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Hydrothermal Synthesis of Lead Indium Selenide

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ABSTRACT: Lead indium selenide ($PbIn_2Se_4$) is a promising chalcogenide semiconductor for optoelectronic and energy applications. We report a hydrothermal synthesis route using ethylene glycol under moderate conditions (433–453 K, 7–12 h), yielding up to 85–87%. The product crystallized into a cotton-like morphology composed of nano- and microparticles. Structural and compositional integrity were confirmed by chemical analysis, thermogravimetric analysis, and transmission electron microscopy. These results demonstrate that hydrothermal synthesis provides an efficient and controllable pathway to high-purity $PbIn_2Se_4$, opening opportunities for its use in advanced functional devices.

KEYWORDS: Thermogravimetric analysis (TGA); lead chalcogenide; hydrothermal method; chemical analysis; thermographic analysis; nano- and microparticles

1 Introduction

The study of lead–indium–selenium (Pb–In–Se) systems has attracted significant attention due to the unique physicochemical properties of their ternary chalcogenides. These compounds, particularly $PbIn_2Se_4$, are characterized by narrow band gaps, high carrier mobility, and strong optical absorption, making them attractive candidates for thermoelectric converters, infrared detectors, and next-generation photovoltaic devices. The versatility of this system is further enriched by its complex phase diagram, which reveals multiple stable and metastable phases with distinct structural and electronic features [1].

Previous investigations of Pb–In–Se alloys have relied predominantly on solid-state reactions, differential thermal analysis, and crystallographic methods to elucidate their equilibrium diagrams and phase stability. While these approaches have clarified the existence of several ternary phases, they often require high temperatures, extended reaction times, and rigorous processing steps. Consequently, developing low-temperature and solution-based synthesis strategies has become crucial for producing these materials with controlled size, morphology, and stoichiometry [2].

A low-temperature chemical bath deposition method (room temperature to 70°C) was developed for preparing submicron PbSe thin films on substrates of various sizes and shapes. The process produced uniform, mirror-like coatings on both glass and transparent polyester films. Structural, optical, and electrical properties of the films were investigated in their as-deposited state as well as after annealing [3].

Hydrothermal and solvothermal techniques have emerged as powerful alternatives, offering the ability to tune particle growth and composition under relatively mild conditions. These methods not only reduce energy consumption but also enable the generation of unique nanostructures unattainable by traditional solid-state synthesis. Despite their potential, systematic studies on the hydrothermal synthesis of $PbIn_2Se_4$ remain limited [4].

In this work, we present a comprehensive investigation into the hydrothermal preparation of $PbIn_2Se_4$ in ethylene glycol and analyze its formation, morphology, and stability. By combining thermogravimetric analysis, X-ray diffraction, and electron microscopy, we provide new insights into the structural

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characteristics of this compound and demonstrate the efficiency of hydrothermal synthesis for fabricating high-purity $PbIn_2Se_4$ with tailored micro- and nanostructures [5].

2 Experimental Details

The phase equilibrium of the Se-rich part of the Pb-In-Se system was studied using metallography, DTA (Differential Thermal Analysis), DCK (possibly Differential Scanning Calorimetry), and RCA methods. Two ternary phases were observed. The crystallization reactions of the alloys for the Se-rich region were determined. Defect formation observed in the binary In-Se and Se-Pb systems also appeared in the ternary system. A reaction scheme for the PbSe-Se-InSe system is provided [6].

The electronic and infrared absorption spectra of In_2Se_3 vapor were studied, co nfirming its congruent sublimation. Thermodynamic functions of $In_2Se(g)$ were calculated from 273.15 to 2000 K, and the saturated vapor pressure of In_2Se_3 (s) was measured [7].

We report the first experimental evidence of out-of-plane piezoelectricity and ferroelectricity in 2D α-In_2Se_3 nanoflakes. Noncentrosymmetric R3m symmetry was confirmed, and opposite polarization domains were observed. Polarization switching is possible down to ~10 nm thickness. The piezotronic effect modulates the Schottky barrier in devices, highlighting α-In_2Se_3 potential for nanoelectronic and photonic applications [8].

2D ferroelectric semiconductor α-In_2Se_3 is notable for vertical polarization, but its in-plane ferroelectricity is disputed. Experimental and simulation results show no in-plane polarization in single-domain α-In_2Se_3. Vertical polarization switching involves unique atomistic mechanisms, and domain walls move with avalanche dynamics under out-of-plane and in-plane fields, following a universal creep behavior with a distinct dynamical exponent. This clarifies misconceptions and advances understanding of 2D ferroelectrics [9].

