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Keywords: parametric rietveld refinement, symmetry mode, CuInSe2

MS05.P19

Acta Cryst. (2011) A**67,** C245

Parametric XRD profile analysis of sno$_2$ crystallite growth

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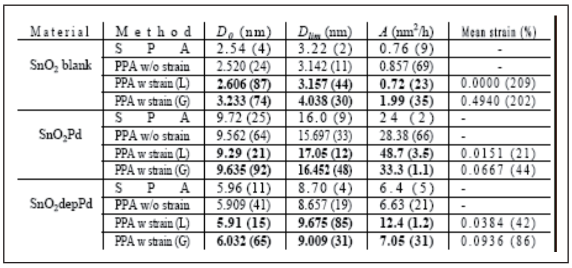
Simultaneous estimation of lattice strain and crystallite size using *sequential profile analysis* (SPA) within one TXRD experiment is difficult due to the high correlation between them, especially with short range diffractograms independently fitted to each other. The problem can be resolved without 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 800^{o}C (for the sake of brevity) are shown in the following table.



Material	Method	D_0 (nm)	D_{lim} (nm)	A (nm^2/h)	Mean strain (%)
SnO$_2$ blank	SPA	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	SPA	9.72 (25)	16.0 (9)	24 (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	SPA	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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Keywords: growth, kinetics, strain

MS05.P20

Acta Cryst. (2011) A**67,** C245-C246

Polarons and distortions in rare-earth molybdates at high temperature

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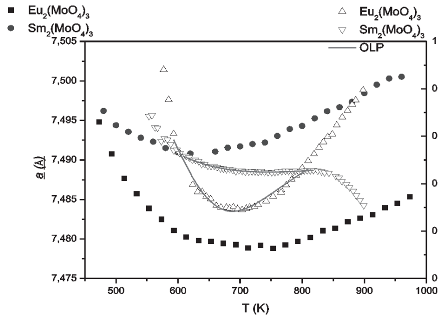
Light rare-earth (RE) molybdates (RE=La-Eu) can occur in differently ordered scheelite-type (CaWO$_4$) structures, where 1/3 of the calcium substituted by the RE are vacancies. At room temperature, are monoclinic with space group *C2/c* and *Z=4* but the molybdates with RE=La-Nd and RE=Sm-Eu have a volume 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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Keywords: rare-earth molybdate, semiconductor, electronic transport

MS05.P21

Acta Cryst. (2011) A**67,** C246

In Situ X-ray Diffraction Study of the Phase Transitons in C4 Olefin Catalysts

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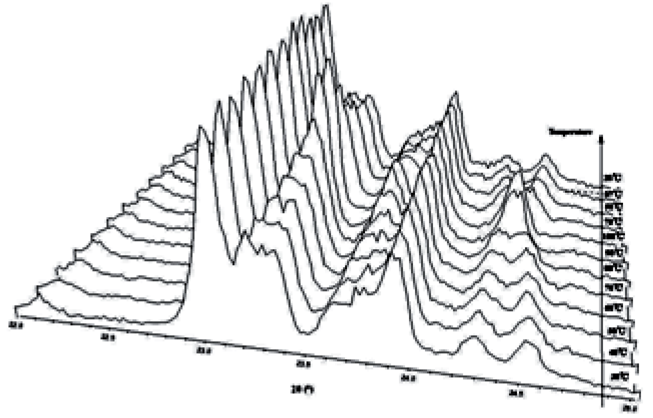
Temperatured-programmed X-ray diffraction technology is employed to study phase transitions of modified ZSM-5 catalysts for C4-olefin cracking reactions to produce propylene. The crystal phase transitions of the fresh, used and regenerated catalysts are investigated respectively with temperature increasing and decreasing under vacuum and air conditions.

The samples were prepared with following steps. HZSM-5 zeolite and Al_2O_3 (as binder) were fully mixed, kneaded and then molded by extruder. Elements of alkaline-earth metals and phosphorus were introduced by impregnation. After drying and calcination, the fresh ZSM-5-based catalyst was obtained. The catalyst for C4 cracking was evaluated in a fixed-bed reactor. The deactivated catalyst was regenerated through combustion with the mixture of air and nitrogen on line.

