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Kevin Keller
Institute of Mineralogy
Brennhausgasse 14
D-09599 Freiberg
Tel.: +49 3731 39 4348
mail: kevin.keller@mineral.tu-freiberg.de

Shock-induced synthesis of spinel-type Ge_3N_4

M. R. Schwarz, K. Keller, J. Heinz, M. Köhler, N. Schreiter, D. Weile, T. Schlothauer, E. Kroke, G. Heide

XII International Symposium
on Explosive Production of New Materials:
Science, Technology, Business, and Innovations
(EPNM-2014)
May 25-30 Cracow, Poland

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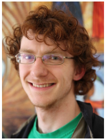

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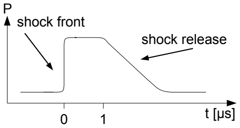
Outline

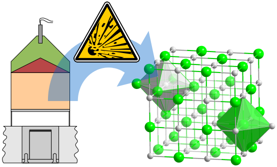
Group IV-nitrides

Experimental
- Shock Synthesis
- Powder Processing

Shock Synthesis of γ-Ge_3N_4
- Scanning Electron Microscopy
- Phase Analysis
- Raman spectroscopy

Conclusion and Outlook

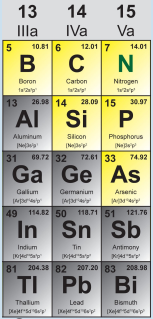




Group IV-nitrides

Structure and properties of M_3N_4 substances

- trigonal $\alpha - M_3N_4$ and hexagonal β-M_3N_4 (α-$M_3N_4 \xrightarrow{HT} \beta$-$M_3N_4$)
- e.g. β-Si_3N_4 ceramic material (high strength, wear resistance, good HT-properties) and microelectronic (dielectric properties)
- β-Si_3N_4 and β-Ge_3N_4 corner-shared SiN_4 or GeN_4 tetrahedra



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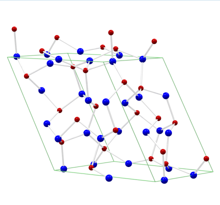
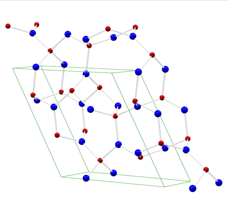
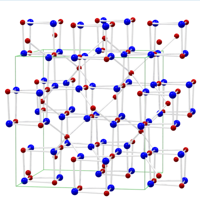


(a) α-M_3N_4



(b) β-M_3N_4

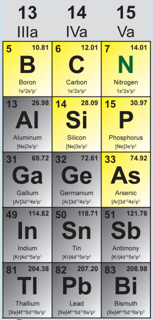


(c) γ-M_3N_4

Group IV-nitrides

M_3N_4 @ high-pressure

- γ-Si_3N_4, γ-Ge_3N_4 and γ-Sn_3N_4: cubic spinel structure ($Fd\bar{3}m$) with octahedral and tetrahedral coordination of Si, Ge and Sn
- β-$Ge_3N_4 \longrightarrow \gamma$-$Ge_3N_4$ at 12-15 GPa + > 1000 °C (kinetic barrier!)
  LEINENWEBER ET AL. (1999)
- shock synthesis for higher sample mass (mass production and comprehensive charcterisation) HE ET AL. (2001)
- γ-Ge_3N_4: band gap in optical region, hardness 34 GPa, bulk modulus 240-295 GPa SHEMKUNAS ET AL. (2004)
- predicted post-spinel phase (in analogy with e.g. Fe_3O_4 and Mg_2SiO_4) with higher coordination
- β-C_3N_4 hypothetical, predicetd for super-hardness, intensive research



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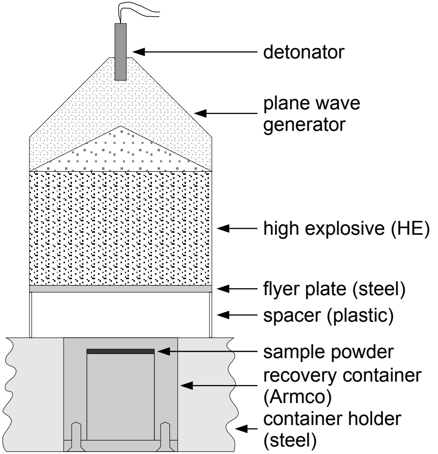
FHP Shock Wave Equipment

- flyer-plate method SCHLOTHAUER ET AL. (2012)
- active plane-wave-generator
- HE = plastified hexogen ($v_D = 8300$ m/s)
- reflection method
- α/β-Ge_3N_4 mixed with copper powder (90 wt%)

