

## MS19.P03

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**Shock wave synthesis and properties of rocksalt-type of aluminium nitride**

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Aluminium nitride is a ceramic material with a high thermal conductivity, a small thermal expansion coefficient and good mechanical properties. Moreover AlN is a wide-bandgap semiconductor ( $E_g = 6.2\text{eV}$ ) and therefore high potential substrate material for high-power electronic applications [1]. At pressure from 14-23GPa the wurtzitic aluminium nitride (wz) undergoes a phase transition to rocksalt structure (rs) at static experiments [2], [3], [4]. A sinterbody of wz-AlN/rs-AlN show high hardness (>4000HV), high electric resistance and a thermal conductivity up to 600W/mK [5]. Though the phase transition through shock waves were verified, shock experiments failed to quench the high-pressure phase so far [6].

Currently rs-AlN were successfully synthesized from AlN nanopowder with shock wave synthesis via flyer-plate method at the Freiberg High-Pressure-Research-Centre (FHP). A 80mm metal plate were accelerated by high explosive to several km/s striking a steel container with the pure AlN sample powder. To obtain good conditions a flat shock wave were produced with a special plane-wave-generator. The fine greyish powder (at the moment up to 2g per shot), which can be gathered from recovery container, shows up to 50% of the high-pressure AlN-phase. Caused by high oxygen content of the commercial AlN nanopowder, the synthesis product consist some percentage corundum and  $\gamma$ -AlON (up to 17%). At a given porosity of 1,68 at about 23GPa the highest yield can be achieved, while at higher pressures or major powder porosity, the post-shock-temperature is too high, so that the new high-pressure phase cannot be quenched and decomposes partly or complete to wz-AlN.

First experiments show good chemical resistance of rs-AlN to acids and bases and a thermal stability higher than 1100°C in air. Further analysis (FTIR, 27Al MAS-NMR, neutron diffraction and in-situ HT-XRD) are in progress.

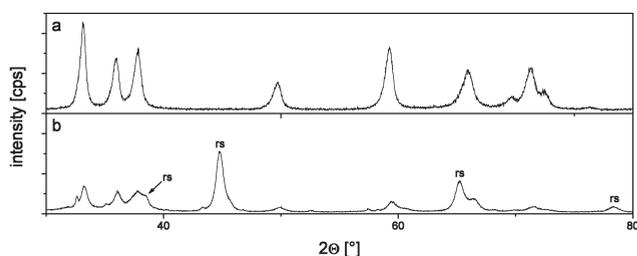


Fig 1: X-ray diffraction of (a) commercial nano-AlN-powder and (b) sample shocked at 22GPa with 50% rs-AlN yield.

[1] W. Werdecker, F. Aldinger, *Components, Hybrids, and Manufacturing Technology* **1984**, 7, 399-404. [2] I. Gorczyca, N.E. Christensen, P. Perlin, P. I. Grzegory, J. Jun, M. Bockowski, *Solid State Communications* **1991**, 79, 1033-1034. [3] M. Ueno, A. Onodera, O. Shimomura, K. Takemura, *Physical Review B* **1992**, 45, 10123-10126. [4] Q. Xia, H. Xia, A.L. Ruoff, *Journal of Applied Physics* **1993**, 73, 8198-8200. [5] H. Vollstadt, H. Recht, *Patent DD000000292903A5* **1991**. [6] K. Kondo, A. Sawaoka, K. Sato, M. Ando, *AIP Conference Proceedings* **1982**, 78, 325-329.

**Keywords:** aluminium nitride, shock wave synthesis, hard material

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**New high-pressure-high-temperature forms in sesquioxides**

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Sesquioxides,  $M_2O_3$  (where  $M$  – is a metal, like Al, Fe, Ti, Cr, Ga, etc.) (Fig.) are the focuses of interests of several fields, such as: geosciences, condensed matter physics and chemistry, industry and others. They show two trends in ambient crystal structure: oxides of metals of small periodic numbers  $Z$  prefer crystallization in a corundum structure, while those of metals of high periodic numbers prefer adopting in a cubic bixbyite lattice.

In this presentation we review new trends in high-pressure-high-temperature (HP-HT) studies in sesquioxides and report some of our new results on HP-HT preparation of novel forms of sesquioxides and examination of their properties. As an examples, we will display several important cases, some of which are listed below:

- (i) ‘**Golden oxide**’: Examination of electron band structure of the recently discovered golden  $\text{Th}_2\text{S}_3$ -type phase of  $\text{Ti}_2\text{O}_3$  [1], [2] by a set of experimental and theoretical methods.
- (ii) ‘**Structural engineering**’: fabrication of new structural forms in ‘mixed’ oxides, e.g. in  $(\text{Ti}_{1-x}\text{M}_x)_2\text{O}_3$  solutions by HP-HT synthesis.
- (iii) ‘**Hidden phases**’: the observation of new intermediate HP-HT phases in seemingly well-studied  $M_2O_3$  materials.
- (iv) ‘**Composites**’: not just mixtures of  $M_2O_3$ , but cases, like: ‘self-organization’, ordering, superstructuring and other puzzling processes in mixtures under HP-HT conditions; ‘hidden’ composite properties of a single structural phase of a single material prepared at HP-HT, etc.

