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Theoretical Structural Characterization of XIn_2Se_4 Ternary Semiconductors Wanted to be Grow Using the Bridgman/Stockbarger Technique

Bridgman/Stockbarger Tekniği Kullanılarak Büyütülen XIn_2Se_4 Üçlü Yarıiletkenlerin Teorik Yapısal Karakterizasyonu

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Abstract

The importance of semiconductors paving the way for nano and optoelectronic technology has recently been increasing. But, producing them easily and having their vast application fields are most important. For that reason, the crystals have a wide application field and their characteristics which are determined are needed. Some researchers (Irie et al., 1979; Shih et al., 1986) have suggested that the crystals grown should be grown in a single ampoule and a single stage, considering the idea that it would cause selenium loss. Considering this situation, it was decided to grow XIn_2Se_4 crystal with this method. XIn2Se4 (X=Cu, Mn, Al, Fe) single crystals used in this research were grown using the Bridgman/Stockbarger method. All of the samples were freshly and gently cleaved with a razor blade from the grown ingots and no further polishing and cleaning treatments were required because of the natural mirror-like cleavage faces. The Samples were cleaved along the cleavage planes (001). In this study, single crystal growth was done in a single step. The structure of XIn_2Se_4 semiconductors was analysed theoretically using x-ray diffractometer (XRD), scanning electron microscopy (SEM), energy dispersive x-ray (EDX) and Raman spectroscopy techniques.

Keywords: Grown XIn_2Se_4, Bridgman/Stockbarger Technique, Theoretical Structural Characterization

Öz

Nano ve optoelektronik teknolojisinin gelişmesinde yarı iletkenlerin önemi son yıllarda giderek artmaktadır. Yarıiletkenlerin kolay büyütülmesi ve geniş uygulama alanlarına sahip olması önemlidir. Kristallerin geniş bir uygulama alanına sahip olması nedeniyle, birçok özelliklerinin belirlenmesi gerekmektedir. Bazı araştırmacılar (Irie et al., 1979; Shih et al., 1986) selenyum kaybına yol açacağı düşüncesiyle büyütülen kristallerin tek ampulde ve tek aşamada büyütülmesi gerektiğini öne sürmüşlerdir. Bu durum göz önünde bulundurularak XIn_2Se_4 kristalinin bu yöntemle büyütülmesine karar verilmiştir. Bu çalışmada tek kristal büyütme tek adımda yapılmıştır. Bu araştırmada XIn_2Se_4 (X=Cu, Mn, Al, Fe) tek kristalleri Bridgman/Stockbarger yöntemi kullanılarak büyütülmüştür. Numunelerin tümü, büyütülen külçelerden (001) düzlemleri boyunca ayrılmıştır. Büyütülen numunelerin yüzey alanları parlak ve pürüzsüz olduğundan parlatma ve temizleme işlemlerine gerek duyulmamıştır. XIn_2Se_4 yarı iletkenlerinin yapısı, x-ışını difraktometresi (XRD), taramalı elektron mikroskobu (SEM), enerji dağılımlı x-ışını (EDX) ve Raman spektroskopisi teknikleri kullanılarak teorik olarak analiz edilmiştir.

Anahtar Kelimeler: XIn_2Se_4 Büyütme, Bridgman/Stockbarger Tekniği, Teorik Yapısal Karakterizasyon

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Introduction

Considering the research on the growth of single crystals, semiconductor technology continues to develop at a dizzying pace. As it is known, ternary and doped semiconductor technology lies at the basis of many applications in the world of technology and science. Most developed countries allocate serious resources for semiconductor technology and work on many different subjects. It is seen that many countries benefit significantly from renewable energy. These application areas are shaped according to certain characteristics of semiconductor compounds.

