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

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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 TiO₂ 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 TiO₂ 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).

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Structural behavior of anhydrous wadsleyite and forsterite

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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 1st 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) Å³, 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 ≈ 2150 K agree with experimental $V(T)/V_0$ [1]. This demonstrates the main advantage of using of 1st 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) Å³, 980(55) K, 1.28(2) and 537.00(13) Å³, 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 MgO₆ layers within the *a-b* plane and its cross linking by Si₂O₇ 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.

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Ordering effects in BiFeO₃-based solid solutions

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In solid solutions of BiFeO₃ multiferroic and KNbO₃ ferroelectric or NaNbO₃ antiferroelectric the different order parameter interactions should occur: magnetic, ferro(-antiferro)electric, and of ferroelastic nature.

X-ray diffraction study in 20≤T≤800°C temperature range of (1-x)BiFeO₃-(x)KNbO₃(BFKNO) and (1-x)BiFeO₃-(x)NaNbO₃(BFNNO) solid solutions systems' samples has allowed to make the (x,T) phase diagrams of the systems. It was established that in BFKNO system the R3c, Pbnm, Pm3m phases' boundaries of pure BiFeO₃ with KNbO₃ doping lessen in transition temperature with the increase of X. The transition temperatures between Amm2, P4mm and Pm3m phases of pure KNbO₃ are also decreased with the decrease of X. The phase boundaries in BFNNO system's solid solutions shift in a similar way.

The comparison of BFKNO and BFNNO phase boundaries shows that in these systems the ferroelectric phase transitions' temperatures of BiFeO₃, KNbO₃ and NaNbO₃ decrease with the increase of secondary component's content. This is also proved by preliminary results of permittivity-temperature dependencies investigations.

Keywords: ferroic, ferroelectricity, X-ray

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Structural study of SrPrMRuO₆ double perovskites by symmetry-mode analysis

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The natural way to study the phase-transitions is the use of the symmetry-mode analysis, to understand in a proper way the microscopic mechanisms responsible for the phase-transitions. For that propose we have used the Bilbao Crystallographic Server [1][2][3] together with FullProf Suit [4].

The SrPrMRuO₆ (M=Zn,Co,Mg,Ni) materials have been elaborated by the conventional Solid State Reaction Method. Rietveld analysis of laboratory X-ray Powder Diffraction (XRPD), Synchrotron Radiation Powder Diffraction (SXPDP) and Neutron Powder Diffraction (NPD) shows that these materials are double perovskites with a primitive space group: $P2_1/n$ (No. 14, non conventional setting). In the four compounds Sr²⁺ and Pr³⁺ are totally disordered in A- and A'-sites; whereas M²⁺ and Ru⁵⁺ are completely ordered, in B- and B'-sites, respectively. For the refinements we have used AMPLIMODES for FullProf [3][5-6]. AMPLIMODES carries out a symmetry-mode analysis of a displace

phase-transition. Starting from the experimental structures of the parent-phase (virtual or real, $Fm-3m$, No. 225 conventional setting) and knowing the metric of the low-symmetry phase ($P2_1/n$), the program determines the symmetry modes compatible with the symmetry break. In the NPD data analysis two modes have been identified as active: the ones responsible to yield the $P2_1/n$ space group: GM_4^+ and X_3^+ . These two modes are related to the rotation of the octahedra (oxygen movements): GM_4^+ generates a rotation around the monoclinic b axis and X_3^+ , around the c axis.

The high-temperature (HT) laboratory XRPD analysis has revealed the following temperature phase-transition sequence [7]: $P2_1/n-R-3-Fm-3m$. HT neutron diffraction data of SrPrMgRuO₆ material has been used to study the phase-transition by the symmetry-mode analysis. According to the theory, the two order parameters actuating in the monoclinic phase are expected to thermally stabilize and become zero at higher temperature. Taking into account that the amplitudes are different, it can be expected that one of them will become zero before the other and, thus, an intermediate phase will appear, before the cubic one. A first order phase-transition has been observed between $P2_1/n$ and $R-3$ (No. 148 conventional setting). None of the amplitudes of the active modes will reach the zero value at the transition temperature. In the symmetry breaking from the prototype cubic phase into the trigonal intermediate (HT) phase a unique active mode has been identified: GM_4^+ , which generates a rotation of the octahedra around the hexagonal c axis.

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High-pressure behavior of high silica ferrierite

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Ferrierite (FER framework topology) is a well-known aluminosilicate zeolite mineral. An understanding of the structure and properties of FER remains important because of its role as a catalyst in commercial reactions. For example, it is important in the petrochemical industry, where it has been used as a shape selective catalyst for the production of isobutene. The thermal behavior of this phase (in its high silica form) was recently studied by Bull et al [1], while its compressibility has never been investigated before.

The high pressure (HP) behavior of synthetic high silica zeolite ferrierite (FER) was investigated by means of in-situ synchrotron X-ray powder diffraction, with the aim to understand the P-induced deformation mechanism. The microporous material was synthesized starting from pure silica and pyridine and propyl-amine as structure directing agents. Here we report the preliminary results on the compressibility of the as synthesized phase. The study of the compressibility of the calcined one will be carried out in the following steps of the project.