Crystals 2020

sciforum

Conference Proceedings Paper

Photoconductivity of the Single Crystals Pb4Ga4GeS12 and Pb4Ga4GeSe12

Hadj Bellagra[1], Oksana Nyhmatullina[2], Yuri Kogut[1], Halyna Myronchuk[2], Lyudmyla Piskach[1]*

[1] Eastern European National University, Department of Chemistry, Voli Ave. 13, Lutsk 43025, Ukraine
[2] Eastern European National University, Department of Physics, Voli Ave. 13, Lutsk 43025, Ukraine
* Correspondence: lyuda0760@ukr.net ; Tel.: +380-50-911-1265
Published: 6 November 2020

Abstract: Quaternary semiconductor materials of the $Pb_4Ga_4GeS(Se)_{12}$ composition have attracted the attention of researchers due to possible use as active elements of optoelectronics and nonlinear optics. The $Pb_4Ga_4GeS(Se)_{12}$ phases belong to the solid solution ranges of the $Pb_3Ga_2GeS(Se)_8$ compounds which form in the quasi-ternary systems $PbS(Se)–Ga_2S(Se)_3–GeS(Se)_2$ at the cross of the $PbGa_2S(Se)_4–Pb_2GeS(Se)_4$ and $PbS(Se)–PbGa_2GeS(Se)_6$ sections. The quaternary sulfide melts congruently at 943 K. The crystallization of the $Pb_4Ga_4GeSe_{12}$ phase is associated with the ternary peritectic process $L_P + PbSe \leftrightarrow PbGa_2S_4 + Pb_3Ga_2GeSe_8$ at 868 K. For the single crystal studies, $Pb_4Ga_4GeS(Se)_{12}$ were pre-synthesized by co-melting high-purity elements. X-ray diffraction results confirm that these compounds possess non-centrosymmetric crystal structure (tetragonal symmetry, space group $P\bar{4}2_1c$). The crystals were grown by the vertical Bridgman method in a two-zone furnace. The starting composition was stoichiometric for $Pb_4Ga_4GeS_{12}$, and the solution-melt method was used for the selenide $Pb_4Ga_4GeSe_{12}$. Obtained value of the bandgap energy for the $Pb_4Ga_4GeS_{12}$ and $Pb_4Ga_4GeSe_{12}$ crystals is 1.86 and 2.28 eV, respectively. Experimental measurements of the spectral distribution of photoconductivity for the $Pb_4Ga_4GeS_{12}$ and $Pb_4Ga_4GeSe_{12}$ crystals exhibit the presence of two spectral maxima. The first lies in the region of 570 nm (2.17 eV) and 680 nm (1.82 eV), respectively, and matches well the optical bandgap estimates. The locations of the admixture maxima at about 1030 nm (1.20 eV) and 1340 nm (0.92 eV), respectively, agree satisfactorily with the calculated energy positions of the defects V_S and V_{Se}.

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

1. Introduction

Recently, series of new compounds were discovered (4-4-1-12 type: $Pb_4Ga_4Ge(S,Se)_{12}$ [1], and 1-2-1-6 type: $PbGa_2Ge(Si)Se_6$, $SnGa_2Ge(S,Se)_6$, $PbGa_2GeS_6$ [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 $AgGa(S,Se)_2$ (record second harmonic generation (SHG) efficiencies) and an order of magnitude higher laser damage threshold. Additionally, they have 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] report that the $Pb_4Ga_4GeS(Se)_{12}$ compounds are isostructural and crystallize in the tetragonal symmetry, space group $P\bar{4}2_1c$, with the unit cell parameters a=1.2673(2), c=0.6128(2) nm for $Pb_4Ga_4GeS_{12}$, and a=1.3064(7), c=0.6310(5) nm for $Pb_4Ga_4GeSe_{12}$. They have bandgap energy of 2.35 and 1.91 eV and are transparent in wide range of IR spectrum 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 $Pb_4Ga_4GeS(Se)_{12}$ compositions were preliminarily synthesized by co-melting the elements in stoichiometric ratio. The batches were composed of high-purity elements Pb, 99.99 wt.%, Ga, 99.9997% (SmiLab Ltd), Ge, 99.9999 wt.%, S, Se 99.999 wt.% (Alfa Aesar). 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, $Pb_4Ga_4GeS_{12}$ was synthesized in 5 g batches followed by the transfer of the powdered obtained alloy to the growth container. $Pb_4Ga_4GeSe_{12}$ 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 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 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 in 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/hr. The furnace was rotated at this temperature for 24 hrs. after stopping the furnace in the vertical position, the alloys were cooled at 20 K/hr to 670 K, and annealed for 240 hrs. The synthesis process was finished by cooling to room temperature in the inertial mode. Obtained alloys were compact ingots.

