

# 行政院國家科學委員會專題研究計畫 成果報告

## 非線性光學晶體 ZGP 合成機制與生長控制之可視化研究 (3/3) 研究成果報告(完整版)

計畫類別：個別型  
計畫編號：NSC 96-2221-E-002-095-  
執行期間：96年08月01日至97年07月31日  
執行單位：國立臺灣大學化學工程學系暨研究所

計畫主持人：藍崇文

計畫參與人員：博士後研究：R. SIVAKUMAR、D.K. RAI  
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處理方式：本計畫可公開查詢

中華民國 96 年 10 月 30 日

行政院國家科學委員會補助專題研究計畫  成果報告  
 期中進度報告

非線性光學晶體 ZGP 合成機制與生長控制之可視化研究

計畫類別： 個別型計畫  整合型計畫

計畫編號：NSC 95-2221-E-002-382-

執行期間：95 年 08 月 01 日至 96 年 07 月 31 日

計畫主持人：藍崇文

共同主持人：

計畫參與人員：王珽玉, R. SIVAKUMAR, D.K. RAI, 徐為哲

成果報告類型(依經費核定清單規定繳交)： 精簡報告  完整報告

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執行單位：國立台灣大學化工系

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## Abstract

A new one-step process for synthesis and growth of zinc germanium phosphide, ZnGeP<sub>2</sub> (ZGP), is reported for the first time herein using a three-zone resistance furnace by the horizontal gradient freeze technique. A safe and proper temperature scheme has been obtained for both synthesis and growth of ZGP crystals via the melt growth route from Zn, Ge and P powder. The prepared material has been investigated using powder X-ray diffraction which shows the correct ZGP tetragonal phase. EPMA results are also obtained to estimate the compositional homogeneity of the grown crystal.

## INTRODUCTION

Zinc-germanium-phosphide, ZnGeP<sub>2</sub> (ZGP) is a semiconducting material of II-IV-V<sub>2</sub> group with band gap of about 2.1 eV. It has a cubic zinc blende type structure with slightly shifted atomic positions with respect to those of the zinc blende structure of space group  $F\bar{4}3m$ , leading to a tetragonal structure of space group  $I\bar{4}2d$ .<sup>1,2</sup> ZGP is one of most promising nonlinear optical materials with a large nonlinear optical coefficient ( $d_{36} = 75$  pm/V) and a large birefringence.<sup>3</sup> These crystals significantly enhance the laser performance by making possible the shifting of wavelength of various laser sources into the mid-infrared ( $\sim 2-8$   $\mu\text{m}$ ) of the spectrum via second harmonic generation (SHG) and optical parametric oscillation (OPO). However, the application of ZGP has been hindered because of various difficulties in synthesis and growth of single crystals namely, high vapor pressure produced by phosphorous, formation of undesired stable binary compounds like ZnP<sub>2</sub> ( $T_m = 1040$  °C) and ZnP<sub>3</sub> ( $T_m = 1193$  °C), zinc diffusion towards the cold junction, cracking and growth of multi-crystals, poor control of stoichiometry, and structural inhomogeneity.

Innumerable amount of work has been done<sup>4-11</sup> and a considerable success has been achieved in understanding of the problems associated with synthesis and growth. Verozubova et al.<sup>11</sup> have addressed the problem of inappropriate yield, zinc diffusion towards cold zone and also formation of thermally stable binary phases by using two-temperature technique for synthesis. They have been able to optimize a standard temperature scheme for synthesis to accomplish the above. They have studied the growth of crystal using the vertical Bridgman and gradient freezing techniques and discussed the effects that may cause polycrystallinity and physical properties inhomogeneity in ZGP. Schunemann et al.<sup>12</sup> have invented a method for growing large, single and crack free crystals. The method contains two steps – one for synthesis of compound material from the constituents zinc (Zn), germanium (Ge) and phosphorous (P) and the other for forming the crystal. They used Horizontal Gradient Freeze (HGF) for seeded growth of ZGP crystal from pre-synthesized polycrystalline ZGP using gold coated transparent furnace. The transparent furnace offers opportunity to see and maneuver the process of melting and subsequent growth of the crystal. The method has been used successfully for the growth of single crystals weighing up to 500 gm for the first time. However, involving a two-step process for synthesis and growth consumes a lot of time and also is not an economically viable approach. Therefore, a new one-step process for synthesis and growth of ZGP crystal has been attempted and studied as a convenient and economically viable possibility. In order to estimate potentiality of the proposed method, properties of the grown crystals have also been studied and reported in the paper.

