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Parametric XRD profile analysis of sno$_2$ crystallite growth

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Simultaneous estimation of lattice strain and crystallite size using *sequential profile analysis* (SPA) within one TXRD experiment is difficult due to the high correlation between them, especially with short range diffractograms independently fitted to each other. The problem can be resolved without performing additional experiments by applying *parametric profile analysis* (PPA) [1], where each diffractogram is linked parametrically to the next one. In this case, crystallite size contribution to peak width is calculated using its mathematical function of time with several refinable parameters, which are common for the whole sequence of diffractograms [2].

In this work we report on the comparison of two methods (SPA and PPA) for crystallite size calculation with or without strain contribution. In our previous paper [3] we showed that growth kinetics of SnO$_2$ crystallites under isothermal annealing can be well described by *size-dependent impediment model* [4]: $D(t) = \sqrt{D_{lim}^2 - (D_{lim}^2 - D_0^2)\exp(-2At/D_{lim}^2)}$, where D_0 and D_{lim} are the initial and limiting crystallite sizes, and A – rate constant. In SPA, the kinetic model was used just to fit the already calculated values of crystallite sizes. In PPA the kinetic model was used to calculate the crystallite sizes by fitting simultaneously all diffractograms obtained as a function of annealing time and considering that the evolution of crystallite size obeys the model given.

Three SnO$_2$ materials (blank SnO$_2$, bulk doped SnO$_2$ with 0.02 wt. % Pd (SnO$_2$ Pd), and surface doped SnO$_2$ with 1.2 wt. % Pd (SnO$_2$ dep Pd)) were analyzed by TXRD under isothermal conditions: at 600, 700 and 800ºC. Overall 31 patterns were collected during 32 hours of annealing. Kinetic parameters were calculated for each temperature using SPA, PPA without consideration of lattice strain (e_0) and PPA with consideration of lattice strain according to Gaussian (G) or Lorentzian (L) contribution. The results for 800ºC (for the sake of brevity) are shown in the following table.

Material	Method	D_0 (nm)	D_{lim} (nm)	A (nm²/h)	Mean strain (%)
SnO$_2$ blank	S P A	2.54 (4)	3.22 (2)	0.76 (9)	-
	PPA w/o strain	2.520 (24)	3.142 (11)	0.857 (69)	-
	PPA w strain (L)	2.606 (87)	3.157 (44)	0.72 (23)	0.0000 (209)
	PPA w strain (G)	3.233 (74)	4.038 (30)	1.99 (35)	0.4940 (202)
SnO$_2$Pd	S P A	9.72 (25)	16.0 (9)	2.4 (2)	-
	PPA w/o strain	9.562 (64)	15.697 (33)	28.38 (66)	-
	PPA w strain (L)	9.29 (21)	17.05 (12)	48.7 (3.5)	0.0151 (21)
	PPA w strain (G)	9.635 (92)	16.452 (48)	33.3 (1.1)	0.0667 (44)
SnO$_2$depPd	S P A	5.96 (11)	8.70 (4)	6.4 (5)	-
	PPA w/o strain	5.909 (41)	8.657 (19)	6.63 (21)	-
	PPA w strain (L)	5.91 (15)	9.675 (85)	12.4 (1.2)	0.0384 (42)
	PPA w strain (G)	6.032 (65)	9.009 (31)	7.05 (31)	0.0936 (86)

The values obtained without strain consideration, using either SPA or PPA, were found to be quite similar to each other. However, if we take into account lattice strain, the values differ remarkably from the previous ones. The rate constant A reflects higher discrepancy compared to other parameters, since it is depended on both D_0 and D_{lim}. The

higher temperature was, the higher the difference was observed, which suggests higher impact of lattice strain at elevated temperatures. This can be explained by the fact that SnO$_2$ possesses a nonstoichiometric surface which upon heating in air readily loses oxygen. In the case of highly dispersed materials, numerous oxygen vacancies diffuse into bulk, creating defects and increasing lattice strain. The highest values of lattice strain were found for blank SnO$_2$.

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Polarons and distortions in rare-earth molybdates at high temperature

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Light rare-earth (RE) molybdates (RE=La-Eu) can occur in differently ordered scheelite-type (CaWO$_4$) structures, where 1/3 of the calcium substituted by the RE are vacancies. At room temperature, are monoclinic with space group *C2/c* and *Z=4* but the molybdates with RE=La-Nd and RE=Sm-Eu have a volume of nine and three times the volume of the scheelite structure, respectively. In particular, in this work we will study Sm$_2$(MoO$_4$)$_3$ [1] and Eu$_2$(MoO$_4$)$_3$ [2] at high temperature. The study of X-ray diffraction patterns reveals an anomalous behavior of its lattice parameter *a* in the range of temperatures from 473 to 973 K (see figure, solid symbol). Rietveld refinements were performed using symmetry adapted modes [3] at 523, 723 and 923 K in order to study the thermal dependence of the distortion from the scheelite structure and to interpret the structural effects that favor the formation of polarons.

We have analyzed the real part of the complex conductivity in the frequency range from 0.1 to 10000 KHz and the temperature range from 550 to 900 K and found that it follows a universal dielectric response [4], [5]. Detailed analysis of the temperature dependence of the adjusted parameters within this model shows that, in the temperature range of 630 to 800 K (see figure, open symbol), the dominant mechanism of electrical transport is by the overlapping large polaron (OLP) model [6].
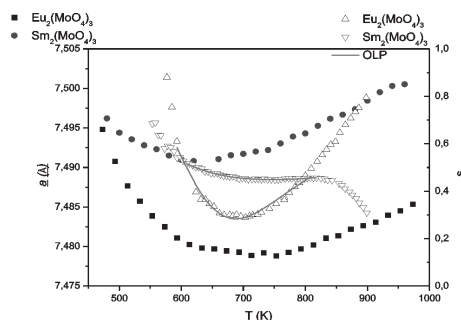
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