

MS05.P07

Acta Cryst. (2011) A67, C240**Noble humidity control system for in-situ X-ray powder diffraction at SPring-8**

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There are many reports on polymorphs of pharmaceutical and/or biological compounds due to humidity-dependent hydration/dehydration processes [1]. For precise analysis of these phase transitions, some important results have been reported using laboratory X-ray systems with humidity controller RIGAKU HUM-1 [2]. For synchrotron experiments, we have introduced a noble humidity control system with HUM-1 on the large Debye-Scherrer camera at the BL19B2 Engineering Science Research I beamline of SPring-8 [3], [4]. Small amount of powdery sample is mounted on a special UV-polyimide device and a humidity controlled mini-chamber adapted with HUM-1 is loaded for *in-situ* X-ray powder diffraction experiment.

For evaluation, we precisely determined phase transitions of nucleosides and nucleotides in wide range of relative humidity (rh) from 0% to 90% at 25°C. Guanosine dihydrate changed to the anhydrous form at 0% rh and it recovered the dihydrate state at 30% rh within 1 hour. Disodium adenosine 5'-monophosphate heptahydrate (Form A) at 50% rh changed to Form B at 80% rh in 1 hour. Form A changed to Form C at 2% rh, and then to Form D at 40% rh.

We expect many polymorph mechanisms of hydrate/dehydrate processes will be cleared using this humidity controlled system near future.

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[1] Y. Sugawara et al., *J. Phys. Chem. B* **2002**, *106*, 10363-10368. [2] T. Furuki et al., *Carbohydrate Research* **2005**, *340*, 429-438. [3] M. Takata et al., *Advances in X-ray Analysis* **2002**, *45*, 377-384 [4] K. Osaka et al., *AIP Conference Proceedings* **2010**, *1234*, 9-12.

Keywords: in-situ X-ray powder diffraction, non-ambient, humidity

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Acta Cryst. (2011) A67, C240**Anisotropy of thermal expansion in borates as a result of collective atomic motion**

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Thermal expansion of a crystal structure may be described as a combination of the thermal behavior of its constituent parts [1]. From this viewpoint we have examined the role of atomic anisotropic vibrations in thermal expansion of borates. In borates boron atoms occur in both triangular and tetrahedral coordination to oxygen and hydroxyl groups in the structures of crystals and glasses. These polyhedra link via the common corners to form rigid boron-oxygen groups that constitute the fundamental building blocks (FBB) of the structure. These groups are considered as rigid structure fragments, moreover it is shown [2], [3] that on heating the BO₃ and BO₄ polyhedra and the FBBs maintain the size and configuration also. Aim of this paper is to clarify how borate

structure affects its thermal expansion.

In a BO₃ triangle oxygen and boron atoms oscillate mainly perpendicular to the B–O bond thus B and O atoms vibrate maximally perpendicular to the BO₃ plane. In response to an increase in temperature borate triangles vibrate in the same direction more intensively as a whole. In the case of a isolated [B₃O₆]³⁻ triborate group composed of three BO₃ triangles B and O atoms vibrate maximally perpendicular to the plane of the a single triborate group. Hence a crystal structure with isolated triangles and triborate groups expands considerably perpendicular to the plane of a group and expands weakly in parallel to plane of a group: as example we observed the same character of thermal expansion of RE-borates isotypical to calcite and aragonite with isolated triangles and α- and β-BaB₂O₄ crystal structures built up from isolated triborate groups. Moreover the triangles as well triborate groups are usually self-arranged by parallel to each other in the 0D-structures. Similar situation occurs in borates with isolated tetra- and pentaborate groups although in last case the internal oxygen and boron atoms of both single rings vibrate perpendicular to planes of these rings while a group as a whole oscillates relative axis of the group – the line drawn parallel to the plane of both rings. Hence strong bonds inside the rigid boron-oxygen groups dictate anisotropy of thermal expansion and self-assembly of rigid groups in a crystal structure formation.

