Preparation and Some Properties of High-Purity PbGa₂Se₄

M. Yu. Rigan

Uzhgorod Department of Optical Information Elements and Structures, Institute of Information Recording, National Academy of Sciences of Ukraine, ul. Zamkovi skhody 4b, Uzhgorod, 88000 Ukraine

e-mail: pet-milyan@yandex.ru Received March 15, 2004

Abstract—Polycrystalline $PbGa_2Se_4$ was synthesized from commercially available and additionally purified Pb, Ga, and Se. As shown by chemical analysis, the material prepared from as-purchased reagents exhibited significant deviations from stoichiometry. According to microstructural analysis, this material contained a second phase. $PbGa_2Se_4$ synthesized from additionally purified Pb, Ga, and Se was uniform in composition. The highest degree of purification was ensured by the Bridgman–Stockbarger method, which enabled growth of stoichiometric single crystals. Attempts to purify $PbGa_2Se_4$ by directional solidification, zone melting, and thermal evaporation led to decomposition of the material. According to mass spectrometry results, the major products of $PbGa_2Se_4$ decomposition are $PbGa_2$, Ga_2Se , Pb, and Se_2 .

INTRODUCTION

PbGa₂Se₄, a IV–III₂–VI₄ compound existing in the PbSe–Ga₂Se₃ join of the ternary system Pb–Ga–Se, is commonly prepared as described by Eholie *et al.* [1], who melted stoichiometric mixtures of Pb, Ga, and Se in silica tubes sealed off under vacuum. They obtained dense black ingots of composition PbGa₂Se₄ as determined by chemical analysis. PbGa₂Se₄ crystallizes in orthorhombic symmetry with lattice parameters a =10.64 Å, b = 10.77 Å, and c = 6.539 Å.

The purpose of this work is to study the behavior of Pb, Ga, Se, and impurities during the synthesis and purification of polycrystalline $PbGa_2Se_4$ and crystal growth. Data are also presented on the dissolution kinetics and temperature-dependent vaporization behavior of $PbGa_2Se_4$ crystals.

EXPERIMENTAL AND RESULTS

Polycrystalline PbGa₂Se₄ was synthesized by a twozone process: Se was maintained at 700–750°C, and Pb and Ga, at 750–800°C. The synthesis duration was 48– 60 h for a sample weight of 0.3 kg. The highest temperature was 900°C. The synthesized material was homogenized at 750 \pm 1°C for 24–30 h and then furnacecooled. The temperature of the furnaces was stabilized to within \pm 0.5°C using VRT-2 precision temperature controllers.

The material was characterized by x-ray diffraction (XRD), microstructural analysis, and differential thermal analysis (DTA), and its composition was determined by chemical analysis.

The XRD pattern of PbGa₂Se₄ could be indexed in an orthorhombic cell with a = 10.638 Å, b = 10.766 Å, and c = 6.357 Å, in agreement with earlier results [1].

Etching with a 1 : 3 mixture of HNO_3 and H_2O revealed a second phase, which was identified as carbon by careful microstructural examination. The sources of carbon were bituminous impurities in selenium. The polycrystalline material was analyzed for Pb, Ga, and Se.

Pb was determined by titration with Trilon B in an acetate buffer solution at pH 5 in the presence of Xylenol Orange as the indicator (relative error of determination, 0.2-0.7%) [2].

Ga was determined by chelatometric titration, with PAN as the indicator (relative error of determination, 0.7-0.9%) [3].

Se was determined spectrophotometrically in the form of a complex with 3,3-diaminobenzidine (relative error of determination, 0.6-1.2%) [4].

Polycrystalline PbGa₂Se₄ was Se-deficient, as determined by chemical analysis: the Se content was found to be 43.35 wt %, against the nominal value of 47.68 wt %. Se losses were also observed earlier in the synthesis of CdGa₂Se₄ and CuAlSe₂ [5, 6]. In all cases, deviations from stoichiometry were associated with the use of as-purchased selenium. The Pb and Ga contents of PbGa₂Se₄ also differed from the stoichiometric values (Table 1).

These results suggest that, to obtain high-purity $PbGa_2Se_4$ crystals, commercially available Pb, Ga, and Se must be purified further.

