

Ca, S and O have been refined from these data, following calibration of the sample to image plate distance with silicon powder.

Keywords: synchrotron X-ray diffraction, high-pressure X-ray diffraction, monochromator

P.20.02.3

Acta Cryst. (2005). A61, C462

High Pressure Synthesis of $\text{EuGa}_{2-x}\text{Si}_{4+x}$ [$x = 1.3(1)$]

Aron Wosylus, Ulrich Burkhardt, Walter Schnelle, Ulrich Schwarz, Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany. E-mail: wosylus@cpfs.mpg.de

The title compound was prepared using a pressure of 8 GPa and a temperature of 1000 °C followed by slow cooling under pressure. After releasing pressure the sample was examined by x-ray powder diffraction, metallographical and EDX analysis. In the sample after the preparation, the compound $\text{EuGa}_{2-x}\text{Si}_{4+x}$ is found to coexist with $\text{EuGa}_{4-x}\text{Si}_x$ (EuGa_4 type) and Si.

$\text{EuGa}_{2-x}\text{Si}_{4+x}$ is the second representative of the EuGa_2Ge_4 structure type [1] and crystallizes in space group *Cmcm* with $a = 4.348(1)$ Å, $b = 10.457(1)$ Å and $c = 11.938(2)$ Å ($V = 542.8$ Å³). Gallium and germanium build up a three-dimensional network of four-bonded atoms with europium located in large voids. By replacing germanium with silicon the volume decreases by about 12 %. This change in volume is pronouncedly anisotropic; the length of the a axis increases by 4.6 % whereas the b and c axis shorten by 7.2 % and 9.3 %, respectively.

Due to a partial replacement of gallium by silicon, the electron balance can be written as $\text{Eu}^{2+}[\text{Ga}(3b)]^{1-0.7}[\text{Si}(4b)]^{0.5,3} \cdot 1.3e^-$. Thus, we expect metal-type conductivity. Magnetic susceptibility, electrical resistance and thermoelectric properties of the silicon compound are currently under investigation.

[1] Carrilo-Cabrera W., Paschen S., Grin Yu., *J. Alloys Comp.*, 2002, 333, 4.

Keywords: high-pressure synthesis, high-pressure crystal structure, physical properties

P.20.02.4

Acta Cryst. (2005). A61, C462

The Phase Transition of Hydrogen-bonded Ferroelectric PbHPO_4 under High Pressure

Yuki Nakamoto^a, Tomoko Kagayama^a, Katsuya Shimizu^a, Kiyoshi Deguchi^b, Takamitsu Yamanaka^c, ^aKYOKUGEN, Osaka Univ., Osaka. ^bDept. Mat. Sci. Inst. Sci. and Tech. Shizuoka. ^cDept. Earth and Space Science, Grad. School Sci. Osaka Univ. Osaka, Japan. E-mail: nakamoto@rcem.osaka-u.ac.jp

PbHPO_4 (LHP), undergoes a phase transition from Phase I to Phase II at $T_c = 310$ K under ambient pressure. The lower-temperature ferroelectric phase (Phase II) with pseudo-one dimensional hydrogen bonded structure has a space group of *Pc*. The paraelectric phase (Phase I) has been assumed to have *P2/c*. The T_c is gradually lowered with increasing pressure and then T_c goes down to room temperature. The transition pressure has been determined to be 0.15 GPa [1]. But the phase transition was no more found over 3 GPa. In this present work, x-ray powder diffraction study of LHP was carried out using synchrotron radiation with diamond anvil pressure cell under hydrostatic conditions at room temperature on BL-18C (KEK), Tsukuba. We could not detect any differences in the diffraction patterns of Phase II and Phase I with increasing pressure up to 5 GPa. By further compression a new pressure-induced phase (Phase III) appears at about 6.5 GPa. We have determined that the structure of Phase III has a possible space group of *Pmmm*, which is stable up to 17 GPa. During decompression cycle, phase III is covered back to the original phase I at 0.7 GPa.

[1] Mylov V. P., et al., *Sov. Phys. - Crystallogr.*, 1979, 24, 738.

