

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**

Diptikanta Swain, T N Guru Row

Indian Institute of science, Solid state and structural chemistry unit., C. V. Raman avenue, Bangalore, Karnataka, 560012, India, E-mail: diptikanta@ssu.iisc.ernet.in

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**

Stanislav K. Filatov

Saint Petersburg State University, Geological Faculty, Department of Crystallography, University Emb. 7/9, St. Petersburg, 199034, Russia, E-mail: filatov@crystalspb.com

Unit cell angles α , β , and γ , not fixed by symmetry, give an additional degree of freedom on the stage of crystal formation. For this reason, monoclinic crystals are the most numerous ones at ambient conditions. The oblique angles play the same role in thermal expansion; in particular they permit to demonstrate sharply anisotropic thermal expansion up to contraction along some directions. In 1982 great jump of the appearance of frequency of crystals, showing negative linear thermal expansion, was discovered between orthorhombic and monoclinic crystals [1]. It occurred that at least one third of monoclinic and triclinic crystals contracts along certain directions on heating due to so-called shears [1, 2]. This fact correlates with the existence of oblique cell angles in monoclinic and triclinic crystals only. Last quarter of a century was test and development period of the thermal contraction concept. Many types of the phenomenon were considered [2, 3 etc.]: shears, hinges, rocking polyhedra and symmetry related types etc. And now we can say that both among chemical compounds and in the earth's crust, shears are the most fruitful case of linear thermal contraction of crystals. Taking into consideration anti-similarity of thermal and pressure deformations of crystals, the same situation should be expected in connection with linear elongation under pressure.

References. 1. Filatov S.K. Proc. Russian Miner. Soc. 111 674-681 (1982). 2. Filatov S.K., Hazen R.M. In: Advanced mineralogy. Ed. A. Marfunin. Berlin etc.: Springer-Verlag, 1994, p. 76-90. 3. Sleight A.W. Inorg. Chem. 37 2854-2860 (1998).

Keywords: negative thermal expansion, high-temperature x-ray diffraction, inorganic compounds

P10.04.17

Acta Cryst. (2008). A64, C495

The structure of type I semiconducting clathrates under pressure

Antonio M Dos Santos, Ling Yang, Christopher A Tulk, Brian C Sales, Bryan C Chakoumakos

Oak Ridge National Lab, Neutron Scattering Science Division, PO BOX 2008 MS6475, Oak Ridge, Tennessee, OAK RIDGE TN 37831, USA, E-mail: dossantosam@ornl.gov

Semiconductor clathrates are compounds consisting of an open framework lattice of mainly, Si, Ge and Ga, containing a second large cation (alkali or alkali-earth) trapped in its cages. In this work, *in-situ* high pressure powder diffraction was performed on two Ge clathrates: $\text{Ae}_8\text{Ga}_{16}\text{Ge}_{30}$, where Ae = Sr, Ba. The pressure was applied to the samples by means of a diamond anvil cell (DAC) to 25 GPa and powder diffraction data were collected with high energy (100 KeV) x-rays at the APS Sector 1 at Argonne National Lab. This technique allows data collection over a wide q range [0.2 \AA^{-1} - 50 \AA^{-1}]. The structure of both samples was analyzed as a function of pressure, particularly with respect to the guest atom electron density and host lattice bonding. Both clathrates show amorphization of the host lattice for pressures in excess of 20 GPa, the structural characteristics of the structure factor functions $S(Q)$ and radial distribution functions $G(r)$ will be presented, elucidating both the local environment of the guest atoms and their short range ordering. This result suggests a promising route for obtaining periodic arrangement of guest atoms embedded in an amorphous semiconductor matrix. Oak Ridge National Laboratory is supported by the Division of Materials Sciences, U.S. D.O.E. (contract DE-AC05-00OR22725 with UT-Battelle, LLC).

Keywords: semiconducting clathrates, *in-situ* high pressure diffraction, pair distribution function

P10.04.18

Acta Cryst. (2008). A64, C495

Magnetic transition and equation of state of iron carbide to 400 GPa

Shigeaki Ono

Japan Agency for Marine-Earth Science and Technology, Institute for Research on Earth Evolution, 2-15 Natsushima-cho, Yokosuka, Kanagawa, 237-0061, Japan, E-mail: sono@jamstec.go.jp

It is known that the Earth's inner core is different from pure iron because the physical properties of pure iron can not explain those of the Earth's inner core estimated by seismological observations. Cosmochemical arguments imply that minor lighter elements should be present to account for the discrepancies of physical properties between pure iron and the seismological observations. C, O, S, Si, and H are considered to be the most probable candidates. Wood (1993) proposed that iron carbide might be the major phase in the inner core based on extrapolations of thermodynamic calculations and an equation of state of iron carbide. Recently, significant advances have been achieved in static high-pressure experiments. Although the P-T range of high-pressure experiments has been extended, it is difficult to achieve extreme conditions corresponding to the Earth's inner core. In contrast, recent developments of the first-principle calculations can provide independent data from high-pressure experiments. In this study, the magnetic properties and the equation of state of Fe₃C were investigated by the first-principle calculations. We performed DFT method using VASP package to calculate magnetic states and equilibrium volumes and pressures. A method of *ab initio* molecular dynamics calculation was also used at high temperatures. The magnetic phase transition was observed at a pressure of ~55 GPa. This indicates that the stable Fe₃C is a paramagnetic phase at pressures corresponding to the Earth's core. The density of Fe₃C estimated by *ab initio* molecular dynamics calculations was sufficient different from seismological data. Our results precluded Fe₃C as the major inner core-forming phase.

Keywords: *ab-initio* calculations, iron compounds, molecular dynamics

P10.04.19

Acta Cryst. (2008). A64, C495-496

Crystallography of intermetallic CaLi₂ at high pressure

Yu Xie^{1,2}, Artem R. Oganov¹, Yanming Ma^{1,2}

¹ETH Zurich, Laboratory of Crystallography, Laboratory of Crystallography, HCI G 515, Wolfgang-Pauli-Str. 10, Zurich, Zurich, 8093, Switzerland, ²National Lab of Superhard Materials, Jilin University, Changchun 130012, China, E-mail: yu.xie@mat.ethz.ch

Lithium and calcium are usually considered as simple metals because of the simple electronic structures with one and two conduction electrons, respectively. Recent studies have indicated that both lithium and calcium have anomalous properties at high pressure. Thus, the high-pressure properties of the Laves-phase CaLi₂, the only intermetallic compound between Li and Ca at ambient conditions, would be very interesting. Recently, Feng *et al* [1] have studied the electronic structure of CaLi₂ under pressure and found the bandwidths of the valence states decrease rapidly under compression just as in Li and Ca. Moreover, they predicted CaLi₂ could be a potential