XIn_2Se_4 (X= Cu, Mn, Al, Fe, vb.) ternary crystals have a layered structure. The layered structures have highly anisotropic properties. Instead of three-dimensional bonding as in group II-VI, II-IV or III-V semiconductors, the molecular bonding in these crystals is first-order ionic or covalent bonds in three dimensions. This bonding mode is key to the unique properties of layered semiconductors. XIn_2Se_4 semiconductors have been widely studied for various nonlinear optical applications. Recently, there has been a renewal of interest in the magnetic properties of XIn_2Se_4 semiconductors. XIn_2Se_4 compounds have different optical and magnetic properties.

The crystallographic parameters of $CuIn_2Se_4$ crystal structure were determined. The obtained $CuIn_2Se_4$ is a black crystalline substance. Its XRD pattern (Figure 1) does not contain any lines of impurity phases; all of the lines were indexed in a tetragonal. The unit cell parameters of $CuIn_2Se_4$ were a = 5.754 Å and c = 11.513 Å, c/a = 2.0008 Å, and V = 382.12 Å (Jackson et al., 2015). Its pycnometer density was 5.319±0.007 gcm^{-3}. The X-ray density of 5.328 gcm^{-3} and the number of $CuIn_2Se_4$ formula units in the unit cell (Z = 1.9995) were calculated from the acquired data. Taking into account reflections in the XRD pattern of $CuIn_2Se_4$, the space group was established as I4-2m (Krauss et al., 1997). The XRD pattern of $CuIn_2Se_4$ (see Figure 1) contains lines 00*l*, wherein *l* is the even number not a multiple of four: *l* = 2, *l* = 6; in the case of a space group I4-2d, these lines are prohibited, while only lines 00(4*l*) are allowed. The closest analogue of $CuIn_2Se_4$ is $ZnIn_2Se_4$, which possesses the structure of unit cell parameters a = 5.7095 and c = 11.449 A, c/a = 2.0053, Z = 2, and space group I4 – 2m (Trah & Krämer, 1985). A comparison of the XRD patterns of $CuIn_2Se_4$ and $ZnIn_2Se_4$ revealed their good correspondence. The structures are almost equal in the compounds $CuIn_2Se_4$ and $ZnIn_2Se_4$.

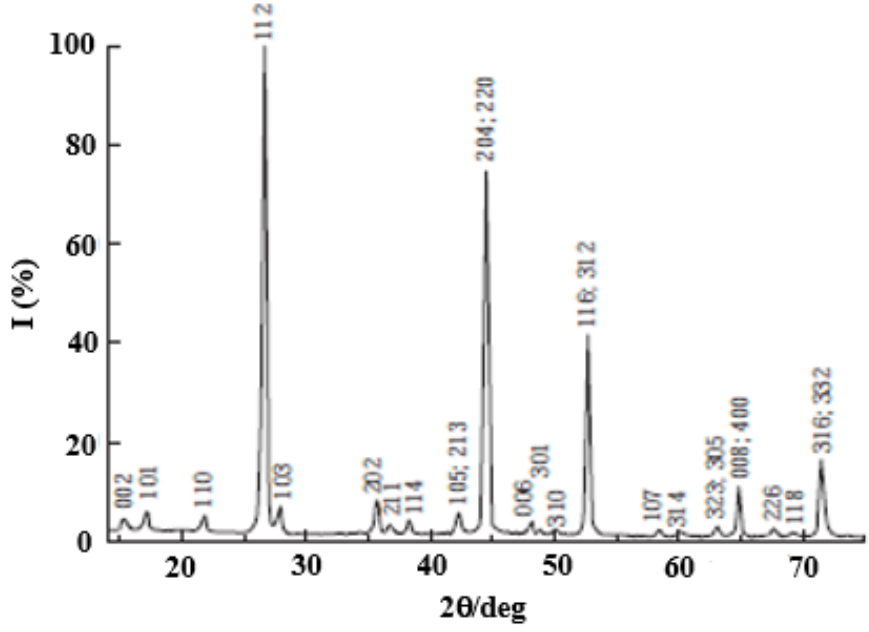

Figure. 1. XRD pattern of $CuIn_2Se_4$ (Odin et al., 2019)

The disorder in the distribution of copper and indium was also observed in the structure of $CuIn_2Se_4$: a part of copper atoms entered into the indium sublattice from its sublattice, and some indium atoms entered the copper sublattice. $CuIn_2Se_4$ is a semiconductor with E_g= 1.08 eV (Jackson et al., 2015). Therefore, the structure of $CuIn_2Se_4$ has been confirmed. The $CuIn_2Se_4$ the tetragonal unit cell parameters were determined.

