

Evaluation Of Microstructural Paramaters Of The Synthesised Γ -Teo2 Nanocrystals Using Xrd Principles

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-----Abstract-----

The synthesised γ -TeO₂ nanocrystals have been indexed in orthorhombic system with lattice energy 81.21 eV. Strain is caused by the presence of dislocations. This has possibility to have dislocations in nanoscale has little significance. The X-ray peak profile study provides peak broadening and asymmetric peak shapes and to understand the micro structural parameters for crystallite size and strain. Present work deals with systematic application of Hall-Williamson method for crystallite size estimation, and the modified Williamson-Hall plot and the modified Warren-Averbach methods yielded physically well justified data for particle size and dislocation densities. The reflections {020}{151} and {002} have the same peak breadth and reflections while {120}{101}{200} and {122} have more or less same peak breadth. The successful application of the new procedures have indicated that even in nanocrystalline particles dislocations are present.

Keyword: Lattice energy, Micro structural parameters, Crystal size and strain, Nanocrystalline particles dislocations.

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I. Introduction

The microstructure of nanomaterials and its relation to macroscopic properties is essential for the development and application of nanomaterials. The structure of TeO₂-based glasses, are promising materials for use in optical fibre or in non-linear optical devices [1]. X-ray diffraction is a promising tool for structural analysis of solid or amorphous materials and approaches such as use of Sherrer equation, integral breadth analysis, single-line approximation, Hall-Williamson method, etc., have been developed for estimation of crystallite size. Numerous experiments have shown that the strain broadening caused by dislocations can be well described by a special logarithmic series expansion of the Fourier coefficients of Bragg reflection peak profiles. X-ray diffraction peak profile analysis is used for the characterization of microstructure either in the bulk or in loose powder materials, which is a nondestructive method yielding a series of interesting microstructural parameters[4]. Present work deals with systematic application of Hall-Williamson method for the estimation of crystallite size and the strain [2] of the synthesised γ -TeO₂ nanocrystals. Also incorporation of the classical methods of Williamson – Hall and Warren –Averbach and the modified Williamson – Hall and modified Warren Averbach methods, for the analysis of particle size and dislocation densities as suggested by Ungar[3] have been attempted for γ -TeO₂.

II. Experimental

Grey color Tellurium metal was mixed in lime water (10ml) and 16 drops of nitric acid was added to it, and after a day, yellow color mineral tellurium dioxide was obtained at room temperature. After 20 days grown crystals were filtered and dried at room temperature. Lime water helps to spread the ions evenly.

III. Results And Discussion

2.1 Powder XRD pattern

The powder sample subjected to X-ray diffractometer within 2 θ range of 20-60 at a scan speed of 7° per minute using a Cu target and Cu-K α radiation of 0.15406 nm wavelength at a powder rating of 40kV, 40mA using Bruker D8 diffractometer. The XRD pattern (Fig. 1a) has been indexed in Table 1 falls in the orthorhombic system whose unit cell parameters are tabulated in Table 2.

A bar diagram is drawn between I/I_{\max} and δ , which is shown in Figure- 1b, suggests that for the plane {020} the density of atom is high compared to other planes and the least in the plane {15 1}. The density of atoms present in one plane is calculated from the formula $\delta = \frac{dN}{V}$, where d is the spacing between each plane, N the number of atoms in the unit cell and V the volume of the atom[6].

2.2 Cohesive energy of ionic crystal γ -TeO₂

Cohesive energy of an ionic crystal can be determined used even if the crystal structure is not known with the help of Kapustinskii equation [15]. Kapustinskii noted an empirical increase in the value of Madeling constant, A, as the coordination number of the ions in the molecular formula of the compound. Any deviation in the rule is compensated by a consequent change in the value of R_e (the sum of the ionic radii for the cation and anion) and the reduced Madelung constant proposed by Kapustinskii (A divided by the number of ions in the formula) to calculate the lattice energy of an ionic crystal to a good approximation, no matter what its geometry may be. Kapustinskii collected the reduced Madeulang constant [15], the length conversion factor, and the energy conversion factor into a simple form of lattice energy equation U.

$$U = \{ Z_c Z_a 287.2 v / (r_a + r_c) \} * \{ 1 - (0.345 / (r_a + r_c)) \} \text{ kcal/mol} \quad \text{--- (1)}$$

where Z_c, Z_a are the charge on cation and anion, $r_a + r_c$ the ionic radii, and v the number of ions in the molecule. This is calculated to be 81.21eV for γ -TeO₂.