## EXPERIMENTAL

The high purity (99.9999 %) powders of constituent elements Zn, Ge and P were taken in molar ratio of 1:1:2. In order to compensate the possible loss of zinc and phosphorous, they were taken in excess of their stoichiometric amount. A specially designed pyrolytic boron nitride (PBN) coated graphite crucible was taken for synthesis and growth. The idea was, first of all, to create a suitable temperature condition such that reaction between the constituents takes place within the crucible with minimum loss of materials. To accomplish this, the mixture of Zn and Ge powder was filled in the crucible. Then, the filled crucible and the third constituent phosphorous were placed separately in a quartz ampoule. To avoid presence of oxygen inside the ampoule, all steps were performed in nitrogen atmosphere. The filled ampoule was then purged with argon as a final attempt to avoid the presence of oxygen. The purged ampoule was then evacuated and sealed for further experiment. A horizontal three zone resistance furnace was used for melt growth of the ZGP crystal. The sealed ampoule containing constituent materials was placed into the furnace in such a way that crucible falls in the hot zone and phosphorous falls in the cold zone. For synthesis of the material, temperature scheme similar to as specified by Veruzobova et. al<sup>11</sup> has been used:

(i) The hot and cold zones of the furnace were heated simultaneously up to 1000 °C and 520 °C respectively. This temperature scheme minimizes the diffusion of Zn vapor towards the cold zone.

(ii) Material was kept for soaking at this temperature for a period of 2-3 hours in order to ensure the complete sublimation of phosphorous and reaction between the constituents.

(iii) The hot zone temperature was further raised up to 1050 °C and cold zone up to 1060 °C. The melt was kept for soaking at this temperature for 10-15 hours in order to ensure the homogeneous melt formation.

The growth of the crystal was performed by cooling the melt at the rate of 1.2 °C/h down to 1000 °C well below the melting point 1027 °C of ZGP. Further cooling of the material was done at the rate of 20.4 °C/h down to the room temperature.

The phase analysis of the grown ZGP crystal was carried out by powder X-ray diffraction (XRD) using X-ray diffractometer (MAC Science, MO3XHF). The compositional analysis in different parts of the ingot was carried out by Electron Probe Micro Analyzer (EPMA) (JEOL, JXA-8200).

## RESULTS AND DISCUSSION

Melt crystallization following the above temperature scheme resulted into a polycrystalline ingot. In a typical experiment an ingot of about 8 cm length and 6mm thickness weighing 28.61 gm with good surface morphology was obtained as shown in figure 1. A weight loss of about 6.5% was observed in the final compound. The weight loss may be attributed to the possible formation of binary compounds like  $ZnP_2$  or  $ZnP_3$  outside the crucible. The obtained ingot is also found to have crack which is because of the polycrystalline nature of the ingot.

The powder X-ray diffraction was recorded for the powders scraped from different parts of the grown crystal. The diffraction pattern and assignment of different peaks are shown in Fig.2. The comparison of the peaks with that of standard pattern of ZGP shows the presence of tetragonal phase in all parts of the crystal. The lattice parameters of the tetragonal phase was calculated to be  $a=b=5.4528 \text{ \AA}$  and  $c=10.6656 \text{ \AA}$  which is consistent with the standard data

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In order to measure composition of constituents at different positions in the grown crystal, EPMA was carried out. The comparative composition variation of the constituents is shown in fig. 3. According to the figure, all the elements Zn, Ge and P are observed to be uniform throughout the length of the crystal. Further, the ratio of the three constituents is also found to be according to the desired stoichiometry of zinc, germanium and phosphorous i.e. 1:1:2.

## **CONCLUSIONS**

A new feasible approach of one-step synthesis and growth of ZGP has been proposed. Using this approach, ZGP crystal has been grown successfully. The grown crystal has been found to have tetragonal structure with  $a=b=5.4528 \text{ \AA}$  and  $c=10.6656 \text{ \AA}$ , which are close to the standard values of ZGP crystal. The crystal is found to possess structural and compositional uniformity throughout the bulk of the crystal.

