# X-RAY LINE PROFILE ANALYSIS OF ANNEALED PbTe THIN FILM

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## ABSTRACT

*Crystallite size, microstrain and dislocation densities of annealed PbTe thin films were determined by using X-ray diffraction line profile analysis. The results at room temperature showed anisotropy in both crystallite size and microstrain along [100] and [111] directions. moreover, the rate of change of crystallite size and microstrain with temperature did not behavesimilarly. These microstructural defects were discussed in term of oxygen diffusion into interstitial holes of the Fcc pbTe structure. The values of the dislocation densities were also found to vary anisotropically along [100] and [111] directions. A phase separation of lead oxide was found at a temperature around 200°C.*

## INTRODUCTION

Thin films are easily affected by variety of defects (concentration variation, microstrain, crystallite size, stacking fault, antiphase domain ..... etc). These defects markedly influence the physical properties of the materials deposited on thin films. The studies of the various defects of thin films are essential for a proper understanding of the film behaviour and accordingly a proper characterization of its physical properties.

The shape and width of a powder diffraction line is very sensitive to the variation of any microstructural defects, so the line profile analysis is used in this work in order to study the types and determine the values of crystallite size, microstrain and dislocation densities present in thin film of PbTe and also to see the effect of annealing temperature on the variation of these defects.

PbTe thin films have high prospects for many applications and its physical properties have been investigated by many works [1-6]. Anamolous discripancies in some of the electrophysical properties of annealed PbTe thin films have been reported, which was explained as a result of the adsorped oxygen molecules during that treatment. The present work is intended to show the effect of introducing oxygen by annealing on the microstructural changes produced in thin films of PbTe.

## 2 - EXPERIMENTAL

PbTe thin films were deposited on clean silica glass substrates by the conventional method of thermal evaporation under vacuum. The rate of deposition was kept low (2 to 5 nm $min^{-1}$) for ensuring uniformity of deposition and a lower density of structural defects in the films. The lateral dimensions of the films were 4 cm x 2 cm. The thickness (198 nm) was measured by using quartz crystal monitor during deposition and by multiple-beam Fizeau's interference method. Four films were prepared under the same conditions to avoid unwanted effects. The films were annealed for the films using the step-scanning method with a step width 0.02' in 2θ and a counting time of 20 seconds per step.

## 3. ANALYTICAL PROCEDURE :

In order to investigate the nature of structural imperfections, reliable parameters defining the positions, breath and shape of all accessible Bragg reflections are required. The technique adapted in this work is as follows :

The measured diffraction profiles were first analyzed with a deconvolution program [ 7] in order to extract the pure, only structurally broadened, diffraction lines. The pure diffraction profile was represented by a Pearson type VII function as :

$$Y(2\theta_i) = I_o \left[1+F(2^{1/m}-1)\frac{(2\theta_i - 2\theta_o)2}{w}\right]^{-m} \qquad [1]$$

where $2\theta_o$ is the peak-maximum position, $I_o$ is the intensity at $2\theta_o$, m is a shape parameter, W is the full width at half maximum and F is an asymmetry function given

by Windsor et al. [ 8]. The goodness of the profile fit is estimated by relaiability index (R) defined as

$$R = \left[ \frac{\Sigma w_i [H(2\theta)_{i\,obs} - H(2\theta i)_{calc}]^2}{\Sigma w H(2\theta_i)^2_{obs}} \right]^{1/2} \qquad [2]$$

where Wi is an appropriate weight usually taken as 1/H $(2\theta_i)$ obs, wher $H(2\theta_i)$obs are observed data points before background subtraction [ 7].