2.3 Methods of profile analysis

For the case that the strain is caused by dislocations, Wilkens computed the mean square strain, assuming that the dislocations are ‘restricted randomly’ and distributed [7][8][9],

$$\langle \epsilon_{g,l}^2 \rangle = \frac{\rho C (b \cdot b)}{4\pi} \ln \left\{ \frac{R_e}{L} \right\} \quad \text{--- (2)}$$

where the b is the length of burger vector, ρ the dislocation density, R_e the outer cut-off radius and C is the contrast factor of the dislocations. The contrast factor depends on the relative orientation of line-burgers- and diffraction vector as well as the elastic constants of the material. Because of the actual dislocation distribution in a sample, it is necessary to average over the screw dislocations, different slip systems and orientation of the slip system with respect to the diffraction vector, denoting the average contrast factor by C. Ungar and Tichy [10], showed that for cubic or hexagonal crystals, if the burgers vector distribution is completely random, the dependence of C on the hkl can be explicitly calculated. The intensity of the profile is given by the convolution of size and strain broadening. Thus in Fourier space, it is possible to separate the contributions via the well known Warren-Averbache equation .

$$\ln A_L = \ln A_L^S + \ln A_L^D \quad \text{--- (3)}$$

Here A_L are the Fourier coefficient computed from the profile, A_L^S and A_L^D are the coefficients associated with size broadening and strain broadening respectively. The strain broadening coefficients are computed using the relation

$$A_L^D = \exp (-2\pi^2 L^2 g^2 \langle \epsilon_{g,l}^2 \rangle) \quad \text{--- (4)}$$

where L is the Fourier length, g is the diffraction vector and $\langle \epsilon_{g,l}^2 \rangle$ is the mean square strain. It depends on the diffraction order and vanishes for $g^2=0$.

Inserting Eq.(4 & 5) in Eq.(3) gives the modified Warren–Averbach equation [11].

$$\ln A_L = \ln A_L^S + \frac{\pi}{2} L^2 b^2 \rho C \ln \left(\frac{R_e}{L} \right) \quad \text{--- (5)}$$

If the strain is caused by dislocations, then the modified Warren-Averbach analysis suggest that $\ln A_L$ must be plotted against $g^2 C$ instead of g^2 . The successful application of this scheme to γ – TeO₂ result a smooth curve is shown in Fig 2.

2.4 Crystallite size estimation

According to the Scherrer equation [14], the broadening due to small crystallite size may be expressed as

$$B_c = k\lambda / t \cos \theta. \quad \text{--- (6)}$$

where B_c is the broadening, solely due to small crystallite size, k a constant whose value depends on particle shape and usually taken as 1.0, t the crystallite size in nanometers, θ the Bragg's angle and λ the wave length of incident X-ray beam in nm. It is found for the synthesized γ - TeO₂ nanostructured material the calculated crystallite size is 170.627 nm for K=1 and crystallite size is 153.565nm for K= 0.9. The Hall-Williamson method is a more accurate method than Scherrer equation for crystallite size estimation of powder samples in view of the ability of the former approach to measure pure breadth of the diffraction peaks i.e., that solely due to smaller crystallite size [2]

