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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]

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

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

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

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

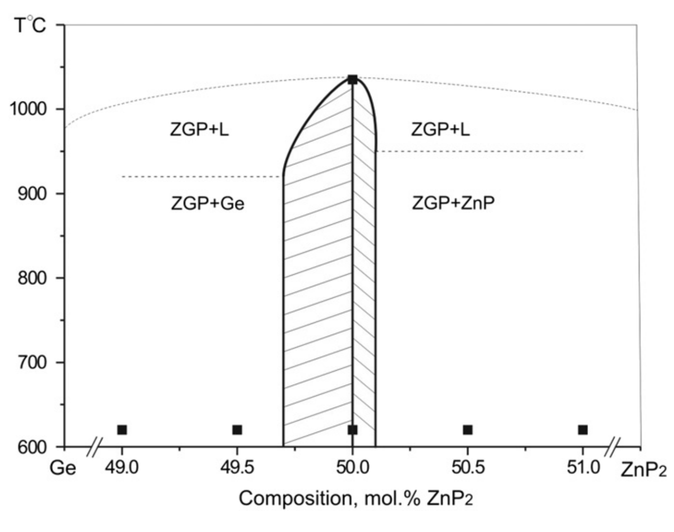

Fig. 1. *T–x* diagram of the ZnP_2–Ge system with the homogeneity range around the $ZnGeP_2$ phase and selected compositions with symbol (■).

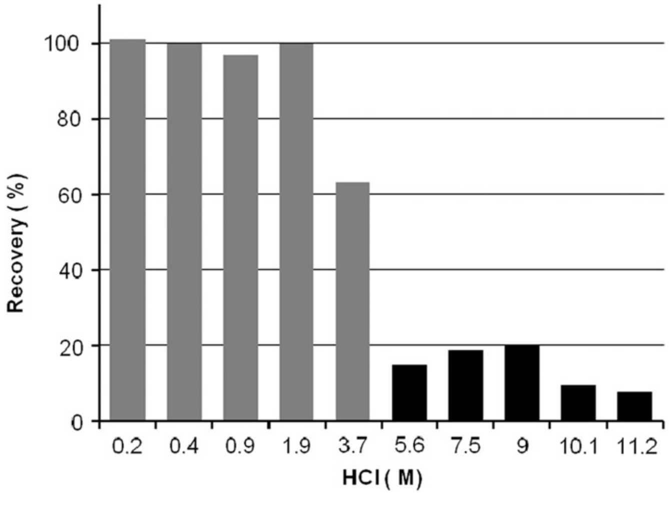

Fig. 2. Effect of the acid concentration (30 ml) on the Ge amount transferred to the solution after matrix dissolution. Conditions: 8 M HNO_3 as gray columns; 8.0, 5.3, 3.2, 1.6, and 0 M HNO_3 as black columns; $m = 50$ mg, 220 °C, $\tau = 1.5$ h.

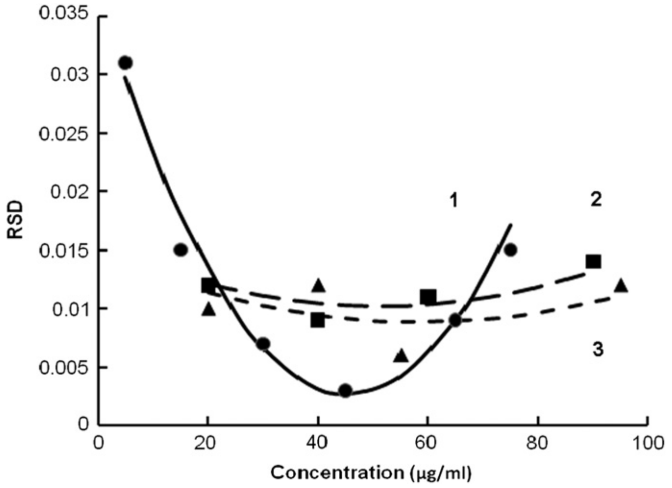

Fig. 3. Relative standard deviation ($n=5$) of the Zn (1), P (2), and Ge (3) determination by ICP AES with the range of the elements concentration for test solutions.

