



Die Ressourcenuniversität. Seit 1765.

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Shock-induced Synthesis and stability of the high-pressure phase of AlN



K. Keller, T. Schlothauer, M. R. Schwarz, G. Heide, E. Kroke



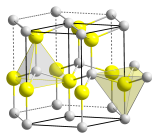
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2.-5.5.2012 Strasbourg, France

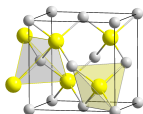


Phase transition to rocksalt structure

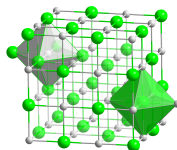
- **Wurtzite** (w), Zinblende (zb) and Rocksalt-Structure (rs)
- rs-AlN discovered 1982 with shock wave experiments ($P_T = 21 \pm 1$ GPa, $\Delta V = 20\%$) KONDO ET AL. (1982)
- first synthesis and recover of rs-AlN with MAP VOLLSTÄDT ET AL. (1990) (quenched from $P = 16.5$ GPa and $T = 1400$ to 1600 °C)
- sintered w-AlN/rs-AlN high hardness (≤ 4500 HV), high electrical resistance and thermal conductivity of 250 to 600 W/m K VOLLSTÄDT AND RECHT (1991)



(a) wurtzite



(b) zinblende



(c) rocksalt

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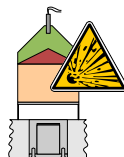
→ almost no knowledge about properties of rs-AlN: thermal and chemical stability, mechanical properties

Shock Synthesis of *rs*-AlN

Experimental Set-up

Parameters and Result of Synthesis

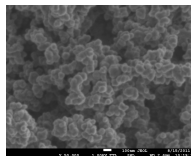
Structural Characterisation



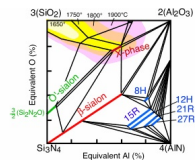
Properties of *rs*-AlN

Thermal Stability

Chemical Stability



Conclusion and Outlook

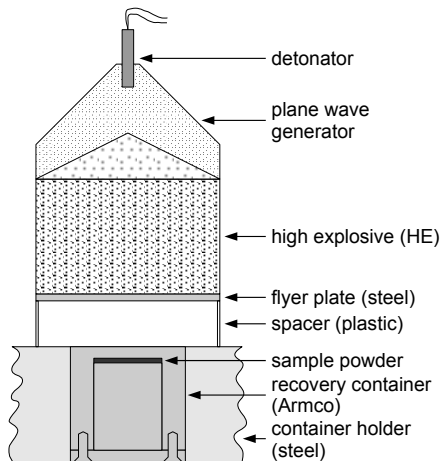


FHP shock wave equipment

- flyer-plate method
- active plane wave generator
- high explosives up to 8.3 km/s
- different materials
- successful synthesis of new materials, e.g.
 - γ - Si_3N_4 SCHLOTHAUER ET AL. (2012)
 - rs-AlN KELLER ET AL. (2011)

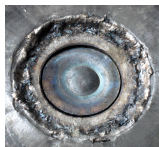
Shock Wave Parameters

- standard: pressures up to 100 GPa, several thousand K
- impedance and reflection method for different p-T-paths

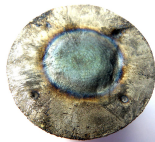


Synthesis Conditions

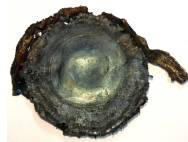
- all sample preparations under nitrogen (glovebox system)
- reflection method, **pressure** 15 to 43 GPa
- w-AlN as starting powder (no additional pressure medium) with varying **porosity** k ($\rho_{\text{solid}}/\rho_{\text{porous}}$) 1.5 to 2.5, **sample height** d 0.5 to 2.0 mm
- nanopowder 20 nm, submicronpowder 0.8 to 1.8 μm



(a) Deformed container holder



(b) Annealing color on shocked sample container



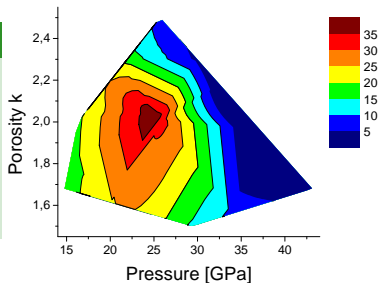
(c) Deformed flyer plate

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Results

- max. yield @ 23 GPa and $k = 2.1$
- sensitiv to conditions caused by thermal reconversion $\text{rs} \rightarrow \text{w}$
- for lower sample heights (0.5 mm) better results (less shock attenuation)