The total peak broadening is given by $B_r \cos \theta = \frac{K\lambda}{t} + \eta \sin \theta$ ---(7)

where η is the strain distribution. Fig. 3 shows a plot of $B_r \cos \theta$ versus $\sin \theta$ with the linear fit yields the slope $\eta = 0.58065$ for the target, with the wavelength of the incident X-ray beam used in 0.154 nm. Following this, the evaluated crystallite size calculated from the intercept is 53.18nm for K=1 and $t = 47.865$ nm for K = 0.9. The peak breadths of the {020}{101}{120}{200}{002}{122} and {151} reflections, scaled in terms of $\cos \Theta \Delta \theta$, where Θ and $\Delta \theta$ are the Bragg angle and half of the FWHM, respectively are shown in Figure 4 with average contrast factors according to modified Williamson Hall plot resulting a slope 0.06487, obtained from the linear fit. The reflections {020}{151} and {002} have the same peak breadth and the reflections {120}{101}{200} and {122} have more or less same peak breadth. This conforms that the peak profiles has peak broadening and asymmetric peak shapes.

2.5 Grain size and dislocation densities

Irrespective of diffraction order, for size broadening and dependence on strain broadening, Williamson and Hall suggested that the FWHM of diffraction peak profiles can be written as the sum of the two broadening effects [12].

It is expressed as $\Delta K = 0.9/D + \Delta K^D$ --- (8)

where ΔK^D is the strain contribution to peak broadening and D is the average grain size or particle size. Here $K = 2 \sin \theta / \lambda$, $\Delta K = 2 \cos \theta \Delta \theta / \lambda$, (θ , $\Delta \theta$, and λ are the diffraction angle, half of the FWHM of the diffraction peak and the wavelength of X-rays, respectively) and $g = K$ at the exact Bragg position. In the conventional Williamson – Hall plot, it is assumed that ΔK^D is either a linear or quadratic function of K [12]. It is expressed as

$$\Delta K = 0.9/D + (\pi A b^2 / 2)^{1/2} \rho^{1/2} (K C^{1/2}) + (\pi A' b^2 / 2) Q^{1/2} (K^2 C) \quad \text{--- (9)}$$

where A and A' are the parameters determined by the effective outer cutoff radius of dislocations, b the burger vector of dislocations, C the contrast factor, ρ the dislocation density and Q correlation factor. Eq. (9) shows that if dislocations are the source of strain in a crystal the proper scaling factor of the breadths (or FWHM) of the peak profiles is $(K C^{1/2})$ instead of merely K. The FWHM according to conventional Williamson- Hall plot is shown in Fig 5. The unsymmetric FWHM follow an apparently unsystematic behaviour as a function of diffraction vector K (or g). Plotting the same data of FWHM according to the modified Williamson-Hall plot , a smooth curve is obtained as expected from Eq.(2) and it is shown in Fig.6 The average contrast factors corresponding to the most common type of edge and screw dislocations in f.c.c and b.c.c crystals were evaluated as a function of the elastic constants of crystals in a wide range of the elastic anisotropy, A_i [where $A_i = 2C_{44} / (C_{11} - C_{12})$ and C_{ij} are the elastic constants] in the range of 7.2405.

$$C \text{ or } q = a \{ 1 - \exp(-A_i/b) \} + c A_i + d \quad \text{--- (10)}$$

where the parameters a,b,c and d are fitted to the calculation. The C factors were averaged by assuming that all slip systems permitted in given crystal are equally populated , and that edge and the screw dislocations are present with equal probability. The contrast factors were calculated using the following elastic constants for γ -

TeO₂ $C_{11} = 29.6$ GPa, $C_{12} = 21.7$ GPa and $C_{44} = 28.6$ [13]. The average C factor used in the present evaluation is listed in Table 3. The insertion at $K = 0$ of the curve in Fig. 6 fitted by the standard least square method provides a particle size to be $D = 12.6275$ nm.

2.6 Scatter matrix

To account the grain size of the sample the study on the peak profile is important. The peak profiles of the observed reflections of the specimen, in the form of scatter matrix are shown in Figure 7. It is the topographical view to study the relation between the intensities and their corresponding ΔK . It is observed that

except {151} reflection all other reflections are confined, the corresponding intensities are normalized to and centered around the maxima of the profiles. The FWHM of {101} and {120} reflections are identical within the experimental error. Similarly the FWHM of {020} and {151} reflections are identical.

