Microstructural Analysis of AgIn₅VI₈ (VI: S, Se, Te) Ternary Semiconductors by X-Ray Diffraction

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This work is a study of the microstructural properties of the polycrystalline ternary compounds AgIn₅S₈, AgIn₅Se₈, and AgIn₅Te₈ by X-ray diffraction technique (XRD). The full-width-half-maximum (FWHM) of the XRD profile is measured as function of the diffraction angle and used to estimate the microstructural parameters. In general, a microstructural characterization by XRD is principally performed by Strain/Size analysis based on the modified Scherrer formula, which in turn, allows for mean grain size and average microstrain to be computed. However, when applied to polycrystalline bulk semiconductors, the modified Scherrer formula gives grain sizes of the order of a few hundreds of nanometers, which is not usually observed in bulk materials. Instead, a new theoretical scheme with misfit dislocations and plastic deformations would be used to calculate the grain size into a bulk. Assuming that these dislocations are of elastic origin, we were able to calculate the misfit dislocations density as function of the elastic constants of the materials. With this, the modified Scherrer formula is corrected to explain the additional XRD line broadening. All microstructure parameters of our samples increase as the atomic radius of the VI-element increases, with elastic constants similar to related semiconducting compounds.

Keywords: Strain/Size analysis, Modified Scherrer Equation, microstructural parameters, ternary semiconductors AgIn₅VI₈, Poisson ratio.

1. Introduction

Ternary semiconductors provide a natural way of tuning the desired band gap and flexibility to control other material parameters by changing the relative composition of the pure elements in the alloy. A special group of ternaries are those based on the groups of elements I-III-VI, such as Ag(In, Ga) (S, Te, Se), CulnSe₂ and AgGaTe₂. These alloys crystallize in the non-centrosymmetric chalcopyrite structure, leading to non-zero second order nonlinear susceptibility. This gives these compounds promising features for technological applications, including infrared optoelectronic devices and solar cells applications. Another group of semiconductors that have gained much attention during recent years are those from the family of I-III-VI₈ compounds. These alloys present a tetragonal or orthorhombic structure depending on the ion of group III, and a cubic-spinel or tetragonal structure depending on the group VI element, and have optical band gaps suitable for optimum energy conversion solar cells, and thermoelectric properties useful for applications in waste-heat recovery, air conditioning, and refrigeration.

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materials is the Strain/Size method. This technique for analysis is based on the interpretation of the broadening of the diffraction lines on the framework of the Scherrer equation, from which, microstructural parameters, such as grain size and average microstrain, are determined. It is apparent that these two parameters are the most relevant in the description of a microstructure; however, when an actual sample is subjected to strain forces, structural defects must be introduced in order to stabilize the crystalline lattice. These structural defects are called misfit dislocations and contribute to an extra broadening in the experimental full-width at half-maximum (FWHM) of the XRD lines. These defects are not usually taken into account in a conventional microstructural analysis based on the Scherrer equation, so some corrections are needed in order to provide a more realistic description of a microstructure.

2. Experimental Methods

Three polycrystalline ingots of AgIn$_5$S$_8$, AgIn$_5$Se$_8$, and AgIn$_5$Te$_8$ were prepared by direct fusion of the stoichiometric mixture (DFSM) of the elements of at least 5N purity, following a synthesis program similar to that outlined by Pérez et al. The samples were synthesized inside evacuated quartz ampoules ($\approx 10^6$ Torr). The ampoules were very slowly heated in a vertical furnace, from room temperature up to 858 °C at a heating rate of about 5 °C/h, lower enough to prevent an explosion due to exothermic reactions between group III and group VI elements. The samples are kept at this temperature during 48 hours, and rocked at regular intervals to achieve a homogeneous mixing of the liquid mixture (DFSM) of the elements of at least 5N purity, and on the XRD absorption.