The crystal structure of $MnIn_2Se_4$ is a rhombohedral structure with lattice parameters of a = 4.056 Å and c = 39.49 Å at 300 K (Döll et al., 1990). $MnIn_2Se_4$ semiconductor is mentioned in different literature on magnetic and optical properties. Twardowski et al. (1987) and Ramirez et al. (1994) reported a paramagnetic behaviour in $MnIn_2Se_4$, whereas Quintero et al. (1997) and J. C. Woolley et al. (1994) reported a spin-glass behaviour at low temperature. The tetragonal compound the layered $MnIn_2Se_4$, with rhombohedral symmetry, is synthesized by melting a stoichiometric mixture of the elements or by chemical vapour transport technique (Döll et al., 1991).

The semiconductor $MnIn_2Se_4$ has an energy gap of E_g = 1,38 eV (Khan et al., 1997) which is suitable for photovoltaic applications. Furthermore, the plate-like habit and easy cleavage of $MnIn_2Se_4$ point to a quasi-dimensional layered structure, which may influence the magnetic properties. From X-ray powder diffraction measurements (Döll et al., 1990) a rhombohedral unit cell was found for this material. From the study of the optical absorption coefficient and photoluminescence spectra of the layer semimagnetic semiconductor $MnIn_2Se_4$ the nature of its fundamental absorption edge is established. It is found that the lowest energy gap of this compound is allowed indirect between parabolic bands that vary from about 1,55–1,43 eV in the temperature range from 10 K to room temperature (Rincón et al. 2015). The structure of XIn_2Se_4 semiconductors was analyzed theoretically using x-ray diffractometer, scanning electron microscopy, energy dispersive x-ray and Raman spectroscopy techniques. On the other hand, its optical and electrical properties were also examined

Experimental Procedures

The structure and melting point of the XIn_2Se_4 ternary compounds have been determined. The grown XIn_2Se_4 samples are shiny and have a layered structure. There has been increased interest in the growth and characterization of derived layered compounds over the last fifteen years. XIn_2Se_4 (X= Cu, Mn, Al, Fe, etc.) single crystals were grown by the Bridgman-Stockbarger method. For the preliminary reaction, the component elements prepared in stoichiometric proportions were sealed in the growth ampoule. Grown ampoules are placed in a cage designed from kanthal DSD-Cr-Al-Fe alloy wire. It is fixed to the shaking furnace by means of connection wires made from both ends of the cage, at the appropriate distance determined, parallel to the furnace tube. Some researchers (Irie et al., 1979; Shih et al., 1986) have suggested that the crystals grown should be grown in a single ampoule and a single stage, considering the idea that it would cause selenium loss. Considering this situation, it was decided to grow XIn_2Se_4 crystal with this method.

