GAUSS-LORENTZ SIZE-STRAIN BROADENING AND CELL PARAMETERS ANALYSIS OF Mn DOPED SnO$_2$ PREPARED BY ORGANIC ROUTE

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Abstract

SnO$_2$ samples doped with x-mol% Mn (x = 0, 0.3, 0.5, 0.7, 1.0) were prepared by organic route, calcined at 800 °C for 4h, and characterized by the Rietveld method with X-ray diffraction data. The Thompson-Cox-Hastings pseudo-Voigt profile function was used as it is in the DBWS 9411 Rietveld analysis software. For the FWHM, were refined only the Gauss and Lorentz coefficients that can be related to size and strain, while the others were kept fixed in the values reached for a WC standard. The Gauss-strain, Lorentz-size and Lorentz-strain broadening coefficients present an almost uniform variation in respect to the Mn inclusion while the Gauss-size coefficient vary disorderly. The crystallite size determined with these coefficients varies uniformly for Lorentz broadening and highly non-uniform for Gauss broadening. The strain determined with the Lorentz coefficient is approximately 5 times smaller than when determined with Gauss coefficient.. The Lorentz and Gauss contributions for crystallite size (also for strain) were weighted in the FWHM formulae of the TCHZ pseudo-Voigt profile function, and used in the evaluation of the mean crystallite size. The crystallite size and strain so determined showed a uniform decrease in the crystallite size and increase in the microstrain with the addition of dopants. It was also observed that the unit cell volume decreases slightly as the amount of added dopant increases. For undoped sample the cell parameters are a = 4.73785(5) Å and c = 3.18667(4) Å and for 1mol% Mn doped SnO$_2$ the cell parameters are a = 4.73577(7) Å and c = 3.18481(6) Å. Based on the cell parameters' variation it is suggested that the Mn dopant occupies the same crystallographic site as Sn, in the SnO$_2$ crystal structure. Considering that the crystallite size decreases with increasing Mn content, this could explain Mn segregation on the grain boundary of sintered samples and the increase in conductivity observed elsewhere.

1. Introduction

Tin dioxide is a ceramic material with many interesting applications, as for example catalysts, gas sensors, optoelectronic or photovoltaic devices [1-5] that require specific characteristics like films, dense or porous materials for technological use.

In Mn doped SnO$_2$ prepared by a chemical route derived from Pechini method, it has been verified the Mn segregation on the powder surface [6,7]. To that materials calcined at 500 °C for 15 h, the cell parameters did not change with the dopant inclusion. Also the strain effect was considered negligible, with the peak broadening being related only to crystallite size effects (called grain in that work). For that analysis, the standard was a coarse ZnO sample and the instrumental contribution was measured only from the (110) ZnO peak at 2θ = 31.74°.

Considering that these results could not be of enough precision, it was decided to prepare a series of Mn doped samples to be characterized more carefully. The Rietveld method (RM) was applied in the structural and microstructural (size-strain) analysis, in the way described by Young & Desai (1989) [8] and in a weighted size-strain broadening described below. The use of the full pattern in the refinements allows obtaining precise unit cell parameters, with which one can analyse small unit cell variations that would be related to the small addition of dopants, in the crystal lattice.

2. Experimental

The samples were prepared by the method of organic solution from citrates. The Sn and Mn solutions were polyesterified at 200 °C and burned at 400 °C for the elimination of organic matter. Concentrations of 0.3, 0.5, 0.7 and 1.0 mol% of Mn were prepared. The resulting material was calcined at 800 °C for 4 h and characterized by the Rietveld method of crystal structure refinements with X-ray diffraction data. The measurements were performed in a D5000 Siemens diffractometer, from 22 to 120° 2θ with Δ2θ = 0.02° 2θ, divergence slit = 2mm and reception slit = 0.6 mm, copper radiation monochromatized by graphite crystal, and step time = 10 s. The instrumental broadening was measured from a tungsten carbide standard sample. The Rietveld refinement program DBWS 9411 [9] with the modified Thompson-Cox-Hastings pseudo-Voigt profile function (TCHZ function - eq.1) was used. A subroutine called SIZE was written, to perform the size-strain analysis, in a way to be unnecessary any change in the original program, unless one line in the subroutine EXPUT, to call the subroutine SIZE. This subroutine reads the U$_i$, X$_i$ and Y$_{ii}$ instrumental FWHM parameters in a separated file named "pattern.dat". This subroutine was compiled together the DBWS 9411 program and is called by the program only if the user enter a flag for this purpose.