Separation of the crystallite size and microstrain was then carried out applying the single-line method developed by Keijser et al. [9 & 10]. The volume-weighted average crystallite size (P) and the microstrain measure (e) are given by

$$p = \frac{\lambda}{\beta f_c \cos\theta} \qquad [3]$$

$$e = \frac{1}{4}\, \beta^f_G\, (e_1 m^{-1} + e_2 m^{-2}) \qquad [4]$$

where $\beta^f_c$ and $\beta^f_G$ are the integral breadths of the Cauchy and Gaussian components of the pure profile, $\lambda$ is the wavelength of the readiation employed $\theta$ and is the Bragg angle. $\beta^f_c$ is assumed to be solely due to finite crystallite size and $\beta^f_c$ is solely due to microstrain. Both are obtained in terms of the integral breadth ($\beta$) and the shape parameter (m) of the pure profile as [ 10] :

$$\beta^f_G = \beta\, (e_1 m^{-1} + e_2 m^{-2}) \qquad [5]$$

$$\beta^f_G = \beta\, (f_0 + f_1 m^{-1} + f_2 m^{-2} + f_3 m^{-3}) \qquad [6]$$

where $e_1$, $f_0$, $f_1$, $f_2$, and $f_3$ are constants given by Keijser et al. [ 10], b and m are obtained from the deconvolution of the measured diffraction profiles.

Single-line methods are dubious in many respects, however, the drawbacks of their applications are far less serious in relative determinations than in determinations on absolute scale [ 11]. This holds in particular if changes occure in either size or strain which is the case of this study.

Since both crystallite size and microstrain are manifestation of the dislocation network in the films, the dislocation density (ρ) as shown by Williamson et al. [ 12] can be written (under certain simplified assumptions) as :

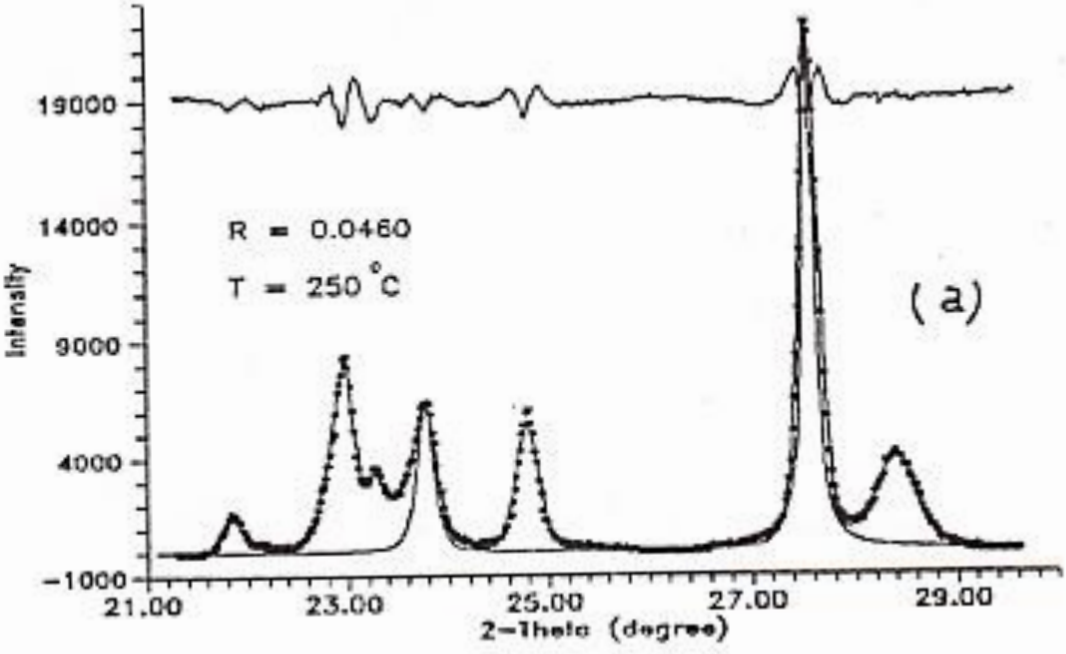
$$\rho = \frac{2\sqrt{3}\,e}{bp} \qquad [7]$$

