Irradiation Effect on the Structure of Indium Sulfide Semiconductor Crystals

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Abstract— In the present work, indium sulfide (InS) single crystals are successfully grown by the modified vertical Bridgman technique. Single crystal X-ray diffraction for the grown crystals shows that the product crystal is the orthorhombic structure of Pnnm space group. The crystals were irradiated with 100, 300 and 500 KGy to reveal the influence of gamma irradiation on their structural properties. The detailed structural analysis was done by Scherrer and Williamson – Hall plot methods. Relations between the irradiation dose and the deformation of the lattice parameters, dislocation density, grain size, microstrain, crystallinity were investigated and discussed. Unique results are found in the present study for the first time as far as we know. This study not only enriches the understanding of structure of indium sulfide crystals but also paves the way in the search for the role played by gamma irradiation on semiconducting compounds.

Index Terms— Crystallite Size, Dislocation, InSe Crystals, Micro strain, Radiation Effects , XRD Analysis

1 INTRODUCTION

Semiconductors AIIIBVI, where A is Ga, In; B is S, Se, have been attracted particular interest in recent years because of their layer-nature and promising applications. Indium sulfide is a semiconducting compound belonging to this family. The crystal structure of InS can be regarded as a three-dimensional network which is slightly different from a layered structure of its counterparts (GaS, GaSe, and InSe). There is very little literature on InS system and even the existing ones reported different crystal structure for the equiatomic InS. This is why, it is not clear if InS system is monoclinic or orthorhombic [1], [2].So single crystal x-ray analysis is strongly recommended to clear this issue, and it should be performed on the grown crystal. It was reported that InS has the orthorhombic structure composed of four molecules in a primitive unit cell and belongs to the space group Pmnn [3]. Optical band gap of 2.09eV is deduced from linear optical measurements [4]. Being a wide band gap semiconductor [2], thin films of In2S3 are investigated for optoelectronics and photovoltaic applications [4]. Nishino and Hamakawa have performed electrical and optical measurements on InS single crystals [5]. They reported that as-grown InS is an n-type semiconductor and have estimated room temperature indirect and direct band gaps to be 1.9 eV and 2.44 eV respectively[5]. Also, the carrier concentration of as-grown crystals is more than 1018 cm-3 and the Hall mobility is about 50 cm2/V. sec at room temperature as appeared in the same previous reference. As far as we know nothing in the literature about the influence of γ- irradiation doses on InS structure, hence on its physical properties.

The purpose of this article is to present the results of the structural properties of the crystals and their relations with the γ- irradiation doses on InS in the 100 - 500 KGy range. The previous experience we had during the work on InSe [6]and analysis of our results indicate that irradiation is an important factor from the point of view of the crystal structure and it improves the crystallinity and hence the crystal quality but until a certain limit.

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2 EXPERIMENTAL DETAILS

2.1 Crystal Growth

InS single crystals were prepared by the modified vertical Bridgman method starting with high purity (5N pure) elements. The chemicals were obtained from Aldrich. This mixture was kept in a quartz crucible and then sealed in a quartz ampoule in 10−6 Torr. The sealed ampoule was placed in the three zone furnace and heated up to 1050o C with the rate of 50 o C/hr in the first zone. The temperature was kept then for 24 hrs. The crystallization was made by cooling the system to 550 C at a rate of 5 C/hr in the second zone. In the third zone, solidification occurs and the as-grown crystals were like cleaved and having a reddish color. The used technique is very simple but it enabled us to obtain high qualities of crystals. This is because of the absence of the motor vibrations which is not beneficial. Details about this technique have already been published [7]. For growing the crystals we followed the phase diagram of In and S that were reported earlier [5], [7], and [8]. The analysis of X-ray diffraction data showed that they crystallize in 1an orthorhombic unit cell with parameters: a = 0.394, b = 0.444 and c = 1.065 nm. in a good agreement with the work published in ref. [3], [5].

2.2 X – Ray Diffraction Technique

Since perfect crystal would extend in all directions to infinity, so no crystals are perfect due to their finite size of the products. This deviation from perfect

crystallinity leads to a broadening of the x-ray diffraction peaks. The two main properties extracted from the peak width analysis are crystallite size (which is a measure of the size of a coherently diffracting domain and lattice strain) [9]. It is an established fact that the x-ray diffraction is a good tool for verifying crystals. Also, the lattice parameters, grain size, strain and dislocation density of a given material can be determined by using x-ray investigations [6]. The measurement of structural parameters by means of x-ray diffraction has therefore of many advantages over the other techniques. For example, it does not require time for sample preparation (tinning) and image analyzing. Utilization of the x-ray diffraction has been done to reveal the influence of irradiation and changes on the crystal structure of the grown InS crystals.

