INVESTIGATIONS OF THE TlInP₂Se₆-In₄(P₂Se₆)₃ SYSTEM AND ITS OPTICAL PROPERTIES

VALERIA TOVT,¹ IGOR BARCHIY,¹* MICHAL PIASECKI,² IWAN KITYK,³ AND ANATOLII FEDORCHUK⁴

¹ Department of Chemistry, Uzhgorod National University, Pidgirna St. 46, 88000 Uzhgorod, UKRAINE
² Institute of Physics, Jan Długosz University, Armii Krajowej 13/15, 42-200 Częstochowa, POLAND
³ Faculty of Electrical Engineering, Częstochowa University of Technology, Dabrowskiego 69, 42201 Częstochowa, POLAND
⁴ Department of Inorganic and Organic Chemistry, Liviv National University of Veterinary Medicine and Biotechnologies, Pekarska St. 50, 79010 Lviv, UKRAINE

The equilibrium phases were investigated and the corresponding phase diagram constructed for the TlInP₂Se₆-In₄(P₂Se₆)₃ system from physical and chemical analyses, namely differential thermal analysis (DTA), X-ray diffraction (XRD), and microstructural analysis (MSA). It was established that this system belongs to the eutectic type and is characterized by the formation of boundary solid phases containing complex compounds. Single crystals of the compounds TlInP₂Se₆ and In₄(P₂Se₆)₃ were grown using the Bridgman method. Both crystals were found to exhibit diffuse reflection spectra and photoinduced dependence of birefringence at various IR wavelengths generated by CO₂ laser irradiation. Birefringence properties were investigated using the Senarmont method.

Keywords: phase diagram, solid solution, crystal structure, optical properties, direct-gap semiconductor, indirect-gap semiconductor, photoinduced birefringence

1. Introduction

Compounds with the formula M₂P₂Se₆ possess promising magneto-electric, piezoelectric, electro-optical, and thermoelectric properties that indicate their suitability as functional materials in optoelectronics [1-2]. Due to their crystal structure, they exhibit anisotropy in terms of their physical properties. In a multilayer structure of M₂P₂Se₆ compounds, metal cations and pairs of phosphorous atoms occupy the octahedral positions between planes of selenium atoms. This structure is characterized by its layered arrangement of atoms, which contributes to the formation of a dipole moment between the layers of cationic and anionic groups. The replacement of the metal cation M²⁺ by other metal cations (M⁺, M³⁺ or M⁴⁺) leads to the deformation of the structure [3-4], changes the magnitude of the dipole moment and, consequently, its physical properties.

The Tl₃Se-In₃Se₃-P₂Se₄ ternary system is composed of binary Tl₃Se-In₃Se₃, Tl₃Se-P₂Se₄, and In₃Se₃-P₂Se₄ systems. The Tl₃Se-In₃Se₃ system is characterized by the formation of two intermediate ternary compounds: TlInSe₂ melts congruently at 1023 K and TlInSe₃ is formed according to the peritectic reaction L + In₂Se₃ ↔ TlInSe₃ at 1029 K [5-6]. In the system Tl₁Se-P₃Se₄ with a ratio of 2 to 1, interoperate components form the compound Tl₁P₃Se₆ which possesses a congruent nature of melting at 758 K [7]. The In₃Se₃-P₂Se₄ system is characterized by the formation of the compound In₄(P₂Se₆)₃ in a syntetic reaction of L₁ + L₂ ↔ In₄(P₂Se₆)₃ at 880 K [8]. In the Tl₁Se-In₃Se₃-P₂Se₄ system at the intersection of incisions, the phases Tl₁P₃Se₆-In₄(P₂Se₆)₃ and TlInSe₂-P₃Se₄ form the complex compound TlInP₂Se₆ [9].

