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Studying of some physical properties of screen printed of hazardous carcinogenic lead iodide thick films doped with aluminum

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Abstract

Lead iodide considers as one of the chemicals that is on the Special Health Hazard Substance List (SHHSL) and it is consider as carcinogenetic substance. In this study films of 12µm thick toxic PbI_2 pure and doped with various atomic volumes doping concentration of Al (1, 2, 3, & 4 mil) were deposited, and their physical properties were investigated different poisonous concentrations of hazardous lead iodide. The films were set by screen printing on glass substrates at room temperatures. X-Ray diffraction of deposited films shows raising the peak intensity with increasing dopant concentration. Energy gap decreases with increasing dopant concentration. Doping of Lead Iodide film with specific amount of Al will increase the electrical resistivity with increasing the dopant concentration, while decrease mobility.

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Introduction

Lead Iodide that usually used in screen printing and photography has a yellow bright colour (Iness *et al.,* 2015), odorless, and usually the pure PbI_2 is a heavy powder (Zuck *et al.,* 2003) it considered as a hazardous material like mercury iodide, the high sensitivity (Park *et al.,* 2007) high stopping power, low humidity and low dark current high-gain conversion properties that make wide band gap polycrystalline (Street *et al.,* 2002) semiconductors toxic materials like HgI_2, PbI_2, PbO, CdTe (Paul *et al.,* 2008) important for manufacturing digital radiography X-ray detectors (Kashikhin *et al.,* 2012).

These Polycrystalline semiconductors materials of high atomic number need low energy for generation of electron-hole pairs with high mobility-lifetime product of the charge carriers (David *et al.,* 1992). The high density of PbI_2 (D=6.2 g/cm3) makes it possible to fabricate a thinner detector (Lin JC; Leez C. 1999). Lead Iodide has a crystal arrangement of different poly types that are generally hexagonal in shape. The polytypism of Lead Iodide seems to be a significant property of this material (Matuchova *et al.,* 2010). The poly types of Lead Iodide are: 2H, 4H, 4R, 6H, 8H, 10H, 12H, 12R, 14H, 15H, 18R, 20H, 20R, 36R , 48R, where R and H indicate rhombohedral and hexagonal poly type respective (Hamza *et al.,* 2013).

The main source of energy levels in PbI_2 seems to be intrinsic structural defects i.e. iodine vacancies which could be associated with two shallow donor levels and lead vacancies which introduce two acceptor levels (Matuchova *et al.,* 2010). It can be noticed in addition that interstitial iodine was suggested to deteriorate the transport properties of nuclear radiation detectors (Williamson; Smallman 1956).

In spite of the effect of lead iodide on eyes (cause irritation), headache, irritability, upset stomach, and weakness in addition to that it may cause brain, lungs, Kidney and stomach cancer in humans, besides it may cause to colic, muscle cramps harm the nervous system. In spite of all that still the lead iodide used in printing because of the performance of all photoconductive detectors which are made from metal iodides (Mousa A; Al-rubaie N 2009), is largely affected by the electrical properties especially the (S/N) ratio and (μ *τ) value (Cullity and Stock 2001). To have high value of (S/N) ratio we need a detector with very low dark current, and to do so the starting material should have high resistivity, while the(μ*τ) value needs higher value for both ,and this means low scattering and recombination centers. (Jamil *et al.,* 2013).

In this study the researcher do not investigate the toxicity and the hazardous of lead iodide on humans being health and biology of the cells alters kinetics of proliferation, metabolic activity and cellular morphology, this study concentrate on the structure in addition to the electrical properties of PbI_2: Al was investigated, while the toxicity and bio effect biological effect was left for further study

Experimental

Deposition of PbI_2 films

It is important to know that the recommended airborne exposure limit (REL) is 0.05 mg/m3 averaged over a 10-hour work shift. Air concentrations should be maintained so that the concentration of Lead in blood must be less than 6% mg/100 grams of total blood. However Lead iodide were deposited on substrate of borosilicate glass, these glasses first washed in distilled water to remove all types of impurities from the surfaces, after that immersing in chromic acid solution for (24hours).

These glasses washed again in distilled water using ultrasonic bath for (20 minutes) to remove the remaining impurities. At last the glasses dried and became ready to be used as cleaned substrate. By mixing so well Lead Iodide with (10%) of Lead Chloride ($PbCl_2$) as an adhesive and an appropriate amount of Ethylene Glycol as a binder we gate PbI_2 paste, Ethylene Glycol as a binder. Lead Iodide film preparation using stainless steel screen by means of adhesive a paste was pressed through the screen by means of squeegee The 120 mesh number of the screen is (120 meshes per inch). After leveling, the printed wet film is dried in Oven at (60 °C) for (60 minutes).

Preparation of PbI_2 solution and impurities

Although the traces amount of lead iodide that was used in the preparation but it has to be aware of the toxicity of the lead iodide and its effect on biology of human being as a hazardous material, however the solubility limit of Lead Iodide in distilled water is relatively low about (0.044 gm per 100 ml) at (0 °C). The solubility limit of Lead Iodide increases with increasing the temperature by about (0.063 gm per 100ml) at (20 ^{5}C), and (0.41 gm per 100 ml) at (100 °C) .The solution is formed by dissolving (0.4 gm) of Lead Iodide in (125 ml) of hot distilled water with applying heat to (93 °C), with continuous shaking to guarantee total dissolution in distilled water.