The grown crystals were identified also by means of x-ray diffraction. The conformation of the product crystal showed that it is the single phase with an orthorhombic structure belongs to the space group Pmnn and the unit cell parameters obtained are the same as reported earlier [3],[5].

The x–ray diffractograms were obtained with scan speed 2 deg. /min. (continuous scan mode) at ambient room temperature with Goniometer type Ultima IV (Germany). The instrument is equipped with a copper anode generating Ni - filtered CuKα radiation (λ= 1.5406 Ao, 40 kV, 40 mA, back monochromator). The equipment was used in a θ - 2θ geometry in the range between 10 and 80o with a divergence slit of 2/3 deg. In the present work, we did utilize the x – ray pattern for determination of many important parameters. It must be mentioned that background subtraction and Ka2 elimination were done before the peak search work. In general, we have followed the same procedures done on InSe semiconductor crystals which already have been published [6].

2.3 Gamma irradiation

The samples were irradiated with γ -rays obtained from 60Co cell available at the research center, faculty of science, King Saud University, Saudi Arabia. The average dose rate from the cell was 1Gy/S. The doses were adjusted to be 100 KGy (corresponding to about 1day), 300 KGy (corresponding to 4 days and 500KGy (corresponding to 6 days). Then utilization of the x-ray diffraction has been done to reveal the influence of irradiation and changes on the crystal structure of the grown InS crystals.

3 RESULTS & DISCUSSION

3.1General analysis of the X-ray diffraction patterns

Fig.1 shows the powder diffract gram of the InS sample. In this figure, we can see strong Bragg peaks of x-ray diffraction pattern which indicate that the sample is crystalline. No other or foreign peaks were detected. The intense peaks in the patterns prove the high crystallinity of the products. The relative intensities of the reflection peaks in all patterns agree well with the XRD pattern of bulk InS. Also, the effect of irradiation on InS structure
appeared in XRD chart. This can be observed as a change in the peak intensities. The variations of the intensities of the main peaks are due to that localized variations in intensity within any individual diffracted spot arise from structural non-uniformity in the lattice planes causing the spot, and this forms the basis for the x-ray topographic technique.

This topographic contrast arises from differences in the intensity of the diffracted beam as a function of position inside the crystal. So this change, simply, is a function of the crystallinity. On the other hand, with increasing irradiation doses from 100 to 300 and 300 to 500 KGy, the crystallinity of the products was changed. In this work, it is desired to establish the extent to which the irradiation treatment plays a significant role in the improvement of the crystal quality. The preferable dose that can be used in this respect lies at 300 KGy where at 500KGy the peak intensity is no longer high. Now if the crystallite is strained then the d spacing will be changed; a compressive stress would make the d-spacing smaller (and a tensile stress would make the d spacing larger), say reducing a given spacing d to d− δd. Then by Bragg's Law the position of the peak will increase from 2θ to 2(θ + δθ). If every crystallite in the sample was strained (compressed) by the same amount it would result in a peak shift from (2θ) to 2(θ + δθ). Based on the above facts and regarding Fig.2 we concluded the following:

1- All the three patterns proved that the understudy crystal is confirmed as InS orthorhombic if compared to data and the d spaces of ref. [3],[5].

2- Under the influence of irradiation the peaks shift upward. Since the peak height depends on the crystal quality, so it is easy to conclude that irradiation changes the crystallinity and hence the crystal quality.

3- In spite of the observable broadening, the peak positions are the same for the different irradiation doses. This indicates that the compressive stress is excluded.

4-Irradiation improves the crystallinity and the crystal quality but until a certain limit (300 KGy). This is concluded where peaks started to decrease above 300 KGy.

3.2 Determination of Crystal Lattice Parameters

The direction of the reflection beams is determined entirely by the geometry of the lattice which in turn governed by the orientation and spacing of the crystalline planes. If for the crystal of symmetry the given size of the structure cell a, b and c, the angle at which the beam diffraction from the crystal plane (hkl) can easily be calculated from the inter-planar spacing relationships. We did so and the obtained data were used to identify the product crystal. Moreover with the aid of Bragg's law: $n \lambda = 2 d \sin \theta$ we calculated, by computational treatments, structure

cell a, b and c substantially free from experimental error by using the extrapolation function F (θ).