Sample	Pb	Ga	Se
Polycrystalline charge synthesized from as-purchased chemicals	33.94	22.35	43.35
Single crystal prepared using as-purchased chemicals	32.33	21.12	46.24
Polycrystalline charge synthesized from additionally purified chemicals	31.34	21.17	47.28
Single crystal prepared using additionally purified chemicals	31.22	20.97	47.59

Table 1. Chemical analysis data (wt %) for polycrystalline and singe-crystal PbGa₂Se₄

Table 2.	Impurity concentration	n in PbGa ₂ Se ₄ crystals	s grown by the Bridgma	an–Stockbarger met	thod using $(1-3)$	as-purchased
and (4–6)	additionally purified	Pb, Ga, and Se				

Crystal portion	Impurity	Weight percent $\times 10^3$	
1. Seed end (single-crystal)	Fe, Si, As, C	1	
	Bi, Na, Ti, Mg, Zn, Mn, Al	0.1	
2. Middle (single-crystal)	Fe, Si, As, Ti, Mg, Al	0.1	
	Sn, Tl, Sb, Te, Bi	0.01	
3. Tail end (single-crystal)	Mn, Cu, Cd, Co, Ag, Zn, Cr, Bi, Ti, Si	10	
4. Seed end (single-crystal)	Fe, Mn, Si, As, Ti, Na, Al, Sb, Ni	0.01	
5. Middle (single-crystal)	In, Tl	0.001	
6. Tail end (polycrystalline)	Zn, Cu, Cd, B, As, Bi, S, Ni, Co, Cr, Ti, Si, Al, Ca, Na	1	
	Hg	0.1	

Pb (V000 grade) was purified by acid etching, hightemperature heat treatment, and zone melting, which reduced the total impurity content to $10^{-5}-10^{-7}$ wt %.

Ga (OSCh V000) was purified by acid etching and high-temperature vacuum heat treatment. The total impurity content after purification was at a level of 10^{-5} wt %. The Cd and Hg contents were below the corresponding detection limits.

Se (OSCh 17-4) was purified by acid etching, vacuum distillation, directional solidification, and zone melting, which reduced the concentrations of major impurities by two to three orders of magnitude and the carbon concentration to below the detection limit.

The polycrystalline growth charge synthesized from the additionally purified Pb, Ga, and Se was phase-pure by XRD. Microstructural examination revealed no carbon. It was more uniform in composition compared to the charge prepared from as-purchased Pb, Ga, and Se (Table 1).

Attempts were made to further purify this material by directional solidification, zone melting, and the Bridgman–Stockbarger method. In the first two purification processes, $PbGa_2Se_4$ decomposed according to the scheme

$$PbGa_2Se_4 \longrightarrow PbSe + Ga_2Se_3.$$

The products, both PbSe and Ga_2Se_3 , had nonstoichiometric compositions.

 $PbGa_2Se_4$ crystals were grown by the Bridgman– Stockbarger method in silica ampules pumped down to 0.1–0.01 Pa. The solidification rate was 0.1–0.5 mm/h, and the temperature gradient was 5°C/mm.

Preliminary results on the purification of the $PbGa_2Se_4$ charge by crystallization indicated that increasing the free space in the ampule led to partial $PbGa_2Se_4$ decomposition. In view of this, in growing $PbGa_2Se_4$ crystals by the Bridgman–Stockbarger method, the free space in the ampules was minimized (10–20%).

In this way, we obtained black ingots similar in shape to the ampules, with a convex upper part. This shape was favorable for driving impurities from the central part of the ingot to its periphery. Indeed, the surface layer that was in contact with silica was found to contain gas inclusions 2 to 3 μ m in size and 4 × 10⁻² to 7 × 10⁻³ wt % Si. As shown by XRD, microstructural examination, and chemical analysis, the ingots were single-crystalline.

The crystals prepared using as-purchased Pb, Ga, and Se had nonstoichiometric compositions. The deviation from stoichiometry was smaller in the neck (Table 1).

