The Structural Properties of Thick Film of PbI_2

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Abstract

Polycrystalline layers of Lead iodide have been prepared using a solution growth method on glass substrates for potential application to nuclear detection .This paper reports on their preliminary characterization in terms of structural properties. The influence of thickness and annealing on the structural properties has been investigated.

Keywords: PbI_2 thin film , The structural properties of PbI_2 film

الخصائص التركيبية لغشاء سميك من يوديد الرصاص PbI_2

الخلاصة

تم تحضير نماذج من يوديد الرصاص متعدد التبلور باستخدام طريقة الانمـــاء بـــالمحلول بالترسيب على قواعد زجاجيه تستخدم في تطبيقات الكواشف النووية . في هذا البحث درس اثر تغيير السمك والتلدين على الخصائص التركيبية للنماذج المحضرة

Introduction

Lead iodide PbI_2 is a wide band gap semiconductors Eg >2.3 eV . Due to the high atomic number of its elements (Z_{Pb}=82, Z_I=53), it is a material with potential use as an ionizing radiation detector (X and γ rays)*[1,2,3]* . Lead iodide is an important and promising P- type semiconductor and crystallizes in an hexagonal cadmium iodide like structure *[4],* atoms are located in layers of Pb and I perpendicular to c-axis in the succession I-Pb-I-I-Pb-I, on account of van der Walls bonding between the iodine atoms*[5]*.

The aim of this work is to prepare a thin polycrystalline lead iodide layers using a simple solution method *[6]*,and studying the structural properties of this material to present preliminary results which in this approach could be a way to develop PbI_2 nuclear imaging devices beside the electrical properties*[3]* .

Sample preparation

Polycrystalline PbI_2 layers samples were prepared on glass substrates by solution growth using PbI_2 powder prepared in the laboratories without further purification ,as checked by x-ray fluorescence the main residual impurity in the base material is Ag. The polycrystalline layers are grown by dissolving the powder in deionized water at 100 ^oC up to the limit of solubility (4.2 g/l at 100 ^oC) *[6]*. Then the solution is slowly cooled down to 0 ^oC, precipitation of small crystallites occurs rapidly. After evaporation of the excess water, thin layers (typically 3-17 μm thick) are obtained on the glass substrates. Undoped samples with and without annealing are prepared from this material. The undoped

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samples without annealing are taken in three different thickness(8.8, 12 ,14.6μm) the annealing samples for one same thickness are annealed at three different temperatures.

Structure properties

The structural properties of the layers were first investigated by using transmittance optical microscopic (TOM) and x-ray diffraction (XRD) measurements. (TOM) shows that the layers are made of hexagonal platelets parallel to the substrata planes as it is shown in figure (1,A,B). XRD were performed using a diffractrometer kind PHILIPS – PW 1840 tube copper of Nickel filter with source radiation of CuKα with (1.54 1^o) wavelength for pure, and annealed PbI_2 films recorded for a range of 2θ from 10^o to 60^o at 2^o glancing angle, the pattern of the XRD were shown in figure (2)and(3).

The main facts of all XRD patterns are the existence of the same peaks through different deposition conditions and dopants. A comparison between our results and those of the ASTM is shown in table (1)-(2). It is clear that a strong peaks are observed at (d= 6.967, 3.486, 2.332 and 1.744 A^o) which corresponds to the reflection planes (001), (002), (003) and (004) respectively, besides that in thicker samples other peaks at 2.609 and 2.010 A^o correspond to (102), (103) reflections appear respectively, the presence of these reflections indicates a high degree crystallization with a preferred orientation perpendicular to the c-axis takes place. These results are in good agreements with data achieved by others *[1,3,7]*. The diffraction patterns preliminary recorded indicates that all investigated films are polycrystalline. An accurate observation of each reflection peak for most samples reveals the presence of two less intense peaks very close to the main one (10-20°). This is probably due to the presence of polytypes *[8,9]*.