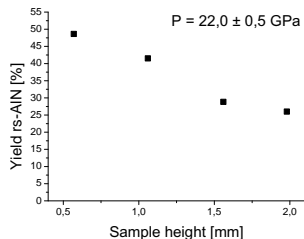


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Nanopowder vs. Submicron-powder

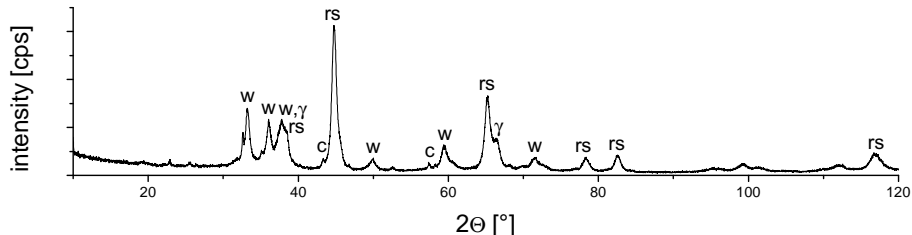
- with submicron-powder at same pressure and experimental set-up no rs-AIN formed (recovered)
- for AIN transition pressure decrease with decreasing grain size [WANG ET AL. \(2004\)](#)
- lower P_T enable recover of rs-AIN (less energy introduced causing less temperature rise)
- other possible effects: more nuclei, reactivity of nanopowder

Phase Analysis

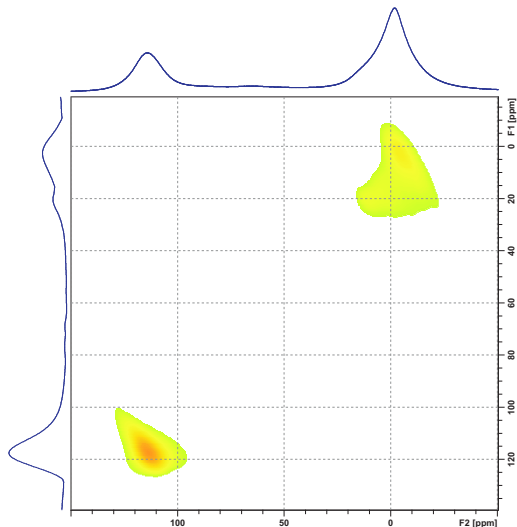
- mixture of rs-AlN (at the moment up to 50%), w-AlN, corundum, γ -AlON
- high oxygen content caused by bad commercial nano-AlN powder-quality \rightarrow Al_2O_3 and γ -AlON in reaction product
- up to 2 to 5% chloride in starting powder

XRD data of AlN

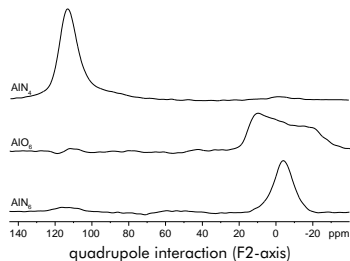
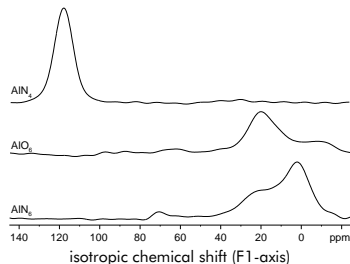
w-AlN:	15 to 30 nm
	$a = 3.1073 \pm 0.0002 \text{ \AA}$
	$c = 4.9806 \pm 0.0005 \text{ \AA}$
rs-AlN:	10 to 25 nm
	$a = 4.0464 \pm 0.0027 \text{ \AA}$



Nuclear Magnetic Resonance Spectroscopy (NMR)

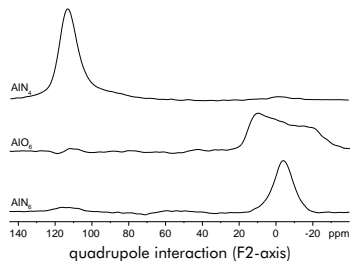
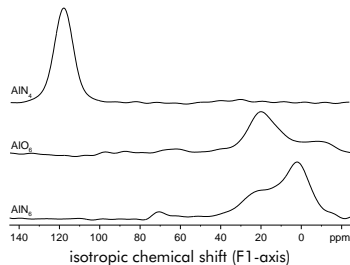