Impurities solution was arranged by dissolve a (0.001) gm of impurities in (50) ml of distilled water (the same weight used for the three impurities). Impurities solutions were introduced in to (25ml) of hot Lead Iodide solution. The concentration (in volume) of impurities solutions was varied from (1ml) to (4ml). Slow cooling of the solution resulted in the precipitation of small hexagonal Lead Iodide crystallites after evaporation of the excess water.

The structural properties

The structural characteristics of Lead Iodide film were investigated using X- ray diffraction system (lab X – XRD – 6000 / Shimadzu) with wave length (λ=1.54°A) from Cu-Kα with scanning speed (8 degree/min.) and incident angle (10-60) degree . From full Width at Half Maximum (FWHM) method of X-Ray spectrum we can compute the Grain size (*D*) of the polycrystalline PbI_2 (Scherer formula) [16].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad \text{.......................................} \quad (1)$$

The extinction coefficients (K) calculate from the relationship [16].

$$K = \frac{\alpha \lambda}{4\pi} \quad \text{.......................................} \quad (2)$$

Thickness of films was measured using weight method as the thickness of the deposited film is more than 1 µm. The difference in weight is calculated by measuring the weight of the substrate before and after deposition process by using sensitive four digit Balance type SARTORIOS TE214S. Thickness was measured according to the relation [18]

$$Thickness\ (d) = \frac{\Delta M}{\rho * A} \quad \text{.......................................} \quad (3)$$

Optical properties

The optical properties of the films were inspected and investigate by measure the optical transmission (T) of the samples as a meaning of the wavelength in the range (400-1100)nm by using Shimadzu UV- Visible Spectrometer (UV-1650PC). UV-Visible spectrophotometry is one of the most often engaged techniques in pharmaceutical investigation.

It comprise measure the total of ultraviolet or visible radiation absorbed by a substance in solution. Instruments that measured the relation of the intensity of two beams of light in the UV-Vis district are called UV-Vis Spectrophotometers. The absorption coefficient (α) has been calculates by using the following equation [19].

$$lin \frac{1}{T} \quad \text{.......................................} \quad (4) \quad \alpha = \frac{1}{d}$$

The absorption coefficient (**α**) and visual band gap (Eg) are related by [19].

$$\alpha h v = A(hv - Eg)^{n} \quad \text{.......................................} \quad (5)$$

Electrical properties

Four Aluminum ohmic contacts were used to make Hall measurements by evaporating of Aluminum electrode established through masks made from Aluminum Foil designed to give for metal contact with (2mm) inter electrode distance. Mean the response of the material to the applied electrical field. Electrical properties were tested using Hall Effect measurement system type (ECOPIA – HMS-300), with magnetic field of value (0.55 Tesla), the device is equipped with computer program, which provides the most important parameters at room temperature.

Result

The recorded X- ray diffraction patterns of undoped, doped Lead Iodide films at a range of 2θ from (10°) to (60°) at (8°) glancing angle represent in Figures (1) , (2).

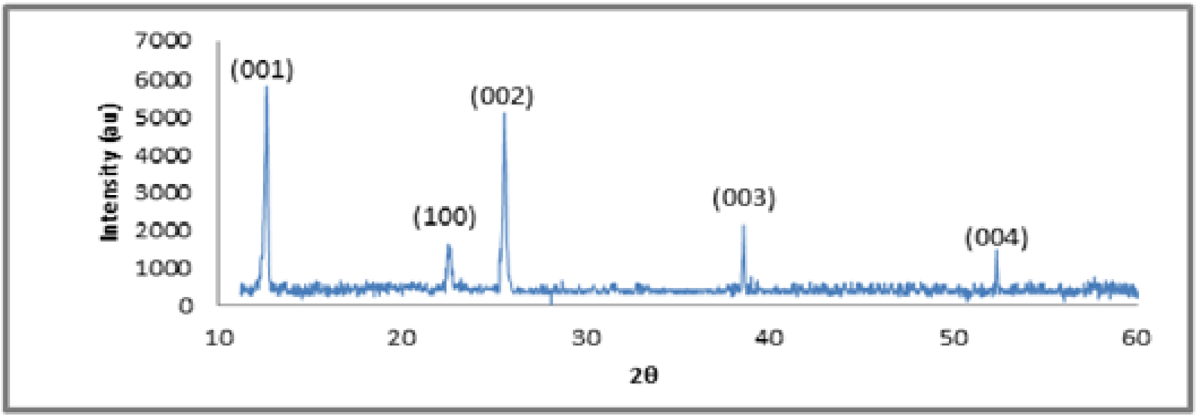

Fig. 1. XRD pattern for undoped Lead Iodide films.