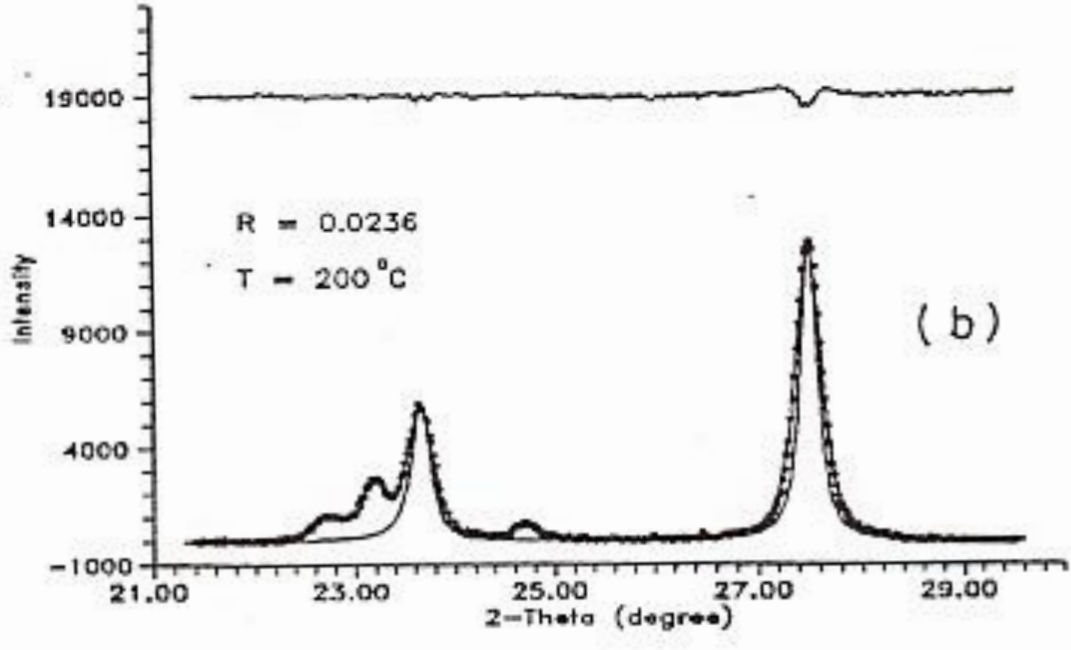
where b is the Burgers vector associated with the Buyrgers circuit. If it is further assumed that $b = a_o$, the lattice parameter of the bulk sample, ρ can be easily calculated which gives the length of the dislocation line per unit volume.

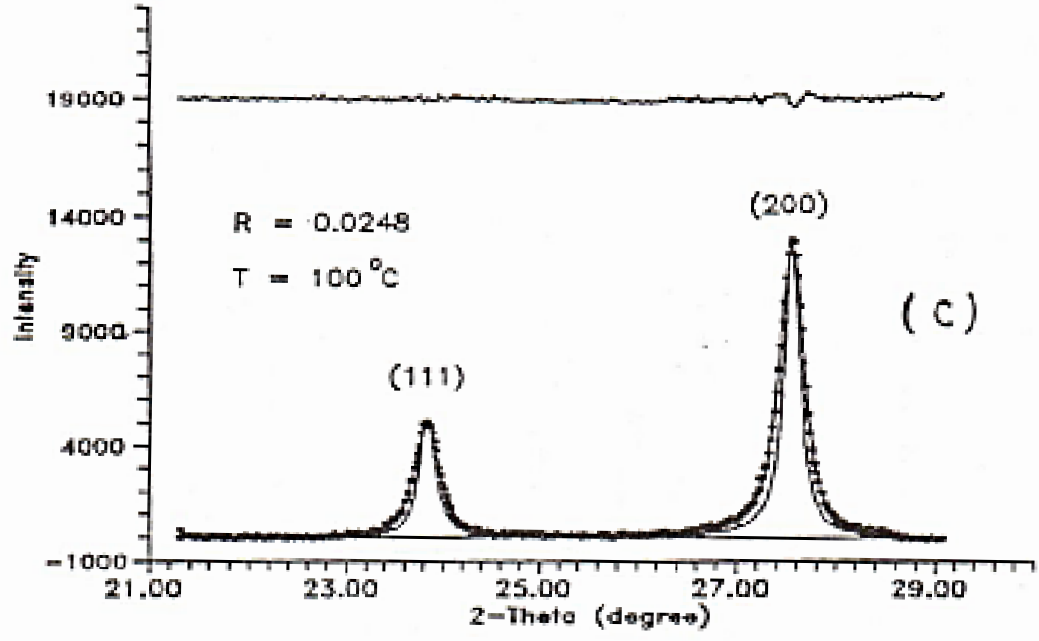
## 4. RESULTS AND DISCUSSION :

The deconvolution of the Bragg reflections (111) and (200) at different annealing temperatures are shown in figure 1. It can be seen that all films analyzed are of the standard polycrystalline PbTe patterns. However, some new lines started to develop at a temperature around 200°C and a complete pattern for this new phase appeared at 250°C. This new phase as Pb is much more probable for oxidation than Te from the activation energy point of view, this new phase didnot correspond to any of the known lead oxides phases so far.