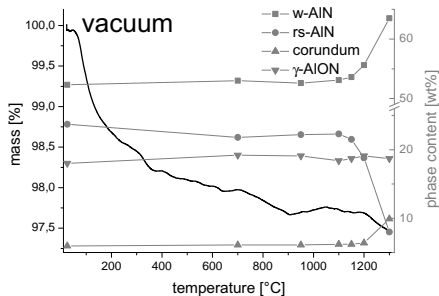
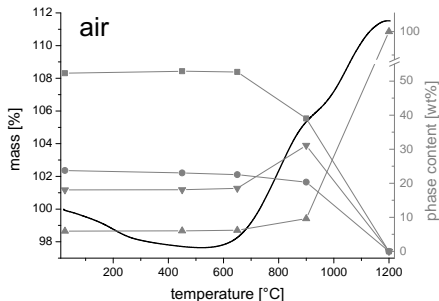
3MQ-MAS NMR spectra of sample AN33 with 48 % rs-AIN



Results of 2D NMR measurement

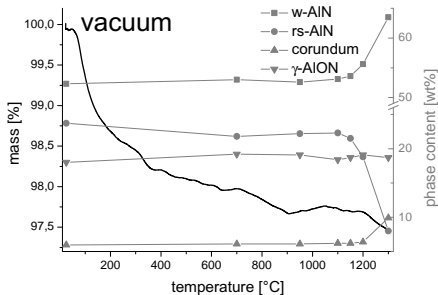
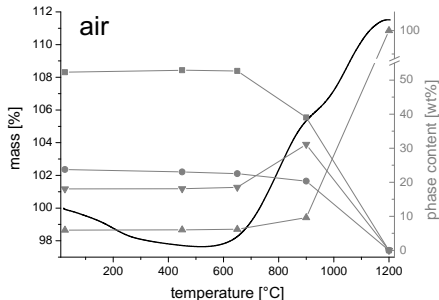
- corrected peak positions: 2 ppm (AlN_6), 20 ppm (AlO_6) and 118 ppm (AlN_4)
- quadrupole splitting of AlO_6 -group
- peak broadening \rightarrow poor crystallinity





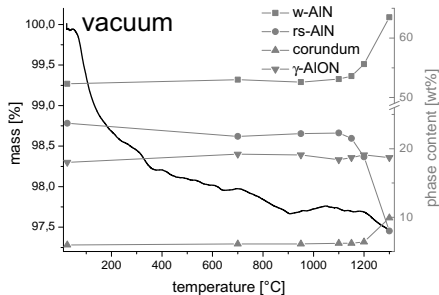
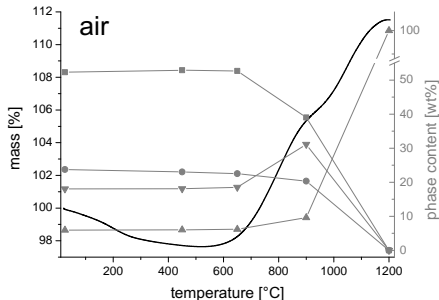
Heat stability in air and vacuum

- weight loss up to 500 °C caused by degassing and decomposition of hydroxides
- stepwise mass increase + positive heat flow indicates oxidation
- rs-AlN oxidised at $T > 600$ °C
- mass decrease of 2.5 % caused by outgassing of volatiles and decomposition
- reconversion of rs-AlN \rightarrow w-AlN at 1100 to 1300 °C
- increase in γ -AlON and corundum (structural bonded oxygen in rs-AlN?)



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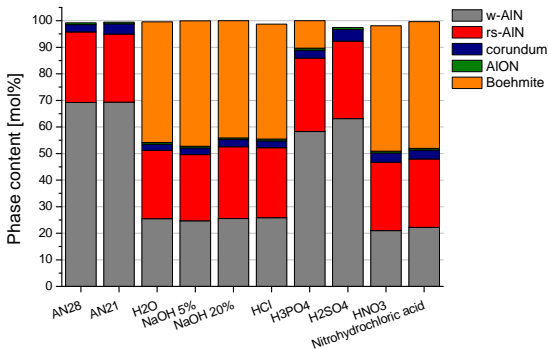


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Chemical resistance against acids and bases

- different chemicals: water, NaOH, HCl, H_3PO_4 , H_2SO_4 , HNO_3 and nitrohydrochloric acid
- 500 mg sample in 4 ml chemical for 1 h
- w-AIN reaction to $\text{AlO}(\text{OH})$, γ -AlON slightly dissolved
- corundum and rs-AIN extreme stable



Just to sum up...