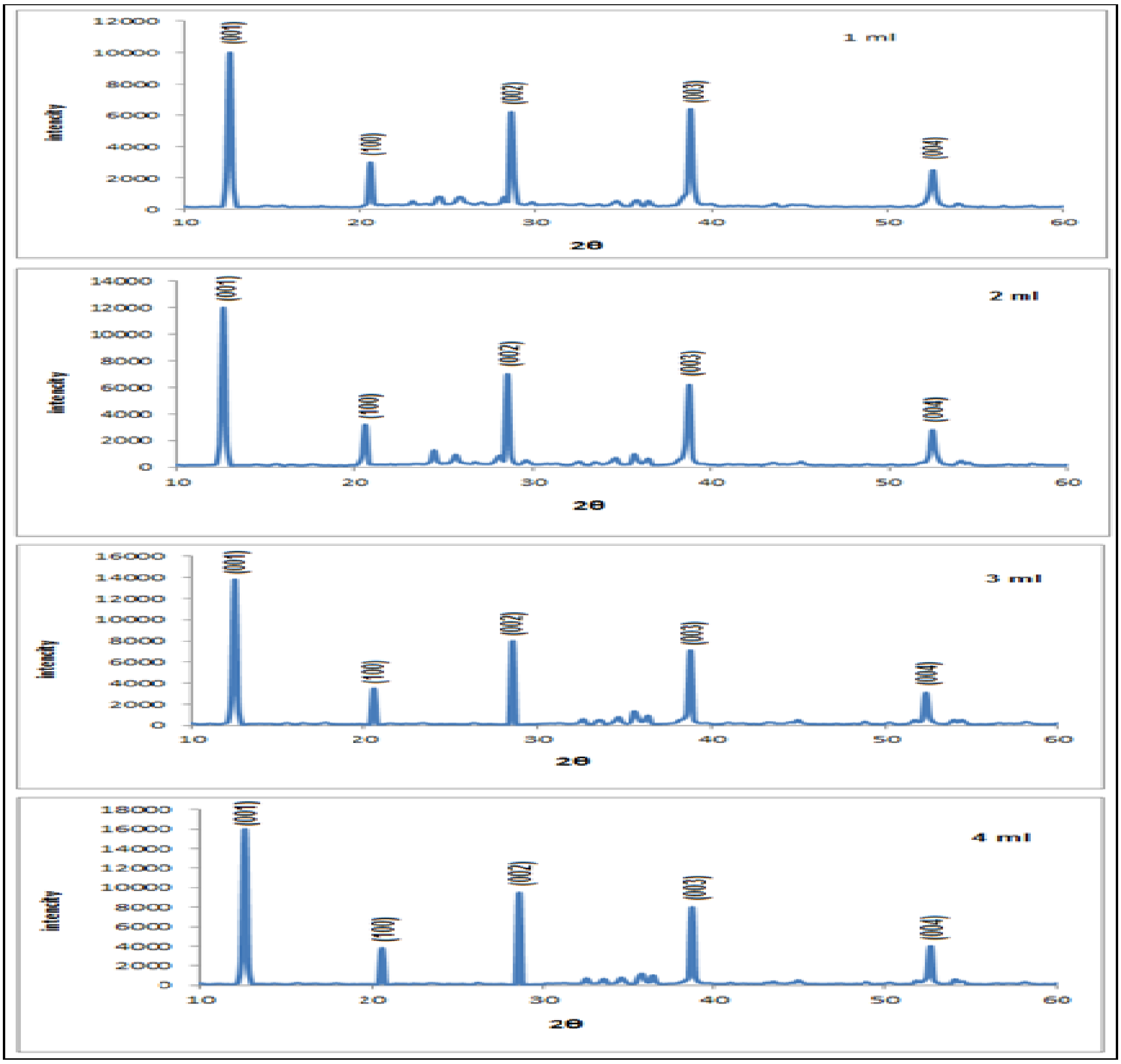

Fig. 2. XRD pattern for doped Lead Iodide films with different atomic volumes doping concentration of Al.

All these Figures shows the main planes of PbI_2 at (001), (100), (002), (003), (004) with compare to ASTM data [ ]. The strong peaks are observed at (d = 6.9775, 3.9345, 3.4821, 2.3305, 1.7452)°A which correspond to the reflection planes (001), (100), (002), (003), (004), respectively, Figure (3) represents the extinction coefficient of PbI_2 films deposited at different overthrow concentrations of (Al).

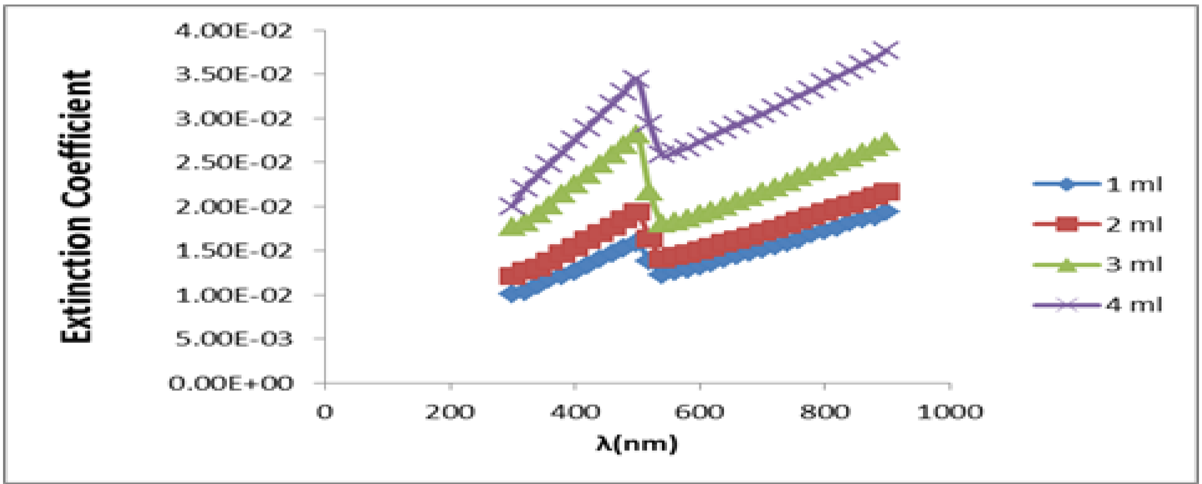

Fig. 3. Extinction coefficient as function of wavelength.