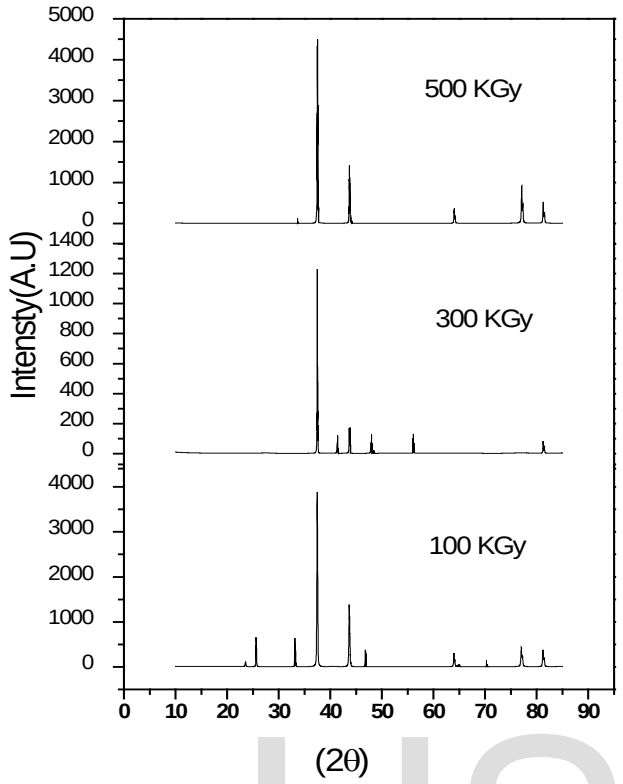

Fig. 1.X-ray charts of InS crystals at 100, 300 and 500 KGy

From the values of d- spaces, for different reflection planes, we calculated the lattice parameters of the orthorhombic InS according to the following equation [10]:

$$\frac{1}{d_{hkl}^2} = \left[\frac{h^2}{a^2}\right] + \left[\frac{k^2}{b^2}\right] + \left[\frac{l^2}{c^2}\right] \quad \text{.....(1)}$$

Where d is interplanar spacing, h, k and l are Miller's indices and a, b and c are the lattice parameters. It is observed in Fig.2 that peak broadenings occur. This is regarded as a result of (a) crystallite size and (b) lattice strain. For more utilization of figure (1), we shall digress with a discussion on the width of the main peak in the three cases. The pre-mentioned three cases corresponding to the three crystals as irradiated with 100,300 and 500 KGy.

In order to obtain the lattice parameters a, b and c of the orthorhombic InS substantially free from experimental error, one should plot the apparent values of a, b and c respectively against the corresponding values of the famous extrapolation function F (θ) which is [11]:-

$$F(\theta) = \frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta} \quad \text{..... (2)}$$

Fig. 2 shows the relation between the lattice parameters a, b and c vs. (θ). The interception of the extrapolation of a straight line with y-axis gives the value of the lattice parameters a, b and c accurately.

The results of lattice parameters as estimated from Fig 2 are listed and compared to the values of references [3],[5].in table 1 below:-

TABLE 3

Dose	Lattice parameter A°			Values in Ref[3],[5].A°		
	a	*b*	*c*	*a*	*b*	*c*
100 kGy)	4.12	4.62	11.11	3.944	4.447	10.65
(300 kGy)	3.75	4.21	10.13			
(500 kGy)	3.62	3.58	10.13			