Considering that indium would react and melt selenium as a result of thermal conductivity in the XIn_2Se_4 (X= Cu, Mn, Al, Fe, vb.) mixture, the lower and upper zone temperatures of the furnace were increased to 150 °C within 30 minutes, respectively. The reaction between In and Se was initiated by ensuring that it was above the melting temperature of indium ($In_{m.t}$: 157 °C) and below the melting temperature of selenium ($Se_{m.t}$: 217 °C). This will prevent the sudden increase in temperature and pressure inside the ampule. After waiting at this temperature for 50 minutes, it was increased to 217 °C within 60 minutes and kept at this temperature for 2 hours. Because the exothermic reaction between In and Se continues at 217 °C, a long time is needed to eliminate risks such as explosion or cracking of the ampule. Since selenium has a high vapour pressure between 600 °C and 950 °C, the lower and upper zone temperatures of the crystal growth furnace were increased to 500 °C within 20 hours, respectively, and waited at 500 °C for 12 hours. It is predicted that the chemical reaction between In and Se will end and the chemical reaction rate will decrease. Then, it was increased from 500 °C to 850 °C in 30 hours and remained at this temperature for 20 hours. It was then reduced to 30 °C in 48 hours. As a result of this pre-reaction process, the vapour pressure of the alloy was reduced and explosion or cracking problems in the next growth step were tried to be minimized.

Considering that the XIn_2Se_4 (X= Cu, Mn, Al, Fe, vb.) mixture will react chemically as a result of thermal conductivity and increase the vapour pressure of selenium, the lower and upper zone temperatures of the furnace were increased to 600 °C within 10 hours and the pressure risk was tried to be eliminated. This prevented the temperature and pressure inside the magnifying ampule from increasing suddenly. It was kept at this temperature for 15 hours. Because the exothermic chemical reaction between the elements In, Se, Cu, Mn, Al and Fe continues at 650 °C, a long time is needed to eliminate risks such as explosion or cracking of the ampoule. Since the selenium element has a high vapour pressure after 600 °C, it was heated to 1000 °C for 20 hours and kept for 10 hours. To ensure homogeneous distribution of In, Se, Cu, Mn and Fe elements, the

furnace was shaken by moving it up and down at an angle of approximately 45° for 5 hours. The enlargement oven is fixed at an angle of 60-70° with the horizontal.

The upper zone temperature of the crystal growth furnace was first kept constant at 1000 °C for 50 hours, then decreased to 800 °C for 70 hours, 650 °C for 50 hours, 250 °C for 40 hours and 30 C for 10 hours. The lower zone temperature of the furnace was reduced to 800 °C in 50 hours, to 650 °C in 70 hours, to 250 °C in 40 hours, to 100 °C in 10 hours and to 30 °C in 10 hours, and the furnace was turned off. Thus, at the same time and using the same growth temperature program, the growth process of XIn_2Se_4 ternary semiconductor crystals was completed in approximately 5 days and 14 days including the reaction. At the end of the growing process, it was removed from the oven. The ampoules were cut with the help of a suitable cutter to ensure that the nugget crystal did not suffer any hardness or deformation. The ingot must be stored in a very clean environment to avoid chemical contamination of the samples (Gürbulak et al. 2021; Gürbulak, 1997; Bodnar et al., 2010; Dotzel & Schafer, 1976).

Growth and Characterization

The first important step in obtaining high quality crystal is the purity of the main materials in the structure. These elements were weighed stoichiometrically to an accuracy of 0.001 mg. The total mass of the ingredients is approximately 100 grams. The main criteria for this selection were, first of all, the cost of a single operation, sufficient need and minimal loss of material in the form of cracking of the ampoule. The elements to be used in the growth (Cu, Mn, Al, Fe, In and Se etc.) were used in high purity (99.999%) pieces with a particle size of approximately 200 mesh. The elements were weighed and loaded into a thick-walled quartz ampoule. Quartz ampoules are sealed under pressure of approximately 10^{-6} Torr. For this purpose, XIn_2Se_4 ((X=Cu, Mn, Al, Fe) etc.) semiconductor was grown with the Bridgman/Stockbarger technique developed in our current crystal growth laboratory.

