

P10.04.13*Acta Cryst.* (2008). A64, C494**Hydrothermal growth and characterization of rare earth vanadate polyscale crystals**Kohei Soga¹, C. K. Chandrashekar², Tadafumi Adschiri³, K. Byrappa²¹Tokyo University of Science, Materials Science and Technology, 2641 Yamazaki, Noda, Chiba, 278-8510, Japan, ²University of Mysore, P.B. No. 21, Manasagangotri, Mysore 570 006, India, ³Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1 Katahira, Aoba, Sendai 980-8577, Japan, E-mail: mail@ksoga.com

Hydrothermal method is one of the best routes to grow polyscale crystals covering an entire range of sizes from bulk single crystals to fine, ultrafine and nano- single crystals. There are several advantages in the hydrothermal method due to highly controlled diffusion, which helps in obtaining defect free bulk single crystals. In recent years, organic ligands, capping agents, chelating agents and surfactants are used extensively in the hydrothermal growth of crystals to achieve a desired shape and size for the crystals. Also these organic ligands can provide the desired surface charge for the crystals, which in turn assist in obtaining a crystal surface either hydrophobic or hydrophilic. In the present work, the authors discuss systematically the growth of polyscale rare earth vanadate crystals under hydrothermal conditions within a wide range of PT conditions starting from mild hydrothermal (T ~ 100°C and P < 30 bars) to supercritical hydrothermal conditions (T = 400°C and P = 30 MPa). The mechanism of the growth of rare earth vanadate polyscale crystals has been discussed in detail. The morphology of the rare earth vanadates has been studied in detail with respect to the experimental conditions. Rare earth vanadates are the potential materials used as diode pumped laser materials, bio-imaging, neutron capture therapy, photocatalytic, etc. The hydrothermal technique is highly suitable for the growth of such polyscale rare earth vanadate crystals. In this work, a systematic characterization of these polyscale rare earth vanadate crystals has been discussed.

Keywords: hydrothermal synthesis, rare earth vanadate, optical properties

P10.04.14*Acta Cryst.* (2008). A64, C494**High temperature borate crystal chemistry**Rimma S Bubnova¹, Stanislav K. Filatov²¹Grebenshchikov Institute of the Silicate Chemistry of the RAS, Makarov Emb. 2, St. Petersburg, St. Petersburg, 199034, Russia, ²Department of Crystallography, St. Petersburg State University, St. Petersburg, 199034, Russia, E-mail: rimma_bubnova@mail.ru

One of distinguishing characteristic of unique borate crystal chemistry is occurrence of rigid groups consisting of the BO₃ triangles and the BO₄ tetrahedra. These rigid groups maintain their configuration in various crystal structures without any essential changes. The great diversity of borate crystal structures arises from rigid boron-oxygen groups condensed to form 0D-, 1D-, 2D and 3D-dimensional anions in crystals and glasses. Thermal expansion of about 50 borates has been investigated by powder X-ray diffraction. More than 3/4 of them demonstrate highly anisotropic expansion, moreover, about half of them show negative linear expansion. To understand that strong anisotropic expansion we examine thermal structural behaviour of six borates by single crystal high temperature X-ray diffraction. The fundamental rules of high-temperature borate crystal chemistry emerge from these studies. (1) BO₃ and

BO₄ polyhedra practically do not change on heating similarly to tetrahedra in silicates (Hazen, Finger, 1982); (2) The rigid groups do not essentially change their configuration on heating in contrast to silicates in which thermally stable are TO₄ tetrahedra only (Hazen, Finger, 1982); (3) the rigid groups might rotate like hinges; (4) breaking strength of bonds inside the rigid boron-oxygen groups and the ability of these groups to rotate relatively to each other round shared oxygen atoms dictate a plastic thermal behavior of borate crystals and glasses. As a result most borates viewed as one-, two- and three-dimensional hinges demonstrate greatly anisotropic thermal expansion including linear negative expansion. If the hinge structure is expanded in one direction on heating, it has to contract synchronously in another one. This research is supported by RFBR (08-03-00232).

Keywords: borates, high-temperature x-ray diffraction, thermal expansion

P10.04.15*Acta Cryst.* (2008). A64, C494**Structural phase transition in a super protonic conductor KHSO₄**

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In situ high temperature structural phase transitions and dehydration of a super fast proton conductor have been analyzed by single crystal X-ray diffraction. The room temperature structure is orthorhombic, Space group *Pbca*, $a=8.415(7)\text{\AA}$, $b=9.790(8)\text{\AA}$, $c=18.967(2)\text{\AA}$, on heating to 463K the structure convert to more symmetric, space group *Cmca*, $a=8.4290(9)\text{\AA}$, $b=9.8938(10)\text{\AA}$, $c=19.1950(2)\text{\AA}$. At 475K dehydration takes place and the compound become K₃HSO₄ (S₂O₇) with space group *P2₁/c* and cell parameters $a=13.1960(5)\text{\AA}$, $b=13.1960(5)\text{\AA}$, $c=9.6560(5)\text{\AA}$, $\beta=97.056(5)^\circ$. The room temperature structure is perfectly ordered but at 463K there are disordered oxygen and hydrogen atoms with a S-O bond distance $\approx 1.753(4)\text{\AA}$. The crystal structure exhibits O-H...O hydrogen bonds forming zero dimensional dimer and infinite polymeric chain at both room temperature and 463K. The presence of hydrogen bond is only responsible for the proton conduction. It was suggested that at high temperature the dimer breaks and forms chains resulting in the observed high proton conductivity [1]. It is shown in our analysis for the first time that the structure of the dimer and infinite polymeric chain of hydrogen bond remain intact, however, disorder in both oxygen and hydrogen atoms resulting in the lengthening of S-O bond length could be the cause of increased proton conductivity. It is of interest to note that the structure at 475K has only dimeric hydrogen bond and not chains.

Reference

[1] M. Sharon and A. K. Kalia, Journal of Solid State Chemistry, 31, 3, 1980.

Keywords: phase transition, proton conductor, dehydration

P10.04.16*Acta Cryst.* (2008). A64, C494-495**The most fruitful type of negative linear thermal expansion of crystals**

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