In figure (2,A,B,C) shows that the increasing the samples thickness leads to increase in the intensity of the peaks, it might be due to the higher orientation and higher crystallization, beside that a small amount of (102) and (103) reflections was observed for higher film thickness, this indicates a large number of Bragg planes and hence a higher diffraction intensity. Figure (3,A,B,C) refers to the effect of annealing on crystallization of the film. In general it shows a higher intensity peak as compared with peaks for sample without annealing having approximately the same thickness of ≈ 8-9 μm. However, the intensity of (001) peak seems to be with limited change for the three annealing temp. Annealing with 200 ^oC shows decreasing of intensity in (002),(003) and (004) reflections, this decrease in intensity could be due to the reduction in c-axis alignment of grains as observed from x-ray analysis. XRD could be used to define many parameters such the preferred orientation, and from the diffrograms one can calculate the average grain size and determine whether the deposited films suffer from stress or not. The parameters which we are studying :

(A) The lattice parameters

The lattice constants (a) and (c) were calculated using the following relationships for hexagonal crystal structure respectively [10]:

$$\frac{1}{d^2}=\frac{4(h^2+hk+k^2)}{3a^2}+\frac{l^2}{c^2}\text{.....(1)}$$

where (d) is the inter planer spacing of (hkl) planes which belong to the (001) , (002) ,(003) ,(004) ,(102) ,(103) planes in the diffraction pattern of undoped, annealed and doped samples for PbI_2 films deposited, it is found that the obtained values of lattice parameters are in a good agreement with that of the ASTM and other researches*[11]*.

From these values the influence of thickness and annealing temperature on the lattice parameters is shown in tables (1) and (2). The increase or decrease in the value of the lattice parameters in general is attributed to the residual stress which was found to be positive (tensile stress) or negative (compressive stress)*[12.13]*.

We have found that increasing thickness causes increasing in lattice parameter (c) for the preferred orientation (001) and they are larger than their values in ASTM, hence,we thought that the samples are under a compressive stress.

For the annealed samples the lattice constant for the preferred orientation decreases with the increasing temperature and its values become smaller than its values in ASTM, which indicate that the samples are under tensile stress (+) figures (4) and (5) show the behavior of the lattice parameters.

(B) FWHM (Δ)

The FWHM is an indication of the existence of dislocation in the material *[14]*. From tables (1) and (2) we can conclude the following:

For undoped samples the FWHM decrease with increasing film thickness and this may due to the better crystallization of the deposited thicker films.

The heat treatment for one hour at temperature ≤ 150 °C has no great influence for all planes except the (004) planes where the FWHM decrease. For temperature > 150°C the FWHM decreases and this is due to the decrease in the defects.

(C) Average grain size (G.S)

The average grain size is determined from the full width at half maximum (FWHM) for the most intense peak using the Scherrers formula*[14]:*

$$G.S=\frac{(0.9l)}{\Delta_{2\Theta}COS\Theta}\text{.....(2)}$$

Figure (6) shows the variation in the average grain size with deposition condition. Average grain size increases with the layers thickness indicating better degree of crystallization and this is already noticed with FWHM. Annealing with temperature (T>100°C) increase grain size.

(D) Texture coefficient (Tc)

Texture coefficient Tc is the best indication of preferred orientation , (which may be defined simply as a condition in which the distribution of crystals orientation is nonrandom), the fabricated film is calculated using relation *[15]*:

$$Tc(hkl)=[(I(hkl)/I_o(hkl)]/[N_r$$

$$/[N_r^{-1}\sum I(hkl)/I_o(hkl)]\text{.....(3)}$$

Figure (7) shows the influence of different deposition condition on (Tc).We think that our results indicate that for pure PbI_2 there is a value of preferred orientation produced by the forming process

itself, it is due to the tendency of the grains in a polycrystalline aggregate to rotate during their growth in complex way that is determined by imposed force adjoining the grains , the result is a preferred orientation. For samples with different thickness the preferred orientation or Tc is (001), it is found that texture becomes stronger with increasing thickness, and with higher thicknesses of crystals are rearranged with a higher orientation distribution relative to the increasing in grain size. For the annealed samples the preferred orientation or Tc is in (001) plane and its value increases when the annealing temperature is increased, this means that annealing operation increases the arrangements of preferred orientation or reduces the degree of disorder, this is in agreement with the results for PbI_2 in *[16],* and it may decrease the stress which accompanies an increase in grain size. this causes more symmetrical or uniform in film smoothness *[17].*

It is thought that these results can be explained in terms of distraction of randomly distributed stacking faults and the nucleation of new set of ordered stacking faults ,or the migration of extended defects to a more stable configuration can be also adopted *[16]*.