In a polycrystalline sample, the assumption that the crystallite size matches the grain size is not always valid. In these materials, grains are made up of small crystallites oriented in all directions. In this case, the size effects could be overwhelmed by an anisotropic microstructure, characterized by the presence of microstrains between atomic planes. In order to stabilize the grain size, the microstrains must be compensated by local elastic forces, as a consequence inducing misfit dislocations and mosaicities, deformations, stacking faults, vacancies, composition gradients, etc. Due to this relaxation process, the lines of the XRD profile display an additional broadening, represented by the expression, where $\varepsilon$ is the microstrain between crystalline planes and is a measure of the elastic deformation; $d$ and $d'$ are the interplanar distances before and after deformation, respectively. Another aspect to be considered in our analysis is the aberration introduced by the diffractometer to the FWHM, or instrumental broadening, $\beta_{int}$. The instrumental broadening is parameterized from a reference silicon data using the Caglioti’s formula.

$$\beta_{int} = U \tan^2 \theta + V \tan \theta + W.$$  

where $U$, $V$, and $W$ are fitting parameters to the base XRD-line. In our case, $U= 0.000010$, $V= 0.0000015$, and
are typically observed when the micro-deformations field line corresponds to a Lorentzian function. These profiles have been a subject of great interest during the past decades.

3.2 Elastic Relaxation. Mechanical Properties

In the following section, the density at mechanical equilibrium, as will be shown in greater detail. The energy density of elastic deformations is given by (within the Hooke’s law approximation)

\[ E_d = \frac{1}{2} B \varepsilon^2. \]

where \( \varepsilon \) is the average microstrain, and \( B \) is the bulk modulus related to the elastic constants of the material, which are,\(^ {23} \)

\[ C_{11}, C_{12}, C_{13} : \text{cubic}, \]
\[ C_{11}, C_{12}, C_{13}, C_{44} : \text{hexagonal}, \]
\[ C_{11}, C_{12}, C_{13}, C_{335}, C_{44}, C_{66} : \text{tetragonal}. \]

In particular, for a single cubic crystal \( B = (C_{11} + 2C_{12})/3 \).

As mentioned above, accurate calculations of the misfit dislocation energy are further complicated, since a dislocation line is a complex structure. In the usual case the energy of an array of dislocations is the elastic energy stored within the dislocation line. If the strain field is distributed along screw and edge dislocations, the misfit dislocation energy density is calculated following the model discussed by Sutton and Balluffi.\(^ {24} \) It is then obtained that,

\[ dE_d(\phi) = \frac{df}{4\pi(1-\nu)} \mu b^2 \rho_0 \ln\left(\frac{L}{a}\right)(1 + \nu \cos^2 \phi), \]

with \( \mu \) being the effective shear modulus, \( \nu \) the Poisson ratio, \( L \) the size of a grain/crystallite intercepting a dislocation line, \( b \) the modulus of the corresponding Burger vector, \( \rho_0 \) the misfit dislocation density per unit area, and \( \phi \) the angle between the Burger vector and the dislocation line, in the range from 0 (screw) to \( \pi/2 \) (edge). The Poisson ratio gives information on the material’s plasticity and is defined as the negative ratio “transversal-strain/longitudinal-strain” for the unit cell (-1 < \( \nu \) < 0.5). Most semiconductors exhibit positive \( \nu \)-values, which indicate that when subjected to a strain force the material elongates longitudinally, while it is compressed transversally. In contrast, there are certain special man-made materials that can exhibit a negative Poisson’s ratio and are called ”auxetic”. In order for any solid structure be stable, elastic energy must be absorbed in the same amount along each crystalline direction. Integrating Eq. (8) gives the total energy density due to misfit dislocations as,
After applying the elastic equilibrium condition, $E_{\text{el}} = E_D$, to energies (6) and (9), we obtain that the misfit dislocation density due to plastic deformations is given by,

$$\rho_D = 4 \left( \frac{1 - \nu}{1 + \nu} \right) \beta \frac{1}{\mu} \ln \left( \frac{L}{b} \right) \frac{e^{\gamma}}{b^2}.$$  \hfill (10)

Considering the constitutive relation $\beta/\mu = 2(1+\nu)/3(1-2\nu)$, and the Burger vector satisfying Bragg’s law, the correction to the XRD line broadening due to misfit dislocations is,

$$\beta'_\text{D} (\theta) = 2\gamma \left( \frac{1 - \nu}{1 + \nu} \right) \ln \left( \frac{2\pi \sin \theta}{L} \right) \frac{e^{\gamma}}{b^2}.$$  \hfill (11)