XIn_2Se_4 (X=Cu, Mn, Al, Fe, etc.) belongs to the family of layered ternary semiconductors known as chalcopyrite compounds. These materials have drawn significant interest due to their promising optoelectronic and photovoltaic properties. To provide a detailed theoretical understanding of the structural characterization of XIn_2Se_4, we'll delve into several key aspects. The crystal structure of XIn_2Se_4 is based on a tetragonal, rhombohedral and hexagonal unit cell. It belongs to the space group I-42d. The lattice parameters vary slightly depending on the specific element X (Cu, Mn, Al, Fe). The unit cell typically contains multiple layers stacked along the c-axis. The crystal structure of XIn_2Se_4 consists of layers of covalently bonded Se atoms sandwiched between layers of metal cations. This layered structure contributes to the anisotropic properties of the material.

The bonding in XIn_2Se_4 is predominantly covalent between Se atoms and metal cations, while there also exist weaker van der Waals forces between adjacent layers. The covalent bonding within the layers provides stability to the crystal structure, while the weaker interlayer interactions allow for easy cleavage along certain crystallographic planes.

The presence of defects, such as vacancies or interstitials, can influence the electronic and optical properties of XIn_2Se_4. Additionally, intentional doping with different elements (Cu, Mn, Al, Fe) can tailor the material's properties for specific applications by altering its electronic band structure and conductivity. Experimental techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDS) are commonly used to characterize the crystal structure, morphology and elemental composition of XIn_2Se_4 samples.

Density functional theory calculations can provide insights into the electronic structure, band gap, and other properties of XIn_2Se_4. Computational simulations can complement experimental observations and aid in the understanding of its behaviour under different conditions. Understanding the structural characterization of XIn_2Se_4 is crucial for optimizing its properties for applications in solar cells, photodetectors, and other optoelectronic devices. Both experimental and theoretical approaches play key roles in advancing our knowledge of this material's properties and potential applications.

Growth and structural characterizations of single crystals like $CuIn_2Se_4$, $MnIn_2Se_4$, $AlIn_2Se_4$ and $FeIn_2Se_4$ typically involve several steps and techniques. Here's a general overview of the process:

i. Crystal growth technique: Single crystals are often grown using methods such as the Bridgman method, chemical vapour transport (CVT), or the flux method. Each method has its advantages and is chosen based on factors like material properties and desired crystal quality.
ii. Material preparation: High-purity starting materials are required for crystal growth. These materials are weighed according to the stoichiometric ratio of the compound and then mixed thoroughly.
iii. Crystal growth: The chosen method for crystal growth is employed. In the Bridgman-Stockbarger method, for example, the mixed materials are loaded into a crucible and melted at high temperatures. Then, a nucleus crystal is slowly pulled from the melt, allowing the desired compound to crystallize around it.
iv. Characterization techniques:
   - X-ray Diffraction (XRD): XRD is used to determine the crystal structure, phase purity, and orientation of the grown crystals. It provides information about lattice parameters, crystal symmetry, and crystal quality.
   - Scanning Electron Microscopy (SEM): SEM is used to study the surface morphology and microstructure of the crystals. It provides high-resolution images that can reveal details about defects, grain boundaries, and surface features.
   - Energy-Dispersive X-ray Spectroscopy (EDS): EDS is often coupled with SEM to provide elemental analysis of the crystals. It helps confirm the stoichiometry and composition of the grown crystals.
   - Raman Spectroscopy: Raman spectroscopy is used to study vibrational modes and lattice dynamics in the crystals. It can provide information about crystal quality, defects, and phonon modes.
   - Optical Characterization: Techniques like UV-Vis spectroscopy and photoluminescence spectroscopy are used to study the optical properties of the crystals, including bandgap energy, absorption spectra, and emission spectra.
   - Electrical Characterization: Electrical measurements such as Hall effect measurements, resistivity measurements, and conductivity measurements are performed to understand the electrical properties of the crystals, including carrier concentration, mobility, and conductivity type.
v. Data analysis: The data obtained from various characterization techniques are analyzed to understand the crystal structure, composition, morphology, and properties of the grown crystals. This analysis often involves comparing experimental data with theoretical models and known reference materials.