Values of the extracted apparent crystallite sizes, microstrain and dislocation densities at different temperatures for the reflecting planes(111) and (200) are given in table 1. Inspection of these value showed that the crystallite sizes extracted from (111) are significantly less than those from (200), this is realy understandable if there is a preferred orientation for the (100) plane. This was found to be a characteristic properties of lead salts as pointed out by Zemel (1969) and was confirmed in this work by measuring the ratios of the integrated intensities $I_{200}/I_{111}$ and $I_{200}/I_{200}$ for the thin films and for the bulk and by comparing them together it was evident that for thin films PbTe crystallities prefer to have (100) oriented growth. Figure 2 shows the variation of the crystallite size with annealing temperature, again there is a considerable increase in the crystallite size along the (100) direction whereas the increase along (111) is negligible in comparison. This finding again confirm still the oriented growth along the (100). On the other hand the results of the microstrains


19000
14000
9000
4000
-1000
Intensity
R = 0.0460
T = 250 °C
(a)
21.00
23.00
25.00
27.00
29.00
2-Theta (degree)


19000
14000
9000
4000
-1000
Intensity
R = 0.0236
T = 200 °C
(b)
21.00
23.00
25.00
27.00
29.00
2-Theta (degree)



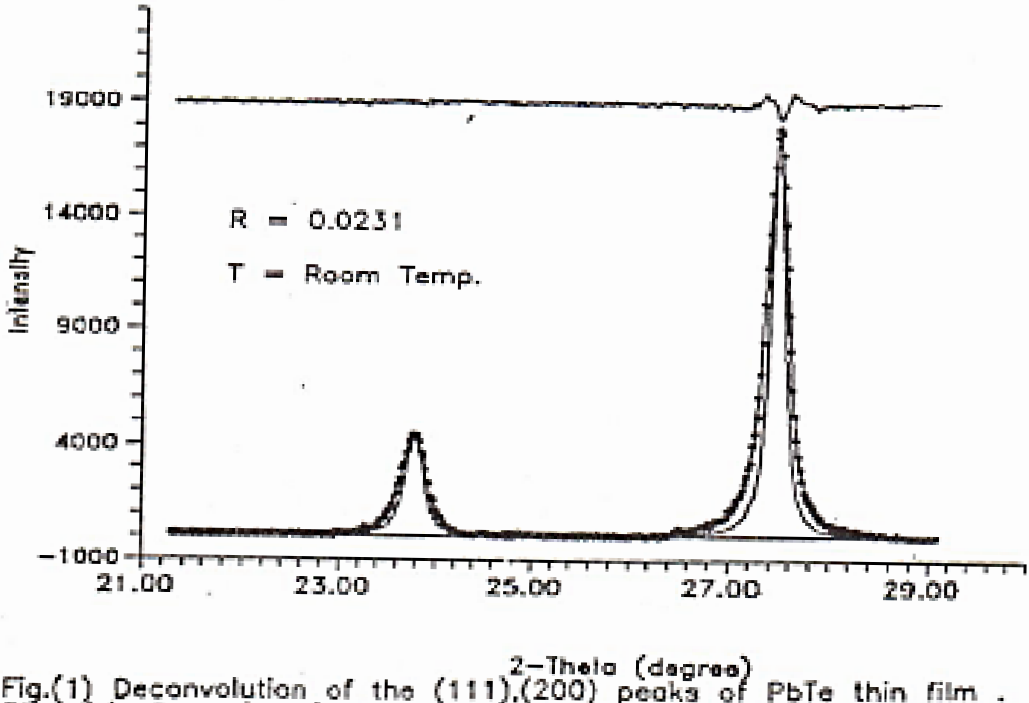




Fig.(1) Deconvolution of the (111),(200) peaks of PbTe thin film . Obs. (•); Calc. (solid); and pure profile (solid).