Shock Wave Parameters

	FP-GN1	FP-GN2
P [GPa]	45 GPa	35 GPa
$P_{first\ shock}$ [GPa]	35 GPa	27 GPa
T [K]	1920 K	1380 K

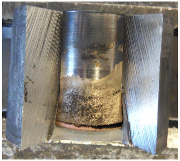


Starting material

- ammonolysis by ball milling of GeO_2 in ammonia atmosphere
- $GeO_2 + 4\,NH_3 \longrightarrow Ge_3N_4 + 6\,H_2O$
- mixture of β-Ge_3N_4 (67 %), α-Ge_3N_4 (23 %) and Ge (10 %)

Processing of sample after shock synthesis

- mechnical opening of container
- etching with HNO_3



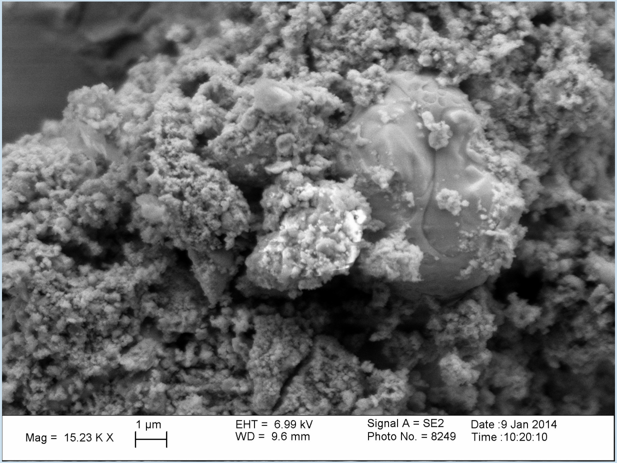
SEM & EDX Analysis (before and after etching)

Before etching

- Ge–Cu intermetallics
- Ge crystals
- Ge–N phases

After etching

- cubic-shaped plates of Ge–O (μm-sized)
- nanosized Ge–N phases



SEM image of sample FP-GN1 before etching

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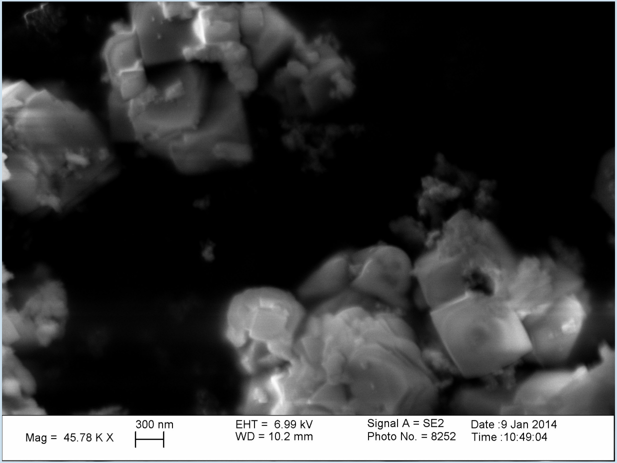
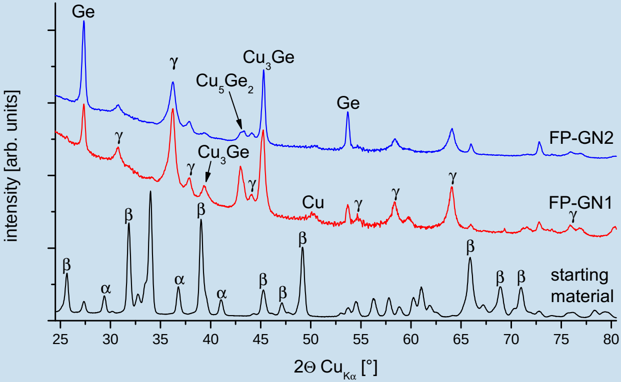


SEM image of sample FP-GN1 after etching

Phase composition after shock (before etching)

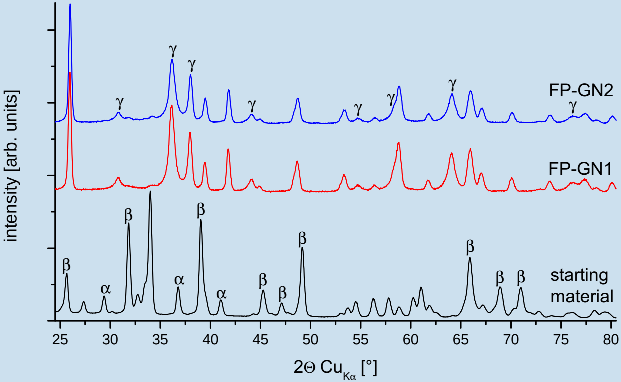
- γ-Ge_3N_4 and Ge (thermal decomposition $Ge_3N_4 \longrightarrow 3Ge + 2N_2$), minor β-Ge_3N_4
- formation of Cu–Ge alloys (Cu_5Ge_2 and Cu_3Ge), some Cu