IV. Conclusions

Though every method has its advantages and disadvantages, yet they are independent to determine set of quantities/parameters. It is always useful to make use of all possibilities of evaluation thereby enhancing the accuracy of the results as well as identifying better procedure. The system has been indexed analytically with reference to [13], in orthorhombic system yields lattice energy as 81.21 eV. For the plane {020} the density of atom is high compared to other planes with the least in {151}. Strain is caused by the presence of dislocations. This has possibility to have dislocations in nanoscale has little significance. The perfect applicability of modified Williamson-Hall plot indicates that in the nanocrystalline γ -TeO₂, strain is caused by the presence of dislocations. This has to be considered as a clear answer to the question raised in the debate about the possibility to have dislocations in nanoscale. From the conventional Williamson Hall plot the calculated $\eta = 0.58065$ from the slope is very close to the both theoretical η value and the cf. [13]. Thus in the sequence of length scales, it is established that grain size is less than crystallite size. The crystallite size is certainly the smallest length scale in microstructure, which is not directly related to dislocation densities or distances between dislocation. Table 4 summarizes the calculated grain size and crystallite size of γ -TeO₂. From the conventional Williamson Hall plot, the reflections {020}{151} and {002} have the same peak breadth and the reflections while {120}{101}{200} and {122} have more or less same peak breadth. The peak profile has peak broadening and asymmetric peak shapes and this value provides the micro structural parameters for crystallite size and strain. From the modified Warren-Averbach analysis, including the contrast factor we got the smooth curve and thus it conforms that the strain is caused by dislocations.

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List of symbols

γ Gamma
 γ -TeO₂ Meta stable form of Tellurium Dioxide
eV Electron volt
ml milli liter
XRD X-ray diffraction
Cu Copper target
K α Radiation line due to energetic K-electrons
nm Nano meter
kV Kilo volt
mA Milli Ampere
 θ Teta
d Inter planar distance
Å Angstrom Unit
I Intensity
I_{max} Maximum intensity
 δ Density of atoms in one plane
g/cm⁻¹ Grams per centimeter inverse
 ρ Density of the unit cell

N Number of atoms in unit cell
hkl miller indices
ln Lograthemic expansion
eq. Equation
FWHM Full width half maximum
f.c.c Face centered cubic crystals
b.c.c Base centered cubic crystals
GPa Giga Pascal
 η Eta

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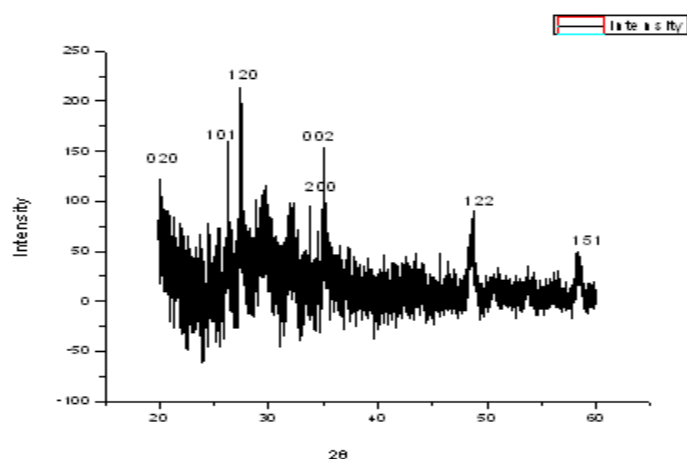


Fig. 1a: Powder XRD pattern

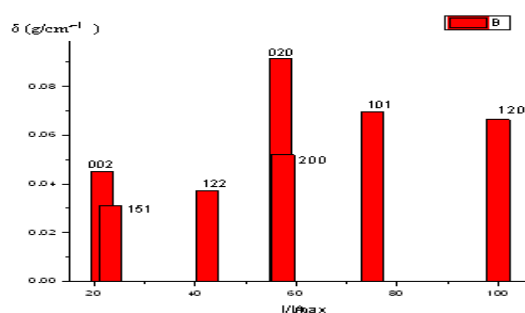


Fig . 1b: Bar diagram representing density of atoms in different reflecting plane