We have shown that rs-AlN...

1. ... can be shock synthesised from AlN nanopowder with a maximum yield of 50 % at 23 GPa and a porosity of 2.1
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Further things to come...

- improved shock wave synthesis for higher amounts and yields (precursor chemistry, cooling medium, cylindrical charge)
- HR-TEM analysis
- ND for further structural characterisation, esp. oxygen in structure
- production of dense sinter body for further characterisation (mechanical, electrical, thermal)

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Financial support

- Dr. Erich Krüger-Foundation - Freiberg High-Pressure Research Centre (FHP)
- Excellence Initiative of the Saxonian Government, promoted by the European Union - ADDE
- DFG Priority Programme 1236

Other support

- Many collaborators
- Team of the Reiche Zeche mine
- Federal Institute for Materials Research and Testing (BAM), Division Explosives
- Saxony explosive ordnance disposal unit (KMBD)





Thank you for your kind attention!

- DECARLI, P. S. AND MEYERS, M. A. (1981): "Shock waves and high-strain-rate phenomena in metals: Concepts and Applications". In: ed. by Meyers, M. A. and Murr, L. E. New York: Plenum Publishing Corporation. Chap. Design of uniaxial strain shock recovery experiments, pp. 341–373.
- DOBRATZ, B. M AND CRAWFORD, P. C. (1985): *LLNL Explosives Handbook. Properties of Chemical Explosives and Explosive Simulants*. Ed. by Dobratz, B. M. and Crawford, P. C. ISEE Explosives Engineers.
- KELLER, K., SCHLOTHAUER, T., SCHWARZ, M., HEIDE, G., AND KROKE, E. (2011): "Shock wave synthesis of aluminium nitride with rocksalt structure". In: *High Pressure Research* 31. 4, in press.
- KONDO, K., SAWAOKA, A., SATO, K., AND ANDO, M. (1982): "Shock compression and phase transformation of AlN and BP". In: *AIP Conference Proceedings* 78. 1, pp. 325–329. URL: <http://link.aip.org/link/?APC/78/325/1>.
- SCHLOTHAUER, T., SCHWARZ, M. R., M., OVIDIU, BRENDLER, E., MOECKEL, R., KROKE, E., AND HEIDE, G. (2012): "Shock wave synthesis of oxygen-bearing spinel-type silicon nitride γ -Si₃(O,N)₄ in the pressure range from 30 to 72 GPa with high purity". In: *Minerals as Advanced Materials II*. Ed. by Krivovichev, S. V. Springer Berlin / Heidelberg, pp. 389–401.
- SEKINE, T. AND KOBAYASHI, T. (2003): "Phase transition in ceramics under shock wave compression". In: *New Diamond and Frontier Carbon Technology* 13. 3, pp. 153–160. URL: <http://www.myu-inc.jp/myukk/NDFCT/archives/pdf/NDFCT423.pdf>.
- VOLLSTÄDT, H. AND RECHT, H. (1991): "Verfahren zur Herstellung von kubischem Aluminiumnitrid [DD000000292903A5]". Deutsch. Patent DD000000292903A5. URL: <http://depatisnet.dpma.de/DepatisNet/depatisnet?action=bibdat&docid=DD000000292903A5>.
- VOLLSTÄDT, H., ITO, E., AKAISHI, M., AKIMOTO, S-I, AND FUKUNAGA, O. (1990): "High Pressure Synthesis of Rocksalt Type of AlN". In: *Proceedings of the Japan Academy, Series B* 66. 1, pp. 7–9. DOI: doi:10.2183/pjab.66.7. URL: http://www.journalarchive.jst.go.jp/english/jnlabstract_en.php?cdjournal=pjab1977&cdvol=66&noissue=1&startpage=7.
- WANG, Z., TAIT, K., ZHAO, Y., SCHIFERL, D., ZHA, C., UCHIDA, H., AND DOWNS, R. (2004): "Size-Induced Reduction of Transition Pressure and Enhancement of Bulk Modulus of AlN Nanocrystals". In: *The Journal of Physical Chemistry B* 108. 31, pp. 11506–11508. ISSN: 1520-6106. URL: <http://dx.doi.org/10.1021/jp048396e>.

