

Photoconductivity of the Single Crystals $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$ and $\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$ †

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Abstract: Quaternary semiconductor materials of the $\text{Pb}_4\text{Ga}_4\text{GeS}(\text{Se})_{12}$ composition have attracted the attention of researchers due to their possible use as active elements of optoelectronics and nonlinear optics. The $\text{Pb}_4\text{Ga}_4\text{GeS}(\text{Se})_{12}$ phases belong to the solid solution ranges of the $\text{Pb}_3\text{Ga}_2\text{GeS}(\text{Se})_8$ compounds which form in the quasi-ternary systems $\text{PbS}(\text{Se})\text{--Ga}_2\text{S}(\text{Se})_3\text{--GeS}(\text{Se})_2$ at the cross of the $\text{PbGa}_2\text{S}(\text{Se})_4\text{--Pb}_2\text{GeS}(\text{Se})_4$ and $\text{PbS}(\text{Se})\text{--PbGa}_2\text{GeS}(\text{Se})_6$ sections. The quaternary sulfide melts congruently at 943 K. The crystallization of the $\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$ phase is associated with the ternary peritectic process $L_p + \text{PbSe} \leftrightarrow \text{PbGa}_2\text{S}_4 + \text{Pb}_3\text{Ga}_2\text{GeSe}_8$ at 868 K. For the single crystal studies, $\text{Pb}_4\text{Ga}_4\text{GeS}(\text{Se})_{12}$ were pre-synthesized by co-melting high-purity elements. The X-ray diffraction results confirm that these compounds possess non-centrosymmetric crystal structure (tetragonal symmetry, space group $P\text{--}42_1c$). The crystals were grown by the vertical Bridgman method in a two-zone furnace. The starting composition was stoichiometric for $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$, and the solution-melt method was used for the selenide $\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$. The obtained value of the bandgap energy for the $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$ and $\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$ crystals is 1.86 and 2.28 eV, respectively. Experimental measurements of the spectral distribution of photoconductivity for the $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$ and $\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$ crystals exhibit the presence of two spectral maxima. The first lies in the region of 570 (2.17 eV) and 680 nm (1.82 eV), respectively, and matches the optical bandgap estimates well. The locations of the admixture maxima at about 1030 (1.20 eV) and 1340 nm (0.92 eV), respectively, agree satisfactorily with the calculated energy positions of the defects vs. and V_{Se} .

Keywords: quaternary chalcogenides; phase equilibria; single crystals; photoconductivity

1. Introduction

Recently, a series of new compounds were discovered (4-4-1-12 type: $\text{Pb}_4\text{Ga}_4\text{Ge}(\text{S},\text{Se})_{12}$ [1], and 1-2-1-6 type: $\text{PbGa}_2\text{Ge}(\text{Si})\text{Se}_6$, $\text{SnGa}_2\text{Ge}(\text{S},\text{Se})_6$, $\text{PbGa}_2\text{GeS}_6$ [2–5]) that possess qualitatively new physical properties and may serve as a basis for the design of non-linear optical materials. The 4-4-1-12 quaternary compounds feature non-linear coefficients exceeding those of $\text{AgGa}(\text{S},\text{Se})_2$ (record second harmonic generation (SHG) efficiencies) and an order of magnitude higher laser damage threshold. Additionally, they have a much longer-wave limit of IR transparency (up to 23 μm) and more suitable double refraction for phase synchronism of the converted radiation in the 1–10 μm range. The authors [1] reported that the $\text{Pb}_4\text{Ga}_4\text{GeS}(\text{Se})_{12}$ compounds are isostructural and crystallize in the tetragonal symmetry, space group $P\text{--}42_1c$, with the unit cell parameters $a = 1.2673(2)$, $c =$

0.6128(2) nm for $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$, and $a = 1.3064(7)$, $c = 0.6310(5)$ nm for $\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$. They have bandgap energy of 2.35 and 1.91 eV and are transparent in a wide range of the IR spectrum at 0.80–22.5 and 0.75–22.5 μm , respectively.

Our research was focused on the technology of the single crystal growth of these compounds, and their possible use in active elements for linear and non-linear optics and optoelectronics.