Keywords: ferroelectrics, high pressure, phase transition

P.20.03.1

Acta Cryst. (2005). A61, C462

High Pressure Structures and Compressibilities of YF_3 and LaF_3

Wilson A. Crichton^a, Pierre Bouvier^b, Andrzej Grzechnik^c, ^aESRF,

B.P. 220, 38043 Grenoble, France. ^bENSEEG, INPG, St. Martin d'Hères, France. ^c Universidad del País Vasco, 48080 Bilbao, Spain.

E-mail: crichton@esrf.fr

Many studies have been devoted to the study of laser-hosting *Ln* (*Ln* = REE, Y, Sc) fluorides; particularly ALnF_4 phases crystallizing in the scheelite structure. Yet, for many *Ln* chemistries the scheelite form is unknown and, in the case of those known compositions, e.g. LiGdF_4 , decomposition, to $\text{LiF} + \text{LnF}_3$, occurs at high- p [1]. We have investigated how the LnF_3 structure controls both the synthesis and the decomposition of the binary fluoride phase at high p conditions.

YF_3 crystallizes in the $\beta\text{-YF}_3$ -type structure at ambient p . It has been proposed [2], though not observed, that the high- p , RT structure is the same as that of LaF_3 , tysonite-type. This conjecture we can confirm, in addition to obtaining compressibilities of high- and low- p forms. These data allow calculation of molar volumes at high- p , e.g. LiYF_4 cf. $\text{LiF} + \text{YF}_3$ and judge the effect of increase in REE-coordination at phase transitions on phase stability.

LaF_3 has no known binary fluoride scheelite forms and undergoes a phase transition at $p > 12$ GPa to a structure previously described in *Cmma* and *I4/mmm* symmetries (subgroups of CaF_2 structure) [3,4]. We will present our determination of the high- p structure of this phase that extends the currently known transition sequence for LnF_3 , thus:

$\delta\text{-UO}_3$ (ReO_3) to dist-ReO_3 to $\alpha\text{-UO}_3$ to $\beta\text{-YF}_3$ to LaF_3 to *Pmmm*.

[1] Grzechnik, et al., *J. Phys.: Cond. Matt.*, 2004, 16, 7779. [2] Atavaeva E.Y., Bendeliani N.A., *Inorganic Materials*, 1979, 15, 1487. [3] Dyuzheva, et al., *J. Alloys Comps.*, 2002, 335, 59. [4] Winkler, et al., *J. Alloys Comps.*, 2003, 349, 111.

Keywords: high-pressure structures, transformation, fluorides

P.20.03.2

Acta Cryst. (2005). A61, C462

Isosymmetric Reversible Phase Transition in Sodium Oxalate

Svetlana N. Ivashevskaya^{a,c}, E.V. Boldyreva^{a,b}, H. Sowa^d, H. Ahsbahs^d, H.-P. Weber^{e,f}, V.V. Chernyshev^g, ^aNovosibirsk State University, REC "MDEST", Russia. ^bInstitute of Solid State Chemistry and Mechanochemistry RAS, Novosibirsk, Russia. ^cInstitute of Geology Karelian Scientific Center RAS, Petrozavodsk, Russia. ^dPhilipps-Universität Marburg/Lahn, Institute of Mineralogy, Germany. ^eESRF, Swiss-Norwegian Beamlines, Grenoble, France. ^fInstitut de Cristallographie, Université de Lausanne, Switzerland. ^gMoscow State University, Chemistry Department. E-mail: sveta@xray.nsu.ru

Oxalate ions are widely used in the design of supramolecular structures. Anhydrous metal oxalates (like sodium oxalate) are interesting because they have not H-bonds and their structures are determined by the interactions in the system "oxalate-anions - metal cations" only.

At 3.8 GPa an isosymmetric phase transition was observed, preserving the *P21/c* space group despite a jumpwise change in cell parameters and volume. The orientation of oxalate-ions and the coordination of sodium-cations by oxygen atoms change jumpwise at the transition point. The packing of the centroids of oxalate-anions remains preserved to a large extent. It distorts anisotropically with increasing pressure.

The study was supported by RFBR (02-03-3358), the BRHE-Program (grant NO-008-XI), the National Science Support Foundation for EVB, CRDF Support of Young Scientists for SNI (grant Y2-CEP-08-07). The diffraction experiment was carried out at the Swiss-Norwegian Beamline at ESRF (experiment 01-02-656).