The crystal structures of the samples were recorded by X-ray powder diffraction analysis on Bruker AXS D8 Advance SSS X-ray diffractometer equipped with a graphite monochromator and scinitillation counter, and using CuKα radiation (40KV and 300mA). Anton Parr XRK 900 reaction chamber was equipped, which was used to heat samples from room temperature to 900℃ and provide certain experimental conditions.

The research results show the crystal phases of all these catalyst are changed into orthorhombic structure when the temperature is increased to a certain degree no matter what kind of their initial crystal structure (monoclinic or orthorhombic)(shown in fig.1). The experimental conditions whether under vacuum or air prove further the water has nothing with phase transitions of these catalysts.



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Keywords: XRD, phase transition, ZSM-5

MS05.P22

Acta Cryst. (2011) A**67,** C246

Neutron diffraction studies of the ferroelectric phase of $CdTiO_3$

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Cadmium titanate ($CdTiO_3$) is relatively poorly studied due to the toxicity of cadmium and difficulties in obtaining pure $CdTiO_3$ since it has only a moderate stability with respect to the oxides. $CdTiO_3$ can be synthesised with either an ilmenite or perovskite type structure. The ilmenite-like phase of $CdTiO_3$ is unstable at high temperatures and undergoes an irreversible reconstructive phase transition to the perovskite phase near 900 °C. The perovskite phase decomposes, through the loss of Cd, if heated above 1000 °C. In recent years, there has been growing interest developing thin films of cadmium for a variety of uses including as a photocatalyst.

The precise structure of the perovskite phase of $CdTiO_3$ is uncertain. This is a consequence of the combination of its ferroelectric properties and the subtleties in the various octahedral tilting schemes observed for perovskites. A ferroelectric structure for $CdTiO_3$ at room temperature in $Pc2_1n$, and a non-polar in *Pbnm* have been reported. Studies showed that $CdTiO_3$ undergoes a displacive ferroelectric phase transition at about 80 K, with X-ray analysis suggesting the low temperature phase is in $Pn2_1a$ or $P2_1ma$ while the room temperature paraelectric phase is in *Pbnm*.

In the present work we have used high resolution neutron diffraction methods to refine the structure of the three phases of $CdTiO_3$, namely the paraelectric ilmenite and perovskite phases and the ferroelectric perovskite phase. It is expected that neutron diffraction will provide a more accurate and precise description of these structures compared with X-ray diffraction methods due to the presence of the heavy Cd cations. To circumvent the high neutron absorption cross section of naturally occurring Cd we used samples enriched in ^{114}Cd. Cooling perovskite-type $CdTiO_3$ to 4 K induces a ferroelectric phase transition, with the neutron data suggesting the low temperature structure is in $Pna2_1$ (Figure 1). Solid solutions of the type $Cd_{1-x}Ca_xTiO_3$ could be prepared. Invariably this required the use of relatively high temperatures resulting in the formation of perovskite-type oxides and we did not find any evidence to suggest appreciable amounts of Ca could be incorporated into the ilmenite type $CdTiO_3$ structure. Interestingly we could not prepare solid solutions of the type $Cd_{1-x}Sr_xTiO_3$ using conventional methods. There are only 5% of Sr and 5% of Ca can be doped in $CdTiO_3$ in the solid solution of $Ca_xSr_xCd_{1-x}TiO_3$. This is somewhat remarkable given the relative ease with which oxides of the type $Ca_{1-x}Sr_xTiO_3$ can be prepared and suggests the A-O bonding is playing a significant, but poorly understood role in stabilising the oxides. There is ample evidence that altering the *A*-cation significantly alters the hybridisation between the B-site metal t_{2g} d states and the O p π orbitals.

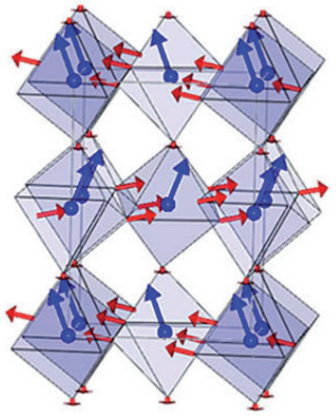

Figure 1. A ferroelectric structure in $Pna2_1$ at 4 K.

Keywords: neutron, Cd-114, ferroelectric