2. Materials and Methods

Polycrystalline alloys of the $\text{Pb}_4\text{Ga}_4\text{GeS(Se)}_{12}$ compositions were preliminarily synthesized by co-melting the elements in the stoichiometric ratio. The batches were composed of high-purity elements Pb, 99.99 wt.%, Ga, 99.9997% (SmiLab Ltd., Svitlovodsk, Ukraine), Ge, 99.9999 wt.%, S, Se 99.999 wt.% (Alfa Aesar GmbH & Co KG, Karlsruhe, Germany). Lead was additionally purified by dripping through crushed quartz under static conditions. The total batch mass was 20 g. The sulfur-containing quartz ampoule was evacuated to 10^{-2} Pa and was locally heated in the oxygen-gas burner flame to complete bonding of sulfur under visual observation of the reaction process. Considering high vapor pressure, $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$ was synthesized in 5 g batches followed by the transfer of the powdered obtained alloy to the growth container. $\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$ was synthesized already in the evacuated growth container. Quartz ampoules with conical bottom were used for the crystal growth.

The results of preliminary experiments suggest the critical importance of the homogeneity of the starting batch and rather high temperature gradient at the solid–melt interface. This is because lead reacts rather poorly with chalcogens. Initial interaction of the elements yields binary lead chalcogenide, which surrounds molten lead and prevents further reaction with other elements or binary chalcogenides of other metals. Additionally, the melts of these systems have high viscosity, as one of the system components (GeS(Se)_2) is a known glass-forming agent. High viscosity hinders the diffusion mixing of the melt above the growing crystal which may lead to the formation of blocs, admixtures of other phases, uncontrolled occlusion, all of which affect the properties of single crystals. Therefore, operations of forced homogenization are necessary, such as furnace rotation or vibration, or crushing the alloy into powder before loading it into the growth container.

Homogenization of the alloys of both phases was achieved by placing the ampoules with the alloys in a rotation furnace and heating to 1170 K at the rate of 50 K/h. The furnace was rotated at this temperature for 24 h. After stopping the furnace in the vertical position, the alloys were cooled at 20 K/h to 670 K and annealed for 240 h. The synthesis process was finished by cooling to room temperature in the inertial mode. The obtained alloys were compact ingots.

The crystal growth was performed by the Bridgman method [6] in a two-zone furnace with steady temperature profile. The growth containers with the synthesized batches were placed in the pre-heated furnace. The temperature of the upper isothermal zone was 1170 K, and that of the lower zone varied from 620 to 670 K. The temperature in the growth zone was controlled with ± 0.5 K accuracy. Independent temperature control and selection of metal discs between the two zones permitted the variation of temperature gradient at the solid–melt interface of 1.2–3 K/cm. The growth rate varied in the range of 5–6 mm/day. After the complete crystallization of the melts, the furnace was cooled to room temperature at the rate of 5 K/h.

3. Results

3.1. Phase Equilibria Related to the Formation of $\text{Pb}_3\text{Ga}_2\text{GeS(Se)}_8$

Our investigations of the quasi-ternary systems $\text{PbS(Se)}-\text{Ga}_2\text{S(Se)}_3-\text{GeS(Se)}_2$ using the XRD and differential thermal analysis (DTA) methods (to be published in detail elsewhere) showed that the $\text{Pb}_4\text{Ga}_4\text{GeS(Se)}_{12}$ compositions belong to the solid solution ranges of the $\text{Pb}_3\text{Ga}_2\text{GeS(Se)}_8$ compounds that form at the crossing of the sections $\text{PbGa}_2\text{S(Se)}_4-\text{Pb}_2\text{GeS(Se)}_4$ and $\text{PbS(Se)}-\text{PbGa}_2\text{GeS(Se)}_6$ (Figure 1).