behave totally different as shown from table 1 and figure 3. At room temperature, strain in the (111) direction is smaller than that along (200) direction. This finding may be due to strain gradient at the substrate-film interface, since most of the crystallite have their (100) planes parallel to the substrate. However, the rate of increase of the strain with temperature and also the rate of decrease is much larger along (111) than (200). Figure 3 shows this difference in the rate of increase and decrease. These observation may be explained if we consider the diffusion of the oxygen to be increased by annealing and to be interstitially diffused into PbTe lattice. PbTe is (fcc) structure with eight interstitial holes in the crystal lattice. These holes are available for oxygen diffusion and are located in pairs along the cube diagonals symmetrical with respect to the unit cell center, i.e. with, tetrahedral symmetry. By raising the temperature the oxygen will diffuse into the interstitial site of PbTe lattice and this in turn will disturb the local and the surrounding configurations and gives rise to an increase in the microstrain. The more the temperature increase in the more the oxygen diffuse and accordingly the more the occupancy of the tetrahedral holes by the oxygen atoms[7]. This increase in oxygen diffusion will certainly increase the microstrain in the lattice and some of them may replace some of the Te atoms that may evaporate. This process will continue by increasing the annealing temperature untill a temperature is reached around 200°C at which phase separation of lead oxide occurs. This phase dissociation inhibit oxygen diffusion and markedly reduces the microstrain to a limit far more below those values of room temperatures along (111) and (200) as can be seen from figure 3. This large decrease in microstrain is due to annealing effect after phase separation. Dislocation denstities (ρ) calculated from equation (7) at different temperature are given in table 1. It can be seen that at room temperature the dislocation densities (ρ) are nearly of the same order along both direction (111) and (200), but it decreases with the temperature continuously along the (100) direction whereas along the direction (111) it. firstly increase up to 150°C and then decreases sharply. This result is in accordance with the microstrain results discussed before. This increase in the dislocation densitities is due to the creation of the antiphase domain created by the introduction of oxygen atoms into the tetrahedral interstitial sites and also due to the creation of stacking faults caused by the

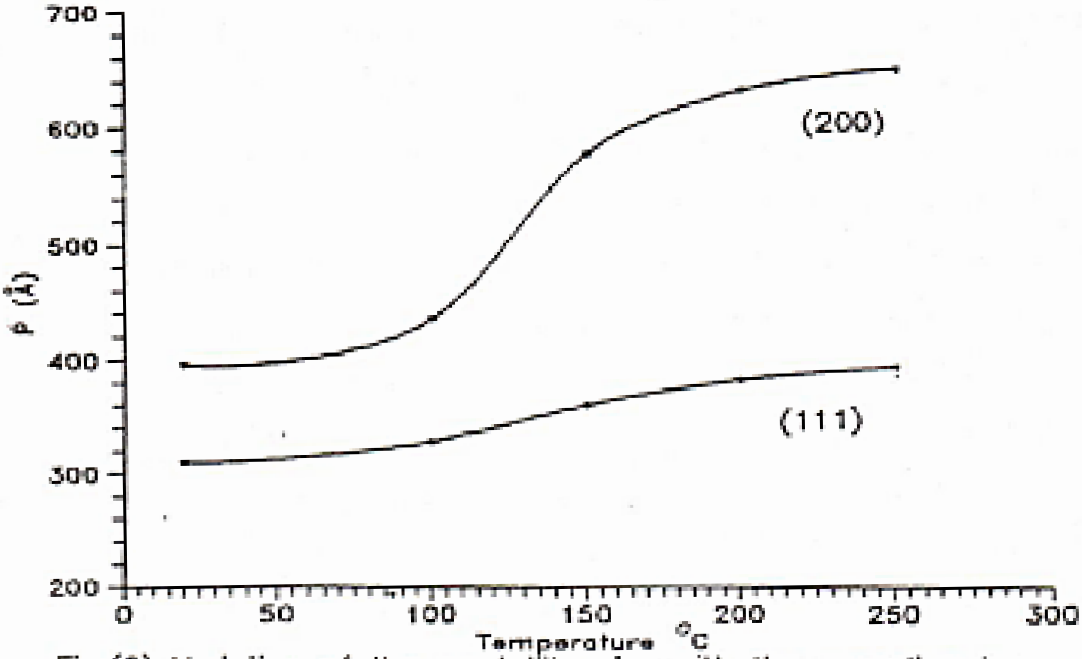



Fig.(2) Variation of the crystallite size with the annealing temp. of PbTe thin films.