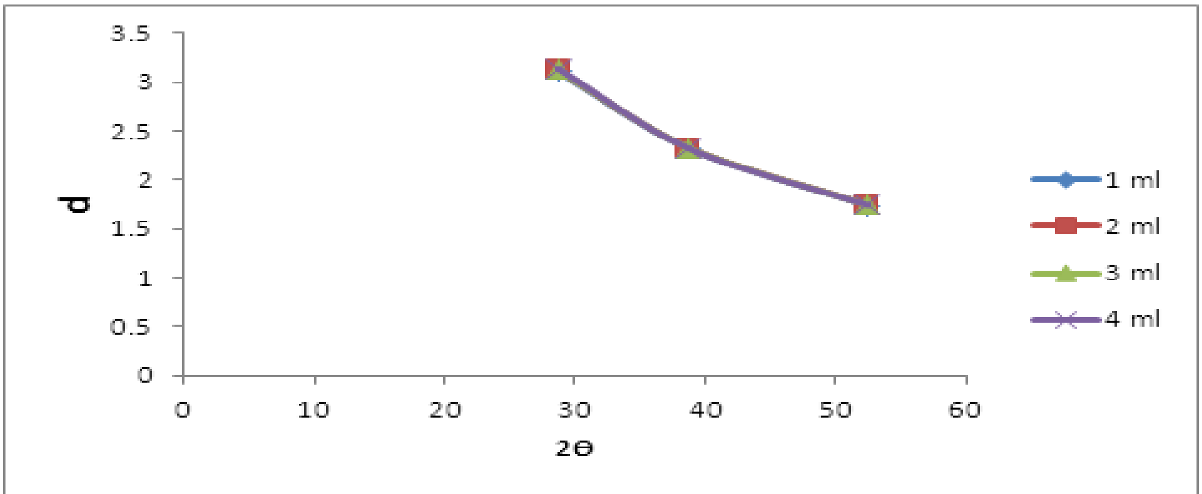

Fig. 4. variation of d-value with 2θ for doped PbI_2 films.

The extinction coefficient symbolize the amount of energy that absorbed in the film, which means the amount of extinction for electromagnetic wave in the material and depend on free electrons density and structure defects. Figure (4) Displays the inter planner spacing (d) as a function of (2 θ) which shows that the d – spacing is strongly dependent on the reflection plane. Doping of Lead Iodide does not lead to change in the inter planner spacing (d). The plot of the variation of average grain size with 2θ is presented in Figure (5). The typical grain size is influenced by added impurities.

The plot of the FWHM as a function of 2θ of doped Lead iodide films is presented in Figure (6). FWHM value of Lead Iodide films influenced by adding impurities, Figure (7) illustrates the relationship of doped Lead iodide films transmittance at wavelength range (200 – 900nm) as a function of 2θ, we can see a decrease in transmittance value with increasing value of doping concentration at wavelength range (300 – 500nm).

Figures (8) show the band gap absorption coefficient for doped Lead Iodide films.

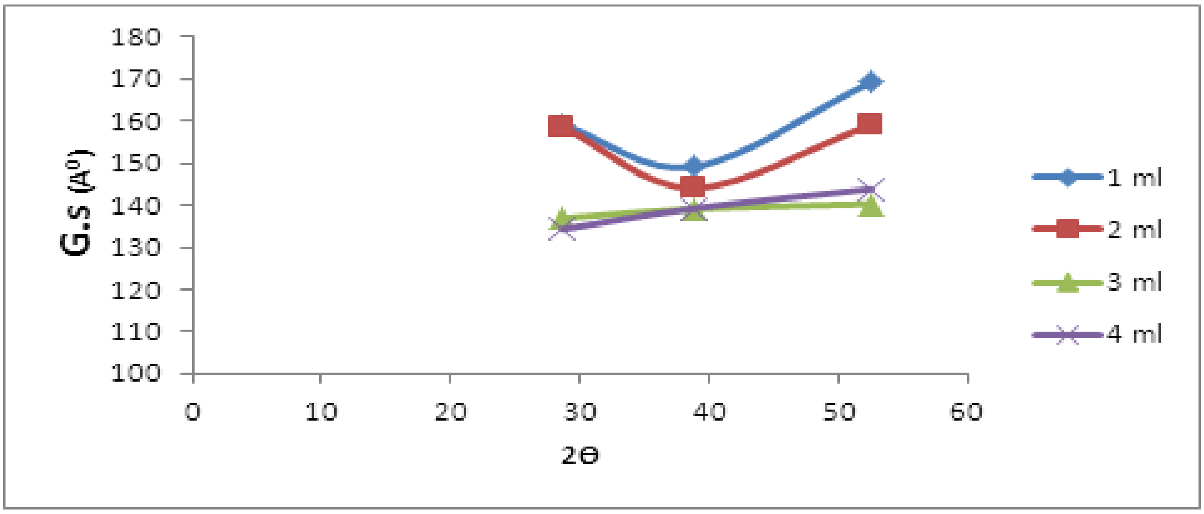

Fig. 5. The average grain size angular dependence of the doped samples at fixed weight of Lead Iodide.