Keywords: phase transitions, pressure, powder method

P.20.03.3

Acta Cryst. (2005). A61, C462-463

Isostructural Transformation and Polymorphism of Thiourea Dioxide at High Pressure

Alistair J. Davidson^a, David R. Allan^a, Francesca P. A. Fabbiani^a, Duncan J. Francis^b, William G. Marshall^b, Colin R. Pulham^a, John E. Warren^c, ^aSchool of Chemistry and Centre for Science at Extreme Conditions, University of Edinburgh, Edinburgh, UK. ^bISIS, Neutron and Muon Facility, Rutherford Appleton Laboratory, Didcot, UK.

^cCCLRC Daresbury Laboratory, Warrington, UK. E-mail: A.J.Davidson-4@sms.ed.ac.uk

With the notable exceptions of water, ammonia and a very limited number of other examples, there have been relatively few high-pressure structural studies of simple molecular compounds. Such studies can provide fascinating information about intermolecular interactions and pressure-induced phase transition, in particular hydrogen-bonding interactions. Recent results for thiourea and urea obtained from the experiments on neutron beamlines at the UK ISIS facilities have shown a very rich high-pressure behaviour [1].

In the light of these results, we have undertaken neutron and synchrotron studies on thiourea dioxide, which has been selected by virtue of its interesting ambient pressure structure [2].

We report a phase transition between a powder sample of orthorhombic phase I of thiourea dioxide to a new monoclinic phase II at a pressure of 0.54 GPa. This transition has also been observed in a single crystal sample at a pressure of 0.45 GPa. We also report an unusual isostructural transformation in thiourea dioxide at 6.8 GPa that involves the formation of a new hydrogen bond.

[1] Marshall W.G., *ISIS Annual Report*, 2003. [2] Sullivan R.A.L., Hargreaves A., *Acta Cryst.*, 1962, **15**, 675.

Keywords: polymorphism, high pressure phase transitions, hydrogen bonding polymorphism

P.20.03.4

Acta Cryst. (2005). A61, C463

The Effect of Pressure, and Formation of new Polymorphs of the Amino Acids L-cysteine and L-serine

Stephen Anderson Moggach, Simon Parsons, David Allan, Carole Morrison, Lindsay Sawyer, *School of Chemistry and CSEC, University of Edinburgh, Scotland*. E-mail: s.moggach@ed.ac.uk

The application of pressure (<10 GPa) has proved a successful way of probing materials, particularly biologically important building blocks such as amino acids to understand the significance of hydrogen bonding interactions in these simple organic molecules [1].

On application of pressure, even systems comparable to each other have been shown to have remarkably different properties. Orthorhombic L-cysteine and L-serine-I, both of which have similar packing arrangements are examples of this. Under pressure, L-cysteine initially undergoes a much larger reduction in volume than L-serine-I, until at much higher pressure (c.a. 4 GPa) a single-crystal to single-crystal phase transition was observed. L-serine-I also undergoes a similar phase transition (c.a. 5 GPa) [2], however, although both phase transitions in L-serine-I and orthorhombic L-cysteine occur through the compressibility of soft interactions, the resulting high-pressure polymorphs are far different.

Pressure studies between ambient and 10 GPa are not only providing a useful way to investigate polymorphism of materials, but the information obtained on increasing pressure is beginning to give us an appreciation of the compressibility of intermolecular interactions under these pressure.

[1] Dawson A., Allan D.R., Clark S.J., Belmonte S.A., David W.I.F., McGregor P.A., Parsons S., Pulham C.R., Sawyer L., 2005, *accepted for publication*. [2] Moggach S., Morrison C.A., Allan D.R., Parsons S., Sawyer L., *Acta Cryst.*, 2005, **B61**, 58-68.

Keywords: high-pressure, polymorphism, amino acids

P.20.03.5

Acta Cryst. (2005). A61, C463

Absence of Halogen Bonding in the High-pressure Structure of Chlorotrimethylsilane

Roman Gajda, Kamil Dziubek, Andrzej Katrusiak, *Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland*. E-mail: katra@amu.edu.pl

Halogen...halogen interactions are usually considered as the next most important cohesion forces, apart from the hydrogen bonds, governing the arrangement of molecules in crystals [1]. Such interactions are observed in many compounds containing halogens.