Table 1
Determination of zinc, germanium and phosphorous by the addition method ($n=6$; $P=0.95$).

Element	Taken (mg)	Found (mg)	s_r (%)
Zn	16.1	(16.1 ± 0.1)	1.0
Ge	18.0	(17.9 ± 0.2)	1.2
P	15.5	(15.6 ± 0.2)	1.2

with an OPTIM 4300 DV apparatus (Perkin Elmer); 2–3 analytical lines were used to average the results. The measurement was performed with external calibration using reference solutions in the concentration range 10–50 μg/ml in HCl (1:10).

To exclude errors of the dilution procedure and non-controlled time fluctuations of spectrometer performing the multielement analysis of a large series of samples, the calculation for each instrumental measurement was made using the atomic ratios of elements, Zn:Ge, P:Ge and P:Zn, rather than the element contents. The molar fraction of ZnP_2 in the test crystals was calculated independently from the Zn:Ge and P:Ge ratios, and then treated statistically. The P:Zn ratio was always equal to 2 within error $< 1\%$, and not used in the calculation.

The analytical procedure was validated by the addition method injecting Zn and P as solutions and Ge as a solid (Russian State Standard No. 16153-80), Table 1. It is seen that all the elements pass into solution nearly completely with a close to zero systematic error ($t_{calc} < t_{table}$ for $P=0.95$) and a minimum relative standard deviation. Blank runs failed to detect any errors attributable to metal contamination above a level of 0.2, 0.1 and 0.005 ppm for Ge, Zn and P, respectively.

2.4. Procedure

Dissolution of 50 mg of the ground crystal in a freshly prepared mixture 15 ml 16 M HNO_3 + 5 ml 11 M HCl + 10 ml H_2O was carried out in a closed AT-2 autoclave by heating at 220 °C during 1.5 h. Transfer of the cooled solution in a 50-ml standard flask was made with 5 ml 11 M HCl and diluting up to the mark with water. A 10-fold dilution with HCl (1:10) was found to be optimal; the dilution was made just before the ICP AES analysis, although the solutions were stable at least for one month.

3. Results and discussion

Characterization of non-stoichiometric crystals is given in Table 2. Note that initial heterogeneity given by the T–x diagram was not supported by XRD, since the crystals were found to have the single-phase structure with the structural parameters varying only slightly. As XRD detection of impurity phases has failed, results of chemical determination of phase heterogeneity became the subject of the study, and special attention was given to the quality of the reference crystal. Results of its characterization together with the literature data for strongly stoichiometric ZGP are listed in Table 3. Virtually a 100% occupation of the structural positions by the Zn, Ge and P atoms allowed determining stoichiometry of the reference crystal with the experimental error of 1%, which provided a higher precision as compared to the chemical analysis. EDXA shows that deviation of the element concentrations from the average value does not exceed 3% and is independent of the scanning direction. With this error, the 50% crystal was assigned to spatially uniform structures, its sampling error being close to zero. And lastly, a good agreement between these and earlier obtained data confirms high quality of the prepared reference crystal concerning its spatial homogeneity and compositional accuracy. Note that reference samples of so high quality are rarely available in the analytical procedures [17]. The progress in the preparation of reference crystal allowed us to demonstrate that chemical analysis is able to detect the phase heterogeneity of test crystals.

The above analytical procedure was applied to analyze the nonstoichiometric crystals simultaneously with the reference crystal. The results for 15 independent weights of the crystals, which were checked previously in terms of 3σ criteria for the absence of huge errors, are shown in Table 4. Here, some results are of special interest. First, the average values of Zn:Ge and P:Ge ratios fall close together, but differ from the given values, especially for the 51.0 and 50.5% crystals; this difference is detected conclusively by chemical analysis. Since some losses of volatile ZnP_2 during the preparation are quite realistic, analysis of the grown crystals becomes a necessary stage of their characterization. Second, a quite low (± 0.01) relative standard deviation of the analysis for the reference crystal is determined with the desired reliability; therefore, the deviations for the test crystals exceeding that for the reference crystal indicate directly that impurity phases with irregular distribution are present in all the nonstoichiometric crystals. This finding correlates well with the phase heterogeneity given by the T–x diagram. The irregularity effect expressed in terms of Zn:Ge and P:Ge ratios for each crystal is illustrated graphically in Fig. 4 showing the results for 15 different sampling areas. The spread of analytical data relative to the average line is observed for each heterogeneous crystal; their graphs differ significantly from that of the homogeneous crystal.