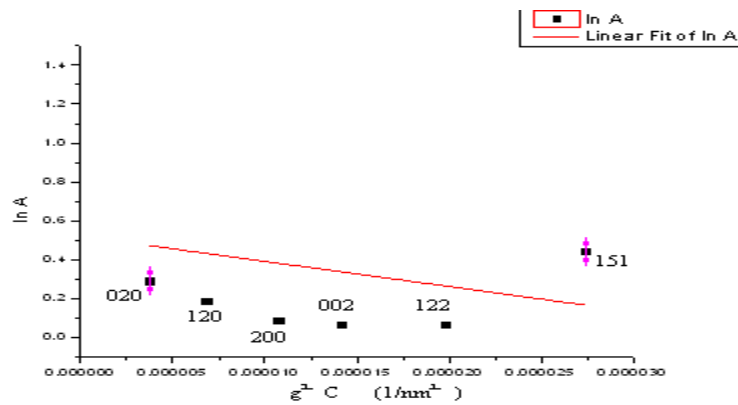


Fig 2: The real part of the Fourier coefficients plotted versus $g^2 C$ according to the modified warren Averbach analysis.

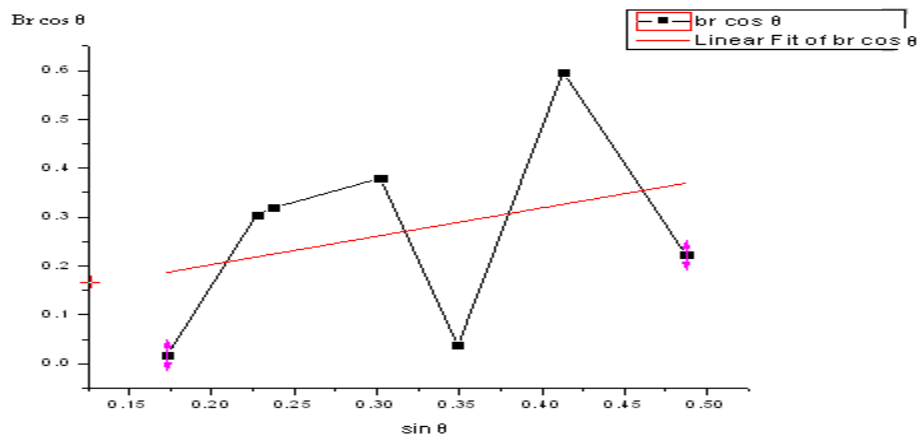


Fig. 3 Hall Williamson plot

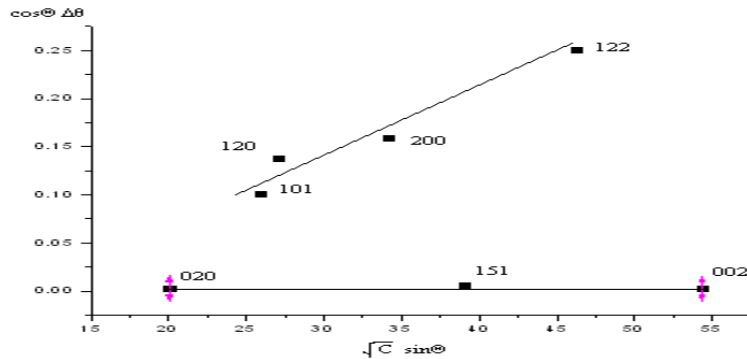


Fig 4: Half of the FWHM scaled in terms of $\cos \theta \Delta \theta$ according to the modified Williamson – Hall plot scaled in terms of $\sqrt{C} \sin \theta$.