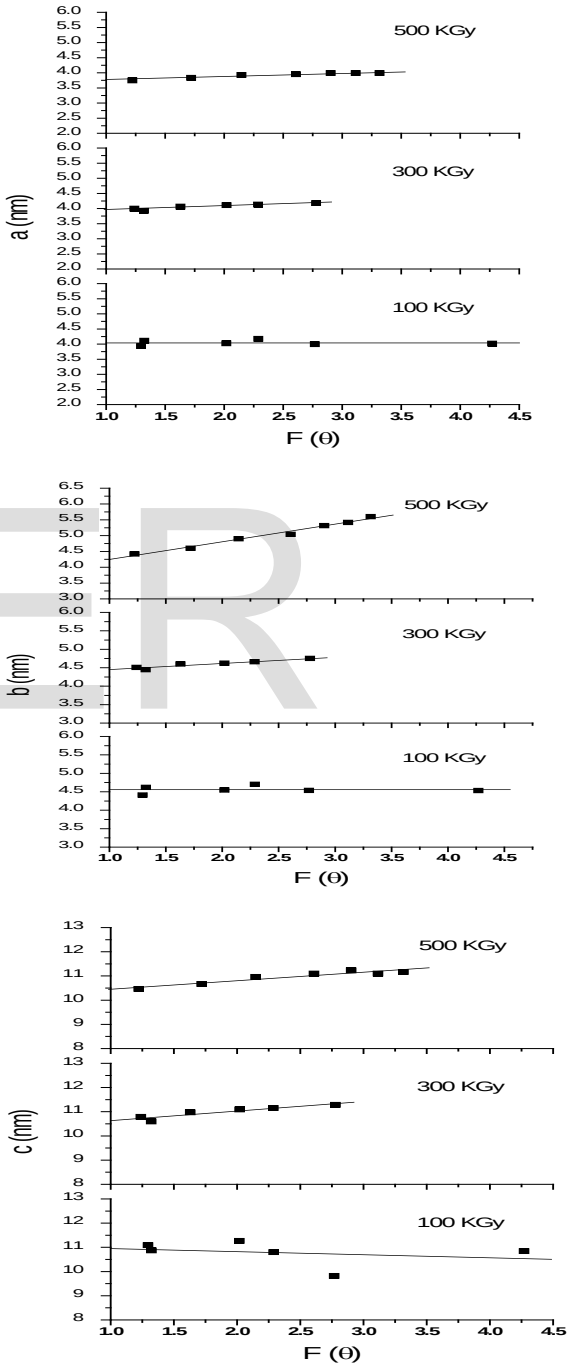

Fig. 2. Relation between the lattice parameters *a*, *b* and *c* and the extrapolation function F (θ) for InS crystals at 100, 300 and 500 KGy.

The data appeared in the above table 1 and Fig. 2 lead to the following comments:

1- Results of a, b and c proved that the understudy InS crystal is orthorhombic.
2- Generally all the lattice parameters are influenced by the exposure of irradiation.
3- Once the crystal is exposed to the dose 100 KGy; all the lattice parameters a, b and c became larger than those reported in references 3, 5.
4- The same estimated parameters value a, b and c was turned to be lower than the standards when the crystal is exposed to the doses 300 KGy and 500 KGy.
5- From the results and calculations, we concluded that the unit cell volume decreases when the radiation dose was increased from 100 KGy to 300 KGy and then abruptly increases at 500 KGy i.e. radiation cause shrinkage first and then the unit cell volume expands. It must be mentioned that we did conclude from section 5. (A) that tensile stress is excluded.
6- The variation of the unit cell volume is attributed to the fluctuation in the lattice parameters under the different irradiation doses, as observed in Fig.2, which in turn can be due to the variation occurred in the quality and/or the lattice imperfections of the crystals resulting from irradiation [11]. This is acceptable if we note that the lowest unit cell volume value was observed at 300 KGy and at this dose the x- ray peak is the shortest one. This, in turn, supports that the high crystallinity observed at 300 KGy means that the crystal contains low defects.

3.3 Determination of Crystallite Size

Using eq. (3) and substituting the values of Γ (the full width at half maximum) for the main peaks we can obtain the values (D_{vol}) (crystal size). This quantity is important because it is proportional to L_{vol} (the column lengths). The primarily obtained column lengths of an ensemble of particles can be transformed into average grain sizes if all the crystallites in the sample have roughly the same shape [12]. The standard assumption is a spherical shape, then [13]: $(D_{vol}) = 4/3\ L_{vol}$

This is why we computed (D_{vol}) and (L_{vol}),for the orthorhombic InS crystals at the different conditions understudy, as listed in table 2 from the following Scherer's equation [14]:-

$$\Gamma = \frac{0.94\lambda}{D_{vol}\cos\theta} \quad \text{..... ..... (3)}$$

The results are as follows:

TABLE 2

Dose	L_{vol}(nm)	D_{vol}(nm)
(100 KGy)	173.13	230.84
(300 KGy)	134.38	179.17
(500 KGy)	143.59	191.45

In spite of Scherer's formula is an approximation and the values of D_{vol} and hence L_{vol} should be inversely proportional to the crystal quality, the above table shows that lowest values of D_{vol} and hence L_{vol} are observed when the crystals are irradiated by300 KGy.