Shock Synthesis of γ-Ge_3N_4— Phase Analysis

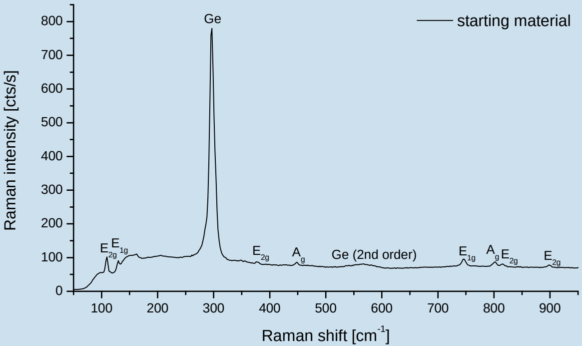
Phase composition after etching

- FP-GN1: 36 % γ-Ge_3N_4, 58 % α-GeO_2, 1 % β-Ge_3N_4
- FP-GN2: 29 % γ-Ge_3N_4, 65 % α-GeO_2, 2 % β-Ge_3N_4



Raman spectroscopy of etched samples

- starting material: β-Ge_3N_4 and Ge PARKER ET AL. (1967)
- shocked samples: α-GeO_2, very weak signal of γ-Ge_3N_4 DONG ET AL. (2000)
- additional line at 779 cm^{-1} and very strong line T_{2g} at $\sim$ 730 cm^{-1} $\rightarrow$ defects and deviation in stochiometry DEB ET AL. (2000); SERGHIOU ET AL. (1999)



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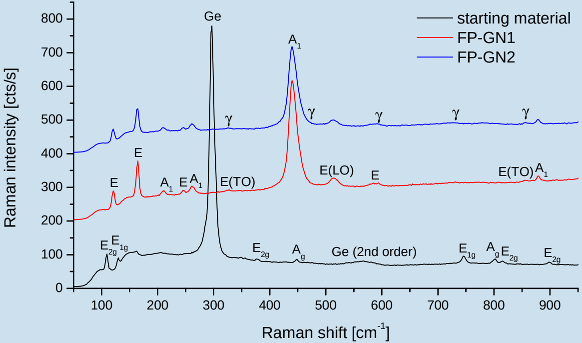

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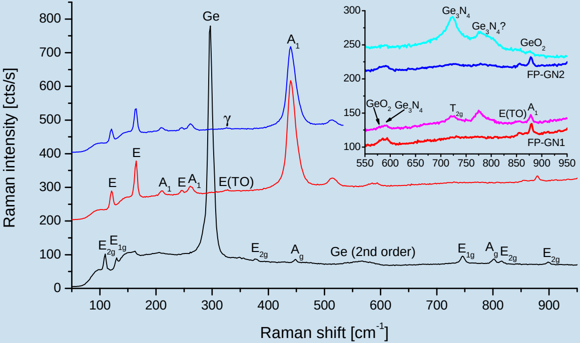

Conclusion and Outlook

To sum it up...

- synthesis of spinel-type γ-Ge_3N_4
- structural inevstigation with XRD and Raman
- shock synthesis causes less-ordered/less-crystalline material (compared to static synthesis)

Further things to come...

- synthesis of pure samples
- investigation of stability of IV-nitrides @ HP (γ-Si_3N_4, γ-Ge_3N_4, γ-Sn_3N_4) $\rightarrow$ post-spinel phase?
- study of spinel defect structure and crystallinity (influence of synthesis method)

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Acknowledgements

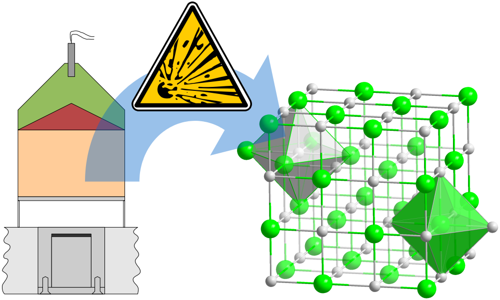
This work was performed as a part of a students course in solid state chemistry.

Financial support

- Dr. Erich Krüger-Foundation
- Excellence Initiative of the Saxonian Government, promoted by the European Union

Further support

- C. Röder (Raman spectroscopy)
- Team of the Reiche Zeche mine



Thank you for your kind attention!

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