In_2Se_3 nanoparticles were hydrothermally synthesized and used to fabricate self-powered photoelectrochemical (PEC) photodetectors. These devices exhibit strong visible-light photoresponse (455–630 nm), high responsivity (25.48 mA/W at 455 nm), fast response (100 ms), and good stability (90% photocurrent retention after 50 cycles), showing promise for underwater optoelectronic applications discotion [10].

Initially, 0.1150 g of indium was precipitated from a 20 mL indium (III) chloride solution using ammonium hydroxide to form indium (III) hydroxide. After thorough washing, the precipitate was transferred to a beaker with ethylene glycol. Then, 0.140 g of lead acetate (0.76 g Pb) was added, and the solution was thoroughly mixed. This mixture was transferred into the reaction vessel, followed by the addition of 0.120 g of a selenizing agent—a selenium solution prepared by dissolving elemental selenium (amorphous or molten) with sodium borohydride in ethylene glycol.

The reaction vessel was placed into a Teflon-lined autoclave, sealed tightly, and heated at 423 K for 5–7 h. After the process, the precipitate was filtered through a glass filter, washed first with diluted hydrochloric acid and then with ultrapure water (UPW). Finally, the sample was rinsed with ethanol and dried under vacuum at 333–343 K. The synthesis yield of lead indium selenide at 453 K was 85–87%. The experiments were conducted using analytically pure reagents.

The composition of the compound (Pb:In:Se) was determined using both chemical (volumetric and gravimetric) methods and the NETZSCH STA 449F3 thermal analysis device from Germany. X-ray phase analysis of $PbIn_2Se_4$ nano- and microparticles was carried out using a D2 PHASER "Bruker" X-ray diffractometer (CuKα radiation, 2θ range: 10–70°). The morphology of the samples was examined with a TEM (Transmission Electron Microscope)—Hitachi TM-3000 (Japan). Images were captured using a high-sensitivity DESKOPT camera.

3 Results and Discussions

It is known that depending on the synthesis environment (organic or aqueous), chalcogenides form compounds with various stoichiometries ($PbIn_2Se_4$, $Pb_2In_2Se_5$, $Pb_3In_2Se_6$, $Pb_4In_2Se_7$, etc.) [11–13]. Therefore, the $PbIn_2Se_4$ samples synthesized by the hydrothermal method were subjected to thermogravimetric analysis using the NETZSCH STA 449F3 device [14]. The results are shown in Fig. 1.

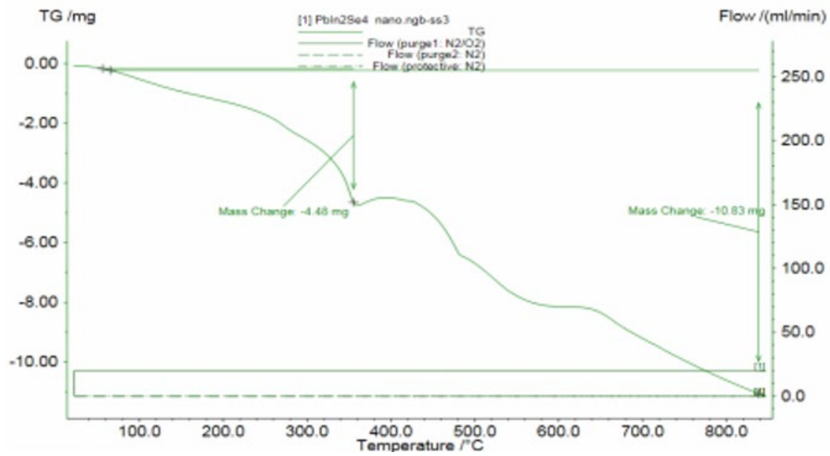


Figure 1: Thermogravimetric analysis of $PbIn_2Se_4$ nanocompound synthesized at 423 K for 7 h.

As observed in the graph, the sample underwent a total mass loss of 10.83 mg when heated from 293 K to 1125 K. Between 293 K and 623 K, the mass loss was 4.48 mg, attributed to the release of free selenium in the sample (due to pH change, during washing, excess selenium solution undergoes partial hydrolysis). The loss of 10.83 mg at 1125 K indicates the oxidation and sublimation of selenium as SeO_2. According to calculations based on the graph data, the weight ratio of lead and indium to selenium was found to be 58.03:41.96.

The compound's elemental composition was analyzed using selected methods for Pb, In, and Se [15,16], and the results are presented in the table.

