Studies of Surface Defect in Microcrystalline α-GaOOH and β-Ga_2O_3

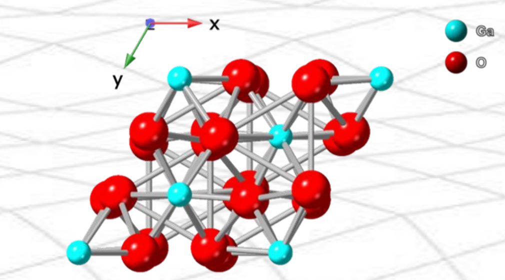
D.A. Johnson[1], P. Ahluwalia[2], Z. Rabine[1,3], T.Y. McHenry[1], M.M. Smit[1], Y.M. Strzhemechny[1]
[1]Texas Christian University, [2]Harmony School of Innovation, [3]Wayne State University

Abstract:

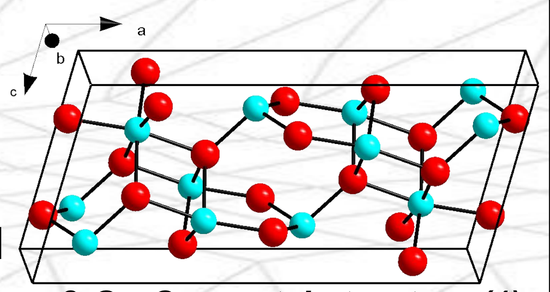
Surface defects in nano- and micro-crystals strongly affect performance of materials in applications, necessitating elucidation and control of those defects. The beta variant of gallium oxide (β-Ga_2O_3) in nano- and microcrystalline form is attracting a strong interest due to its potential applications in such critical areas as biological therapeutics, optoelectronics, and catalysis. In our studies, β-Ga_2O_3 crystals are produced through a simple bottom-up hydrothermal method, which yields, as a first step, an α-GaOOH precursor, which then undergoes calcination to bear the final product. Variation of growth parameters allows for a synthesis of particles with tunable morphologies and surface structures. Optoelectronic and physicochemical properties of both α-GaOOH & β-Ga_2O_3 samples are studied by a range of experimental techniques. These investigations address, among others, the surface defect properties. We also evaluate the impact of surface defects and particle morphologies on the antibacterial action α-GaOOH.

Introduction

- The internal crystalline structure of solid state materials governs external behaviors
- At the micro and nanoscale, surface defects in strongly affect the performance of these materials in application
- Gallium oxide is a polymorphic material though the beta variant (β-Ga_2O_3) and its precursor (α-GaOOH) are attracting strong interest due to their potential in critical areas including biological therapeutics, optoelectronics, and catalysis.



