



**HAL**  
open science

# Elastic moduli, anisotropy and refractive index of $\gamma$ -Ge<sub>3</sub>N<sub>4</sub> via laser ultrasonics, Brillouin light scattering, and first-principles calculations

Chen-Hui Li, Philippe Djemia, Nikolay Chigarev, Siham Sodki, Y. Roussigné, Samuel Raetz, Vitalyi Gusev, Andreas Zerr

## ► To cite this version:

Chen-Hui Li, Philippe Djemia, Nikolay Chigarev, Siham Sodki, Y. Roussigné, et al.. Elastic moduli, anisotropy and refractive index of  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub> via laser ultrasonics, Brillouin light scattering, and first-principles calculations. The Joint 28th AIRAPT and 60th EHPRG International Conference 2023, Jul 2023, Edinburgh, United Kingdom. pp.17. hal-04241737

**HAL Id: hal-04241737**

**<https://hal.science/hal-04241737>**

Submitted on 13 Oct 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Public Domain

# Elastic moduli, anisotropy and refractive index of $\gamma$ -Ge<sub>3</sub>N<sub>4</sub> via laser ultrasonics, Brillouin light scattering, and first-principles calculations

Dr. Chen-Hui Li<sup>1</sup>, Prof. Philippe Djemia<sup>1</sup>, Dr. Nikolay Chigarev<sup>2</sup>, Ms. Siham Sodki<sup>1</sup>,  
Prof. Yves Roussigné<sup>1</sup>, Prof. Samuel Raetz<sup>2</sup>, Prof. Vitaliy E. Gusev<sup>2</sup>, Dr. Andreas Zerr<sup>1</sup>

<sup>1</sup>Laboratoire des Sciences des Procédés et des Matériaux - CNRS, Villetaneuse, France, <sup>2</sup>Laboratoire d'Acoustique de l'Université du Mans, Le Mans, France

Poster Session 2 and Refreshments, July 27, 2023, 16:00–17:30

Germanium nitride having cubic spinel structure,  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub>, is a wide band-gap semiconductor,  $E_g=3.65(5)$  eV, with a large exciton binding energy [1,2] which exhibits high hardness, elastic moduli and elevated thermal stability to  $\sim 700^\circ\text{C}$ . Experimental data on its bulk and shear moduli ( $B_0$  and  $G_0$ , respectively) are strongly limited [3–6], inconsistent and, thus, require verification. Moreover, earlier first-principles density functional calculations provided significantly scattering  $B_0$  values but consistently predicted  $G_0$  much higher than the experimental one [7–9]. Here, we investigated the elastic behaviour of  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub> experimentally, using the techniques of laser ultrasonics (LU) and Brillouin light scattering (BLS), and theoretically, using the first-principles calculations. We measured velocities of the Rayleigh surface acoustic waves (RSAWs) and of the longitudinal acoustic waves (LAWs) in our low-porosity polycrystalline sample using the LU-technique and derived its isotropic elastic moduli  $B_p$  and  $G_p$  (here and below, the subscripts p and 0 indicate values for the porous and densified sample, respectively). Applying the Hashin-Shtrikman approach, we obtained  $B_0=322(44)$  GPa and  $G_0=188(7)$  GPa for the dense  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub>. The significant error in  $B_0$  is explained by the low amplitude of the LAW-signals in our LU-measurements. Nevertheless, it agrees, within experimental uncertainties, with the  $B_0=295(5)$  GPa [3] obtained from the EOS measured upon quasi-hydrostatic compression. Both the previous and the present first-principles calculations underestimated  $B_0$  while the GGA-PBEsol functional with a hard PAW potential showed the least deviation from the experiment.

Our experimental  $G_0$  exceeds by  $\sim 1.5$  times the previous experimental value,  $G_0=124$ -129 GPa derived from the nanoindentation testing [4, 5]. The calculated  $G_0$  values, typically around 170 GPa, were underestimated but much less significant than the  $B_0$ , between 211-269 GPa. However,  $G_0=186(10)$  GPa calculated using the GGA-PBEsol functional with a hard PAW potential agreed with our measurements. Comparison of the RSAW-velocity values,  $VR_0$ , measured using the LU- and BLS techniques confirmed the theoretically-predicted elastic anisotropy of  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub>. The anisotropy led to the asymmetric RSAW peaks in our BLS measurements resulting in the  $VR_0$  underestimation by  $\sim 10\%$ . Combining our LU- and BLS results for the LAWs, we determined the refractive index of the dense  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub> to be  $n_0=2.4(1)$ . This value ranks  $\gamma$ -Ge<sub>3</sub>N<sub>4</sub> in the class of very-high-refractive-index materials transparent for visible light, such as diamond, GaN or TiO<sub>2</sub> having anatase structure.

- [1] Boyko T.D., et al., Phys. Rev. Lett. 111, 097402 (2013)
- [2] Feldbach E., et al., Electron. Mater. Lett. 17, 315-323 (2021)
- [3] Somayazulu M.S., et al., in Proceedings of AIRAPT-17, M. Manghnani, W.J. Nellis, M. Nicol, 663-666 (2000)
- [4] Shemkunas M.P., et al., J. Mater. Res. 19, 1392-1399 (2004)
- [5] Zerr A., J. Mater. Res. 23, 3273-3274 (2008)
- [6] Nishiyama N., et al., J. Am. Ceram. Soc. 102, 2195-2202 (2019)
- [7] Dong J.J., et al., Phys. Rev. B 67, 094104 (2003)
- [8] Luo Y.S., et al., Comput. Condens. Matter 1, 1-7 (2014)
- [9] Xiang H.M., et al., Sci. Rep. 8, 14374 (2018)

# 28<sup>th</sup> AIRAPT and 60<sup>th</sup> EHPRG

23–28 July 2023

Edinburgh International Conference Centre,  
Edinburgh, UK