Williamson-Hall relations are helpful to spotlight on the microstrain and dislocation density in the crystal. The Williamson-Hall equation can be given as [15]:-

$$\Gamma\cos\theta = \frac{0.94\lambda}{D_{vol}} + 4\varepsilon\sin\theta \quad \text{..... (4)}$$

Where Γ is the full width at half-maximum of x – ray peak at diffraction angle θ and ε is the micro-strain. We utilized Williamson- Hall relation because it takes into account that the total width of the x-ray diffraction peak is due to both size and strain effects. For the separation, the different dependence is helpful: the size broadening is proportional to cos-1θ and the strain broadening is proportional to tanθ. Accordingly, from plotting the relation between Γ cos θ and sinθ, we can get from the intercept the value of Dvol and from the slope the value of ε (the micro-strain). This is done in Fig 4 regarding Williamson-Hall relation. From the figure and the results we can conclude the data listed as shown in the following table:

TABLE 3

Dose	L_{vol} (nm)	D_{vol} (nm)	Microstrain (ε)	Dislocation density (m^2)
100 KGy	210	280	0.00055	$1.37\text{x}10^{-26}$
300 KGy	75.92	101.23	0.00026	$2.59\text{x}10^{-27}$
500 KGy	204.97	273.92	0.00047	$1.15\text{x}10^{-26}$

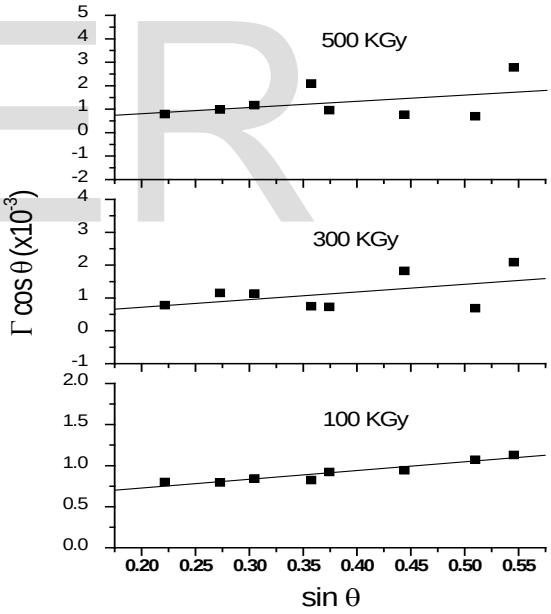

Fig 3: Γ cosθ as a function of Sin θ

As for the obtained results in table 3, we have the following comments:-

1- Both Dvol and Lvol are influenced by the irradiation.
2- Both Dvol and Lvol have the highest values when the crystals are irradiated to 100 KGy while the lowest are corresponding to300 KGy.
3- The above result is acceptable if we consider the peak broadening appeared in Fig.1. Again XRD peaks are broadened by small crystallite size and lattice distortion caused by lattice dislocations.
4- Generally the values of crystallite size calculated by Scherrer's method are different from those obtained

by Williamson-Hall method. This difference is attributed to the strain values and hence it confirms that the role of strain is a crucial factor.

5- This difference should be considered in the calculation of crystalline size. Thus, calculations by using the Scherrer's method without considering strain may yield inaccurate results.

3.4 Determination of the microstrain and the dislocation density

It is mentioned that Williamson Hall technique takes into account both size and strain effects. The formula which is between Γ cos θ and sin θ is a linear relationship as predicted. From the intercept of the line, we got above the crystal size. The slope of the fitted line provides the micro-strain.

The average dislocation density R_e can be determined from the following equation [16]:-

$$\varepsilon^2 = (\pi A b^2 / 2) R_e C \quad \text{..... (5)}$$

Where (b2/2) is the Burgers vector, A is a constant defined by the effective outer cut-off radius of dislocations R_e and C is the contrast factor.

The results of the microstrain and the dislocation density are listed in the previous table. The results reveal the following:-

1- Both values of the microstrain and the dislocation density are influenced by the irradiation.

2- Both the microstrain and the dislocation density behave in the same manner.

3-They reach the maximum values at irradiation of 500 KGy while the lowest values are observed at 300 KGy.

4- From the dislocation density (ρ) relations, the average distance between the adjacent dislocations L_c (as appeared in the previous table) can be checked simply as with the aid of the following formula:-

$$L_c = 1/\sqrt{\rho} \quad \text{.....(6)}$$

4 Conclusion

InS crystals were grown by a special modification of the vertical Bridgman technique. Via X-ray diffraction examinations it was proved that the grown samples are the crystalline InS in their orthorhombic form. The crystals were irradiated with 100 - 500 KGy. The crystallite size and lattice strain were estimated from broadening of XRD peaks by using Scherrer and Williamson-Hall methods. A lot of structural work

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