The crystal growth was performed by 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, the lower zone varied within 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 compete crystallization of the melts, the furnace was cooled to room temperature at the rate of 5 K/hr.

3. Results

3.1. Phase equilibria related to the formation of $Pb_3Ga_2GeS(Se)_8$

Our investigations of the quasi-ternary systems $PbS(Se)–Ga_2S(Se)_3–GeS(Se)_2$ by XRD and DTA methods (to be published in detail elsewhere) showed that the $Pb_4Ga_4GeS(Se)_{12}$ compositions belong to the solid solution ranges of the $Pb_3Ga_2GeS(Se)_8$ compounds that form at the crossing of the sections $PbGa_2S(Se)_4–Pb_2GeS(Se)_4$ and $PbS(Se)–PbGa_2GeS(Se)_6$ (Figure 1).

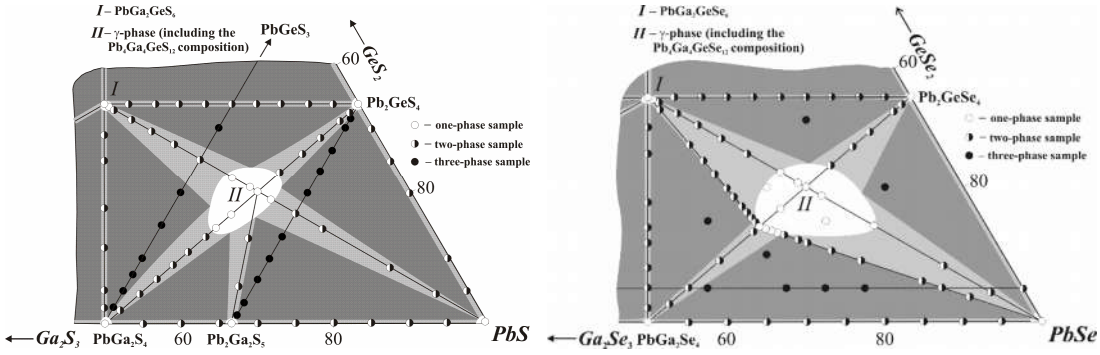


Figure 1. Isothermal sections of the PbS(Se)–$Ga_2S(Se)_3$–$GeS(Se)_2$ systems in the PbS(Se)–$Pb_2GeS(Se)_4$–$PbGa_2GeS(Se)_6$–$PbGa_2S(Se)_4$ part at 670 K.

Vertical sections $PbGa_2S(Se)_4$–$Pb_2GeS(Se)_4$ were investigated to consider the conditions for the crystal growth of $Pb_4Ga_4GeS(Se)_{12}$ as the sections demonstrate the nature of the formation of these phases (Figure 2). The sulfur-containing section $PbGa_2S_4$–Pb_2GeS_4 is quasi-binary in the entire concentration and temperature range, while the selenide section $PbGa_2Se_4$–Pb_2GeSe_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 $Pb_4Ga_4GeS(Se)_{12}$ phases each occupies at the studied sections $PbGa_2S(Se)_4$–$Pb_2GeS(Se)_4$ the range of ~32–57 mol.% $Pb_2GeS(Se)_4$.

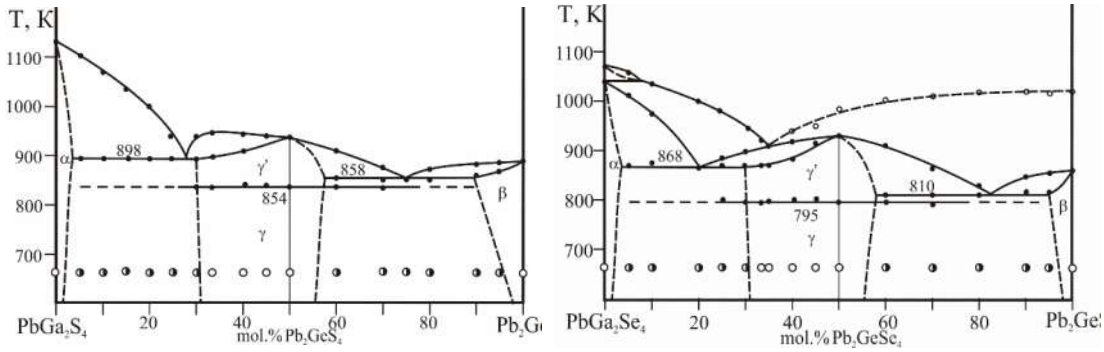


Figure 2. Phase diagrams of the $PbGa_2S(Se)_4$–$Pb_2GeS(Se)_4$ systems.