(E) Micro strain (d**)**

When a polycrystalline piece is deformed by any force effect , slip occurs in each grain causing a change in shape , becoming flattened and elongated in the direction. Beside each grain retains contact on its boundary surface with all its neighbor, and because of this interaction between grains , no single grain in a polycrystalline mass is free to deform in the same way as an isolated crystal would , if subjected to the same deformation acts . As a result of this restraint by its neighbors, a plastically deformed grain in a aggregate solid usually has regions of its lattice left in an elastically bent or twisted condition or, more rarely, in a state of uniform tension (+) or compression (-) *[18].* The micro strain depends directly on the constant (c), and its value related to the shift from the ASTM standard value ,and could be calculated using the relation below:

$$d = [|C_{ASTM} - C_{XRD}| / C_{ASTM}] * 100\% \quad .....(4)$$

Generally there is increase in the value of the lattice parameters for the preferred orientation (001) with higher thickness, which means that increasing thickness makes the samples under the effect of compression strain (-) as compared with the state of smaller thickness where the strain is (+) as shown in figure(8).

Conclusions

The X- ray diffraction analysis confirm that PbI_2 films are polycrystalline, having hexagonal structure. The inception of the data for undoped thin film of lead iodide indicates that the observed (d) values closely matched with the existing standard values for hexagonal structure. The low fluctuation in the value of structure parameters are due to the fluctuation in lattice parameters which is attributed to the stress (positive or negative) which is accompanies with the increase or decrees in grain size .The reproducibility in making thin films of PbI_2 is very good by the present method.

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Table (1) The structural values with different thickness for undoped layers PbI_2 with ASTM

Samples	2q	d_{XRD} (A^o)	d_{ASTM} (A^o)	hkl	FWHM (deg.)	a_{XRD} (A^o)	c_{XRD} (A^o)	Average G.S (A^o)	Tc	d%
Undoped PbI_2 8.8mm	12.5	6.967	6.98	001	0.85	4.549	6.967	93.6033	1.621	0.18
	25.5	3.486	3.489	002	0.76	4.552	6.972	106.9174	0.184	0.085
	38.5	2.332	2.325	003	0.79	4.544	6.96	110.4887	1.205	0.30
	52.3	1.744	1.743	004	0.79	4.555	6.976	116.1808	1.012	0.04
Undoped PbI_2 12mm	12.5	7.040	6.98	001	0.76	4.547	7.04	105.6621	2.264	-0.85
	25.5	3.446	3.489	002	0.96	4.597	6.969	85.6836	0.410	0.12
	34.2	2.609	2.614	102	0.57	4.536	6.947	154.3580	0.373	0.43
	38.5	2.326	2.327	003	0.76	4.603	6.978	110.5347	1.476	0.042
	45.0	1.999	2.0052	103	0.57	4.559	6.955	155.1416	0.286	0.40
	52.3	1.741	1.7449	004	0.76	4.589	6.964	117.0611	1.232	0.22
Undoped PbI_2 14.6mm	12.5	7.017	6.98	001	0.5714	4.582	7.017	147.9230	1.938	-0.53
	25.5	3.446	3.489	002	0.9523	4.550	6.969	85.6325	0.484	0.12
	34.2	2.615	2.614	102	0.3809	4.557	6.979	218.4601	0.358	-0.02
	38.5	2.333	2.327	003	0.57	5.550	6.969	151.7105	1.589	0.17
	45.0	2.010	2.0052	103	0.3809	4.541	6.955	226.606	0.271	0.46
	52.3	1.747	1.7449	004	0.666	4.555	6.96	133.1503	1.357	0.27

Table (2) The structural values at different annealing temp. for undoped PbI_2 with ASTM

