem is solvable by means of seeds.

Yet, in the latter case the growth pattern disturbance, the emergence of crystalline blocks and the physical properties heterogeneity do sometimes occur. The reason is the change in the growth rate. This is especially characteristic of quartz crucibles, which is presumably related to the wetting of the quartz ampoule walls or to the temperature redistribution due to radiation. The use of PBN crucibles decreases considerably the block formation probability. In this case, however, there is a problem associated with ZnP₂ precipitation in the cold part of the system due to loose mating between the PBN crucible and the quartz jacket. The ZnP₂ precipitation can be prevented by means of liquid encapsulation of the melt. Using elevated cold zone temperatures can solve the problem as well.

4. Optical quality of ZnGeP₂ monocrysalts

The optical transmittance measurements have been carried out by a spectrophotometer ‘SPECORD’ at \( \lambda = 2.5-12 \, \mu\text{m} \) and a single-beam spectrometer at \( \lambda = 0.8-1.8 \, \mu\text{m} \).

The data obtained indicate that losses at \( \lambda = 0.8-1.8 \, \mu\text{m} \) depend on monocrystal production conditions. In particular, the optical losses are reduced as the growth and postgrowth cooling rates are slowed down (Fig. 6).

Optical losses at \( \lambda = 3-8 \, \mu\text{m} \) depend but slightly on the production conditions. The optical loss distribution along the monocrystal boule shows that the absorption coefficient increases at \( \lambda = 5 \, \mu\text{m} \) and decreases at \( \lambda = 2.5 \, \mu\text{m} \) (Fig. 7). Similar correlation is observed with a long-term (3 months) low-temperature degradation of the optical quality of the ZnGeP₂ monocrystal at high cooling rate (Fig. 8). The degradation can be accounted for by relaxation of point defects.

We have noticed the effect of the absorption coefficient anisotropy in ZnGeP₂ (Fig. 9). The effect is less pronounced with higher optical losses and a shift to the short wavelength region. The origin of this phenomenon remains unknown.

The ZnGeP₂ composition produced in our laboratory has been studied at the Research Institute of Materials Science in Moscow. The microprobe analysis of ZnGeP₂ cleavage has shown the composition stability of the matrix.
Fig. 8. Change in optical loss spectrum for ZnGeP₂ at high cooling rate (100°C h⁻¹).

However, there are inclusions in a number of crystals (Fig. 10). The core of the inclusions abounds in Ge (90%), while the periphery shows higher content of Zn and P as compared with the matrix. The inclusions may be caused by Zn and P losses or by thermodynamic factors, depending on the shape of the ZnGeP₂ homogeneity range. The problem of the origin of the inclusions may be caused by Zn and P losses or by thermodynamic factors, depending on the shape of the ZnGeP₂ homogeneity range. The problem of the origin of the inclusions calls for the knowledge of phase equilibrium in the vicinity of ZnGeP₂ in the close Zn-Ge-P system.

Fig. 9. Effect of absorption coefficient anisotropy in ZnGeP₂.

Fig. 10. Element distribution near inclusions in ZnGeP₂: (1) Ge, (2) P, and (3) Zn.

5. Concluding remarks

A modified two-temperature method for ZnGeP₂ synthesis has been examined. The method allows the charge amount to be increased (by at least 500 g) and the synthesis time to be reduced. Hopefully, exact calculations and experimental evidence for the Zn and P mass transport and P-T-x diagrams will help determine the most optimum synthesis conditions.

Despite the neglect of the radiative heat exchange in our model it does provide an adequate qualitative description of the temperature distribution and is consistent with our experimental data. The calculations show that thermal conditions can be selected by choosing ampoule surroundings whose thermal conductivity is lower than that of ZnGeP₂ to provide the isotherm convexity and to decrease the change in the growth rate in different parts of the ampoule.

References

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