The quaternary sulfide melts congruently at 943 K. The melting point maximum falls onto the $Pb_4Ga_4GeS_{12}$ composition, while the stoichiometric composition of the quaternary solid solution corresponds to $Pb_3Ga_2GeS_8$. The eutectic between $PbGa_2S_4$ and HT-$Pb_4Ga_4GeS_{12}$ lies at 27 mol.% Pb_2GeS_4, 898 K; the eutectic between HT-$Pb_4Ga_4GeS_{12}$ and Pb_2GeS_4 is at 75 mol.% Pb_2GeS_4, 858 K.

The crystallization of the $Pb_4Ga_4GeSe_{12}$ phase is related to the ternary peritectic process Lp_1 + PbSe ↔ $PbGa_2Se_4$ (α-solid solutions) + $Pb_3Ga_2GeSe_8$ (γ'-solid solutions) at 868 K in the PbSe–Ga_2Se_3–$GeSe_2$ system. The other ternary peritectic process Lp_2+ PbSe ↔ $Pb_3Ga_2GeSe_8$ (γ'-solid solutions) + Pb_2GeSe_4 (β-solid solutions) takes place at 810 K.

3.2. Optical properties of the $Pb_3Ga_2GeS(Se)_8$ single crystals

Two experiments of the growth of each of the crystals were performed. The increase of the temperature gradient proved quite advantageous. Using optimized growth condition, crystals of up to 11 mm diameter and 58 mm ($Pb_4Ga_4GeS_{12}$) and 55 mm length ($Pb_4Ga_4GeSe_{12}$) were obtained. It should be noted 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 L + δ + γ. XRD

results confirm that the low-temperature modifications of these compounds have non-centrosymmetric crystal structure (tetragonal symmetry, space group $P\bar{4}2_1c$).

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 (Fig. 3 b, d). Obtained bandgap energy value is equal to 2.28 eV and 1.86 eV for $Pb_4Ga_4GeS_{12}$ and $Pb_4Ga_4GeSe_{12}$ crystals, respectively, which is close to the results of [1].

A study of the spectral distribution of photoconductivity for $Pb_4Ga_4GeS_{12}$ and $Pb_4Ga_4GeSe_{12}$ crystals was undertaken for additional confirmation of 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.

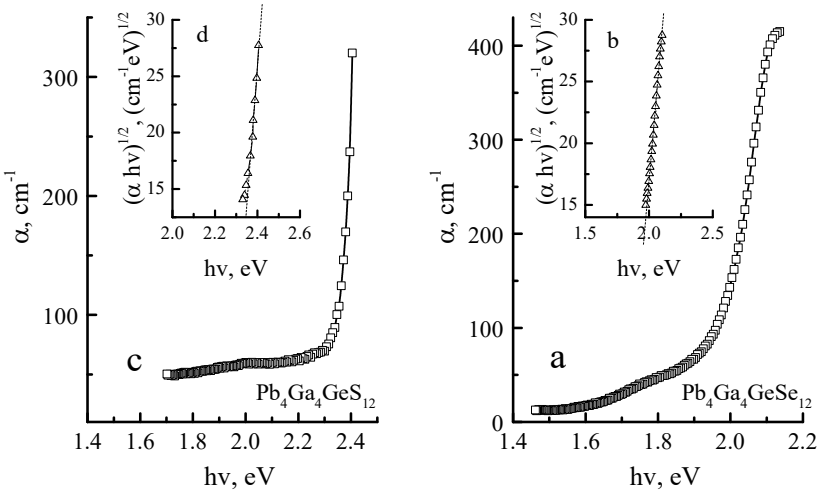
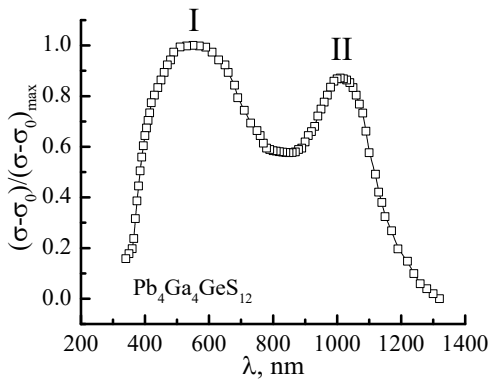


Figure 3. Typical absorption spectra (a, c) versus photon energy and extrapolated (b, d) spectra for the $Pb_4Ga_4GeS_{12}$ and $Pb_4Ga_4GeSe_{12}$ samples.