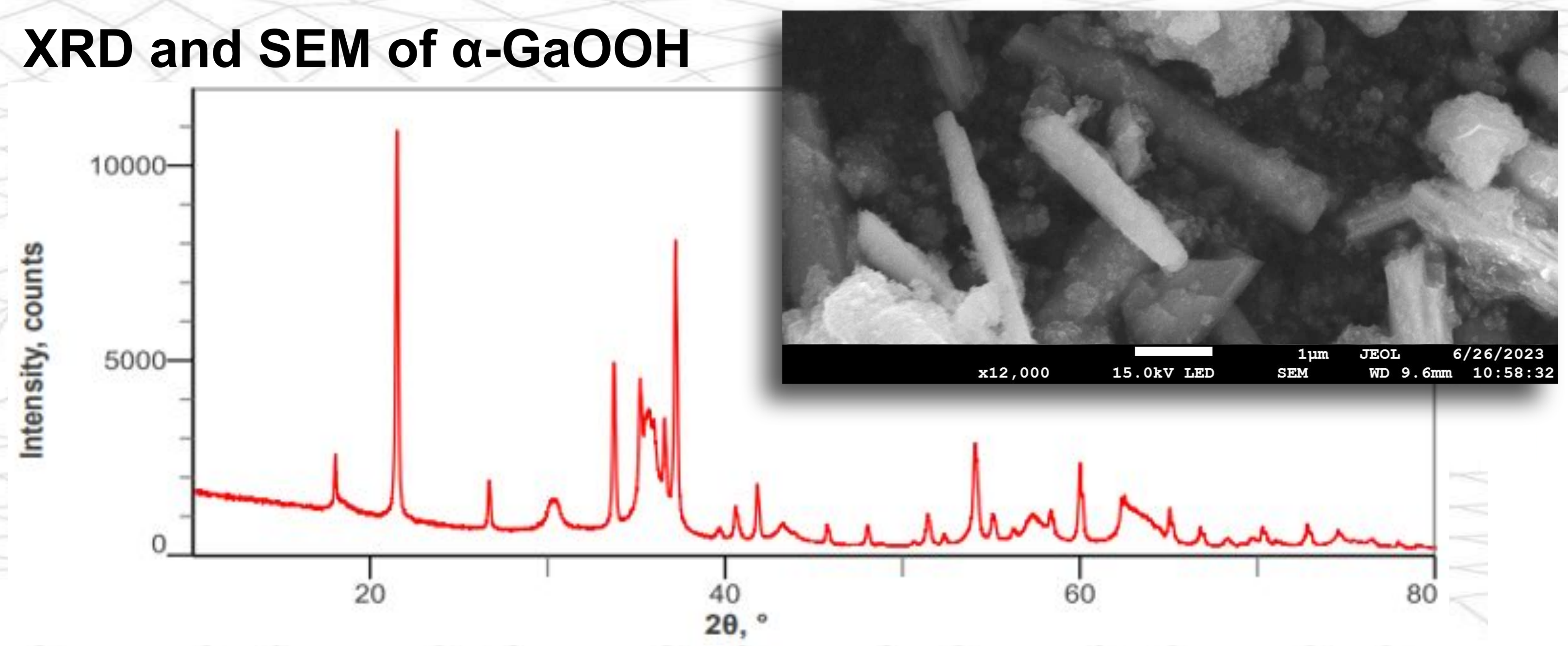
α-GaOOH crystal structure (1)



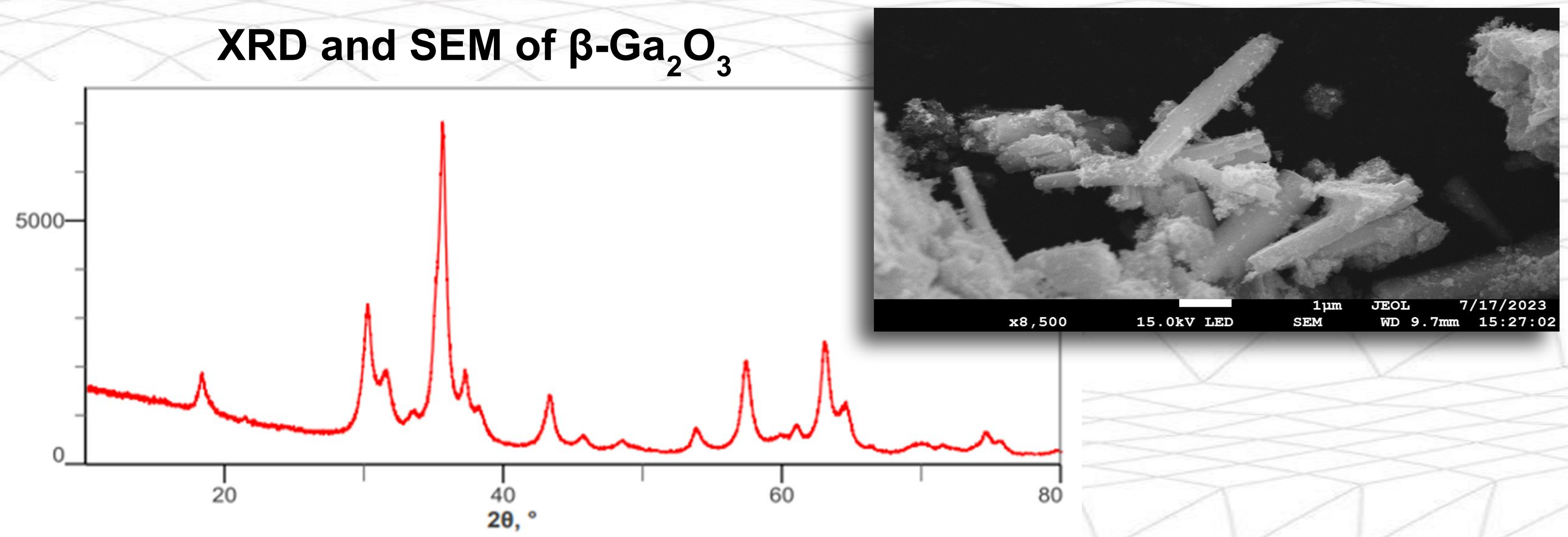
β-Ga_2O_3 crystal structure (1)

