

[1] S. Baroni, S. de Gironcoli, A. Dal Corso, P. Giannozzi, *Rev. Mod. Phys.* **2001**, *73*, 515–562. [2] P. Giannozzi *et al.*, *J. Phys. Condens. Matter* **2009**, *21*, 395502. <<http://www.quantum-espresso.org>>. [3] A. Otero-de-la-Roza, V. Luaña, *Comput. Phys. Commun.* (accepted).

Keywords: thermodynamics, calculation, fitting

MS40.P12

Acta Cryst. (2011) **A67**, C503

Pressure-induced phase transitions in L-alanine and DL-alanine, revisited

Nikolay Tumanov,^a Elena Boldyreva,^b Alexander Kurnosov,^{a,c} Raul Quesada Cabrera,^{d,e} ^a*Novosibirsk State University*. ^b*Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk*. ^c*Bayerisches Geoinstitut, University of Bayreuth (Germany)*. ^d*Swiss-Norwegian Beamline ESRF, Grenoble (France)*. ^e*University College London, Christopher-Ingold Laboratories (United Kingdom)*. E-mail: n.tumanov@gmail.com

The effect of pressure on L-alanine and DL-alanine has been studied by X-ray powder diffraction, single-crystal X-ray diffraction, Raman spectroscopy and optical microscopy. No previously reported structural phase transitions in L-alanine and DL-alanine have been observed up to 12.3 and 8.3 GPa, respectively. In both compounds at about 1.5–2 GPa (close to the pressure of the previously reported phase transition in L-alanine into a tetragonal phase, 2.3 GPa [1], [2]), the cell parameters *a* and *b* become accidentally equal to each other, but without a change in the space group symmetry. Neither could be a polymorphic transformation in L-alanine from tetragonal into a monoclinic phase at about 9 GPa confirmed, the changes in the cell parameters till the highest measured pressures being continuous and the cell metrics remaining orthorhombic. Our Raman experiments confirmed the effects described previously for the spectra of L-alanine [1] and DL-alanine [3], but we have shown that the spectral changes are continuous and are not related to structural phase transitions. During a slow decompression of L-alanine single crystal (in a methanol-ethanol 4:1 mixture as a pressure-transmitting liquid) from about 6 GPa, new phases crystallized in the diamond anvil cell in the pressure range between 0.8–4.7 GPa, which recrystallized into L-alanine below 0.8 GPa. These previously unknown phases were characterized by powder X-ray diffraction and Raman spectroscopy and seem to be a solvate of L-alanine.

The study was supported by a grant from RFBR (09-03-00451), a BRHE grant RUX0-008-NO-06, a FASI Contract № 02.740.11.5102 and Integration Projects SB RAS (№13 & 109).

[1] A.M.R. Teixeira, P.T.C. Freire, A.J.D. Moreno, J.M. Sasaki, A.P. Ayala, J. Mendes Filho, F.E.A. Melo, *Solid State Commun.*, **2000**, *116*, 405–409. [2] J.S. Olsen, L. Gerward, P.T.C. Freire, J. Mendes Filho, F.E.A. Melo, A.G. Souza Filho, *J. Phys. Chem. Solids*, **2008**, *69*, 1641–1645. [3] E.A. Belo, J.A. Lima Jr., P.T.C. Freire, F.E.A. Melo, J. Mendes Filho, H.N. Bordallo, A. Polian, *Vibr. Spectr.*, **2010**, *54*, 107–111.