Transaction during shock consolidation

- compaction and filling of voids - just in the width of the shock front → possibility to compact powders in bulk
- shattering and heavy deformation of grains
- raising dislocation density
- plastic deformation → strong heating
- local softening up to melting
- phase transition 10^{-11} to 10^{-12} s
- specific effects (particle surface melting, jetting, high local deformation)
- different thermodynamical route compared to static →
 - large increase of internal energy at shock wave compaction
 - heterogenous temperature distribution (before and after shock front)
 - melting of just a fraction, high cooling rates (often resulting in amorphous phases)

Comparison of static and dynamic processes

- different timescale → shock processes in order of microseconds
- compaction just in the width of the shock front → possibility to compact powders in bulk (high volume)
- particles accelerated to hundreds of meter per second → particle surface melting, jetting, high local deformation
- different thermodynamical routes →
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Impedance vs. Reflection method

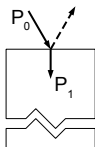
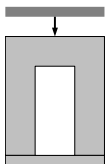
impedance method

precursor mixed with pressure medium
medium to high pressure
high temperature

reflection method

pure precursor
high to ultrahigh pressure
medium temperature

impedance method



reflection method

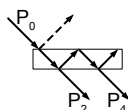
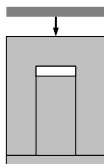


Fig. 1: Sample geometry

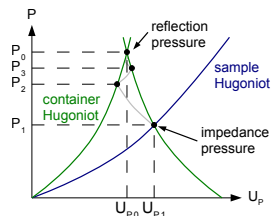


Fig. 2: Sample pressure

Impedance vs. Reflection method

impedance method

precursor mixed with pressure medium
medium to high pressure
high temperature

reflection method

pure precursor
high to ultrahigh pressure
medium temperature

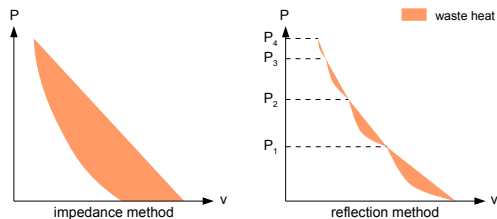


Fig. 1: Sample geometry

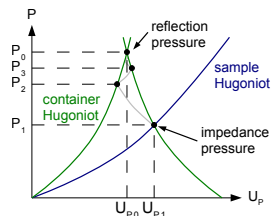


Fig. 2: Sample pressure

Flyer plate speed and sample pressure

The speed of the flyer plate can be estimate with the Gurney velocity $\sqrt{2E}$ [DECARLI AND MEYERS (1981)]:

$$v_{fp} = \sqrt{2E} \sqrt{\left(\frac{3}{1 + 5 \left(\frac{m}{c}\right) + 4 \left(\frac{m}{c}\right)^2} \right)} \quad (1)$$

The pressure can be calculated from the sample impedance Z:

$$P = \rho_0 U_P U_S = Z U_P \quad (2)$$

with:

$$U_S = A + B U_P \quad (3)$$

Gurney velocities

Tab. 1: Gurney velocities for some explosives after DOBRATZ AND CRAWFORD (1985)

explosive	density [g/cm ³]	v _D [km/s]	$\sqrt{2E}$ [km/s]
Comp. A-3	1,59	8,14	2,63
Comp. B	1,72	7,92	2,71
Comp. C-3	1,60	7,63	2,68
Cyclotol 75/25	1,75	8,25	2,79
H-6	1,76	7,90	2,58
HMX	1,84	8,83	2,80
LX-14	1,89	9,11	2,97
Octol 75/25	1,81	8,48	2,80
PBX 9404	1,84	8,80	2,90
PBX 9502	1,89	7,67	2,38
PETN	1,76	8,26	2,93
RDX	1,77	8,70	2,83
Tacot	1,61	6,53	2,12
Tetryl	1,62	7,57	2,50
TNT	1,63	6,86	2,44
Tritonal 80/20	1,72	6,70	2,32
NSP-711 ^a	1,45	7,50	2,36
NSH-711 ^a	1,60	8,30	2,64

a verwendete Sprengstoffe, $\sqrt{2E}$ von BAM bestimmt

The essential aim of the Freiberg High-Pressure Research Centre (FHP) is the application of high pressures for the material development and synthesis, the optimisation and comprehensive characterisation and understanding of the materials properties as well as to convey the gain of knowledge in saleable products.

