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Chemical analysis of $ZnGeP_2$ as a new line of research of heterogeneity in bulk crystals

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ABSTRACT

Chemical analysis coupled with the inductively coupled plasma atomic emission spectroscopy is proposed as a suitable method for determination of the phase heterogeneity of bulk $ZnGeP_2$ crystals, which are excellent materials for non-linear infrared technique. The crystal phase heterogeneity is resulting from impurity phases ZnP_2 or Ge, which are undetectable by traditional x-ray diffraction method because of their low content. The precise analytical procedure was developed using a well characterized homogeneous $ZnGeP_2$ crystal as a standard reference material to analyze a series of bulk $ZnGeP_2$ crystals with a low content of ZnP_2 or Ge. In this case, all static (instrumental and methodical) errors of the analysis were corrected, and dispersion of the analytical results (random errors) for crystals tested was related to a spatial variation of the impurity phase content and its irregular distribution. The spread of the analytical results found for 15 independent weights of each test crystal is demonstrated graphically.

1. Introduction

The preparation of $ZnGeP_2$ (ZGP) crystals of high optical quality has attracted great interest due to their excellent optical properties, but is very complex since the production of transparent materials is achieved by precise control of the stoichiometry, which is often disturbed during crystallization because of vaporization of ZnP_2 as the most volatile component [1–3]. The nonstoichiometry of $ZnGeP_2$ is manifested mainly along the quasi-binary ZnP_2–Ge section of the ternary Zn–Ge–P diagram, where the homogeneity range for ZGP was found to be too small to go beyond its boundaries upon crystal growth [4–9]. Therefore, the presence of impurity phases, ZnP_2 or Ge, is typical of as-grown $ZnGeP_2$ crystals. The phases with content ≤ 1 mol% and irregular spatial distribution can hardly be detected by conventional x-ray diffraction method, x-ray spectral microprobe analysis and especially chemical analysis [4,5]. However, the tremendous progress in analytical chemistry based on improved metrological characteristics of chemical methods makes it possible to characterize not only the composition of solids, but also their phase heterogeneity [10,11].

In this paper, the ability of chemical analysis coupled with ICP AES for determining the phase heterogeneity of bulk $ZnGeP_2$ crystals is demonstrated for the cases where low-content impurity phases ZnP_2 or Ge are undetectable by conventional x-ray diffraction method.

2. Experimental

2.1. The proposed approach

To make chemical analysis applicable for objective testing of the phase heterogeneity, some procedures should be performed.

(i) A minimum content of the impurity phases ZnP_2 or Ge in nonstoichiometric ZGP crystals should be preset in advance based on the known ZnP_2–Ge diagram.
(ii) The elemental composition of ZGP should be determined with high accuracy.
(iii) A standard reference sample—homogeneous, with accurately characterized composition and exactly matrix-matched with the test crystals—should be prepared.
(iv) The reference sample and test samples should be analyzed simultaneously under identical conditions and with the same number of parallel weights.
(v) The difference in results of analysis between the reference sample and each test sample should be used to estimate the content and spatial distribution of impurity phases.

2.2. Preparation and methods of characterization

The choice of initial compositions of the samples was based on the T-x diagram of the ZnP_2–Ge system, where the homogeneity range of ZGP was determined precisely by the tensimetric method [9]. According to this diagram, samples with 49.0, 49.5, 51.5 and 52.0 mol% ZnP_2

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lying outside of the homogeneity range (deviation to both Ge and ZnP_2 sides) should be heterogeneous with the content of ZnP_2 or Ge below 1.0 mol%. The 50.0% sample, being inside the range, fits best of all to be the homogeneous reference material, Fig. 1.

Powdered polycrystalline $ZnGeP_2$ synthesized from high purity elements taken in predetermined amounts was the starting material for the single growth of 50.0% ZGP. The single crystal of $ZnGeP_2$ was grown from the melt at 1060 °C by directional crystallization, annealed at 600 °C for 400 h, and cooled at a rate of 5 °C/h. The cone shaped crystal was ca. 5.6 g in weight.

The crystals with deviated compositions were also grown by directional solidification from a melt and annealed at 600 °C for 400 h. To do this, 1.000 g of the ground single-crystal $ZnGeP_2$ was intimately mixed with powdered high purity Ge or ZnP_2 in predetermined amounts and charged into cleaned and dried silica tubes. A tightly fitting silica rod was inserted into the tubes to eliminate most of the vapor space. The sealed samples were heated to 1060 °C and kept for 8 h with rotation to homogenize the products. The temperature was then decreased to 1050 °C, kept for 2 h, and with a 1−0.5 °C/cm temperature gradient along the ampoule the furnace was cooled at a rate of 0.5 °C/h to 1020 °C, 10°/h to 900 °C and 50°/h to 600 °C with subsequent annealing for 400 h. The large-grain crystals having the conic form were obtained. More details on the preparation of ZGP crystals can be found in [12].

A key stage for the chemical analysis was sampling from the heterogeneous crystals. Therefore, before failure of as-grown crystals, their density was measured. Then they were crushed to powder and mixed very thoroughly in ethanol. For well-mixed powders, the representative weight was found to be ca. 25 mg.