[1] D. Nishio-Hamane, M. Katagiri, K. Niwa, A. Sano-Furukawa, T. Okada and T. Yagi, *High Pressure Res.* **2009**, 29, 379. [2] S. V. Ovsyannikov, X. Wu, V. V. Shchennikov, A. E. Karkin, N. Dubrovinskaya, G. Garbarino, and L. Dubrovinsky, *J. Phys.: Condens. Matter*, **2010**, 22, 375402.

**Keywords:** pressure, oxide, transition

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**Phase stability of boron relative to  $\beta$ -boron at high pressure and high temperature**

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Boron is one of the nonmetal elements that have been widely studied due to its complex polymorphism and fascinating chemical and physical properties. [1], [2] Boron’s three valences are too localized to make it metallic and insufficient in number to form a simple covalent bond. As a result, boron atoms form  $B_{12}$  icosahedra link together in a variety of ways. Until now, probably four of the reported boron phases correspond to the pure element. [1], [2]:  $\alpha$ -boron (rhombohedral, within a 12-atom unit cell),  $\beta$ -boron (high temperature form, rhombohedral, structure is not fully understood and consists of 105 or 108 atoms in

the unit cell), T-192 (tetragonal, with 190-192 atoms per unit cell), and  $\gamma$ -boron (high pressure phase, orthorhombic, with 28 atoms per unit cell). The new phase turned out to be a key to understanding the phase diagram of boron—the only element for which the phase diagram was unknown since its discovery 200 years ago.

Here, we report the synthesis of  $\gamma$ - and T-192 boron from  $\beta$ -boron at pressures up to 18 GPa and temperatures up to 2200 °C using a multianvil apparatus combined with x-ray diffraction (XRD) and Raman spectra. Based on the XRD and Raman results, we give the phase boundary of  $\beta$ -,  $\gamma$ -, and T-192 boron. Fig.1 shows the phase relations between  $\beta$ -boron (open circles),  $\gamma$ -boron (solid circles) and T phase (inverse triangles) based on the results of the multianvil quenched experiments. The semi-solid circles represent  $\beta$ -boron and  $\gamma$ -boron in coexistence. The line is a phase boundary between  $\beta$ -boron and  $\gamma$ -boron, and the inset show the theoretical phase boundary from Oganov *et al.*[1] and the tentative phase boundary from Zarechnaya *et al.*[2]. Additionally, the two open inverse triangle represent P-T conditions of T-192 phase from Oganov *et al.*[1] and Ma *et al.*[3] respectively. Combined with the previous results [1], [2] and our study,  $\gamma$ -boron phase becomes stable under a certain pressures (above ~8.5 GPa), and  $\beta$ -boron can transform into  $\gamma$ -boron above ~8.5 GPa and using heating to overcome kinetic barriers, and the kinetic barriers decrease with increasing pressure. However, at higher temperatures,  $\beta$ -boron and T-192 phase are more stable than  $\gamma$ -boron, thus  $\gamma$ -boron transforms back to  $\beta$ -boron (~9 GPa) or continues to transform into T-192 phase (above ~10 GPa) with increasing temperature depend on undergoing high pressure.