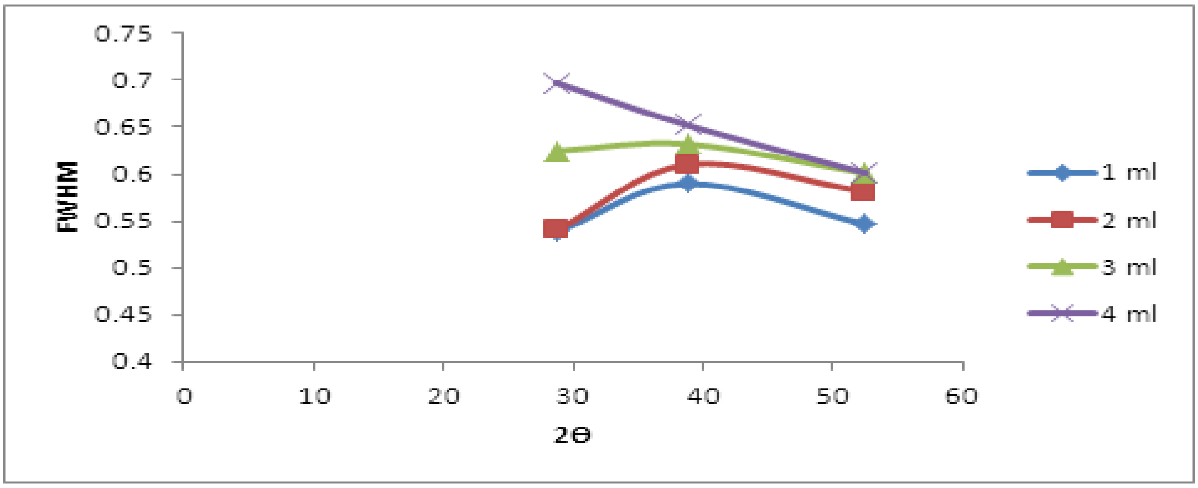

Fig. 6. Dependence of FWHM on the 2θ for doped PbI_2 films.

The absorption coefficient observed indicates the type of the transition is a direct type the band gap is calculated from the plots of the linear region of the $(\alpha h\gamma)^2$ versus $(h\gamma)$, where the extrapolation of the straight line region is used to calculate the band gap.

Figure (9) represents relationship between optical energy gaps of Lead iodide films with doping concentration. Hall mobility decreases more than three times as Al increases whereas it increases about one order of magnitude with increasing Al percentage in PbI_2 thin films deposited at Room temperature DC resistivity increases with dopant volume concentration reaching (5.082×10^8 Ω .cm) at (4ml) of Al Figure (10). The significant change of the electrical properties of Lead Iodide with introduction of Al, could be explained on the biases that influence of carrier mobility and carrier concentration reported in Figures (11) and (12) respectively.

Discussion

Figure 1 indicates that all films are poly crystallites in nature which have a strong preferred orientation along the c-axis in accordance with data reported in literature.

The additional impurity of both charges produced due to the compensation process will be the source of the so–called ionized impurity scattering for the majority free carriers and it reduces their lifetime and hence their mobility as shown in Figures (1, 2). The intensity of all reflection planes increases as the degree of crystallization increases (Street *et al.*, 2002).

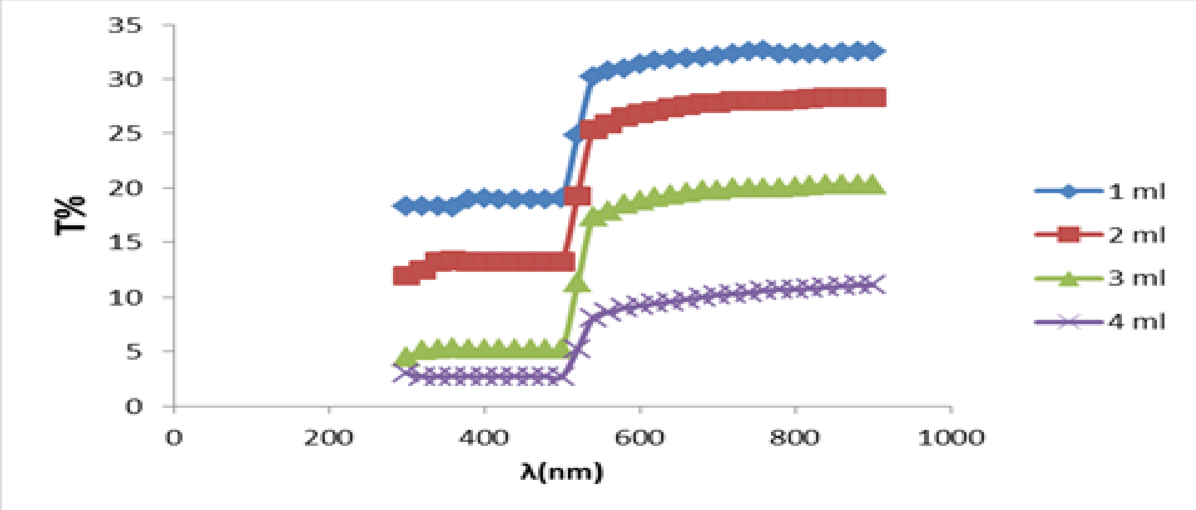

Fig. 7. Optical transmittance spectrum for doped Lead Iodide films.