2. Experimental

Ternary Tl₁P₃Se₆ and In₄(P₂Se₆)₃ compounds were prepared by melting stoichiometric quantities of binary Tl₁Se with elementary indium, phosphorous and selenium under a vacuum of 0.13 Pa in quartz ampoules using a single temperature method. In all syntheses, components were used that possess a purity greater than 99.999 %. The maximum temperatures of synthesis were 993 and 893 K for In₄(P₂Se₆)₃ and TlInP₂Se₆, respectively. The rate of heating up to the maximum temperature was 50 K h⁻¹. The melts were maintained at the maximum temperature for 72 hours. Cooling was performed at a rate of 50 K h⁻¹ down to an annealing temperature of 573 K. The linearity of the heating and cooling processes was achieved by a RIIF-101 temperature controller. The homogenization process occurred over 120 hours. Identification of the complex compounds and alloys was conducted by differential thermal analy-
sis (DTA) (PRA-01, chromalumina thermocouple ±5 K), X-ray diffraction (XRD) (DRON-3 diffractometer, CuKα radiation, Ni filter) and microstructural analysis (MSA) (metallurgical microscope Lomo Metam R-1). Crystal structural calculations were conducted using the software package WinCSD [10]. Optical properties were investigated using an SF-18 spectrophotometer within the wavelength range of 400 – 750 nm. A CO₂ laser was used for photoinduced electrons in samples employing 200 ns pulses with a pulse repetition frequency of about 10 Hz, a fundamental frequency of 10.6 μm and a frequency doubling of 5.3 μm beams. The birefringence was measured using a Er:glass cw laser at 1540 nm by application of the Senarmont method.

3. Results and Analysis

3.1. Phase diagram of the TlInP₂Se₆—In₄(P₂Se₆)₃ system

The TlInP₂Se₆—In₄(P₂Se₆)₃ system is a quasi-binary section of the Tl₂Se-In₃Se₇—P₂Se₆ ternary system (Figs. 1 and 2). It belongs to the eutectic type (V-type diagram by Rozeboom). The complex compounds TlInP₂Se₆ and In₄(P₂Se₆)₃ melt congruently at 875 K and 963 K, respectively. TlInP₂Se₆ is characterized by two polymorphic transformations hTlInP₂Se₆ ↔ mTlInP₂Se₆ at 680 K and mTlInP₂Se₆ ↔ hTlInP₂Se₆ at 711 K. The prefixes hTl—in, mTl— and hTl— represent low-, medium-, and high-temperature modifications, respectively. In₄(P₂Se₆)₃ is also characterized by two polymorphic transformations hIn₄(P₂Se₆)₃ ↔ mIn₄(P₂Se₆)₃ at 665 K and mIn₄(P₂Se₆)₃ ↔ hIn₄(P₂Se₆)₃ at 903 K. When the temperature rises above 791 K, an invariant eutectic process is observed L ↔ hTlInP₂Se₆ + mIn₄(P₂Se₆)₃ (in the presence of 15 mol% In₄(P₂Se₆)₃).

The system is described by the sequence of the efficient peritectic processes hTlInP₂Se₆ + mIn₄(P₂Se₆)₃ ↔ mTlInP₂Se₆ (714 K) and mTlInP₂Se₆ + mIn₄(P₂Se₆)₃ ↔ hTlInP₂Se₆ (689 K) based on the polymorphic transformation of TlInP₂Se₆. The polymorphism of In₄(P₂Se₆)₃ produces metatectic hIn₄(P₂Se₆)₃ ↔ L + mIn₄(P₂Se₆) (884 K) and eutectic mIn₄(P₂Se₆)₃ ↔ L + hIn₄(P₂Se₆) (652 K) processes. Regions of homogeneity in solid solutions, based on the batched complex chalcogenides during annealing at a temperature of 573 K, do not exceed 10 mol%.

3.2. Crystal structure of the compounds In₄(P₂Se₆)₃ and TlInP₂Se₆

The crystal structures of the compounds TlInP₂Se₆ and In₄(P₂Se₆)₃ were solved using the Rietveld method. As an initial model for TlInP₂Se₆ [2], the parameters of In₄(P₂Se₆)₃ were used [8]. Analysis of the crystalline structures of the investigated compounds (Table 1) showed that it is possible to define the structural group of the anionic group [P₂Se₆]₄⁻, which is formed by two single tetrahedra (Fig. 3). Cationic atoms occupy positions between the anionic groups and none are located between the layers.