The modified TCHZ function is given by:

$$TCH\text{-}pV = \eta L + (1-\eta)G \qquad (1)$$

with

$$\eta = 1{,}3660q - 0{,}47719q^2 + 0{,}1116q^3 \quad (2)$$

and

$$q = HL/H \quad (3)$$

The *FWHM H* given by Thompson, Cox and Hastings is [10]:

+ + + + +

(3)

Where
A = 2.69269, *B = 2.42843*, *C = 4.47163*, *D = 0.07842*, and the Gauss (H_G *- modified by Young & Desai* [8]) and Lorentz (H_L) FWHM components are

$$H_G = (U \tan^2\theta + \tan\theta + W + Z/\cos^2\theta)^{1/2} \quad (5)$$

$$H_L = X \tan\theta + Y/\cos\theta \quad (6)$$

After reading the FWHM standard parameters, they were subtracted from the sample FWHM parameters (U_s, X_s, Y_s) to get

$$\Delta U = U_s - U_i \quad (7a)$$

$$\Delta X = X_s - X_i \quad (7b)$$

$$\Delta Y = Y_s - Y_i \quad (7c)$$

One can get, from equation (5), the Gauss-strain and Gauss-size broadening component (H_{dG} and H_{pG}) and, from equation (6), the Lorentz strain and size broadening component (H_{dL} and H_{pL}), as below

$$H^2_{dG} = (\Delta U) \tan^2\theta \quad (8a)$$

$$H^2_{pG} = Z/\cos^2\theta \quad (8b)$$

$$H_{dL} = (\Delta X) \tan\theta \quad (8c)$$

$$H_{pL} = (\Delta Y) \cos\theta \quad (8d)$$

These values can be used to compute the Gauss r.m.s. microstrain and crystallite size (Å), and Lorentz r.m.s. microstrain and crystallite size, using the equations (11) and (12) below, after converting them to radians. They are also used in a weighted calculus of the mean size (p) and strain (d) broadening from equation (4), i.e.,

+ +

+ + +

+ +

+ + +

(9)

(10)

The weighted crystallite size p, with units in Å, is then calculated, after converting H_p to radians, by the Scherrer equation (11),

$$H_p(2\theta) = k\lambda / (p \cos\theta) \quad (11)$$

and the r.m.s. microstrain is given by (12)