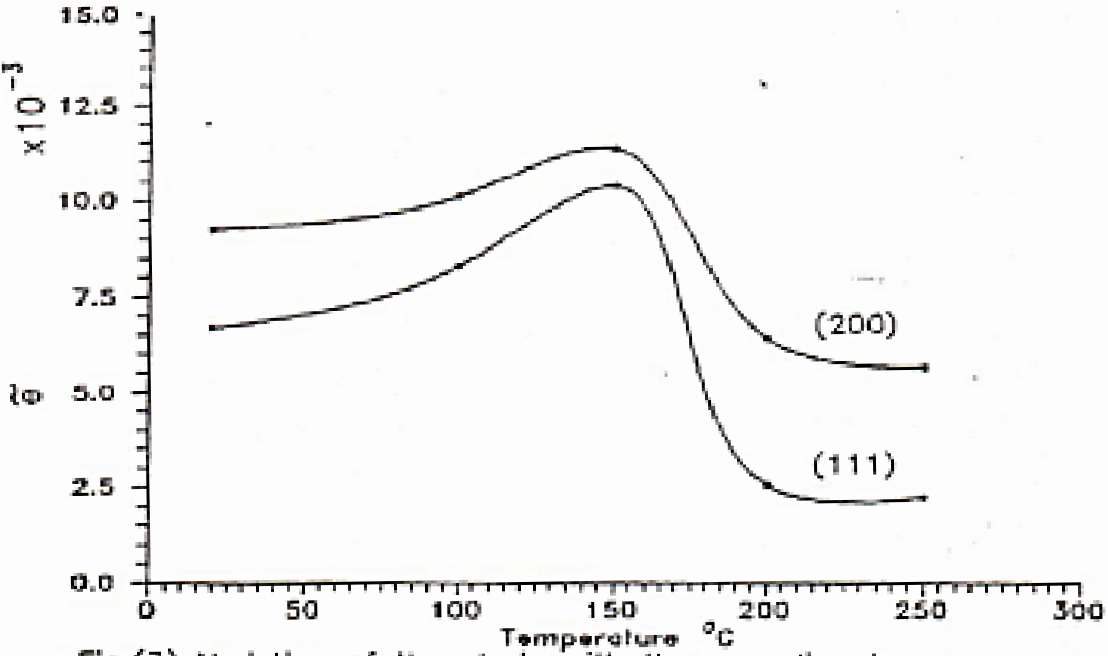



Fig.(3) Variation of the strain with the annealing temp. of PbTe thin films.

distrubance in the local ordering. But at phase separation of lead oxide the PbTe structure goes back to its standard structure and the dislocation densities decrease again to a value less than those at room temperature due again to annealing effect.

## 5 - CONCLUSION :

Annealing PbTe causes oxygen to diffuse into the tetrahedral interstitial holes. This diffusion causes increase in microstrain and disloction densities along (111) direction up to a temperature just below the lead oxide phase separation after which a sudden decrease in microstrain and dislocation densities were markedly sharp. Crystallite size increase with annealing temperature than those along (111). This was due to the preferred orientation growth along (100) and annealing effect enhanced this growth. At 200°C a new phase of lead oxide was developed.

| Temp°C | Apparent Crystallite size ( ) | | Strain ($10^{-3}$) | | Dislocation density ($m^{-2}$) x $10^{15}$ | |
|---|---|---|---|---|---|---|
| | (100) | (111) | (100) | (111) | (100) | (111) |
| Room | 397 | 311 | 9.28 | 6.68 | 1.257 | 1.115 |
| 100 | 436 | 329 | 10.13 | 8.32 | 1.249 | 1.360 |
| 150 | 579 | 361 | 11.36 | 10.41 | 1.055 | 1.550 |
| 200 | 632 | 383 | 6.43 | 2.59 | 0.547 | 0.364 |
| 250 | 651 | 395 | 5.68 | 2.27 | 0.469 | 0.309 |

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