Samples	2q	d_{XRD} (A^o)	d_{ASTM} (A^o)	hkl	FWHM (deg.)	a_{XRD} (A^O)	C_{XRD} (A^o)	Average G.S(A^o)	Tc	d%
Undoped PbI_2 50 ^oC 1h	12.5	6.989	6.98	001	0.76	4.564	6.989	104.4683	1.509	0.64
	25.5	3.476	3.489	002	0.57	4.539	6.952	142.6012	0.183	0.37
	38.5	2.332	2.327	003	0.66	4.568	6.996	126.3774	1.283	-0.21
	52.3	1.744	1.7449	004	0.76	4.555	6.976	116.2143	1.023	0.04
Undoped PbI_2 150 ^oC 1h	12.6	6.967	6.98	001	0.76	4.555	6.967	104.9427	1.520	0.18
	25.4	3.496	3.489	002	0.57	4.565	6.992	146.8150	0.188	-0.20
	38.6	2.325	2.327	003	0.66	4.556	6.975	151.707	1.257	0.08
	52.4	1.743	1.7449	004	0.76	4.557	6.972	132.9350	1.030	0.05
Undoped PbI_2 200 ^oC 1h	12.5	6.979	6.98	001	0.71	4.588	6.979	113.3894	1.550	0.143
	25.5	3.476	3.489	002	0.55	4.539	6.952	148.0676	0.188	0.37
	38.5	2.332	2.327	003	0.53	4.568	6.996	157.9038	1.287	-0.21
	52.3	1.744	1.7449	004	0.57	4.557	6.976	155.06911	1.051	0.04

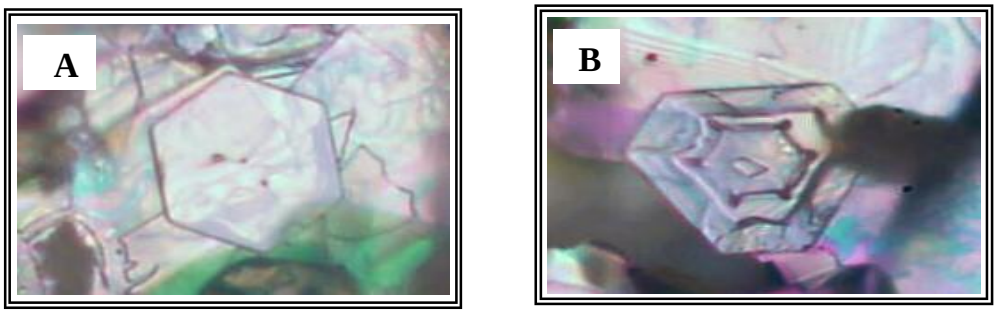

Figure (1) (A ,B) Optical transmission microscopic showing PbI_2 platelets (x=540)