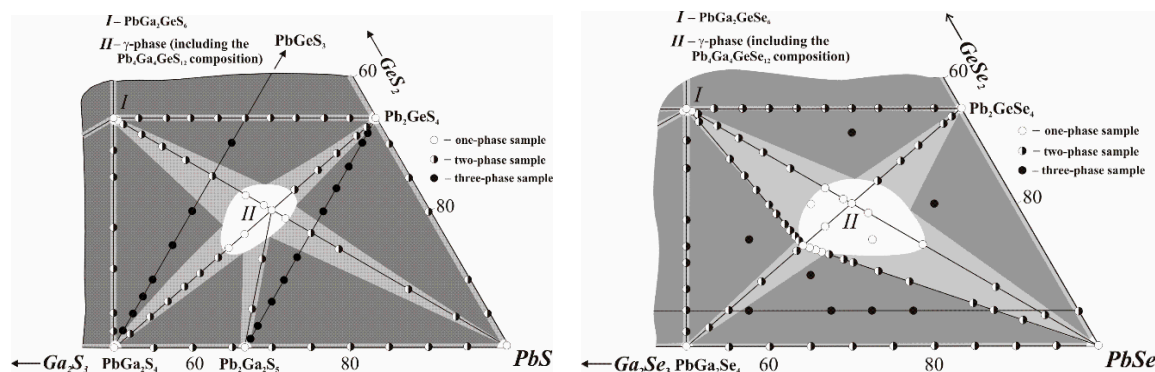


Figure 1. Isothermal sections of the $\text{PbS(Se)-Ga}_2\text{S(Se)-GeS(Se)}_2$ systems in the $\text{PbS(Se)-Pb}_2\text{GeS(Se)}_4\text{-PbGa}_2\text{GeS(Se)}_6\text{-PbGa}_2\text{S(Se)}_4$ part at 670 K.

Vertical sections of $\text{PbGa}_2\text{S(Se)}_4\text{-Pb}_2\text{GeS(Se)}_4$ were investigated to consider the conditions for the crystal growth of $\text{Pb}_4\text{Ga}_4\text{GeS(Se)}_{12}$ as the sections demonstrate the nature of the formation of these phases (Figure 2). The sulfur-containing section $\text{PbGa}_2\text{S}_4\text{-Pb}_2\text{GeS}_4$ is quasi-binary in the entire concentration and temperature range, while the selenide section $\text{PbGa}_2\text{Se}_4\text{-Pb}_2\text{GeSe}_4$ is quasi-binary only in the sub-solidus region due to incongruent melting of the starting ternary compounds PbGa_2Se_4 and Pb_2GeSe_4 . Each of the 4-4-1-12 compounds is dimorphous, with the phase transitions taking place at 854 K for the sulfide and 795 K for the selenide. The $\text{Pb}_4\text{Ga}_4\text{GeS(Se)}_{12}$ phases each occupy at the studied sections of $\text{PbGa}_2\text{S(Se)}_4\text{-Pb}_2\text{GeS(Se)}_4$ the range of ~32–57 mol.% $\text{Pb}_2\text{GeS(Se)}_4$.

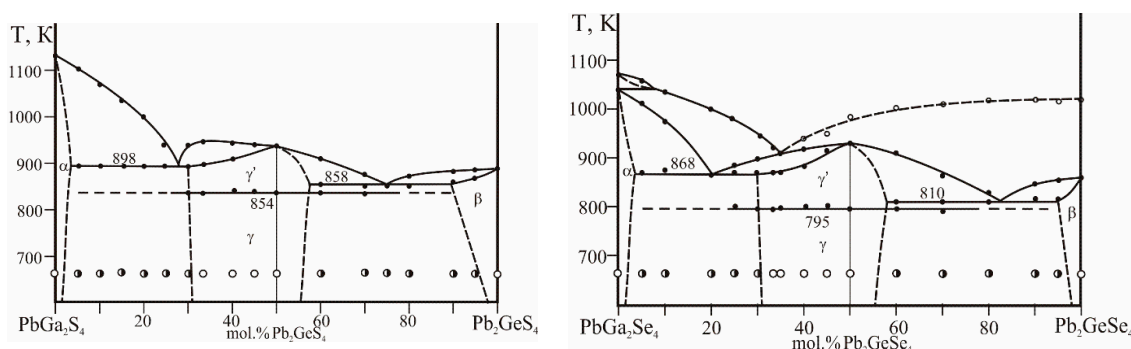


Figure 2. Phase diagrams of the $\text{PbGa}_2\text{S(Se)}_4\text{-Pb}_2\text{GeS(Se)}_4$ systems.