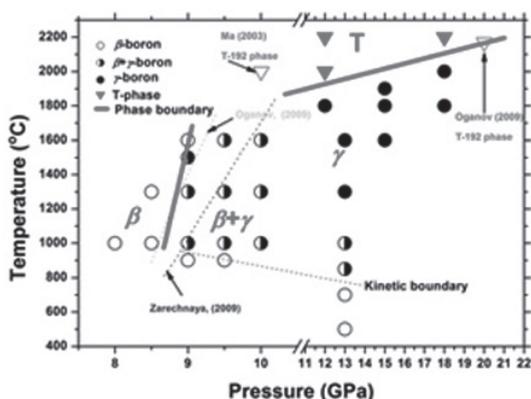


Fig.1 Phase relations between  $\beta$ -boron,  $\gamma$ -boron and T phase

[1] A.R. Oganov, J. Chen, C. Gatti, Y.Z. Ma, Y.M. Ma, C.W. Glass, Z. Liu, T. Yu, O.O. Kurakevych, V.L. Solozhenko, *Nature* **2009**, *457*, 863-867. [2] E.Y. Zarechnaya, L. Dubrovinsky, N. Dubrovinskaia, Y. Filinchuk, D. Chernyshov, V. Dmitriev, N. Miyajima, A. El Goresy, H.F. Braun, S. Van Smaalen, I. Kantor, V. Prakapenka, M. Hanfland, A.S. Mikhaylushkin, I.A. Abrikosov, S.I. Simak, *Phys. Rev. Lett.* **2009**, *102*, 185501. [3] Y.Z. Ma, C.T. Prewitt, G.T. Zou, H.K. Mao, R.J. Hemley, *Phys. Rev. B.* **2003**, *67*, 174116

**Keywords:** boron, phase boundary, high pressure and high temperature

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### Structural anomaly in a novel iron-based perovskite

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Recent discovery of iron-based perovskites  $ACu_3Fe_4O_{12}$  ( $A = Ca$  and  $La$ ) has been attracting much interest due to the fascinating and unexpected properties. A charge disproportionation (CD) of  $Fe^{4+}$  into  $Fe^{3+}$  and  $Fe^{5+}$  occurs in  $CaCu_3Fe_4O_{12}$  (CCFO) [1], whereas an intersite charge transfer (CT) between Cu and Fe results in a large volume change in  $LaCu_3Fe_4O_{12}$  [2]. The different electronic phases resulted from CD/CT imply that further anomalous properties can be achieved in this system.

A novel iron-based perovskite  $SrCu_3Fe_4O_{12}$  (SCFO) was successfully synthesized using high-pressure of 15 GPa. The structural and physical properties of SCFO were in contrast to those of the known  $ACu_3Fe_4O_{12}$  ( $A = Ca$  and  $La$ ) perovskites. SCFO demonstrated a large negative thermal expansion (NTE) with a linear expansion coefficient (ca.  $-2 \times 10^{-5} K^{-1}$  at maximum) in a temperature range of 170–270 K. The Rietveld refinement based on the synchrotron X-ray powder diffraction data revealed that the NTE was attributed to a continuous intersite CT between Cu and Fe. Mössbauer spectroscopy exhibited that SCFO resulted in a charge disproportionated state below ~200 K. The relative abundance of  $Fe^{3+} : Fe^{5+} = 4 : 1$ , which is different from the ratio of 1 : 1 for CCFO, implies the electron doping into Fe through intersite charge transfer.

[1] I. Yamada *et al.*, *Angew. Chem. Int. Ed.* **2008**, *47*, 7032–7035. [2] Y.W. Long *et al.*, *Nature* **2009**, *458*, 60–63.

**Keywords:** novel perovskite, negative thermal expansion, high-pressure synthesis

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### Electron and magnetic properties in high temperatures magnetic semiconductors at high pressure up to 7 GPa

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In high-temperature ferromagnetic semiconductors  $Cd_{1-x}Mn_xGeAs$  ( $x=0\div 0.36$ ) and  $Cd_{1-x}Mn_xGeP_2$  ( $x=0\div 0.225$ ) there is carried out a complex investigation of electric and magnetic properties. The baric dependences of the specific resistance  $\rho$ , Hall coefficient  $R_H$ , and relative magnetic susceptibility  $\chi/\chi_0$  are measured. The  $\rho(P)$  and  $R(P)$  are measured in high-pressure device of “Toroid” type [1], [2] when pressure rises and falls up to 7 GPa. The magnetic susceptibility is estimated by a method described in the work [3]. Structural phase transitions are found in baric dependences of  $\rho(P)$  and  $R_H(P)$  in both compounds at increase and decrease in pressure. A position of phase transitions sifts towards the high pressures when a percentage of Mn increases. All phase transitions are reversible in  $Cd_{1-x}Mn_xGeAs_2$ , in  $Cd_{1-x}Mn_xGeP_2$  samples with  $x \leq 0.135$  the phase transition is accompanied by partial decomposition of a substance, what confirms the X-ray diffraction study before and after pressure applying on dependences  $(\chi/\chi_0)P$ . In all samples of both compounds there are observed the magnetic phase transitions which shift towards high pressures with increase in percentage of Mn. When pressure decreases the hysteresis emerges. A magnetic phase transition is not revealed in base samples of  $CdGeAs$  and  $CdGeP$ . We interpret the observed phase transitions as non-magnetic phase transition [4]. The temperature dependences of normal and abnormal Hall coefficients are calculated from magnetic-field dependences of Hall resistance for  $Cd_{1-x}Mn_xGeAs_2$  ( $x=0\div 0.36$ ) by the method of interactive graphical plotting.