Keywords: amino acids, high pressure, phase transitions

MS40.P13

Acta Cryst. (2011) **A67**, C503

Phase Changes of H₂ and He Hydrates under High pressure and Low Temperature

Hisako Hirai,^a Akiko Umeda,^a Kousuke Shimizu,^a Taku Fujii,^a Shin-ichi Machida,^a Ayako Shinozaki,^a Taro Kawamura,^b

Yoshitaka Yamamoto,^b Takehiko Yagi,^c ^a*Geodynamics Research Center, Ehime University, Matsuyama*. ^b*National Inst. Advanced Industrial Science and Technology, Tsukuba*. ^c*Institute for Solid State Physics, Tokyo University, Kashiwa, Chiba (Japan)*. E-mail: hirai@sci.ehime-u.ac.jp

Three phases of hydrogen hydrate have been known so far. One is a clathrate hydrate, sII [1], and others are filled ice II structure and filled ice Ic structure [2]. The ratio of water to hydrogen molecules for these phases are 1:3, 1:6, 1:1, respectively. sII hydrogen hydrate is expected to be a hydrogen storage material, because it can contain relatively high hydrogen and its synthetic condition is mild comparable to industrial production. At room temperature, above about 1 GPa filled ice II and above 3 GPa filled ice Ic are formed. The latter one survives at least up to 90 GPa [3]. However, phase relations among them under high pressure and low temperature region have not yet been clarified. In this study, high pressure and low temperature experiments were performed by using diamond anvil cells and a helium-refrigeration cryostat in a region of 0.2 to 4.5 GPa and 130 to 300 K. X-ray diffractometry revealed a series of phase change from sII to filled ice Ic via filled ice II. For example, at 220K, sII transformed to filled ice II at approximately 0.6 GPa and further transformed to filled ice Ic structure at about 2.0 GPa. The present results experimentally confirmed the previous prediction.

Helium hydrate is known to form filled ice II structure [4], but the synthetic conditions reported have been limited. Similar experiments were carried in a region of 0.2 to 5.0 GPa and 200 to 300 K. The results showed that the filled ice II structure did not transform to filled ice Ic structure, but decomposed into helium and ice VI or VIII.

[1] W.L. Mao *et al.*, *Science* **2002**, *297*, 2247–2249. [2] W.L. Vos *et al.*, *Phys. Rev. Lett.* **1993**, *71*, 3150–3153. [3] H. Hirai *et al.*, *Amer. Mineralogist* **2006**, *91*, 826–830. [4] D. Londono *et al.*, *J. Chem. Phys.* **1992**, *97*, 547–552.

Keywords: hydrogen hydrate, helium hydrate, phase changes

MS40.P14

Acta Cryst. (2011) **A67**, C503–C504

Study of the behavior of alkali sulfides under pressure

David Santamaría-Pérez,^a Angel Vegas,^b Claus Muehle,^c Martin Jansen,^c ^a*Department of Physical Chemistry I, University Complutense, Madrid (Spain)*. ^b*Instituto de Química Física "Rocasolano", CSIC, Madrid (Spain)*. ^c*Max-Planck Institute for Solid State Research, Stuttgart (Germany)*. E-mail: dsantamaria@quim.ucm.es

Pressure-induced phase transitions in antiferrotype M₂S sulfides (M = Li, Na and K) into anticotunnite-type structures have recently been reported and, some of them, further transform into Ni₂In-type structures [1–3]. This high-pressure phase-transition path involves the increase of the cation coordination number from 8 in the antiferrotype structure, through 9 in anticotunnite to 11 in Ni₂In-type structure.

Theoretical *ab initio* total-energy calculations have allowed to completely characterize the high-pressure phases observed experimentally in Li₂S, Na₂S and K₂S and to predict the most likely phases that are expected to be stable below 100 GPa for all alkali metal sulfides [4].

In the present work we have studied the behavior of both, Rb₂S and Cs₂S at high-pressure and room temperature using angle-dispersive X-ray powder diffraction in a diamond anvil cell (DAC). Our measurements have allowed us to identify the existing phase transitions and confirm the previously proposed antiferrotype → anticotunnite → Ni₂In-type sequence of stable structures for M₂S sulfides with increasing pressure [5]. Strong luminescence is observed in Rb₂S above 2.6 GPa (band maximum at 703 nm) when the transition to the Ni₂In-type phase starts

to occur, the band maximum showing a non-linear blue shift with pressure.