With this, the modified Scherrer formulae for Lorentzian and Gaussian profiles are now corrected and expressed in the form,

$$\beta (\theta) = \frac{K \lambda}{L \cos \theta} + 4\pi \tan \theta + 2\gamma \left( \frac{1 - \nu}{1 + \nu} \right) \sqrt{\ln \left( \frac{2\pi \sin \theta}{L} \right)} + \beta_\text{FWHM}$$  \hfill (12)

$$\beta (\theta) = \frac{K \lambda}{L \cos \theta} + (4\pi \tan \theta)^2 + 2\gamma \left( \frac{1 - \nu}{1 + \nu} \right) \sqrt{\ln \left( \frac{2\pi \sin \theta}{L} \right)} + \beta_\text{FWHM}$$  \hfill (13)

According to this framework, the effect of the strain forces is two-fold: as the material is stretched/compressed, misfit dislocations and plastic deformations are necessarily introduced in order for the lattice structure can be sustained. In this new scheme, the modified Scherrer equations are redefined and now allow estimation not only of grain sizes and micro strains, but also of the fundamental Poisson ratio.

### 4. Results and Discussion

The XRD spectrum of the ternary semiconductor AgIn$_5$S$_8$ is shown in Fig. 1. This profile corresponds to a cubic-spinel structure with lattice parameter $a = 10.8217 \ \text{Å}$, in agreement with previous reports.\(^8\) The cubic-spinel crystalline structure is characteristic of a class of minerals called aluminum spinels, whose general crystalline formula is $A^{2+}B^{3+}O_2^-$ at $L$, with characteristic $c/a = 2.005$ tetragonal distortion in both samples. As in the case of AgIn$_5$S$_8$, these profiles are almost Gaussian, as is demonstrated by the continuous curves shown in the inserted panels. This fact assures that the FWHM of the XRD profile and the diffraction angle satisfy the relation (13).

On the other hand, the XRD spectra for AgIn$_5$Se$_8$ and AgIn$_5$Te$_8$ are shown in Figs. 2-3 and are in agreement with results published earlier.\(^{26,27}\) Both systems display tetragonal structures with lattice parameters $a = 5.795224 \ \text{Å}$, $c = 11.622806 \ \text{Å}$ in AgIn$_5$Se$_8$, and $a = 6.2120 \ \text{Å}$, $c = 12.4561 \ \text{Å}$ in AgIn$_5$Te$_8$, with characteristic $c/a \approx 2.005$ tetragonal distortion in both samples. As in the case of AgIn$_5$S$_8$, these profiles are almost Gaussian, as is demonstrated by the continuous curves shown in the inserted panels. This fact assures that the FWHM of the XRD profile and the diffraction angle satisfy the relation (13).

The values of the XRD FWHM, $\beta_{\text{FWHM}}$, determined from the experimental spectra of all samples, are plotted in Fig. 4. It is observed that $\beta_{\text{FWHM}}$ is almost constant at small diffraction angles, up to a critical value, $\theta_C$, at which the line broadening increases nonlinearly. Similar behavior has
Microstructural Analysis of AgIn\textsubscript{5}VI\textsubscript{8} (VI: S, Se, Te) Ternary Semiconductors by X-Ray Diffraction

Figure 3. Profile of the XRD spectrum of the compound AgIn\textsubscript{5}Te\textsubscript{8}. The lineshape of the diffraction peaks fit in general to a Gaussian profile, as observed from the inserted figure.

been reported in related semiconducting compounds such as AgIn\textsubscript{4}GaTe\textsubscript{8}.\textsuperscript{16} Notice that the $\theta_c$ value coincides with the strongest reflection peak, with a shift from $\approx 13.65^\circ$ to $\approx 12.39^\circ$ as the atomic number, $z$, of the anion VI increases from 16 up to 54. This shift can be understood considering Bragg's law, $\sin \theta_c = \lambda / 2d(z)$, from which we can verify that the interplanar distance calculated at $\theta_c$ satisfies the inequality $d(S) < d(Se) < d(As)$. The continuous curves in Fig. 4 are non-linear numerical fits to the experimental data using Eq. (13), following a Levenberg-Marquardt scheme.\textsuperscript{28} The values of the parameters obtained from these fits are listed in Table 1. The agreement between theory and experiment is good for the set of parameters $(L, \varepsilon, \nu)$, satisfying the theoretical conditions discussed in section 3.2. Notice that both grain size and microstrain increase along with the atomic number of the anion VI, with increasing Poisson ratio. This means that our samples are highly anisotropic with the Poisson ratio typical of other related ternaries.\textsuperscript{29} The grain sizes obtained with our model are of the order of a few microns, which is reasonable in bulk polycrystalline materials.\textsuperscript{30,31}