Table 2
Characteristics of nonstoichiometric samples.

Initial composition, mol% ZnP_2 Phase state given by the T–x diagram		XRD data			Density (g/cm^3)
		a and c in	Å $\pm$ 0.0004	V (cm^3)	
49.0	$ZnGeP_2$ + 0.04Ge	Single phase	5.4667 10.7104	320.06	$4.16_{(3)}$
49.5	$ZnGeP_2$ + 0.02Ge	Single phase	5.4666 10.7104	320.06	$4.16_{(1)}$
50.5	$ZnGeP_2$ + 0.02ZnP_2	Single phase	5.4664 10.7109	320.07	$4.14_{(2)}$
51.0	$ZnGeP_2$ + 0.04ZnP_2	Single phase	5.4664 10.7116	320.08	$4.14_{(2)}$

Table 3
Characteristics of the 50% stoichiometric sample.

Technique and results	Literature data
Thermal analysis, $T_{m.p.}=1032\pm5$ °C	Thermal analysis: $T_{m.p.}=1035$ °C [4–6]
Structural data	*Structural data* [6]
Cell parameters, Å: $a=5.4662_{(4)}$, $c=10.7099_{(5)}$	Cell parameters, Å: $a=5.469_4$, $c=10.714_6$
Composition: $Zn_{1.00(1)}Ge_{1.00(1)}P_{2.00(2)}$	Composition: $Zn_{1.0(1)}Ge_{1.0(1)}P_{2.0(2)}$
Calculated and experimental density, g/cm^3 4.150 and $4.153_{(3)}$	No data
EDXA: the spread of results of the element distribution was normally within ±3%	No data

Table 4
Composition of the ZGP samples in mol% ZnP_2. ($m=50$ mg, $n=15$, $P=0.95$).

Given/ foundcomposition		Composition calculated from the element ratios and standard deviation			
		P:Ge	s_r	Zn:Ge	s_r
50.0	50.00	50.01 ± 0.10	0.005	50.00 ± 0.10	0.004
51.0	50.67	50.64 ± 0.10	0.004	50.71 ± 0.11	0.004
50.5	50.2	50.2 ± 0.3	0.009	50.2 ± 0.3	0.010
49.5	49.70	49.72 ± 0.18	0.006	49.69 ± 0.14	0.005
49.0	48.92	48.87 ± 0.20	0.007	48.98 ± 0.20	0.007

Table 5
Compositions calculated as two-phase mixtures and solid solutions.

Total composition mol% ZnP_2	Molar fractions of the phases in two-phase mixtures		Composition of solid solutions
48.95	$ZnP_2\cdot1.012Ge+0.007Ge$	(0.7% Ge)	$ZnP_2\cdot1.04Ge$
49.60	$ZnP_2\cdot1.012Ge+0.001Ge$	(0.1% Ge)	$ZnP_2\cdot1.02Ge$
50.20	$1.0012ZnP_2\cdot Ge+0.002ZnP_2$	(0.2% ZnP_2)	$1.02ZnP_2\cdot Ge$
50.67	$1.0012ZnP_2\cdot Ge+0.0067ZnP_2$	(0.6% ZnP_2)	$1.04ZnP_2\cdot Ge$
50.02	$ZnP_2\cdot Ge$		$ZnP_2\cdot Ge$