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## Figure captions



Fig. 1 Photograph of grown ZGP crystal

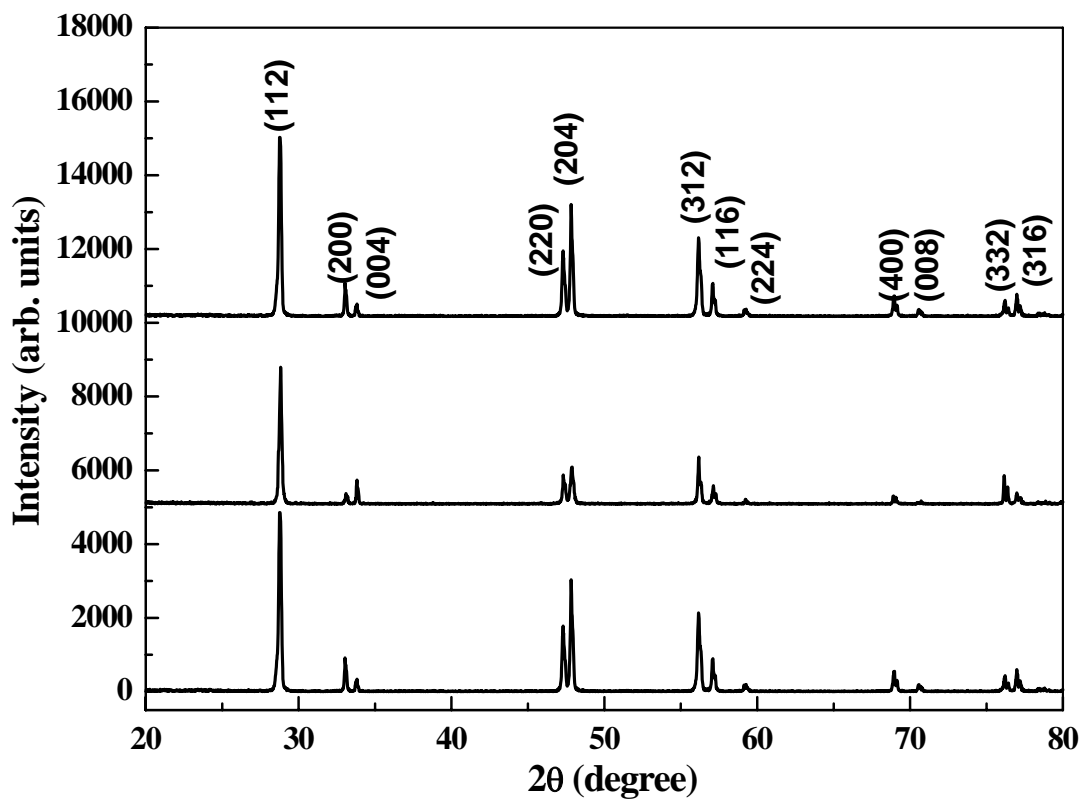


Fig. 2 X-ray diffraction patterns of different parts of ZGP crystal.

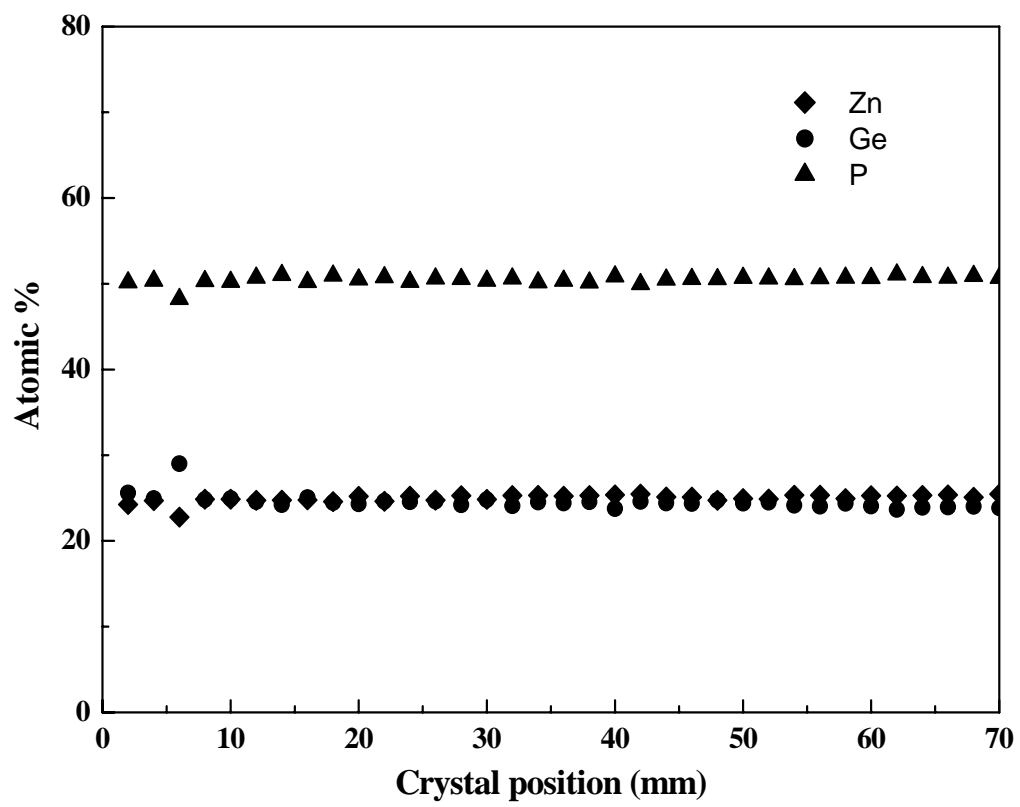


Fig. 3 EPMA result of Zn, Ge and P in the crystal.



## 可供推廣之研發成果資料表

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技術/創作名稱	
發明人/創作人	
技術說明	中文：  (100~500 字)
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技術特點	
推廣及運用的價值	

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