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Rietveld refinements of SnO_2 ceramic powders doped with ZnO, WO_3, CoO, Nb_2O_5 and MoO_3

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Abstract. Polycrystalline materials of SnO_2 doped with ZnO, WO_3, CoO, Nb_2O_5, and MoO_3. were synthesized by solid state reaction. X-ray powder diffraction data were collected with Cu K_α radiation from a Rigaku-Rint 2000 rotating anode source. The structural and profile parameters were refined by the Rietveld method using GSAS [2]. The obtained residual parameters are $R_{wp} = 11,93\%$ and $R_{Bragg} = 4,19\%$. The refined profile parameters indicate no anisotropic crystallite microstrain. The refinement results and Fourier differences calculations indicate that the dopants do not occupy interstitial sites in the crystal structure of SnO_2.

Introduction

Tin dioxide (SnO_2) is an n-type semiconductor with a low densification rate, due to its high surface tension, high diffusion coefficient at low temperatures and high SnO_2 partial pressure at high temperatures [3]. Dense SnO_2-based ceramics can be achieved by introducing dopants or by hot isostatic pressure processing [4]. The SnO_2-based system has been intensively studied as the main candidate to substitute multicomponent ZnO varistors with $\alpha \approx 40$ [5]. In this work we present the results of the structure refinements of SnO_2 with ZnO_2 and WO_3, Nb_2O_5, MoO_3 and CoO dopants, using the Rietveld method.

Experimental

The powder samples were prepared using the mixed oxide method in alcoholic medium. All the oxides used were analytical grade. The molar composition of the studied systems was SnO_2 doped with ZnO_2 with concentration ranging from 0,5 to 2,0 mol%, WO_3 from 0,01 to 0,05 mol%, CoO from 0,75 to 1,00 mol%, MoO_3 from 0,025 to 0,075 mol%, and Nb_2O_5 0,05 mol%. The powders were homogenized in a mixture with i-propanol in a mill during 1 hour. The dried powder was pressed into pellets by uniaxial pressing followed by isostatic pressing at 210 MPa. The pellets were sintered at 1400°C for 4h in oxygen atmosphere and slowly cooled to room temperature (5°C/min) [1].

X-ray powder diffraction data were collected with Cu K_α radiation from a Rigaku-Rint 2000 rotating anode source. The diffractometer is equipped with a graphite monocromator, a scintillation detector and a divergence slit of 0.5°, a dispersion slit of 0.5° and a reception slit of 0.3 mm. Diffraction data were collected for 5 s at each 0.02° step-width over a 2θ range from 20° to 80°. The data were compared with the standards of ICDD-PDF. The Rietveld analysis was performed with the program GSAS [2]. The profile function used was the Thompson-Cox-Hasting pseudo-Voigt.

Table 1. Refined structural parameters and residuals.

Dopants in SnO_2	**x/a of O atom**	**Uiso O($Å^2$)**	**Uiso Sn($Å^2$)**	***a (Å)* *c(Å)***	**R_{wp} R_{Bragg}**	**χ^2**
0.5%ZnO	0.3041(7)	0.005(1)	0.0054(3)	4.73722(4) 3.18610(4)	15.89 8.47	2.325
1%ZnO	0.3069(4)	0.0035(7)	0.0027(1)	4.73806(2) 3.18695(2)	11.93 4.19	2.910
1.2%ZnO	0.3131(6)	0.001(1)	0.0006(1)	4.73791(1) 3.18715(2)	16.63 8.84	4.395
2%ZnO	0.3164(7)	0.0045(1)	0.0002(1)	4.73819(1) 3.18721(1)	17.88 10.34	5.255
1%ZnO+0.01%WO_3	0.3076(6)	0.008(1)	0.0003(1)	4.73735(2) 3.18664(2)	13.27 3.36	3.431
1%ZnO+0.05%WO_3	0.3062(6)	0.006(1)	0.0006(1)	4.73723(2) 3.18645(2)	16.9 7.1	4.430
2%ZnO+0.01%WO_3	0.3071(6)	0.0067(9)	0.0003(1)	4.73743(2) 3.18667(2)	14.39 5.42	3.370
2%ZnO+0.05%WO_3	0.3077(6)	0.006(1)	0.0017(2)	4.73730(2) 3.18652(2)	15.34 6.94	3.660
1%CoO+0.05%Nb_2O_5 +0.075%MoO_3	0.3083	0.011(4)	0.0018(6)	4.7372(1) 3.1864(1)	23.13 8.71	1.153

Results and discussion

The structure of SnO_2 is rutile type, tetragonal with space group $P4_2/mm$. The unit cell contains two tin atoms and four oxygen atoms. Small amounts of the impurity $ZnAl_2O_4$ were detected in the powder patterns of some samples. This impurity was considered in the refinements but with fixed structural parameters. Powder diffraction data and refined profile parameters, as well as interatomic distances and angles are summarized in CIF – files generated using GSAS [2]. The unit cell changes isotropically since no significant alteration was observed in the tetragonality factor (c/a). The refinement details are given in Table 1. The best fitting was achieved for SnO_2 with 1%ZnO data (showed in Figure 1), with