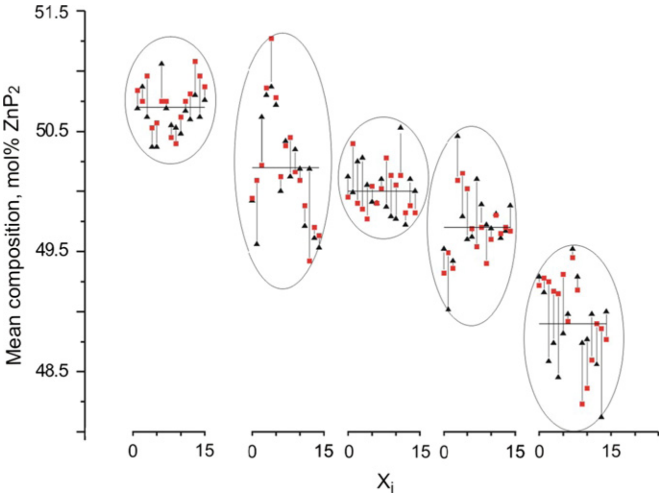

Fig. 4. Graphical images of the results determining total amount of Zn, Ge and P in 15 independent weights in terms of the Zn:Ge (squares) and P:Ge (triangles) ratios for the test samples.

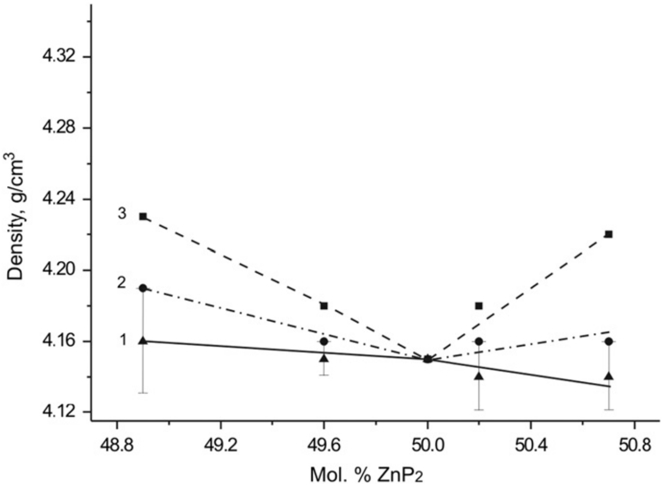

Fig. 5. Experimental (1) and calculated density for the samples as the phase mixtures (2) and as solid solutions (3).

This implies that chemical analysis detects the impurity phases ZnP_2 and Ge with such a low content that cannot be detected by XRD method.

The phase heterogeneity of the test crystals can be presented quantitatively in accord with the T–x diagram data. According to Fig. 1, ZGP as a two-sided phase of varying composition can dissolve 0.03 mol% of ZnP_2 or 0.3 at% Ge. Hence, molar fractions of the main and impurity phases were calculated from the total composition that was determined chemically (within experimental error), Table 5. To verify the proposed phase state of the test crystals, their density was calculated by Eq. (2) and compared with experimental density, Fig. 5. The density calculated for the single phase state of the crystals as a solid solution of $(ZnP_2)_xGe_{1-x}$ type is also shown in Fig. 5. It can be seen that experimental density within its experimental error agrees well with the density of the two-phase mixtures, while the density of solid solutions lies somewhat higher.

So, the analytical procedure proposed here can determine quantitatively and with a high sensitivity the phase heterogeneity and irregular distribution of the impurity phases in bulk crystals. The only disadvantage of the analytical procedure is related to consumption of the material due to parallel sampling. However, this is not an essential limitation, because very useful information on the real composition, the presence of impurity phases and their irregular distribution is extracted at once.

Both the uncontrolled and irregularly distributed impurity phases with the content less than <1 mol% have a decisive influence on the optical quality of bulk ZGP serving as scattering centers. The proposed analytical procedure will be very useful for phase heterogeneity detection. In our opinion, the same approach and analytical determination can be applied with an obvious advantage to other optical crystals from the family $A^{II}B^{IY}C^{Y}{}_2$ (A=Zn, Cd; B=Si, Ge; C=As, P), since their appropriate T–x diagrams and some physicochemical properties are well known.

4. Conclusions

A new direction of chemical analysis coupled with ICP AES for the detection of impurity phases ZnP_2 and Ge with a low content and irregular distribution is considered by an example of bulk crystals $ZnGeP_2$, which are an important optical material for nonlinear technique. High efficiency of the analysis was achieved due to development of a technique for precise composition determination of the test heterogeneous crystals simultaneously with a specified reference crystal under identical conditions. In this case, the use of chemical analysis in tandem with ICP AES provides information on the content and space distribution of impurity phases in bulk crystals, whereas conventional XRD technique is not able to detect such phases.

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