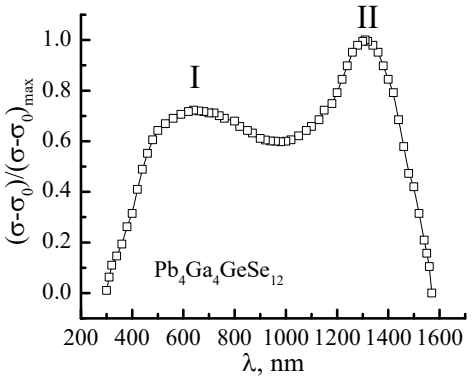


Figure 4. Spectral distribution of photoconductivity for the $Pb_4Ga_4GeS_{12}$ and $Pb_4Ga_4GeSe_{12}$ crystals.

A characteristic feature of the spectral distribution of photoconductivity is the presence of two spectral maxima. The first lies in the region of λ_1=570 nm (2.17 eV) and 680 nm (1.82 eV) for the $Pb_4Ga_4GeS_{12}$ and $Pb_4Ga_4GeSe_{12}$ 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 the peak I of the spectral dependence $\Delta\sigma/\Delta\sigma_{max}$ is due to the intrinsic photoconductivity of the studied crystals. The impurity level is located in the region of λ_2=1030 nm (1.20 eV) and 1340 nm (0.92 eV) for $Pb_4Ga_4GeS_{12}$ and $Pb_4Ga_4GeSe_{12}$ crystals respectively. One can see from obtained results that the location of impurity maximum satisfactorily agrees well with the calculated energy positions of intrinsic defects V_S 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 V_S formation favours the prevalence of the peak II of the impurity photoconductivity in the $Pb_4Ga_4GeSe_{12}$ 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.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Chen Y.K.; Chen M.C.; Zhou L.J.; Chen L.; Wu L.M. Syntheses, structures, and nonlinear optical properties of quaternary chalcogenides: $Pb_4Ga_4GeQ_{12}$ (Q = S, Se). *Inorg Chem.* **2013**, *52*, 8334-8341.

2. Luo, Z.-Z.; Lin, C.-S.; Cui, H.-H.; Long, W. $PbGa_2MSe_6$ (M = Si, Ge): Two Exceptional Infrared Nonlinear Optical Crystals. *Chem. Mater*. **2015**, *27*, 914–922.
3. Fedorchuk, A.O.; Parasyuk, O.V.; Cherniushok, O.; Andriyevsky, B.; Myronchuk, G.L.; Khyzhun, O.Y.; Lakshminarayana, G.; Jedryka, J.; Kityk, I.V.; El-Naggar, A.M.; Albassam, A.A.; Piasecki, M. $PbGa_2GeS_6$ crystal as a novel nonlinear optical material: Band structure aspects. *J. Alloys. Compds.* **2018**, *740*, 294–304.
4. Yousaf, N.; Khan, W.; Khan, S.H.; Yaseen, M.; Laref, A.; Murtaza, G. Electronic, optical and thermoelectric properties of $SnGa_2GeX_6$ (X = S, Se) compounds. *J. Alloys Compds.* **2018**, *737*, 637-645.
5. Huang, Y.-Z.; Zhang, H.; Lin, C.-S.; Cheng, W.-D.; Guo, Z.; Chai, G.-L. $PbGa_2GeS_6$: An Infrared Nonlinear Optical Material Synthesized by an Intermediate-Temperature Self-Fluxing Method. *Cryst. Growth Des.* **2018**, *18*, 1162-1167.
6. Vilke, K.-T. *Crystal Growth*, Nedra; Leningrad, Russia, 1977.
7. Piasecki, M. (Jan Dlugosz University, Czestochowa, Poland); Rudysh, M. (Ivan Franko National University of Lviv, Lviv, Ukraine). Personal communication, 2019.