Keywords: parametric rietveld refinement, symmetry mode, CuInSe2

**MS05.P19**  
*Acta Cryst.* (2011) A67, C245

Parametric XRD profile analysis of sno, crystallite growth

F. Gispert-Guirado,* R.G. Pavelko,* E. Llobet,* † Scientific Resources Service, Univ. Rovira i Virgili, Tarragona, (Spain), † Institute of Physical Chemistry, Univ. of Tübingen, Tübingen, (Germany). ‡MINOS-EMaS, Univ. Rovira i Virgili, Tarragona, (Spain). E-mail: francesc.gispert@urv.cat

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 diffractions 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 with 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 SnO₂ crystallites under isothermal annealing can be well described by size-dependent impendiment model [4]: \( D(t) = D_0 \times \left[ 1 - \left( \frac{D_{\infty}}{D_0} \right)^{n} \right] \), where \( D_0 \) and \( D_{\infty} \) are the initial and limiting crystallite sizes, and \( n \) is 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 SnO₂ materials (blank SnO₂, bulk doped SnO₂, with 0.02 wt. % Pd (SnO₂-Pd), and surface doped SnO₂ with 1.2 wt. % Pd (SnO₂ dep Pd)) were analyzed by TXRD under isothermal conditions: at 600, 700 and 800°C. 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 \((e)\) and PPA with consideration of lattice strain according to Gaussian \((G)\) or Lorentzian \((L)\) contribution. The results for 800°C (for the sake of brevity) are shown in the following table.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( D_0 ) (nm)</th>
<th>( D_{\infty} ) (nm)</th>
<th>( n )</th>
<th>( e ) (%)</th>
<th>( \Delta D_0 ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>5.52 (12)</td>
<td>3.72 (12)</td>
<td>0.78</td>
<td>0.9</td>
<td>0.78</td>
</tr>
<tr>
<td>SnO₂-Pd</td>
<td>3.90 (7)</td>
<td>4.30 (7)</td>
<td>1.72</td>
<td>0.9</td>
<td>1.72</td>
</tr>
<tr>
<td>SnO₂-depPd</td>
<td>3.73 (12)</td>
<td>4.20 (12)</td>
<td>0.78</td>
<td>0.9</td>
<td>0.78</td>
</tr>
</tbody>
</table>

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 \( n \) reflects higher discrepancy compared to other parameters, since it is dependent on both \( D_0 \) and \( D_{\infty} \). 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 SnO₂ 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 SnO₂.

**MS05.P20**  

Polarons and distortions in rare-earth molybdates at high temperature

M. C. Guzmán-Afonso,* M. E. Torres,* C. González-Silgo,* E. Mateosanz,* N. Sabalisck,* † Departamento de Física Fundamental y Experimental, Electrónica y Sistemas, ‡Departamento de Física Básica, †Departamento de Física Fundamental II, Universidad de La Laguna, La Laguna, S/C Tenerife (Spain). ‡C.A.I. Difracción de Rayos X, Universidad Complutense de Madrid, Madrid (Spain). E-mail: mcguzman@ull.es

Light rare-earth (RE) molybdates (RE=La-Eu) can occur in differently ordered scheelite-type (CaWO₄) 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 Snₓ(MoO₄)₂ [1] and Euₓ(MoO₄)₂ [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].

**References**


C245
In Situ X-ray Diffraction Study of the Phase Transitions in C4 Olefin Catalysts

Huanru Wang, Yuanyuan Ji, Xiaoliang Zeng, Xi Zhao, Wenqing Huang. Beijing Research Institute of Chemical Industry, SINOPEC, Beijing (China). E-mail: wanghr.bjhy@sinopec.com

Temperature-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 Al2O3 (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.

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 scintillation 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°C and provide certain experimental conditions.

The research results show the crystal phases of all these catalyst are nothing with phase transitions of these catalysts.

Keywords: XRD, phase transition, ZSM-5

Neutron diffraction studies of the ferroelectric phase of CdTiO3

Qingdi Zhou.1,2 Brendan J. Kennedy,3 Maxim Avdeev,4 1School of Chemistry, The University of Sydney, Sydney, NSW 2006 (Australia). 2Bragg Institute, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menao NSW 2234 (Australia). E-mail: zhou_q@chem.usyd.edu.au

Cd1-xMoxTiO3 (M = Ca, Sr, Ba) is relatively poorly studied due to the toxicity of cadmium and difficulties in obtaining pure CdTiO3 since it has only a moderate stability with respect to the oxides. CdTiO3 can be synthesised with either an ilmenite or perovskite type structure. The ilmenite-like phase of CdTiO3 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 CdTiO3 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 CdTiO3 at room temperature in Pn̅21m, and a non-polar in Pm̅3n have been reported. Studies showed that CdTiO3 undergoes a displacive ferroelectric phase transition at about 80 K, with X-ray analysis suggesting the low temperature phase is in Pn̅21a or P21ma while the room temperature paraelectric phase is in Pm̅3n.

In the present work we have used high resolution neutron diffraction methods to refine the structure of the three phases of CdTiO3, 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 114Cd. Cooling perovskite-type CdTiO3 to 4 K induces a ferroelectric phase transition, with the neutron data suggesting the low temperature structure is in Pn̅21a or P21ma while the room temperature paraelectric phase is in Pm̅3n.

To circumvent the high neutron absorption cross section of naturally occurring Cd we used samples enriched in 114Cd. Cooling perovskite-type CdTiO3 to 4 K induces a ferroelectric phase transition, with the neutron data suggesting the low temperature structure is in Pn̅21a or P21ma while the room temperature paraelectric phase is in Pm̅3n.

Figure 1. A ferroelectric structure in Pn̅21a at 4 K.

Keywords: neutron, Cd114, ferroelectric