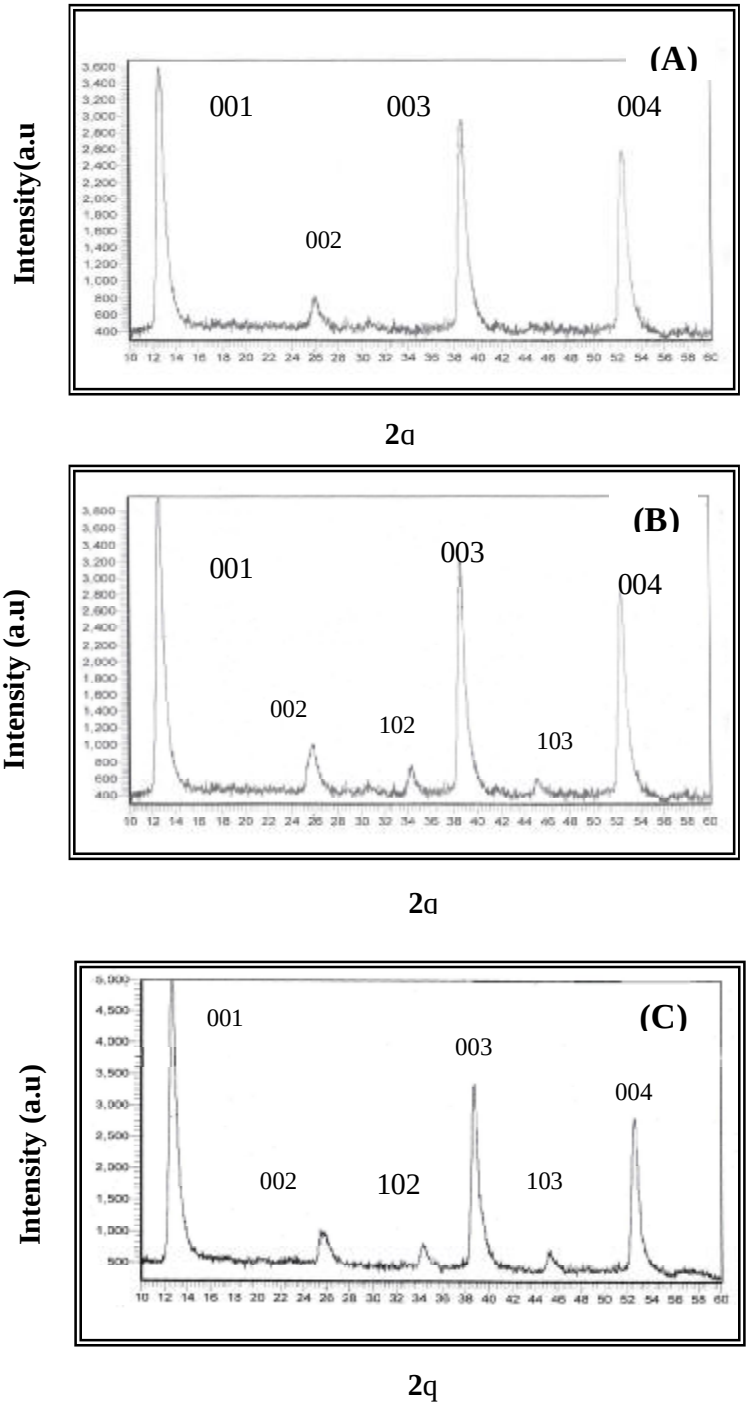

Figure (2,A,B,C) XRD spectrum of pure PbI_2 sample as a function of thickness (A) 8.8 μm, (B) 12 μm, (C) 14.6μm