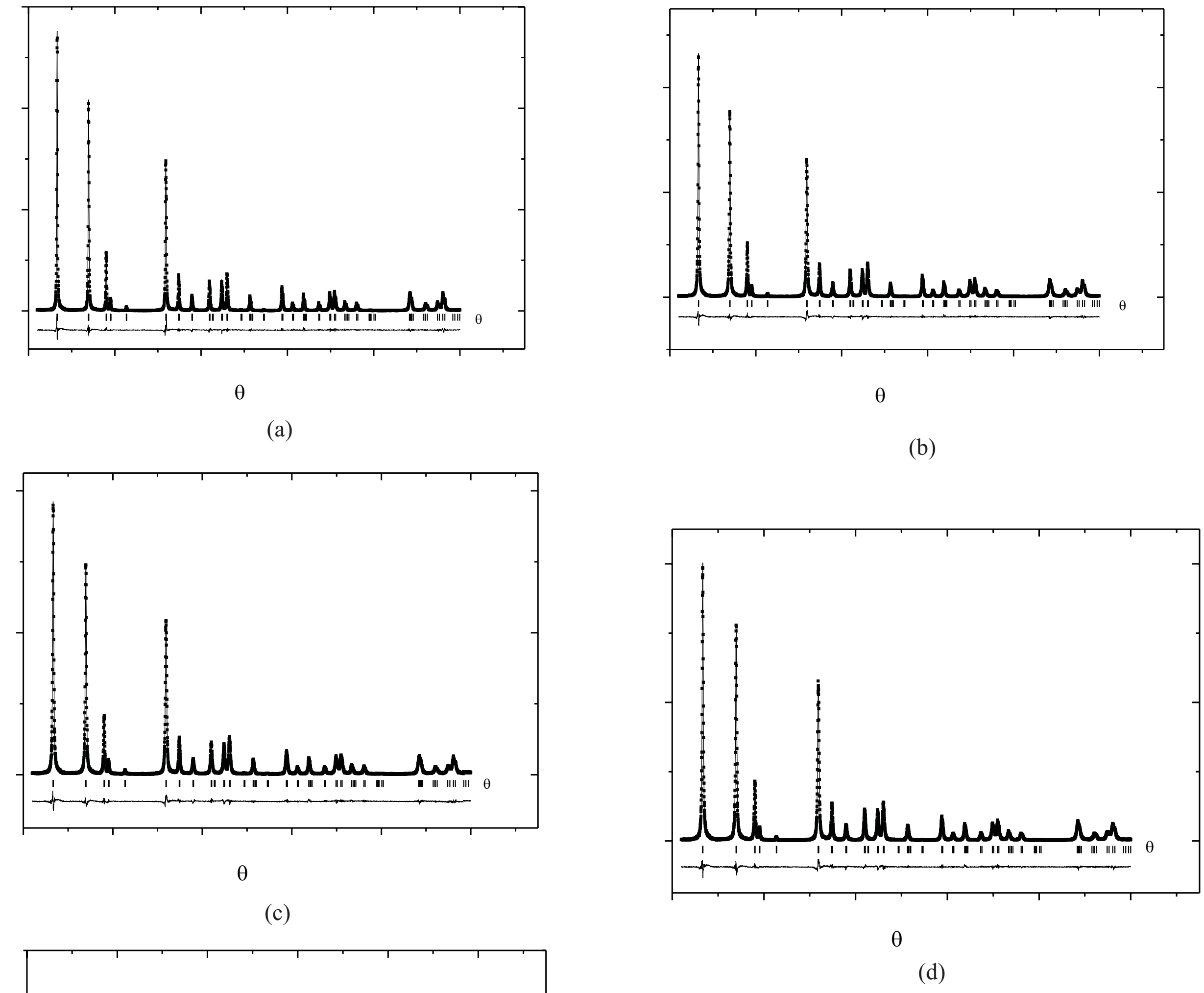
$$H_d(2\theta) = k_d \langle\varepsilon\rangle \tan\theta \quad (12)$$

This method was also used in the crystallite size and r.m.s. microstrain analysis of Mn doped tin dioxide samples. In all cases, only the SnO_2 phases were observed. The initial FWHM parameters were that of the standard sample. At the beginning, the scale factor, sample displacement, cell parameters and background were refined. After that, the U, Z, X and Y were released to refine and then fixed again. Then the individual thermal parameters were refined. After that, also the FWHM parameters the oxygen positional parameters were released to refine. The refinement was considered complete when all the shifts of parameters were less than 10% of the standard deviations. For the case of 0.5mol% of Mn, the X FWHM parameter converged to negative values when released. Since it does not make sense, that parameter was fixed during the refinement. For pure sample, the U FWHM parameter converged to a value less than the instrumental one and for this reason was kept fixed in the instrumental value.

2. Results and Discussion

The final Rietveld indexes and parameters are in Table 1. The Rietveld plots are in Figures 1a-e for undoped, 0.3mol%, 0.5mol%, 0.7mol% and 1.0mol% doped samples respectively. The Williamson-Hall plot build with the FWHM in the reciprocal space ($FWHM^* = FWHM.\cos(\theta)/\lambda$, for all samples, can be seen in figure 2. One can see in table 1 that all refinements reached reasonable goodness of fit index (*S*). Also, in Figures 1, it is possible to observe that no other phase was present in all samples. The Bragg intensity index (R_B) for all refinements are very low, indicating that the crystal structure model refined is in good agreement with the observed data. The d-statistics reached values quite distant from the ideal value of 2, meaning that the standard deviations are underestimated, i.e., the accuracy does not represent the precision of the experiment. One can observe that the unit cell parameters decrease systematically with the increase of dopant addition. The unit cell volume decreased from 71.532(1) $Å^3$ for the pure sample, to 71.427(2) $Å^3$ for 1.0 mol% Mn doped sample.