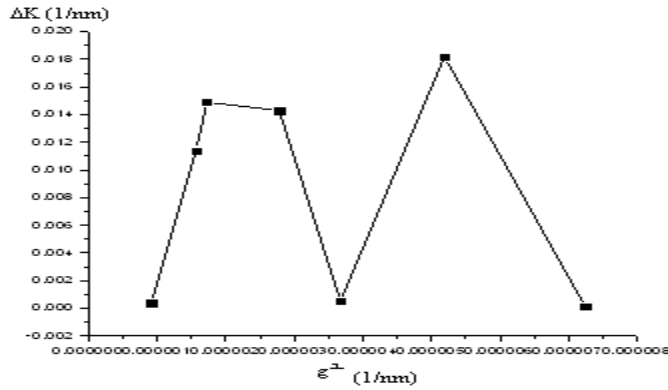


Fig 5: The FWHM according to conventional Williamson Hall plot

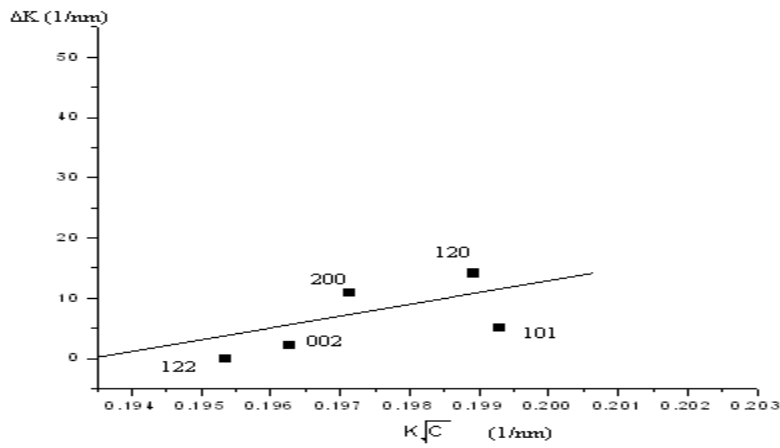


Fig. 6: The FWHM according to the modified Williamson-Hall plot

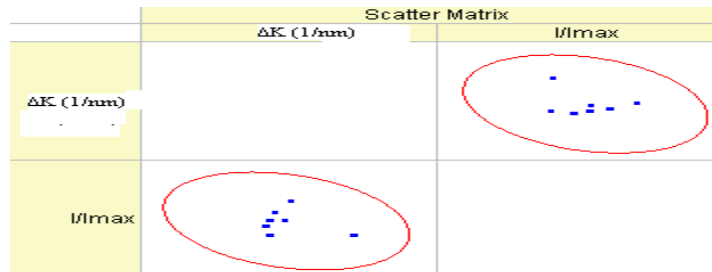


Fig. 7: Scattering matrix for selected reflection of γ -TeO₂

Table 1: Indexing the XRD pattern γ -TeO₂

$2\theta(^{\circ})$	Hkl	$d_{obs}(\text{Å})$	$d_{cal}(\text{Å})$	I/I_{max}	$\delta \text{ (g/cm}^{-1}\text{)}$
19.94	020	4.430741	4.29	56.96	0.09553
6.25	101	3.365718	3.253	75.04	0.07257
27.46	120	3.21741	3.226	100	0.06937
35.14	200	2.514231	2.449	57.32	0.05421
40.62	002	2.175039	2.175	21.55	0.04689
48.77	122	1.811566	1.8036	42.39	0.03906
58.34	151	1.5144	1.5172	23.17	0.03265

δ stands for density of atoms in one plane

Table 2: Data collection through XRD

Unit cell parameter	
a (Å)	5.0085
b (Å)	8.5151
c (Å)	4.3501
Volume (Å ³)	185.5225
ρ (g/cm ⁻¹)	5.7141
Molecular weight	159.6
System	Orthorhombic
N	4

Table 3 : The values of the average contrast factors C for the different diffraction vectors g, used in the present evaluation

g	{200} {002} {122}	{151}	{020}	{101} {120}
C	0.38	0.37	0.40	0.39

Table 4: Grain size and Crystallite size of γ -TeO₂

Method	Size (nm)	
Scherrer equation	K=1	170.627
	K=0.9	153.563
Conversional Williamson Hall plot	K=1	53.18
	K=0.9	47.865
Modified Williamson Hall plot	12.6275	