[1] A. Grzechnik, A. Vegas, K. Syassen, I. Loa, M. Hanfland, M. Jansen, *Solid State Chem.* **2000**, *154*, 603-611. [2] A. Vegas, A. Grzechnik, K. Syassen, I. Loa, M. Hanfland, M. Jansen, *Acta Cryst. B* **2001**, *57*, 151-156. [3] A. Vegas, A. Grzechnik, M. Hanfland, C. Muehle, M. Jansen, *Solid State Sci.* **2002**, *4*, 1077-1081. [4] J.C. Schön, Z. Cancarevic, M. Jansen, *J. Chem. Phys.* **2004**, *121*, 2289-2304. [5] D. Santamaría-Pérez, A. Vegas, C. Muehle, M. Jansen, *Acta Cryst. B* **2011**, *67*, 109-115.

Keywords: high-pressure, phase transitions, alkali sulfides

MS40.P15

Acta Cryst. (2011) **A67**, C504

Pressure-induced B1-B2 phase transition in AgX : revisited

Jennifer Kung, Chia-Hui Lin, *Department of Earth Sciences, National Cheng Kung University (Taiwan)*. E-mail: jkung@mail.ncku.edu.tw

A large number of known AB compounds adopt the B1 (NaCl) structure. Under pressure, most of them transform to the B2 (CsCl) structure directly or via intermediate phase(s). The computational investigations suggest that the dense B2 phase is favored at high pressure for silver halides with the B1-structure (AgX, X=Cl, Br and I). The experimental studies have shown that AgCl transforms from B1 to B2 at 17 GPa, 200 °C [1]. In-situ X-ray work [1] showed two intermediate phases existing between the B1 - B2 phase transition in AgCl, with the structure of KOH and TII, respectively. As for AgBr and AgI, both are known to undergo B1- KOH-type structural transitions [2] in the pressure range between 13 - 16 GPa. In this study, we extended the experimental conditions to higher pressure to investigate the phase transitions in AgBr and AgI and to find out if they share the same topological transition as AgCl under high pressure.

The silver halides were studied in the diamond anvil cell (DAC) by angular dispersive X-ray powder diffraction technique. The high-pressure phase transformations of AgCl, AgBr and AgI were investigated up to 28, 41 and 56 GPa, respectively. In AgCl, a phase transition sequence B1 → KOH → TII → B2 was observed at high pressure, room temperature. The pathway of transformations in AgBr was found to be B1 → (unknown phase) → KOH → TII at high pressure. The "unknown phase" observed in AgBr was found for the first time and has been detected in three consecutive runs carried out in this study. At 35.5 GPa, we applied the laser heating (estimated temperature ~ 500 °C) and found that TII-type AgBr maintained the same structure type (TII). For AgI, the KOH-type high-pressure phase was observed up to 27 GPa. Upon further compression to the pressure of 56 GPa, and after annealing by laser heating (estimated temperature ~ 500 °C), AgI did not transform to the B2 phase. Based on the current experimental results, we conclude that the topological transition of B1-KOH-TII-B2 type AgCl can be achieved by applying pressure along. The occurrence of the TII phase in AgBr at high pressures, shows that the structural transition sequence of B1-B2 in AgBr is similar to the one found in AgCl. Yet, an additional new low-pressure phase is found to exist in AgBr between the B1 and KOH phase.

Computational studies confirm the same transition sequence for the B1-B2 transition of AgI [3]. Within the experimental data resolution, KOH-type AgI is identified to be stable up to 27 GPa, at least. Compared with AgCl and AgBr, the stability range of the KOH-type AgI is surprisingly wide, an effect which has also been noted in the computational study [3]. However, our x-ray diffraction data of AgI above 40 GPa do not confirm the TII structure type, which was predicted to be the stable polymorph in the computational studies [3].