Table 1:

$PbIn_2Se_4$, Tem., K	Example, mg	Components, mg					
		Pb		In		Se	
		Theor.	Prac.	Theor.	Prac.	Theor.	Prac.
433	370	140	136	110	105	120	110
453	372	140	133	110	108	122	112

As seen in the table, the chemical analysis confirms that the sample corresponds to the formula $PbIn_2Se_4$.

The influence of temperature (433 K) on the formation, growth, and morphology of nano- and microparticles of $PbIn_2Se_4$ synthesized via the solvothermal method was studied, and the particle images were recorded (Fig. 2, TM-3000 Hitachi electron microscope) [17,18].

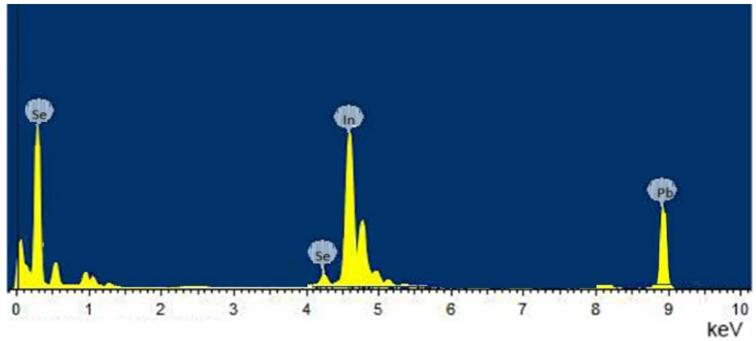
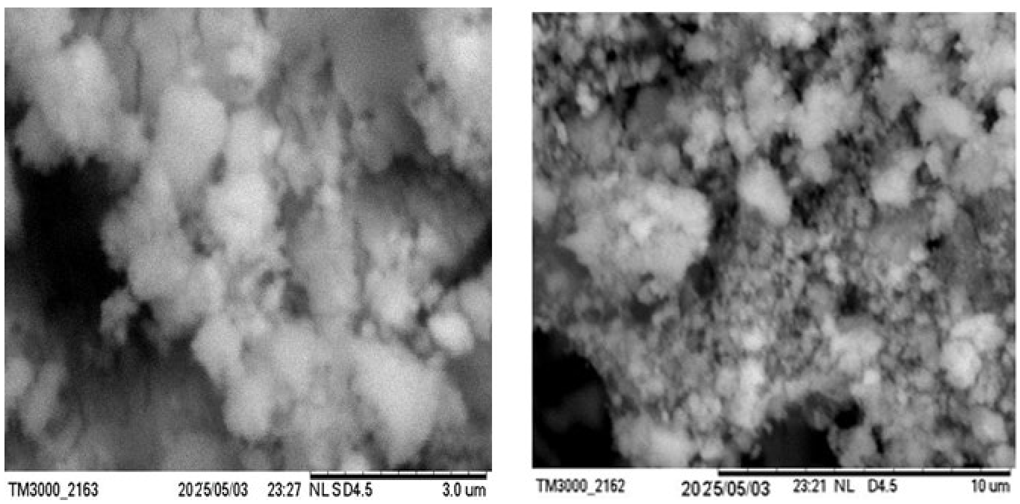


Figure 2: Energy-dispersive spectra of thin films of $PbIn_2Se_4$ obtained by chemical precipitation method.



(**a**) (**b**)

Figure 3: Nanoparticles of $PbIn_2Se_4$ synthesized at 433 K for 5–7 h: (**a**) growth 3.0 μm, (**b**) growth 10.0 μm.

The images show that the $PbIn_2Se_4$ compound forms in cotton-like nano- and microparticle structures.

4 Conclusion

The present study confirms that $PbIn_2Se_4$ synthesized hydrothermally develops a unique cotton-like morphology with stable nano- and microstructures. Beyond demonstrating high yields under mild conditions, the analysis revealed strong phase purity and thermal stability, underscoring the reliability of this method. Importantly, the distinctive morphology obtained through hydrothermal conditions suggests new pathways for tuning the electronic and optical behavior of Pb–In–Se compounds. By linking synthesis parameters to structural features, this work contributes to the broader understanding of ternary chalcogenides and highlights the potential of $PbIn_2Se_4$ in optoelectronic and energy-conversion devices

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Availability of Data and Materials: The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

Ethics Approval: Not applicable.

Conflicts of Interest: The authors declare no conflicts of interest to report regarding the present study.

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