The quaternary sulfide melts congruently at 943 K. The melting point maximum falls onto the $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$ composition, while the stoichiometric composition of the quaternary solid solution corresponds to $\text{Pb}_3\text{Ga}_2\text{GeS}_8$. The eutectic between PbGa_2S_4 and HT- $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$ lies at 27 mol.% Pb_2GeS_4 , 898 K; the eutectic between HT- $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$ and Pb_2GeS_4 is at 75 mol.% Pb_2GeS_4 , 858 K.

The crystallization of the $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$ phase is related to the ternary peritectic process $\text{Lp}_1 + \text{PbSe} \rightleftharpoons \text{PbGa}_2\text{Se}_4$ (α -solid solutions) + $\text{Pb}_3\text{Ga}_2\text{GeSe}_8$ (γ' -solid solutions) at 868 K in the $\text{PbSe-Ga}_2\text{Se}_3\text{-GeSe}_2$ system. The other ternary peritectic process $\text{Lp}_2 + \text{PbSe} \rightleftharpoons \text{Pb}_3\text{Ga}_2\text{GeSe}_8$ (γ' -solid solutions) + Pb_2GeSe_4 (β -solid solutions) takes place at 810 K.

3.2. Optical Properties of the $\text{Pb}_3\text{Ga}_2\text{GeS(Se)}_8$ Single Crystals

Two experiments examining the growth of each of the crystals were performed. The increase in the temperature gradient proved quite advantageous. Using optimized growth condition, crystals of up to 11 mm diameter and 58 mm ($\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$) and 55 mm length ($\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$) were obtained. It should be noted that the lower conical bottom of the selenide sample (up to 2 mm diameter) contains blocs of other phase composition, due to the field of the secondary crystallization $\text{L} + \delta + \gamma$. The XRD results confirm that the low-temperature modifications of these compounds have non-centrosymmetric crystal structure (tetragonal symmetry, space group $P-42_1c$).

Obtained boules were cut using Ni-Cr wire into separate plates that were polished to parallel-plane, optical quality samples of 0.2 mm thickness. These samples were used for the measurements of physical properties such as optical absorption and photoconductivity.

The data from experimental absorption spectra (Figure 3) are comparable to the theoretical calculations of the band gap energy [7]. The band gap of the studied materials was determined by the extrapolation of the linear part of the absorption curve to the energy axis (Figure 3b,d). The obtained bandgap energy value is equal to 2.28 and 1.86 eV for $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$ and $\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$ crystals, respectively, which is close to the results of [1].

A study of the spectral distribution of photoconductivity for $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$ and $\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$ crystals was undertaken for additional confirmation of the obtained results (Figure 4). Experimental measurements were performed using Keithley 6514 Sub-Femtoamp SourceMeter electrometer. Sensitivity of experimental setup was not worse than 1 pA. An MDR-206 monochromator with the diffraction grating with 600 lines/mm and spectral resolution 0.2 nm was used as a spectral device. The electrical contacts were applied by fusing of Ga-In eutectic and were ohmic for all considered compositions.