Solvent	Insoluble residue %	1			Dissolution	
Solvent	insoluble residue, 70	Pb	Ga	Se	Dissolution	
HNO ₃ (conc/dilute)	_	_	_	_	Yes	
H_2SO_4 (conc)	40	12.50	8.42	19.07	Partial	
$H_2SO_4(1:1)$	95	29.70	19.98	45.30	Partial	
HCl (conc)	96	30.05	20.19	45.78	Partial	
KOH (50%)	92	28.88	19.39	43.86	Partial	
Benzene	97	30.36	20.40	46.24	Partial	
H ₂ O	100	31.3	21.04	45.78	No	

Composition of the residue, wt %

Table 3. Chemical stability of PbGa₂Se₄ single crystals in different solvents (50°C, 1 h)

respectively.
The dissolution behavior of single-crystal PbGa ₂ Se ₄
was studied in inorganic and organic solvents (Table 3).
The highest dissolution rate was observed in concen-
trated HNO ₃ . With decreasing HNO ₃ concentration, the
dissolution rate of PbGa ₂ Se ₄ decreases. Increasing the
temperature accelerates PbGa ₂ Se ₄ dissolution in nitric
acid. In benzene and concentrated H ₂ SO ₄ , HCl, and
KOH, PbGa ₂ Se ₄ dissolves only partially. PbGa ₂ Se ₄ sol-
ubility in H ₂ O, acetic acid, toluene, acetone, ethanol,
and Trilon B is insignificant.

Vaporization PbGa₂Se₄ single crystals was studied

using an MI-1201 mass spectrometer fitted with a band-

shaped ion source for analysis of solids [7]. In the gas

source, one of the cathodes was replaced by an effusion

cell. The crystals were vaporized from tantalum Knud-

sen cells in the range 600–1300 K.

and Se were 778 ± 5 and 786 ± 5 °C, respectively. The PbGa₂Se₄ melt solidified after supercooling, which attained 34 and 21°C for the growth charges prepared from as-purchased and additionally purified chemicals,

polycrystalline PbGa₂Se₄ growth charges prepared from as-purchased and additionally purified Pb, Ga,

impurities were Cu, Fe, Al, Cd, As, Mg, Zn, and Mn

According to DTA results, the melting points of the

(Table 2).

and other impurities. The PbGa₂Se₄ crystals prepared using purified Pb, Ga, and Se had nearly stoichiometric compositions (Table 1) and displayed good cleavage properties parallel to the basal plane. The middle (highest purity) portion of the crystals contained evenly distributed Tl and In impurities. In the upper part of the ingots, the major

Those crystals exhibited cleavage in the basal plane,

breaking into several parts, which indicated that impurities resided predominantly in the gaps between the layers and that the crystals were structurally imperfect (Table 2). The highest purity was achieved in the middle portion of the ingots, which contained Fe, Si, As, Ti,

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J, arb. units

Fig. 1. Ionization efficiency curves for vapor species over PbGa₂Se₄: (1) PbGa₂, (2) Pb, (3) GaSe, (4) Ga, (5) Ga₂Se, (6) Se₂, (7) Se.

Since mass spectra depend on the ionizing-electron energy, we measured the ionization efficiency curves of the forming ions in order to identify the ions and major vapor species (Fig. 1). From the initial portion of the curves, we determined the appearance potentials of the ions by linear extrapolation. The major vapor species were identified by comparing the fusion and ionization potentials. Calibration was performed against the appearance potential of Hg (10.4 eV).

According to the present experimental results, PbGa₂Se₄ vaporizes quantitatively starting at 950 K. Below 1070 K, the dominant vapor species is PbGa₂. At higher temperatures, the vapor phase also contains Ga₂Se, Se₂, and Pb. In addition, the mass spectrum shows signals from Ga, Ga₂, Se, and GaSe₂, due to dis-





Fig. 2. Temperature dependences of ion currents for $PbGa_2Se_4$.

sociative ionization. Between 1200 and 1300 K, the vapor composition remains unchanged. These findings indicate that $PbGa_2Se_4$ vaporizes according to the scheme

$$3PbGa_2Se_4 \longrightarrow PbGa_2 + 2Ga_2Se + 2Pb + 5Se_2$$
.

From the temperature-dependent ion currents for the major vapor species (Fig. 2), we evaluated their partial heats of vaporization [8, 9].

CONCLUSIONS

The present results demonstrate that, to obtain homogeneous, high-purity PbGa₂Se₄ growth charges

and crystals, high-purity starting chemicals and optimized synthesis and growth procedures are required.

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