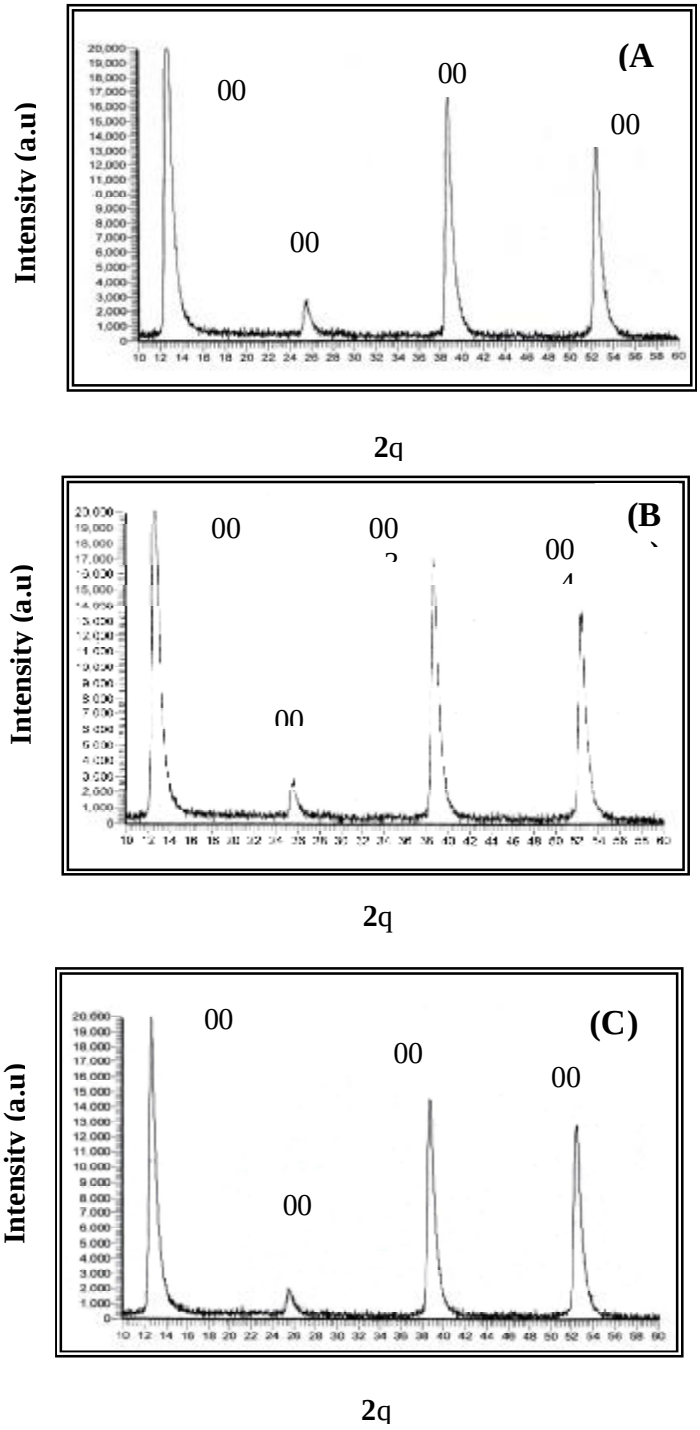

Figure (3)Fig (3,A,B,C) XRD spectrum of annealed PbI_2 sample as a function of annealing temp for 1hr ,
(A) 50 °C, (B) 150 °C, (C) 200 °C