The FWHM parameters: The Gauss-strain component U and the Lorentz-strain component X increase with the dopant addition, except for the sample doped with 0.5 mol% Mn where a slight discontinuity is observed. This discontinuity does not cause a significant variation in the gaussian microstrain between 0.5 and 0.7 mol% Mn doped samples. The Gauss-size component Z varies significantly

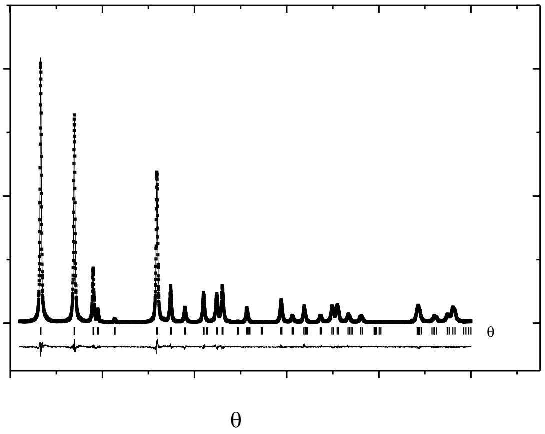


(a)

(b)

(c)

(d)



(e)

Figure 1. Rietveld plots for SnO_2 (a) pure, (b) 0.3 mol% Mn doped, (c) 0.5 mol% Mn doped, (d) 0.7 mol% Mn doped, (e) 1.0 mol% Mn doped samples.

with the increase of dopant, and the Gauss crystallite size computed do not present a regular variation. The Lorentz-size component Y also increases regularly with the addition of Mn, that means that the Lorentz crystallites size decrease regularly. Then, for all samples, the only coefficient that do not present a uniform variation is the size component for the Gauss Broadening. The strain-Gauss are approximately 5 times greater than the Lorentz crystallite size, although they are all very small (Gauss and Lorentz). The computed weighted crystallite size decrease while the weighted microstrain increase with the addition of dopant.

The weighted results were the expected ones because the increase of Mn concentration also increases the Mn segregation in the SnO_2 surface. The Mn is then incorporated in the SnO_2 crystal lattice and, due to the difference in the valence and ionic radius between tin and manganese, the decrease of the unit cell volume and the increase of the microstrain occur.

The results obtained from weighted Gauss and Lorentz crystallite size (and r.m.s. microstrain) by the Rietveld method agree with the Williamson-Hall plot (Fig.2). One can note there that the mean crystallite size decreases as the mean strain increases except for the case of 0.7 mol%, where the crystallite size is larger than for the 0.5 mol% one.

3. Conclusions

From the “weighted” size-strain analysis, based on the Young & Desai method, it was possible to study the variation in the crystallite size and microstrain in the Mn doped SnO_2 samples. The results agree with the qualitative analysis performed with the Williamson-Hall plot. This method can be used for isotropic size and strain analysis in powders.

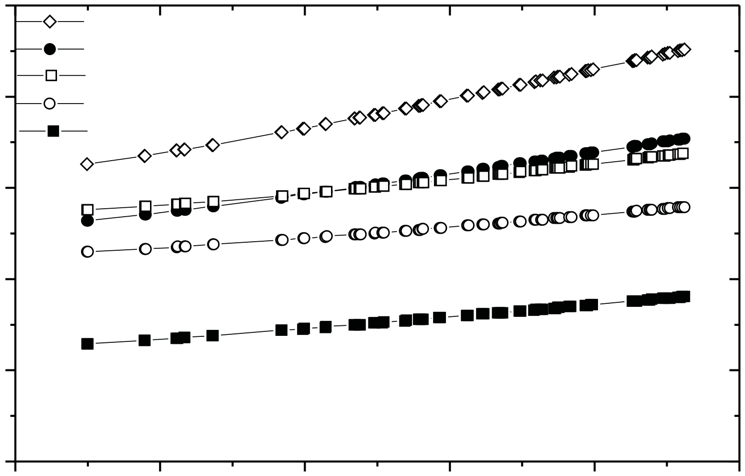


Figure 2. Plot of FWHM* versus d* for all SnO_2 samples.

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Acknowledgments

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