

LETTERS TO THE EDITOR

On the Existence of MgGeP_2

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Present attempts to prepare MgGeP_2 , a scantily characterized phase which was reported in 1961, have led to the growth of crystals for which the X-ray data agree with that reported previously for MgGeP_2 . The X-ray diffraction experiments and chemical analysis by SEM indicate that the crystals obtained here are pure germanium. Reasons are presented for the possible nonexistence of MgGeP_2 . © 1987 Academic Press, Inc.

Introduction

Considerable interest has existed in the synthesis and properties of II-IV- V_2 and I-III- VI_2 semiconductors as ternary analogs of the well-known III-V and II-VI binaries (1). The structures displayed by the binary compounds are diamond-like with the two elements occupying alternate tetrahedral sites. This structural theme is maintained by the ternary compounds, but cation-ordering usually occurs which results in the anisotropic (tetragonal) chalcopyrite structure. Compared to the binary analogs, the ternary compounds display a wide range of band gap values; in addition, some of them possess nonlinear optical properties. These materials have therefore received considerable attention for electronic and optical applications.

The preparation of MgGeP_2 was first reported in 1961 by Folberth and Pfister (2); a sphalerite-type cell with statistical cation disorder was reported with $a = 5.652 \text{ \AA}$ —

neither the preparative method nor a chemical analysis was given. This work is cited by Wyckoff (3) and the "Crystal Data Determinative Tables" (4). Spring-Thorpe and Pamplin (5, 6) reported the preparation of single crystals of II-IV- V_2 semiconducting compounds using solution growth from molten tin. The authors report the preparation of MgGeP_2 as a cubic phase with $a = 5.654 \text{ \AA}$; an optical energy gap of 2.0 eV is tabulated, but no further characterization is given. MgGeP_2 is mentioned in three non-experimental papers (7-9), and the work described above is summarized in the text by Shay and Wernick (1).

Our interest in MgGeP_2 stemmed from its possible physical and chemical properties; although its existence was reported 25 years ago, little or no characterization has been published. It also appeared unusual and interesting that MgGeP_2 would adopt a sphalerite-type structure with a random cation distribution. Only MgGeP_2 is reported to adopt this cubic structure as the

room-temperature equilibrium phase, although four of the other chalcopyrite-type ternaries undergo structural phase transitions to the sphalerite structure at elevated temperatures (1). Folberth and Pfister (10) suggest that sphalerite-type ZnSnAs_2 occurs because the polarizabilities of the Zn-As and Sn-As bonds are similar, as would be expected according to periodic proximities. In contrast, in MgGeP_2 , the Mg-P bond should be significantly more ionic than the Ge-P bond. In ZnGeP_2 , with zinc and germanium only two atomic numbers apart, cation-ordering occurs and only the chalcopyrite structure is observed. The occurrence of a random distribution of magnesium and germanium in MgGeP_2 therefore seems quite unusual. A study was initiated to prepare this phase and determine its properties.

Experimental Methods

The procedure of Spring-Thorpe and Pamplin (5) was repeated to the extent that the reported information permitted; since the melting point of MgGeP_2 is not known, it was not possible to deliberately heat to "within about 100°C of the normal melting point of the compound," as the authors state in their generic procedure (5). Stoichiometric quantities of red phosphorus, germanium, and magnesium were ground together for 30 min in an agate mortar and pestle. The reactant mixture and sufficient tin shot for a 10 mole% solution were placed in a carbon crucible enclosed in a heavy-walled fused silica sample which was then evacuated and sealed at 6×10^{-5} Torr. Heating was carried out in a 3-zone tube-type furnace: the mixture was heated over 3 days to 1100°C, held there for 12 hr, then cooled at 2.5°/hr to 320°C. It was then quickly reheated to 1000°C, held there 24 hr, and cooled to 620°C at 2.5°/hr; the furnace was then turned off and the ampule removed after cooling to room tempera-

ture. The gray reaction plug was placed in concentrated HCl and warmed slightly until all the tin had dissolved as indicated by no further effervescence. A silver-gray granular powder and shiny black pyramidal crystals were isolated. The products were characterized by X-ray diffraction (powder: Scintag PAD V diffractometer, $\text{CuK}\alpha$ radiation; crystals: Gandolfi method, $\text{CuK}\alpha$ radiation) and a chemical analysis was performed by SEM (Amray Model 1400, Tracor Northern Model TN2000 X-ray Analyzer).

Results and Discussion

The Gandolfi X-ray diffraction data for the crystals were indexed with a face-centered cubic unit cell, yielding $a = 5.659(1)$ Å. This result is in good agreement with the unit cell parameters of 5.652 (2) and 5.654 Å (5) which have been reported for MgGeP_2 . Qualitative chemical analysis of the crystals by SEM, however, indicated that they were pure germanium. The unit cell parameter for pure Ge is 5.65763(4) Å (4), and the X-ray diffraction pattern, both d -spacings and line intensities, of the crystals obtained in the present study is essentially identical to that of elemental germanium (11). Chemical analysis by SEM of the granular powder product indicated that it was rich in phosphorus and magnesium; the X-ray diffraction pattern indicated the presence of MgP_4 and Ge.

The crystals prepared in the present study are elemental germanium, not MgGeP_2 . In fact, all the reported X-ray data for MgGeP_2 are also consistent with that of elemental Ge. In light of (1) the paucity of characterization studies on MgGeP_2 despite the report of its isolation 25 years ago, (2) the absence of a specific preparative procedure for the compound, (3) the absence of analytical data on any of the phases previously reported to be MgGeP_2 , (4) the structural-chemical arguments given above that

it would be unusual for MgGeP_2 to form in the sphalerite structure, and (5) the lack of success in the present study to prepare the compound under the given conditions, it is our conclusion that the existence of MgGeP_2 is doubtful.

Acknowledgment

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Note added in proof. We appreciate the comment of a referee who pointed out that MgSiP_2 is reported (12) to decompose in HCl, and therefore so might MgGeP_2 . Even though no other solvent for the tin flux is mentioned in the single reported synthetic procedure for MgGeP_2 (5), it was decided to check this point experimentally. Crystal growth of MgGeP_2 from the elements in tin flux was again attempted, with a heating/cooling regime according to the procedure for MgSiP_2 (12). No large crystals were observed in the tin ingot. Elemental phosphorus was present which ignited during decanting of excess tin. The granular product contained extremely small, shiny black crystals; it was divided, and a portion was treated as usual with hot HCl while the remainder was leached with hot mercury (12) to remove the tin. The product from the HCl-treatment was a mixture of germanium and MgP_4 , as obtained previously. The product from the Hg-treatment, according to X-ray diffraction, contained the same phases.

In a ^{31}P MAS NMR study (with R.A. Nissan) of three-dimensional inorganic phosphides (to be published), we have prepared and obtained the ^{31}P NMR spectra of a number of the II-IV-V₂ chalcopyrite-type semiconductors—including ZnSiP_2 , ZnGeP_2 , and ZnSnP_2 —and the related sphalerite-type GaP. As a final check for the presence of MgGeP_2 , we compared the ^{31}P MAS NMR spectra of the products obtained

from the HCl- and the Hg-treatments. The spectra indicated that the phosphorus-containing phases in both samples were the same, and no indication of sphalerite- or chalcopyrite-type MgGeP_2 was observed. We believe that these additional results further confirm the nonexistence of MgGeP_2 , to date.

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