In general, the transition pressures of this multiple series of solid-solid phase transformation are increasing with decreasing ionicity of

this series of AgX compounds. The ionicities for AgCl, AgBr and AgI are 0.869, 0.847 and 0.775, respectively. The predicted pressures to reach the stability region of the B2-type structures for AgBr and AgI are above 35 GPa [4] and 105 GPa [5], respectively.

[1] K. Kusaba, Y. Syono, T. Kikegawa, O. Shimomura, *J. Phys. Chem Solids* **1995**, *56*, 751-757. [2] S. Hull, A. Keen, *Phys. Rev. B*, **1999**, *59*, 750-760. [3] M. Catti, *Phys. Rev. B*, **2006**, *74*, 174105. [4] P.T. Jochym, K. Parlinski *Phys. Rev. B*, **2001**, *65*, 24106. [5] Y. Li, L.J. Zhang, T. Cui, Y.W. Li, Y. Wang, Y.M. Ma, G.T. Zou *J. Phys. Condens. Matter*, **2008**, *20*, 195218.

Keywords: high pressure, phase transition, silver halide

MS40.P16

Acta Cryst. (2011) **A67**, C504

Polymorphism of 1,4-diazabicyclo[2.2.2]octane complexes with HI and HBr

Anna Olejniczak, Waldemar Nowicki, Andrzej Katrusiak, *Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, (Poland)*. E-mail: aniao@amu.edu.pl

Materials with dielectric constant exceeding 1000 are most coveted for electronic applications in miniature devices. Such properties are exhibited by ferroelectric relaxors, which are mainly the doped lead-containing perovskite ceramics. Therefore organic relaxors are sought, which would be easier in production and more environment friendly: less energy is required for their production and deposition on substrates and they are easier for disposal. Most recently the giant dielectric response was found in NH⁺...N bonded 1,4-diazabicyclo[2.2.2]octane hydroiodide (dabcoHI) and hydrobromide (dabcoHBr) [1, 2].

A multitude of new polymorphs of dabcoHI has been obtained at elevated pressure and temperature [3]. The crystal symmetries identified for the nonsolvated dabcoHI crystals so far are: *P6m2*, *Pbcm*, *Pmc2₁*, *Pmm2*, *Cmm2*, *P2/c*. In all the structures determined by X-ray diffraction linear or nearly linear chains of cations are linked by NH⁺...N hydrogen bonds. The main structural differences between the polymorphs are in the arrangement of the poly-cationic chains and iodide anions, and in the conformation of dabco cations. When crystallized from methanol, up to 1.70(5) GPa dabcoHI forms unsolvated crystals, and at higher pressure solvates could be obtained only.

Only three phases of dabcoHBr could be obtained: phase I (*Pca2₁*), phase II (*Cmc2₁*) and phase III (*P6m2*). The NH⁺...N hydrogen bonded chains, which are characteristic for all dabcoHI structures, are present only in phase III of dabcoHBr. In phases II and III they are broken and NH⁺...Br ionic pairs are formed. Moreover, pressure 1.30 GPa led to N-methylation of dabco.

[1] M. Szafranski, A. Katrusiak, *J. Phys. Chem. B* **2008**, *112*, 6779-6785. [2] M. Szafranski, *J. Phys. Chem. B* **2009**, *113*, 9479-9488. [3] A. Olejniczak, A. Katrusiak, M. Szafranski, *CrystGrowth&Des.* **2010**, *10*, 3537-3546.

Keywords: hydrogen bonding, phase transition, high pressure

MS40.P17

Acta Cryst. (2011) **A67**, C504-C505

Amorphization in rare earth tungstates with modulated scheelite-type structure under pressure

N. Sabalisk,^a L. Mestres,^b X. Vendrell,^b E. Cerdeiras,^b D. Santamaría,^c V. Lavin,^d A. Muñoz,^e P. Rodríguez-Hernández,^e J. Lopez-Solano,^c E. Matesanz,^f M. C. Guzman-Afonso^d ^a*Departamento de Física Básica-Universidad de La Laguna, S/C Tenerife, (Spain)*. ^b*Departamento de*