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Hydrogen motions of Mg(OD)₂ and Ca(OD)₂ at several temperatures

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Mg(OH)₂ and Ca(OH)₂ have a CdI₂ type structure and one of the most simple hydrous minerals. The crystal structure can be described as stacked layers of distorted edge-sharing Mg(or Ca)O₆ octahedra along the *c* axis. Each hydroxyl group is linked with three Mg(or Ca) atoms in an octahedral layer and surrounded by three other hydroxyl groups belonging to the adjacent layer. Previous studies suggested that the H atoms behavior at room temperature is well described by a three-site split-atom model and the transformation to a frozen disordered phase could occur at a low temperature[1,2] At high temperature, some previous studies suggested that slight structural modifications occur at about 50 K below the onset temperature of dehydration of Ca(OH)₂ and discuss the possibility of formation of H₂O molecules[3]. Although such interesting behaviors could be expected, a series of diffraction measurements of Mg(OH)₂ and Ca(OH)₂ from low to high temperature are surprisingly scarce[4]. In this study, we carried out *in situ* neutron diffraction measurements on Mg(OD)₂ and Ca(OD)₂ at several temperatures from 200 K to 600 K.

Deuterated samples were prepared via hydrothermal treatment with MgO (or CaO) fine powders and excess D₂O water in a Teflon lined stainless steel autoclave at 493 K for 4 days. After the hydrothermal treatment was completed, precipitates were filtered out, washed with D₂O water, and then dried at 383 K under vacuum for 3 hours. The products were confirmed to have a CdI₂-type structure by conventional powder X-ray diffraction measurements and were checked to be deuterated by IR absorption spectra. Neutron powder diffraction measurements of Mg(OD)₂ and Ca(OD)₂ were carried out from 200 K to 600 K with the US-Japan Wide-Angle Neutron Diffractometer (WAND) of the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. The neutron beam is monochromated to be the wavelength of 1.4805 Å. The deuterated samples were loaded in a Vanadium-can under vacuum, and cooled down and heated up in a top-loading type cooling system. The measurement time at each targeted temperature was about 1 hour after the temperature reached equilibrium.

Since no diffraction peaks of MgO(or CaO) could be observed in obtained neutron diffraction patterns in this study, the samples of Mg(OD)₂ and Ca(OD)₂ were stable up to 600 K under the present conditions. Both unit-cell parameters *a* and *c* increase on heating. However, the unit-cell expansion is quite anisotropic and the *c* expands more rapidly than the *a* as reported before[4,5]. Furthermore, the *c* changes the expansion rate at around 400 K and 300 K for Mg(OD)₂ and Ca(OD)₂, respectively, although the *a* changes monotonically as a function of temperature. This anomaly could be due to a change in the thermal motion of D atoms. The detailed structure parameters refined by the Rietveld method will be discussed.

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Unexpected flexibility and coordination change in porous borosilicates upon heating

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The aim of this work is to study the thermal behaviour of boron-substituted zeolites (referred to as “boralites” or “borosilicates” [1]) with different framework topologies. Boralites are interesting for their great degree of flexibility in the coordination conversion between tetrahedral and trigonal boron which occurs reversibly upon dehydration and rehydration. Information regarding boralites response to heating is essential not only for their characterization but also for their industrial applications. For this purpose, the following boralites were studied:

- B-leucite (LEU) (s.g. *I-43d*): K₁₆[B₁₆Si₃₂O₉₆]
- B-ZSM-5 (MFI) (s.g. *Pnma*): Na_{4.6}[B_{9.3}Si_{86.7}O₁₉₂]·11.5EN·6H₂O
- B-levyne (LEV) (s.g. *R-3m*): Na_{0.27}[B₃Si₅₁O₁₀₈]·4.5Q·29H₂O
(where EN=ethylenediamine=C₂H₈N₂, Q=quinuclidine=C₇H₁₃N).

The step by step thermal dehydration processes of these materials were studied *in situ* by synchrotron radiation powder diffraction (GILDA beamline, ESRF, Grenoble). This technique has never been used to study structural modifications induced during the thermal activation of boron substituted zeolites. Rietveld refinements were carried out on consecutive powder patterns in the 25°C to 800°C temperature range. Thermal analyses (TG, DTA and DTG) of the as-synthesized samples were carried out in the same temperature range under a constant flux of air (heating rate 5°/m in). B-ZSM-5 unit-cell parameters increase with increasing temperatures up to about 700°C. This result is at complete odds with the case of boron-free MFI materials, both in their as-synthesized [2] and calcined forms [3]. B-ZSM-5 represents the *first example of positive thermal expansion in MFI topology*. According to Fild et al. [4], the variations of the O-T-O and T-O-T angles in all the range investigated clearly indicate that boron preserves its tetrahedral coordination. A similar behaviour is observed in B-LEU, where the presence of counterions such as potassium also stabilises boron in tetrahedral coordination. In this case, the evolution of unit-cell parameters suggests a displacive polymorphic transition at about 560°C, thus indicating a *I-43d* → *Ia-3d* change in symmetry. This process is accomplished by a twisting in the tetragonal prism, constituting a leucite framework, which leads to the formation of more regular apertures when the dehydration is completed. In the case of B-levyne, a dramatic change in the unit-cell parameters is observed at about 500°C, when the decomposition and expulsion of quinuclidine molecules occurs. Interestingly, upon calcination a portion of the boron atoms is transformed to trigonally coordinated boron, as reported by NMR and IR analyses [5]. This is the *first example of tetrahedral to trigonal boron conversion detected by XRD analysis*.

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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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