Table 1. Crystal data of TlInP₂Se₆ and In₄(P₂Se₆)₃ compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal system</th>
<th>Space group</th>
<th>Lattice constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>In₄(P₂Se₆)₃ [8]</td>
<td>trigonal</td>
<td>R3h (146)</td>
<td>a = 6.362(3), c = 19.929(6) Å</td>
</tr>
<tr>
<td>In₄(P₂Se₆)₃</td>
<td>trigonal</td>
<td>R3h (146)</td>
<td>a = 6.3808(8), c = 20.014(4) Å</td>
</tr>
<tr>
<td>TlInP₂Se₆ [2]</td>
<td>triclinic</td>
<td>P1 (2)</td>
<td>a = 6.4310, b = 7.5002, c = 12.124 Å</td>
</tr>
<tr>
<td>TlInP₂Se₆</td>
<td>triclinic</td>
<td>P1 (2)</td>
<td>a = 100.553, β = 93.735, γ = 113.451</td>
</tr>
</tbody>
</table>
The structure of In\(_4\)(P\(_2\)Se\(_6\)) can be derived from the structure of Sn\(_2\)P\(_2\)Se\(_6\) [11]. It is composed of multiple substitutions of the isovalent cations according to 2M\(^{2+}\) ↔ M\(^{4+}\). The crystal structure of the compound In\(_4\)(P\(_2\)Se\(_6\)) can be presented based on the composition of the anionic group [P\(_2\)Se\(_6\)]\(^{4+}\) (Fig.4), in which the indium atoms occupy the space between the anionic groups.

The second coordination environment (SCE) [12] is of cuboctahedron form. Indium cations are surrounded by a triangular environment of anionic atoms of the group [P\(_2\)Se\(_6\)]\(^{4+}\) and within the frames of its environment bonding exists with six atoms of selenium while the coordination form is octahedral (Fig.5).

The structural and chemical properties of the Me\(^{III}\)Me\(^{III}\)P\(_2\)Se\(_6\) compositions are related to the important role concerning the dimension of the cation on its location between the layers of the anionic [P\(_2\)Se\(_6\)]\(^{4+}\) groups. Crystallographic analysis showed that smaller cations occupy a position in the plane perpendicular to the main axis. Atoms located in a second coordination environment of anionic groups in the structure of TlInP\(_2\)Se\(_6\) compounds can be presented as a strongly distorted hexagonal-equivalent cuboctahedron (Fig.6).

The atoms of metallic cations, located in the cavities between the atoms of the anionic groups, are within an asymmetric environment (Fig.7). In\(^{3+}\) cations move toward tetrahedral cavities on the boundary between tetrahedral and octahedral cavities, and Tl\(^{+}\) cations move in the direction of the octahedral cavities.

Moreover the In\(^{3+}\) cations are located in the same plane together with the centres of the anionic [P\(_2\)Se\(_6\)]\(^{4+}\) groups (Fig.8) and some Tl\(^{+}\) cations are shifted relative to the plane. Therefore, this arrangement is a source of the interesting electro-physical and optical properties of materials based on compounds of this type.

**3.3. Optical response of single crystals of TlInP\(_2\)Se\(_6\) and In\(_4\)(P\(_2\)Se\(_6\))\(_3\)**

The most important parameter of the energy spectra of semiconductors is the width of the band gap, \(E_p\), which is defined by the difference in energy between the bottom of the conduction band, \(E_C\), and the top of the valence band, \(E_V\). All semiconductors can be divided into two groups. In the first group, the minimum of the conduction band and the maximum of the valence band occupy the same point in the Brillouin zone, i.e. at an identical location in the space of quasi-moments. In this case, the optical transitions of electrons from the valence band to the conduction band (with the absorption of a quantum of light) and from the conduction band to the valence band (with the emission of a quantum of light) occur so that the electrons practically do not change their quasi-moments. Such transitions are characteristic of direct-gap semiconductors. For the second group, the absolute minimum of the conduction band and the absolute maximum of the valence band are at different points in the Brillouin zone, and optical inter-
band transitions must be accompanied by a large change in the electron quasi-moment. These are characteristic of indirect-gap semiconductors. Since the photon moment is negligibly small compared with the electron quasi-moment, the latter case is possible only when the electron interacts with the phonon.

