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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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