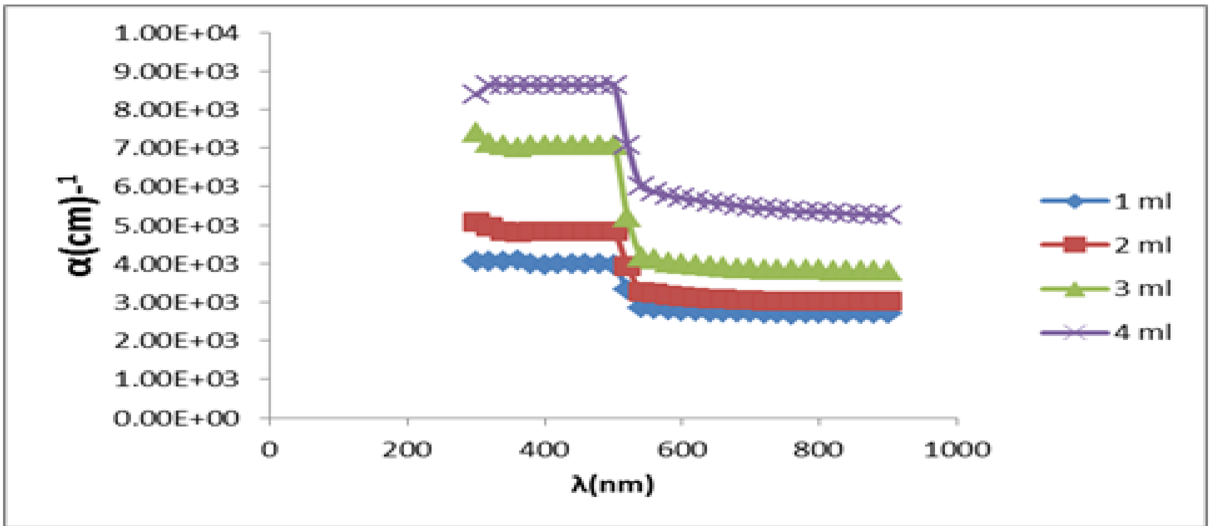

Fig. 8. Absorption coefficient as a function of incident photon energy for doped sample.

The extinction coefficient for films in Figure 3 deposited with doping concentration of (AL) (1ml) is much less than that deposited with (2, 3, and 4) at wavelength 300< λ <500nm, and sharp decrease in 500nm at IR region, this may be due to decrease the energy gap for films (Reiss *et al.*, 1988).

The constancy in the d- values in Figure 4 suggests that the lattice of the host is neither shrinking nor expanding, thus, the cell symmetry is not distributed by doping. It is clear from Figure 5 that the grain size in of the different reflections planes decreases with 2θ. This trend is more pronounced in (003) reflection plane, the increasing in the grain size in fixed doping weight could be attributed to the preferentially substitution incorporation of dopant atoms (Kucytowski and Wokulska, 2005).

The FWHM in Figure 6 increases as 2θ increase. The FWHM is larger for Al. This trend is more pronounced in (003) reflection plane. Increasing the FWHM at fixed doping weight may be due to the increasing of structural defects of the deposited film. The intensity of peaks increase with increasing the doping concentration, according to decreasing the grain size and the defects that produce due to the packing match because of impurities during deposition.

All of this could be attributing to the residual stresses that generate intrinsic defects which casing deformations like dislocations in the film.