According to the phase diagram, the single crystals of TlInP$_2$Se$_6$ and In$_4$(P$_2$Se$_6$)$_3$ were grown using the Bridgman method in two vertical zone furnaces. Experimental studies of optical spectra in the absorption region yielded information on the energy spectrum of electrons near the edges of the conduction band and band gap. Studies concerning the dependence of diffuse reflection on wavelength ($R = f(\lambda)$) have shown that the compound TlInP$_2$Se$_6$ refers to indirect-gap semiconductors. On the graph there are two rectilinear sections, one of which (for small wavelengths, $\lambda$, and large values of $E$) characterizes the interband transitions of electrons with phonon emission, and the other (for large $\lambda$ and small $E$) describes the processes of phonon absorption (Fig.9).

The intersection of the first section with the wavelength axis, $\lambda$, yields the value of $E_g + E_{\text{phonon}}$ ($\lambda = 560$ nm, $E = 2.21$ eV), and the intersection of the second characterizes $E_g - E_{\text{phonon}}$ ($\lambda = 605$ nm and $E = 2.05$ eV). The length of the segment between the points of intersection of both straight lines with the wavelength axis, $\lambda_e$, is equal to the doubled energy of the phonons, $2E_{\text{phonon}}$ (0.16 eV), interacting with the electron. The middle of this segment corresponds to the photon energy equal to the width of the band gap of the indirect-gap semiconductor, $E_g$. Experimental calculations in terms of the compound TlInP$_2$Se$_6$ have shown that $E_g = 2.13$ eV and $E_{\text{phonon}} = 0.08$ eV.

The compound In$_4$(P$_2$Se$_6$)$_3$ refers to direct-gap semiconductors, which characterizes the interband transitions of electrons in terms of photon absorption (Fig.10). The intersection of the line with the wavelength axis, $\lambda$ ($\lambda = 651$ nm), yields the value of $E_g = 1.91$ eV.

The crystals of In$_4$(P$_2$Se$_6$)$_3$ and TlInP$_2$Se$_6$ were illuminated by 10.6 μm and (its second harmonic) frequency doubling of 5.3 μm beams. Each channel of the beam was split by 200-ns CO$_2$ laser pulses with a pulse repetition frequency of about 10 Hz. The angle between these two laser beams was changed from 18° to 22°. Figs.11 and 12 present these dependences. Treatment with a 10.6 μm beam achieved a smaller maximum birefringence (about 1.55×10$^{-9}$) in comparison to the 5.2 μm beam. This indicates a different photoinduced anisotropy for the In$_4$(P$_2$Se$_6$)$_3$ and TlInP$_2$Se$_6$ crystals.
4. Conclusion

Differential thermal analysis, X-ray diffraction and microstructural analysis were used to construct a phase diagram for the TlInP₂Se₆–In₄(P₂Se₆)₃ system, which can be characterized by a eutectic-type interaction. The invariant eutectic process L → hTlInP₂Se₆ + mtIn₄(P₂Se₆)₃ (15 mol% In₄(P₂Se₆)₃) occurs at 791 K. Two polymorphic transformations were identified for TlInP₂Se₆ at 680 K and 711 K and for In₄(P₂Se₆)₃ at 665 K and 903 K. New compounds were not detected in the binary system. The regions of solid phases of the complex compounds TlInP₂Se₆ and In₄(P₂Se₆)₃ do not exceed 10 mol%. Single crystals of both test compounds were achieved by the Bridgman method. Investigations concerning the dependence of the diffuse reflection spectrum showed that the compound TlInP₂Se₆ is characteristic of indirect-gap semiconductors (E₉ = 2.13 eV, E₂phonon = 0.08 eV), while the compound In₄(P₂Se₆)₃ is characteristic of direct-gap semiconductors (E₀ = 1.91 eV, E₂phonon = 0.08 eV). The dependence of the birefringence was photoinduced by wavelengths of 5.3 μm and 10.6 μm, which is indicative of different photoinduced anisotropy.

Acknowledgement

We are grateful for the financial support of this work by the Ministry of Education and Science of Ukraine under the project DB874P_0117U000380.