By comparison, the curves obtained from the Scherrer (S) and the Modified Scherrer (MS) equations are also shown in Fig. 4. Notice that the agreement between experimental data and the MS equation is also reasonable for the corresponding pair of parameters $(L_{MS}, \varepsilon_{MS})$ listed in Table 1. Although the average microstrain, $\varepsilon_{MS}$, is comparable to the value of $\varepsilon$, the grain size, $L_{MS}$, is of the order of $\approx 250$ nm. However, as mentioned before, such small grain sizes are not usually observed in bulk polycrystalline materials. On the other hand, the conventional Scherrer formula (1), can only fit the experimental line broadening at diffraction angles smaller than $\theta_c$, and departs from the experimental data at diffraction angles $\theta > \theta_c$, giving much smaller grain sizes of the order of $\approx 50$ nm.

Figure 4. Full-Width-Half-Maximum ($\beta_{FWHM}$) as function of the diffraction angle for each sample. The solid curves are numerical fits to the experimental data using equation (13). The fitting parameters obtained from these fits are listed in Table 1. The dashed-dotted curve is calculated with the modified Scherrer formula (5), and the dashed curve corresponds to the conventional Scherrer formula.

Table 1. Microstructural parameters $(L, \varepsilon, \nu)$ of the system AgIn$_{5}$VI$_{8}$ determined from numerical fits with Equation (13), as discussed in Section 4. For comparison, the parameters obtained from the modified Scherrer (MS) and conventional Scherrer (S) formulae are also included.

|            | AgIn$_{5}$S$_{8}$ | AgIn$_{5}$Se$_{8}$ | AgIn$_{5}$Te$_{8}$ |
|------------|------------------|--------------------|--------------------|
| $L$ (µm)   | 1.56             | 5.51               | 8.51               |
| $\varepsilon$ (%) | 0.17          | 0.21               | 0.28               |
| $\nu$      | 0.125            | 0.23               | 0.30               |
| $L_{MS}$ (nm) | 245.0           | 258.0              | 262.0              |
| $\varepsilon_{MS}$ (%) | 0.15          | 0.22               | 0.24               |
| $L_{S}$ (nm)  | 48.0            | 46.0               | 50.5               |
5. Conclusions

The microstructural properties of polycrystalline semiconductors AgIn\textsubscript{1-x}VI\textsubscript{x} (VI=S, Se, Te) are studied applying the Strain/Size method to the Full-Width-Half-Maximum of the x-ray diffraction profiles. From our analysis we can conclude:

1. The FWHM of the diffraction line as a function of \( \theta \) cannot be explained by the modified Scherrer formulae in their original forms, since these give in most cases unrealistic grain sizes for a polycrystalline sample.

2. In order to give a more realistic interpretation of the FWHM, misfit dislocations must be included explicitly. In this framework, plastic deformations are important. The Poisson ration, \( \nu \), then appears as a fundamental microstructural parameter beside the mean grain size, \( L \), and the average microstrain, \( \varepsilon \). In this way, the modified Scherrer formulae are then corrected with an additional line broadening, \( \beta_0' \).

3. The values of the microstructural parameters \((L, \varepsilon, \nu)\) for the ternary system AgIn\textsubscript{1-x}VI\textsubscript{x} depend on the atomic radius of the VI element. In particular, according to our model, the Poisson ration is positive in all samples and of the same order than those found in related semiconducting materials, which indicate that all these semiconductors have similar mechanical properties.

The detection and quantification of microstrains and microstructural defects in polycrystalline compounds and granular systems are, in general, complex tasks, since several parameters are involved, requiring highly sensitive techniques and more fundamental theoretical studies. However, the results reported here could be of relevance for future applications of AgIn\textsubscript{1-x}VI\textsubscript{x} in diverse semiconducting processes and microelectronic devices.

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