All the crystals were examined by various methods. The phase state was determined by the x-ray powder diffraction technique (CuK_α, $\lambda=1.540598$ Å, silicon with $a=5.4304$ Å as a calibration standard); lattice parameters were calculated using both the full-profile analysis and the definite individual reflexes operating with Si. The experimental density of as-grown crystals was measured by hydrostatic weighing according to the formula [13]

$$D_{exper.} = \frac{m \times D_l}{m - m_l} \quad (1)$$

where $D_{exper.}$ (g/cm^3) is the sample density, D_l is the liquid density (here, ethanol with $D=0.8020$ g/cm^3), m and m_l are the sample weight in air and in the liquid.

The theoretical density of the two-phase samples was calculated by Eq. (2) from the structural measurement data obtained in our study or taken from the literature for ZnP_2 and Ge

$$D_{total} = x(M_{ZGP}Z/V_{ZGP}N_A) + y(M_{ZnP_2 \text{ or } Ge}Z/V_{ZnP_2 \text{ or } Ge}N_A) \quad (2)$$

where V is the cell volume (cm^3), Z and M are the number and mass of atoms (g-atom), N_A is the Avogadro number, x and y are the molar fractions in ZGP+ZnP_2 or ZGP+Ge mixtures.

Other methods were employed to determine reliably the homogeneity and composition of the 50% stoichiometric crystal: thermal analysis measuring the melting point, the structural full-profile analysis with the PCW program [14] giving the lattice parameters and occupancy of the structural sites with a fixed isotropic thermal factor, and an energy-dispersive x-ray spectrometry with a 2 nm electron probe attached to SEM presenting the intensity maps for the Zn, Ge and P elements. Besides, the elemental composition of ZGP was determined accurately and precisely by a special analytical technique.

2.3. Analytical technique

The analytical technique (for details, see [15]) includes two stages (dissolution and chemical analysis) prone to error which should be minimized. The autoclave dissolution without any element losses was achieved by using an effective solvent represented by a high purity solution of HNO_3, HCl and deionized H_2O, which converted all the P^{3-} ions to PO_4^{3-}. On the other hand, at $C_{HNO3}=8.0$ M and C_{HCl} ranging from 0.2 to 1.9 M, a highly volatile species $GeCl_4$ was turned into non-volatile complex $H_2[Ge(OH)_3Cl_3]$ known from [16]. Optimization of the Ge transfer into solution is shown in Fig. 2. To determine the elemental composition with high precision, the errors of element detection were minimized and the accuracy of the analysis was controlled. The dependence of the error determination (relative standard deviation) of the found element concentrations on their concentration in the test solutions was studied after the decomposition of a stoichiometric sample, Fig. 3. The obvious dependence of the accuracy and error of the determination on the element concentration in the solution was noted only for zinc. Therefore, 30–40 μg/ml of Zn, Ge, and P was chosen as the optimal element concentration for ICP AES analysis. The following standard solutions were employed: State Reference Sample GSO No. 7791-2000 for phosphate, State Reference Sample No. 7770-2000 for zinc, and Ekoanalitika for germanium. The ICP AES measurements were made

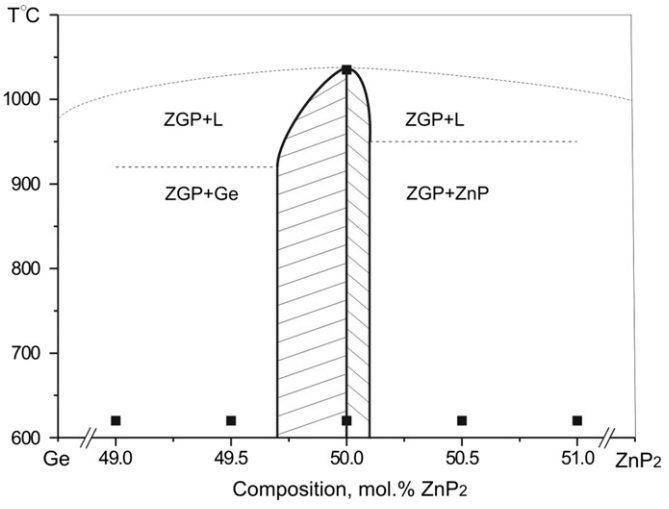

Fig. 1. T–x diagram of the ZnP_2–Ge system with the homogeneity range around the $ZnGeP_2$ phase and selected compositions with symbol (■).

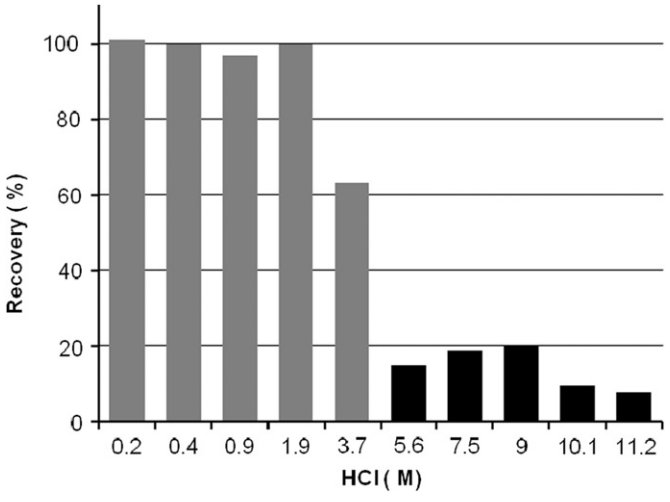

Fig. 2. Effect of the acid concentration (30 ml) on the Ge amount transferred to the solution after matrix dissolution. Conditions: 8 M HNO_3 as gray columns; 8.0, 5.3, 3.2, 1.6, and 0 M HNO_3 as black columns; $m=50$ mg, 220 °C, $\tau=1.5$ h.