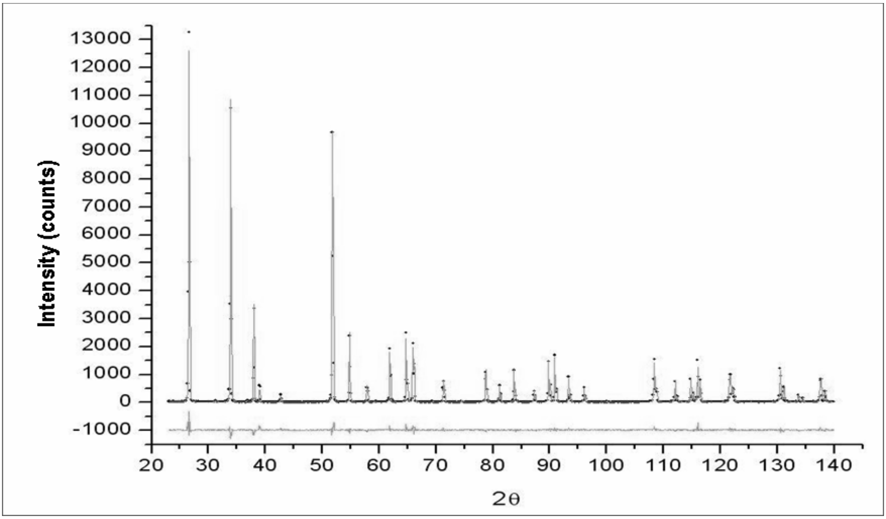

Figure 1. Rietveld refinement of SnO_2 doped with 1%ZnO

R_{wp} = 11.93% and R_{Bragg} = 4.19%. Figure 2 shows the difference Fourier map for SnO_2+2ZnO, the sample with greater amount of dopant ZnO. The refinement results and the inspection of the Fourier differences indicate that the dopants do not occupy interstitial sites in the crystal structure of SnO_2 which indicates that Zn^{2+} and W^{6+} ions substitute the Sn^{4+} ions.

Conclusions

The results confirmed that the unit cell volume increases when ZnO is added to the system and decreases for the samples doped with WO_3. The reason for this modification is attributed to ionic radius differences: 0.69 Å for Sn^{4+}, 0.74 Å for Zn^{2+} and 0.60 Å for W^{6+} [1] [6]. The refined profile parameters indicate no anisotropic crystallite microstrain.

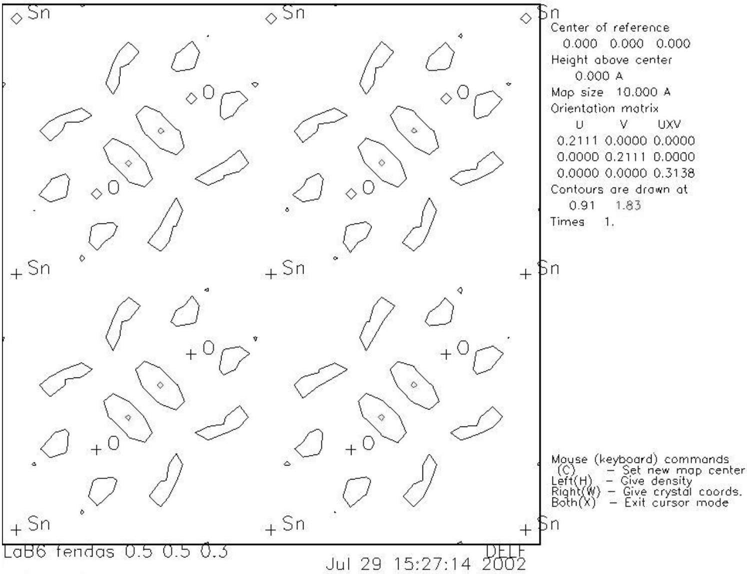

Figure 2. DifferenceFourier map for sample SnO_2+2ZnO

References

1. Perazolli. L., Simões, A. Z., Coleto, U., Gutierrez-Antonio, F. M. Jr. S., Carrió, J. A. G., Paiva-Santos, C.O., Marques, R. F. C., Longo, E., Varela, J. A., 2005, *Materials Letters*, **59**, 1859.
2. Larson. A.C. and Von Dreele, R.B., 1993, GSAS. *Document LAUR 86-748* (Los Alamos National Laboratory. Los Alamos).
3. Pianaro, S.A., Bueno, P.R., Longo, E., Varela, J.A., 1995, *Journal of Materials Science Letters*, **14**, 692.
4. Fagan, J.G., Amarakoon, V.R.W., 1993, *American Ceramic Society Bulletin*, **72**, 119.
5. Park, S.J., Hirota, K., Yamamura, H., 1984, *Ceramics International*, **10**, 115.
6. Shannon, R.D., 1976, *Acta Cryst. A*, **32**, 751.

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