

**Keywords:** borosilicates, thermal behaviour, “in-situ” synchrotron powder diffraction

## MS05.P12

*Acta Cryst.* (2011) A67, C242

### Study of crystallization of different titania thin films by in-situ XRD measurements

Radomír Kužel,<sup>a</sup> Zdeněk Matěj,<sup>a</sup> Lea Nichtová,<sup>a</sup> Zdeněk Hubička,<sup>b</sup> Josef Buršík,<sup>c</sup> <sup>a</sup>*Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University in Prague, (Czech Republic).* <sup>b</sup>*Institute of Physics, Academy of Sciences of the Czech Republic, Prague, (Czech Republic).* <sup>c</sup>*Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, Rez near Prague (Czech Republic).* E-mail: kuzel@karlov.mff.cuni.cz.

Titania is well-known material of great interest because of its low cost, good chemical stability, nontoxicity, mechanical hardness and optical transmittance with high refractive index, and in particular because it is a unique material that connects two distinct photo-induced phenomena: photocatalytic activity and photo-induced superhydrophilicity after UV illumination. However, desired properties are strongly influenced by the crystallinity and/or their particular microstructure, presence of residual stresses in the films etc. Temperature evolution of the film structure and microstructure is of high interest also because of need of different substrate. In our previous studies [1-4], magnetron-deposited nanocrystalline and amorphous films of different thickness were investigated. A strong influence of film thickness on composition and crystallization of TiO<sub>2</sub> thin films on Si(111) substrates was found. In very thin amorphous films (below about 200 nm) the crystallization is significantly slower than for thicker layers. This was probably related to the tensile stresses (> 300 MPa) generated during the crystallization and inhibiting further crystallization. They also increased drastically for very thin films. Crystallization started at temperature below 200 °C. Texture developed at the beginning of crystallization was suppressed with higher thickness and XRD line widths were very small close to the instrumental broadening from the very beginning of crystallization indicating relatively fast growth of larger (> 100 nm) crystallites.

In this contribution, the results are compared with similar studies of TiO<sub>2</sub> films prepared by other methods – plasma jet sputtering and spin coating. The former films are less dense, tensile stresses are smaller more complicated due to the developed texture. However, the XRD line broadening is the same as for magnetron sputtered films. Crystallized anatase phase seems to be very stable. Below 900 °C, no indication of transformation into rutile appeared. Crystallization of the plasma jet sputtered films (thicker than 200 nm) appeared only at 260 °C.

Annealing of amorphous spin coated films leads to very different results. Crystallization starts at higher temperatures (390 °C) by forming small crystallites which reach specific size at specific temperature after definite time. For further size reduction, the temperature must be increased. The XRD line widths reach values of instrumental broadening only at very high temperatures above 750 °C when also transformation of anatase into rutile can be observed.

Time evolution of crystallization in terms of the integrated intensity of anatase diffraction peaks can be quite well described for all the films by the well-know Johnson-Mehl-Avrami-Kolmogorov equation (see [3], for more details).

[1] Z. Matěj, R. Kužel and L. Nichtová, *Powder Diffraction*, **2010**, 25, 125-131. [2] R. Kužel, L. Nichtová, Z. Matěj, D. Heřman, J. Šícha and J. Musil, *Z. Kristallogr.* **2007** Suppl. 26, 247-252. [3] R. Kužel, L. Nichtová, Z. Matěj and J. Musil, *Thin Solid Films* **2010** 519(5), 1649-1654. [4] Z. Matěj, R. Kužel

and L. Nichtová, *Metallurgical and Materials Transactions A*, **2011** in press, DOI: 10.1007/s11661-010-0468-z.

**Keywords:** thin films, titanium dioxide, crystallization

## MS05.P13

*Acta Cryst.* (2011) A67, C242-C243

### Structural behavior of anhydrous wadsleyite and forsterite

Dmytro M. Trots, Alexander Kurnosov, Tiziana Boffa Ballaran, Daniel J. Frost, *Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, (Germany).* E-mail: d\_trots@yahoo.com

Forsterite and wadsleyite are the major minerals in the Earth's upper mantle and transition zone. The forsterite-wadsleyite phase transition is thought to produce a seismic discontinuity at 410 km depth. In order to calculate stability fields of mantle minerals, a useful approach is to refine thermodynamic parameters using high-pressure (HP) experimental phase relations. Such calculations benefit if parameters used in calculations, such as thermal expansivity and bulk modulus, can be accurately determined independently. However, significant divergences occur between results of previous thermal expansion studies of wadsleyite. Therefore, the high-temperature (HT) expansivities of the anhydrous wadsleyite and, for comparative purposes, forsterite were reinvestigated. An analysis of HT structural variations in wadsleyite was also undertaken.

Samples were synthesized at HP HT conditions at the BGI–multianvil facility (wadsleyite sample numbers z626, z627). *In situ* structural studies on wadsleyite were performed at the synchrotron facility HASYLAB/DESY (Hamburg, Germany) with the powder diffractometer at beam-line B2 up to 1083 K. The thermal expansion of forsterite was measured using a furnace mounted on the Philips Xpert powder diffractometer up to 1313 K.

The HT thermal expansion of wadsleyite and forsterite was parameterized on the basis of the 1<sup>st</sup> order Grüneisen approximation using a Debye function for the internal energy. The values for hypothetical volume at  $T=0$  K, Debye temperature and Grüneisen parameter of forsterite equal 288.80(2) Å<sup>3</sup>, 771(9) K, 1.269(2), respectively, with a fixed to 125 GPa bulk modulus. The extrapolation of  $V(T)/V_0$  values to melting of forsterite at  $\approx 2150$  K agree with experimental  $V(T)/V_0$  [1]. This demonstrates the main advantage of using of 1<sup>st</sup> order Grüneisen approximation for forsterite and confirms validity of such model for expansivity parametrization. The values for hypothetical volume at  $T=0$  K, Debye temperature, Grüneisen parameter for wadsleyite equal 536.86(14) Å<sup>3</sup>, 980(55) K, 1.28(2) and 537.00(13) Å<sup>3</sup>, 887(50) K, 1.26(1) for z626 and z627, respectively, with a fixed to 161 GPa bulk modulus. The best agreement of the expansivity is observed with results of references [2, 3].

Larger compressibility of the *c*-axis of wadsleyite was attributed to the pseudo-layering features with MgO<sub>6</sub> layers within the *a-b* plane and its cross linking by Si<sub>2</sub>O<sub>7</sub> dimers along *c*-axis [4]. By the analogy, the same structural features might explain the large expansivity along the *c*-axis. However, Mg-O bonds response in different ways to temperature than to the pressure increase. The temperature-induced changes in interpolyhedral angles correlate well with significantly larger expansivity along the *c*-axis of wadsleyite and in contrast to anisotropic compression, can not be neglected in their contribution to the anisotropic thermal expansion.

Support from the ERC advanced grant no. 227893 “DEEP” funded through the EC 7th Framework Programme. The measurements with synchrotron radiation were carried out during beamtime allocated to Project I-20090287 at HASYLAB/DESY.

[1] M.A. Bouhifd, D. Andrault, G. Fiquet, P. Richet, *Geophysical Research Letters* **1996**, 23, 1143-1146. [2] I. Suzuki, E. Ohtani, M. Kumazawa, *Journal of*