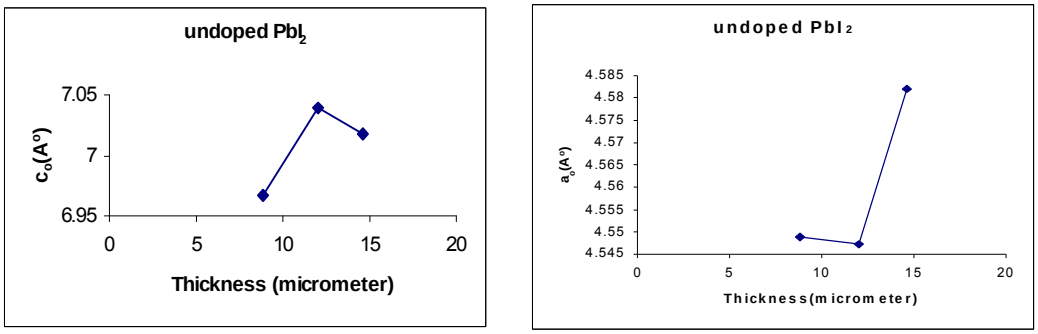

Figure (4) Lattice parameters of different thickness undoped PbI_2 samples

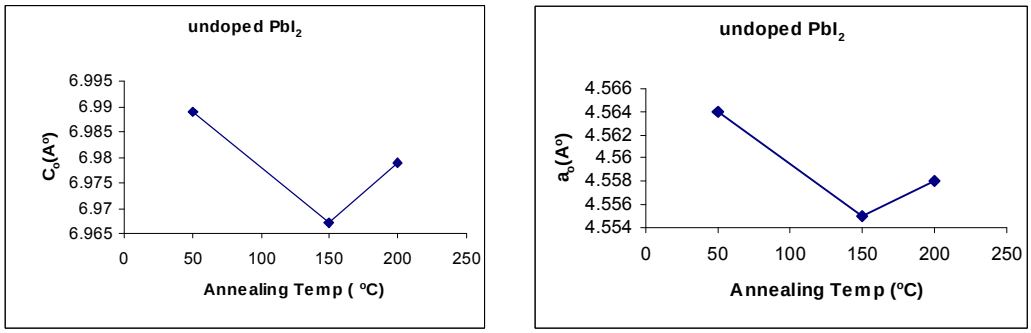

Figure (5) Lattice parameters of annealing undoped PbI_2 samples

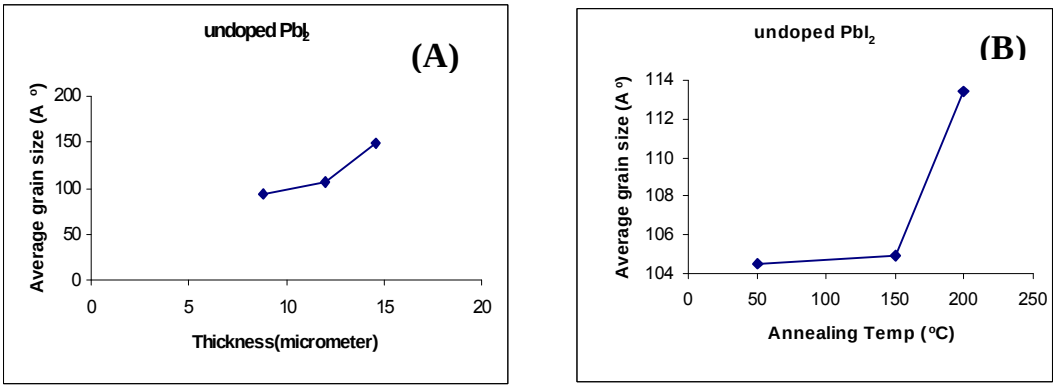

Figure (6) Variation in average grain size with (A) thickness, (B) annealing temp

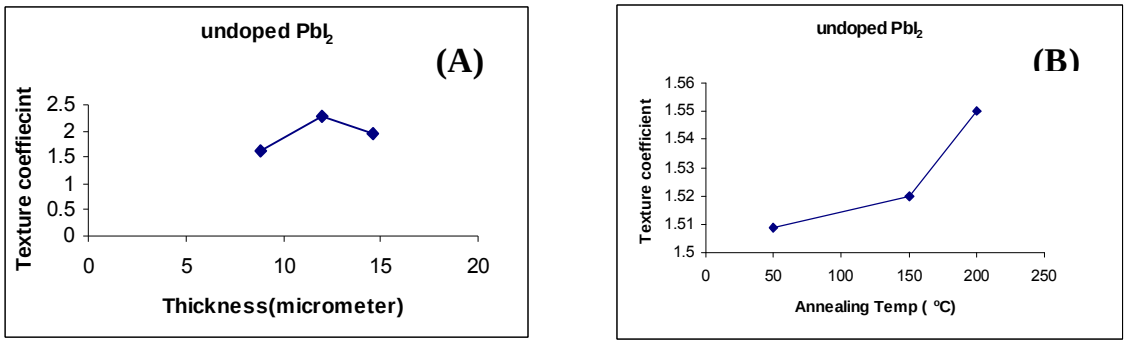

Figure (7) Variation in texture coefficient with (A) thickness, (B) annealing temp.

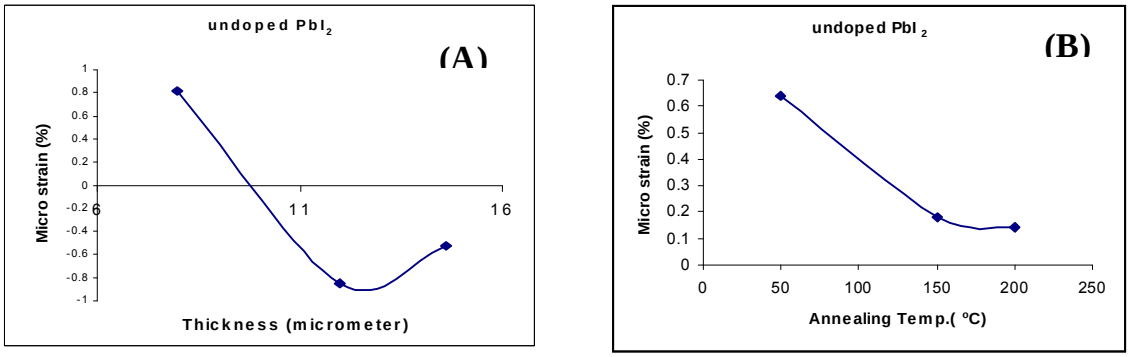

Figure (8) Variation in Micro strain with (A) thickness, (B) annealing temp.