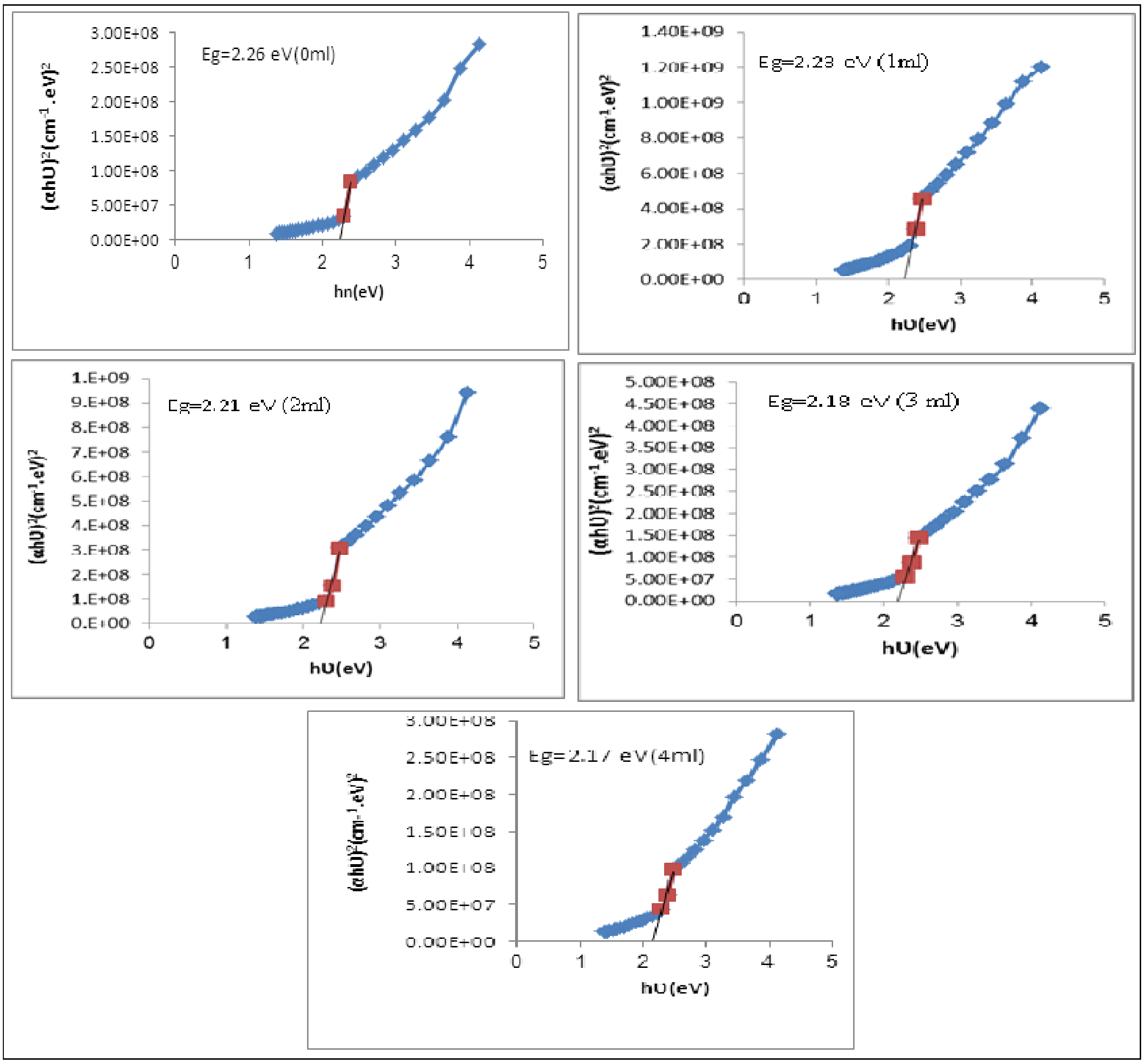

Fig. 9. $(\alpha h\gamma)^2$ versus $(h\gamma)$ plot of Lead Iodide film doped with Al.

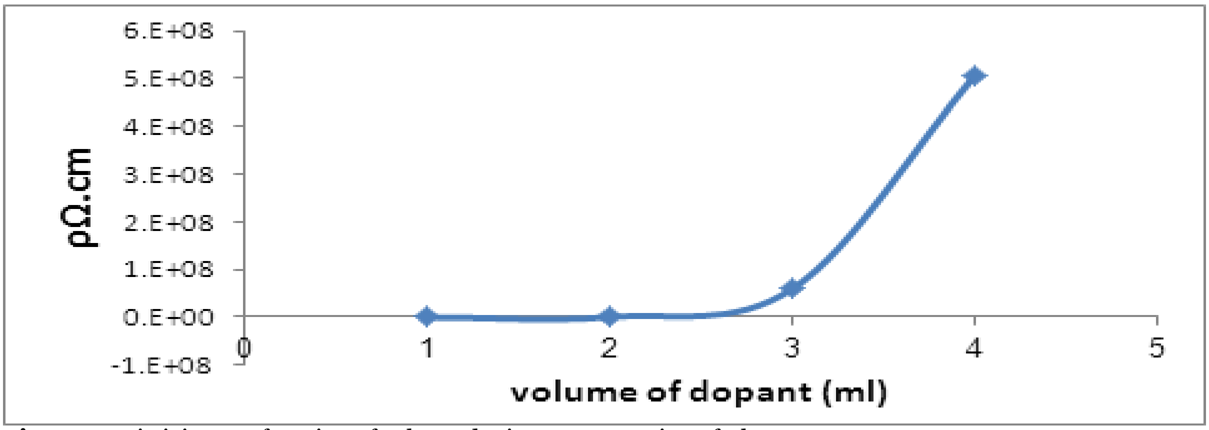

Fig. 10. Resistivity as a function of volume doping concentration of Al.

The band gap in Figure 7 decreases with adding Al to Lead Iodide films, and decreases with adding Nickel and Boron. While Figure 8 shows Increasing the doping concentration of (Al) lead to decrease energy gap may be due to creating defects or vacancies which lead to change in energy gap and also due to grain size (Hamza *et al.*, 2013).

By doping Al compensating effect, which is properly the residual shallow acceptor level (about 0.1 e .V above the valence band) and the presence of Lead vacancies (0.3 e .V) both give P-type conductivity. The net concentration of active centers is able to contribute each a free carrier and this comes from the annihilation of a concentration by compensation, which leads to a spontaneously generated, oppositely charged native defect forms, which compensates and negates the effect of intentional dopant and hence the crystal is over saturated that can limit doping.