In conclusion; by employing these techniques and methods, researchers can gain valuable insights into the growth and structural characteristics of single crystals like $CuIn_2Se_4$, $MnIn_2Se_4$, $AlIn_2Se_4$ and $FeIn_2Se_4$, which are important for various applications such as photovoltaics, thermoelectric, and spintronics

Results and Discussions

XIn_2Se_4 (X= Cu, Mn, Al, Fe, etc.) single crystals were grown by the Bridgman-Stockbarger method. The structure and melting point of the XIn_2Se_4 ternary compounds have been determined. The grown XIn_2Se_4 samples are shiny and have a layered structure. In recent years, interest in the growth and characterization of derived layered compounds has increased. $FeIn_2Se_4$, $MnIn_2Se_4$ and $CuIn_2Se_4$ semiconductor compounds belong to the $II\text{-}III_2\text{-}VI_4$ semiconductor family. Semiconductor samples crystallize in rhombic, hexagonal and tetragonal crystallographic structures, respectively.

The choice of growth technique for a given sample depends on many factors. In summary, these factors are;

- Chemical reactivity components of the compound and elements,
- Decomposition vapour pressure of the compound at the growth temperature,
- The melting point of the elements and the melting point of the compound,
- It depends on the presence or absence of phase transformations.

The general procedure for cleaning semiconductor compound ampoules is as follows.

- The magnification ampoules should be cleaned with diluted $HN0_3$ for approximately four hours to remove metallic contamination on the surface.

- Then it should be rinsed repeatedly with deionized water.
- The inner surface of the magnifying ampoule should be washed with liquid gel for 30 hours to remove dust particles and oils.
- It should be rinsed again with deionized water.
- The inner and outer surfaces of the growth ampoule should be etched with HF (45% diluted) for 6 minutes to further remove residual contaminations.
- The magnification ampoule should be rinsed once again with deionized water.
- Then it should be washed with acetone.
- The magnification ampoule should be washed ultrasonically in deionized water.
- In the growth oven, the ampoule should be baked at 750 °C for 30 hours.
- Plastic gloves should be worn to prevent contamination of the growth ampoules.

As a result, the following procedures must be applied to grow quality single crystals.

- The purity of the elements used in the compound must be approximately 6N.
- A very precise scale must be used to weigh the elements.
- Plastic holders should be used for weighing chemical elements and transferring them via ampoules.
- It should be known whether chemical elements are harmful to the researcher.
- It should be known whether chemical elements react with the ampoules.
- The ampoules used in the growth process must be clean.
- Gloves must be used when transferring chemical elements to ampoules.
- Growth ampoules should be prepared according to the layered or chain structure of the semiconductor sample.
- Growth ampoules should be coated with carbon.
- Pre-reaction should be done to ensure homogeneity of the compound.
- The optical and electrical properties of the grown compound must be known very well.
- If the compound has a phase, the vapour pressure and melting point of the elements must be known.
- The growth laboratory should be clean and noiseless.
- The growth laboratory should be located away from vibration.
- Since the semiconductor sample growth process takes 5-25 days, an uninterruptible power supply must be used (Gürbulak et al., 1999).

As a result, it is important to grow XIn_2Se_4 (X=Cu, Mn, Al, Fe) semiconductors using the Bridgman-Stockbarger method. While enlarging these samples to be enlarged;

- ✓ Factors affecting the selection of the growth technique,
- ✓ General procedures for cleaning growth ampoules,
- ✓ Recommended procedures for growing single crystals, must be taken into consideration.

Conclusions

Both experimental and theoretical approaches play a key role in gaining scientific knowledge about the structural properties and potential applications of this material. Understanding the theoretical structural characterization of layered XIn_2Se_4 (X=Cu, Mn, Al, Fe) is crucial for optimizing its properties for applications in solar cells, photodetectors, and other optoelectronic devices. On the other hand; both experimental and theoretical approaches play a key role in gaining scientific knowledge about the structural properties and potential applications of this material.

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