[1] R.M. Hazen, L.W. Finger, *Comparative crystal chemistry*, Berlin: Springer-Verlag, **1982**. [2] R.S. Bubnova, S.K. Filatov, *Phys. Stat. Sol.* **2008**, *245(b)*, 2469–2476. [3] R.S. Bubnova, S.K. Filatov, *High-Temperature Crystal Chemistry of Borates and Borosilicates*. **2008**, St. Petersburg: Nauka (in Russ.).

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Acta Cryst. (2011) A67, C240-C241**General conception of increasing symmetry of crystals with rising temperature**

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Well known tendency of thermal increasing of crystal symmetry is related usually to polymorphic transitions [1–3]. The general conception includes both polymorphic transition (I or II order) and thermal expansion. It means that the process of thermal crystal structure rearrangement is considered here as single process at all temperature interval of existence of a compound [4–6].

Although thermal expansion of each polymorphic modification is not accompanied by changing of symmetry, the crystal structure transforms usually in the direction of increasing symmetry.

Comparative analyses of atomic rearrangement of thermal expansion and final polymorphic transition can be used for mutual explanation or prediction a character of thermal behaviour for each of these components [4, 7]; this is special problem for I order transformations.

The general conception of thermal increasing of symmetry may be formulated following way. *Symmetry of crystal matter increases usually with rising temperature: vibration symmetry of atoms and molecules increases → crystal structure rearrangements in the direction of increasing its symmetry → more symmetrical modification forms.*

[1] R.M. Hazen, L.W. Finger. *Comparative crystal chemistry*. Berlin: Springer-Verlag **1982**. [2] S.K. Filatov. *High temperature crystal chemistry*. Leningrad: Nedra **1990** (in Russ.). [3] R.M. Hazen, R.T. Downs, C.T. Prewitt, *Rev. Mineral.* **2000**, *41*, 1–33. [4] S.K. Filatov In: *Crystallography and Crystal Chemistry* **1973**, *2*, 5–12. Ed. V.A. Frank-Kamenetsky. Leningrad: State University (in Russ.). [5] S.K. Filatov *Proc. Russian Miner. Soc.* **1982**, *111*, 674–681 (in Russ.).

[6] S.K. Filatov *Dokl. Akad. Nauk SSSR* **1985**, 280, 369–372 (in Russ.). [7] S.K. Filatov *Phys. Stat. Sol.* **2008**, 245(b), 2490–2496 (in Russ.).

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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.

[1] L. Desgranges, D. Grebille, G. Calvarin, G. Chevrier, N. Floquet, J.C. Niepce *Acta Cryst.* **1993**, B49, 812-817. [2] O. Chaix-Pluchery, J. Bouillot, D. Ciosmak, J.C. Niepce, F. Freund *J. of Solid State Chem.* **1983**, 50, 247-255. [3]

L. Desgranges, D. Grebille, G. Calvarin, K. Chhor, C. Pommier, N. Floquet, J.C. Niepce *J. Phys. Chem. Solids* **1994**, 55, 161-166. [5] H. Xu, Y. Zhao, S.C. Vogel, L.L. Daemen, D.D. Hickmott *Solid State Chem.* **2007**, 180, 1519-1525.

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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*.

[1] R. Millini, G. Perego, G. Bellussi, *Topics in Catalysis* **1999**, 9, 13. [2] Milanesio, G. Artioli, A.F. Gualtieri, L. Palin, C. Lamberti, *Journal of the American Chemical Society* **2003**, 125, 14549-14558. [3] D.S. Bhang, V. Ramaswamy, *Microporous and Mesoporous Materials* **2007**, 103, 851-860. [4] C. Fild, D.F. Shantz, R.F. Lobo, H. Koller, *Physical Chemistry Chemical Physics* **2000**, 2, 3091-3098. [5] R. Millini, A. Carati, G. Bellussi, *Zeolites* **1992**, 12, 265-268.