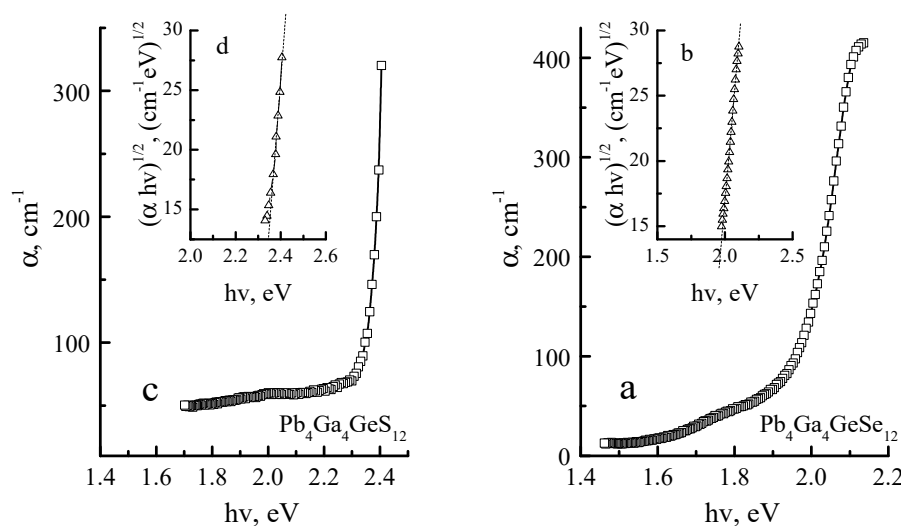


Figure 3. Typical absorption spectra (a,c) versus photon energy and extrapolated (b,d) spectra for the $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$ and $\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$ samples.

A characteristic feature of the spectral distribution of photoconductivity is the presence of two spectral maxima. The first lies in the region of $\lambda_1 = 570$ (2.17 eV) and 680 nm (1.82 eV) for the $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$ and $\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$ crystals, respectively, and show a good match with the band gap estimated from the spectral dependence of the absorption coefficient. Therefore, we can assert that peak I of the spectral dependence $\Delta\sigma/\Delta\sigma_{\text{max}}$ is due to the intrinsic photoconductivity of the studied crystals. The impurity level is located in the region of $\lambda_2 = 1030$ (1.20 eV) and 1340 nm (0.92 eV) for $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$ and $\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$ crystals, respectively. One can see from the obtained results that the location of impurity maximum satisfactorily agrees well with the calculated energy positions of intrinsic defects vs. and V_{Se} [7], which is close to the center of the band gap. The lower formation energy of V_{Se} in comparison with the energy of vs. formation favors the prevalence of peak II of the impurity photoconductivity in the $\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$ crystals.

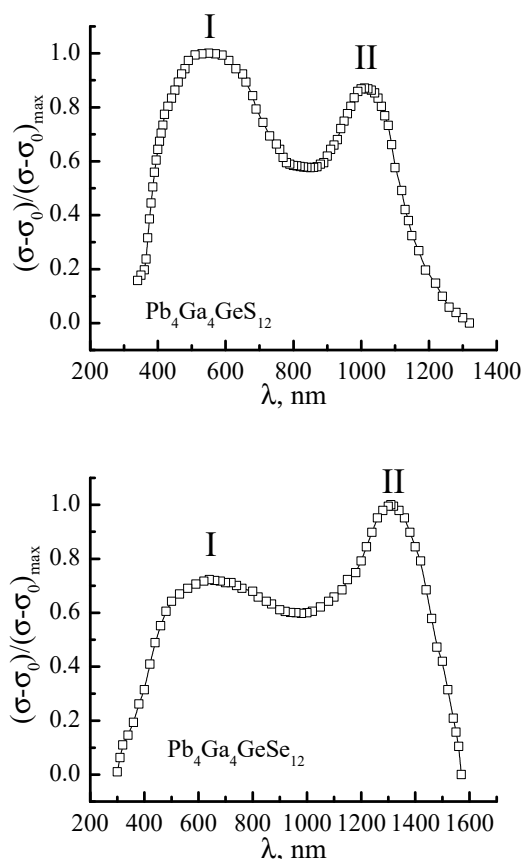


Figure 4. Spectral distribution of photoconductivity for the $\text{Pb}_4\text{Ga}_4\text{GeS}_{12}$ and $\text{Pb}_4\text{Ga}_4\text{GeSe}_{12}$ crystals.

Author Contributions: Conceptualization, L.P. and H.M.; methodology, L.P., Y.K. and H.M.; sample synthesis, H.B. and O.N.; single crystal growth, Y.K. and H.B.; DTA and XRD data collection and analysis, Y.K. and H.B.; optical absorption and photoconductivity data collection and analysis, O.N. and H.M.; writing—original draft preparation, H.B., Y.K. and O.N.; writing—review and editing, Y.K., L.P. and H.M.; supervision, H.M.; project administration, L.P. All authors have read and agreed to the published version of the manuscript.

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