The interactions of one halogen atom with the lone pair of another halogen atom forms intermolecular bridges. The chlorine...chlorine interactions belong to the most fundamental supramolecular synthons [2].

Meanwhile in the structure of chlorotrimethylsilane determined at low temperature [3] no halogen...halogen interactions are observed. Therefore we have undertaken the high-pressure study of this compound to check if short chlorine...chlorine contacts would exist in the compressed crystal. We have determined the crystal structure of chlorotrimethylsilane at 0.3 and 0.6 GPa. At these pressures the crystal is orthorhombic, space group Pmn2₁, whereas the crystal frozen at low temperature crystallized in monoclinic space group P2₁/m. It occurs that also in this new high-pressure phase of C₃H₉ClSi no close chlorine...chlorine contacts are observed.

[1] Metrangolo P., Resnati G., *Chem. Eur. J.*, 2001, **7**, 2511. [2] Bosch E., Barnes C.L., *Cryst. Growth Des.* 2002, **4**, 299. [3] Bushmann J., Lentz D., Luger P., Röttger M., *Acta Cryst.*, 2000, **C56**, 121.

Keywords: weak interactions, high-pressure crystallography, noncovalent bonding

P.20.03.6

Acta Cryst. (2005). A61, C463

High-pressure Crystal Phase of 1,2-ethylenediamine

Armand Budzianowski, Anna Olejniczak, Andrzej Katrusiak, *Faculty of Chemistry, Adam Mickiewicz University in Poznań, Poland*. E-mail: katra@amu.edu.pl

1,2-Ethylenediamine (H₂N CH₂ CH₂ NH₂) is the simplest of α,ω -alkanediamines. Its m.p. is 284.29 K [1], and it was crystallized at low temperature and its structure determined at 213 K [2] and 130 K [3]. The crystals are monoclinic, space group P2₁/c, $a = 5.047(2)$, $b = 7.14(2)$, $c = 5.475(2)$ and $\beta = 115.36(3)$ [3] (hereafter phase II).

In our study we have crystallized C₂H₈N₂ by pressure-freezing in Merrill-Bassett diamond-anvil cell. In this way three distinct phases of C₂H₈N₂ have been obtained and their structures determined: phase II with the unit cell parameters similar to those listed above for the low-temperature phase; phase I (which is stable at lower pressure and higher temperature, than for phase II) – monoclinic, space group P2₁/c $a = 5.031(10)$, $b = 5.132(3)$, $c = 7.167(5)$, $\beta = 110.60(12)^\circ$ at 0.3 GPa and 293(2) K; at 1.5 GPa the crystal is transformed to phase III with the unit-cell doubled.

The structures have been solved by direct methods and refined by full matrix least squares.

[1] Messerly J.F., Finke H.L., Osborn A.G., Douslin D.R., *J. Chem. Thermodyn.*, 1975, **7**, 1029. [2] Jamet-Delcroix P.S., *Acta Cryst.*, 1973, **B29**, 977. [3] Thalladi V.R., Boese R., Weiss H.-C., *Angew. Chem. Int. Ed.*, 2000, **39**, 918.

Keywords: crystal growth, high-pressure structure determination, hydrogen bonds in organic crystals

P.20.03.7

Acta Cryst. (2005). A61, C463-C464

Probing Polymorphism with High Pressure

Francesca P. A. Fabbiani^a, Colin R. Pulham^a, Simon Parsons^a, David R. Allan^a, John E. Warren^b, ^a*School of Chemistry, The University of Edinburgh, Edinburgh, UK*. ^b*CCLRC Daresbury Laboratories, Warrington, UK*. E-mail: F.P.A.Fabbiani@ed.ac.uk

In recent years, work at Edinburgh has shown that pressure-induced crystallisation of simple organic compounds from the pure liquid results in the generation of new polymorphs [1]. Attempts to induce polymorphism in more complex, higher melting compounds (such as pharmaceuticals) have been much less successful. This is because thermal decomposition usually occurs long before the pressure-elevated melting temperature is reached.

We have instead developed a technique for growing single crystals from solution at high pressure that removes excessively high temperatures and provides an opportunity to study high-pressure crystallisation from different solvent systems [2]. We report how the power of this technique, in combination with ambient-pressure conventional polymorph screening processes, is not only successful in