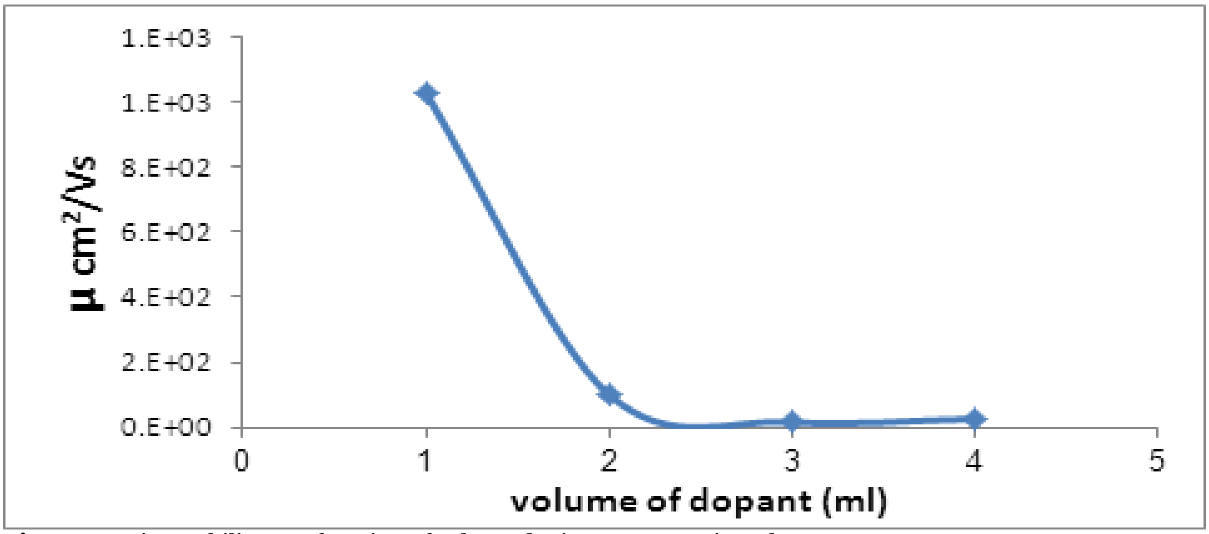

Fig. 11. Carrier mobility as a function of volume doping concentration Al.

The additional impurity of both charges produced due to the compensation will be the source of the so – called ionized impurity scattering for the majority free carriers and it reduces their lifetime and hence their mobility as shown in Figures (9, 10, 11 and 12) (Hong *et al.,* 2008).

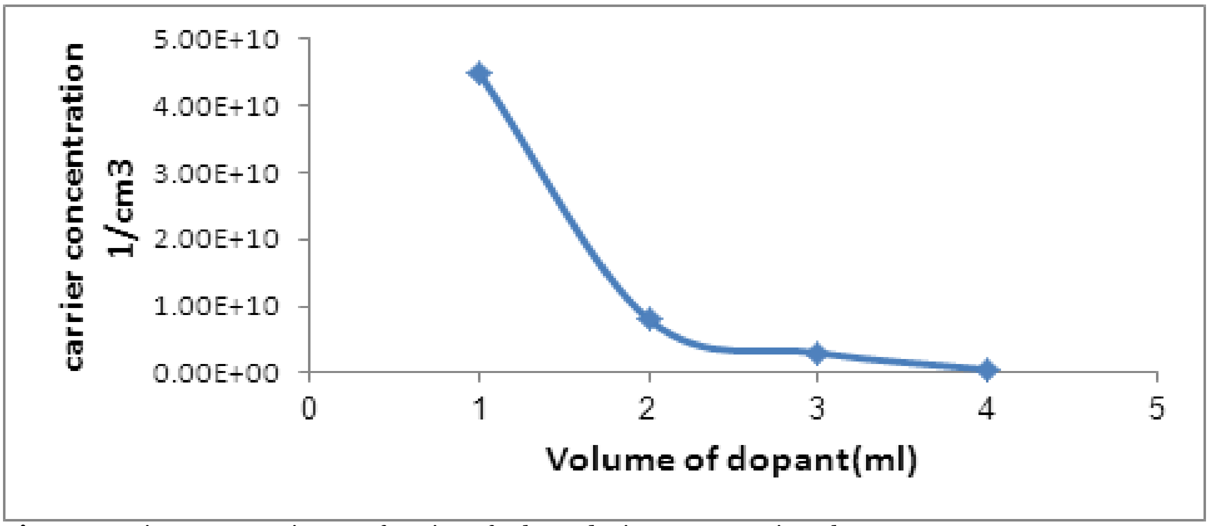

Fig. 12. Carrier concentration as a function of volume doping concentration Al.

Conclusion

Lead iodide is very toxic chemical material and hazard and harmful, thus general ventilation must be applied to control exposures to skin and eye irritants. The optical and structural properties of PbI_2 films before and after doping with Al were investigated. XRD results showed that the intensity of doped PbI_2 films of all reflection peaks Increase as the degree of crystallization increases with increasing doping concentrations.

Sharp decrease in films transmission at wavelength (550-500nm).with increasing absorption coefficient which makes it a good sensitive to X-Ray and ϒ-Ray. The electrical resistivity of films increase with increasing doping concentrations with decreasing carrier mobility.

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