

## MS05.P07

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

Keiko Miura,<sup>a</sup> Keiichi Osaka,<sup>a</sup> Shigefumi Yamamura,<sup>b</sup> Yoko Sugawara,<sup>b</sup> <sup>a</sup>*Industrial Application Division, Japan Synchrotron Radiation Research Institute, Hyogo (Japan).* <sup>b</sup>*School of Science, Kitasato University, Kanagawa (Japan).* E-mail: miurakk@spring8.or.jp

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.

These experiments were performed with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2009B2068, 2010A1849 and 2010B1803).

[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

## MS05.P08

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

Rimma Bubnova,<sup>a</sup> Stanislav Filatov,<sup>b</sup> <sup>a</sup>*Institute of Silicate Chemistry of the RAS, St. Petersburg (Russia).* <sup>b</sup>*Department of Crystallography, St. Petersburg State University (Russia).* E-mail: rimma\_bubnova@mail.ru

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 BO<sub>3</sub> and BO<sub>4</sub> 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 BO<sub>3</sub> triangle oxygen and boron atoms oscillate mainly perpendicular to the B–O bond thus B and O atoms vibrate maximally perpendicular to the BO<sub>3</sub> 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 [B<sub>3</sub>O<sub>6</sub>]<sup>3-</sup> triborate group composed of three BO<sub>3</sub> 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-BaB<sub>2</sub>O<sub>4</sub> 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.).

**Keywords:** thermal expansion, atomic vibration, borate

## MS05.P09

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

Stanislav Filatov, *Department of Crystallography, St. Petersburg State University, Saint Petersburg (Russia).* E-mail: filatov.stanislav@gmail.com

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.).