Crystalline Structure

XRD and SEM of α-GaOOH

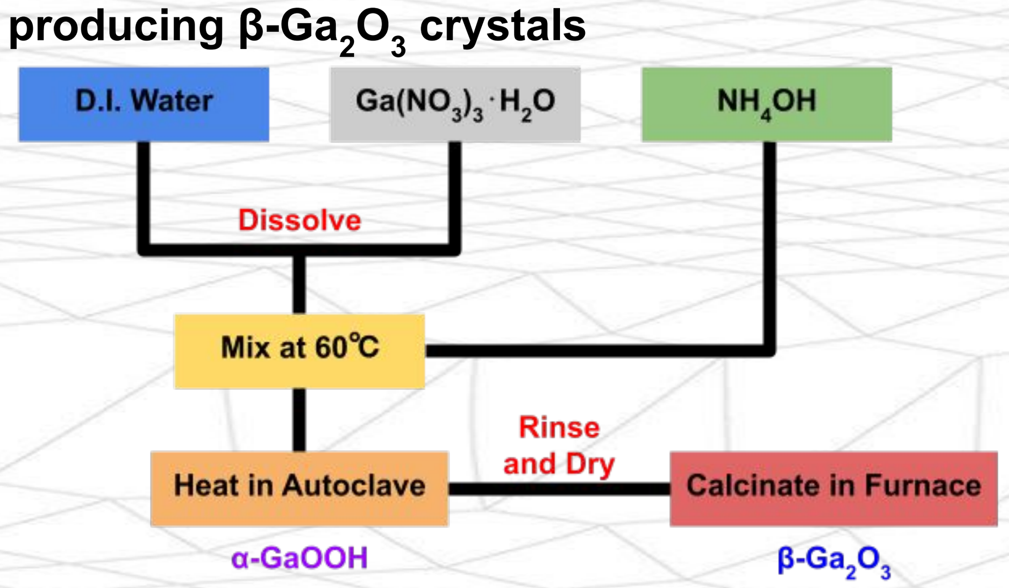


XRD and SEM of β-Ga_2O_3



Synthesis

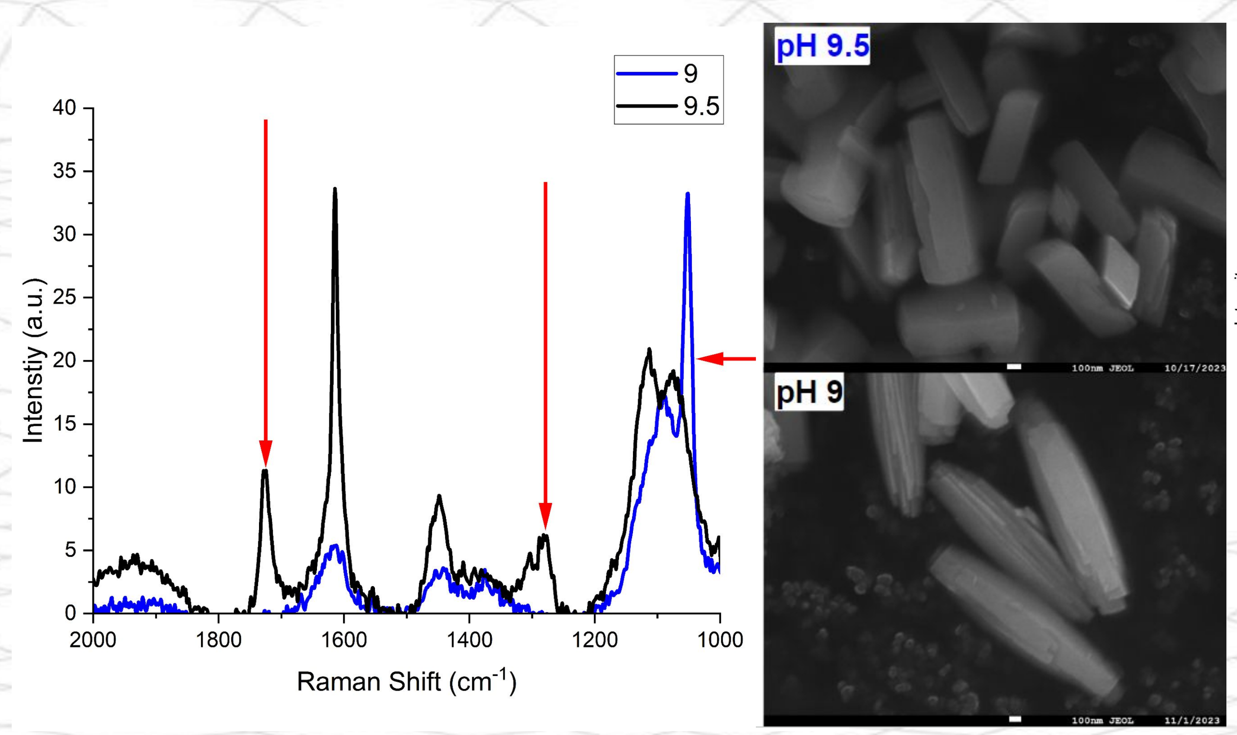
- Hydrothermal growth in which Gallium salt is mixed with ammonium hydroxide at 60℃
- Reaction is catalyzed within an autoclave in an forced air oven
- The resulting powder is α-GaOOH and is rinsed and dried at 70℃
- The powder is then calcinated at 750℃ for 5h, producing β-Ga_2O_3 crystals



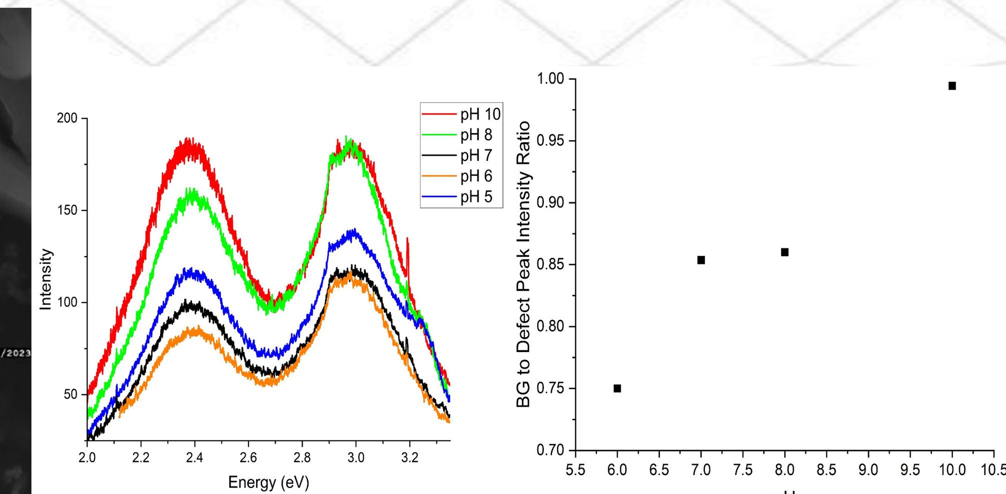
SciCom
Let's Talk Science

Nano and microscale technologies are becoming increasingly utilized for emerging applications. β-Ga_2O_3 and its less studied precursor α-GaOOH in particular are of interest for their potential applications in high frequency electronics and biological therapeutics amongst others. Performance of materials at these scales are heavily reliant on the nature and abundance of surface level defects. Here we look at the origins of these defects in regards to particle growth conditions, determine their nature and evaluate their impact on the performance of α-GaOOH as an antibacterial agent.

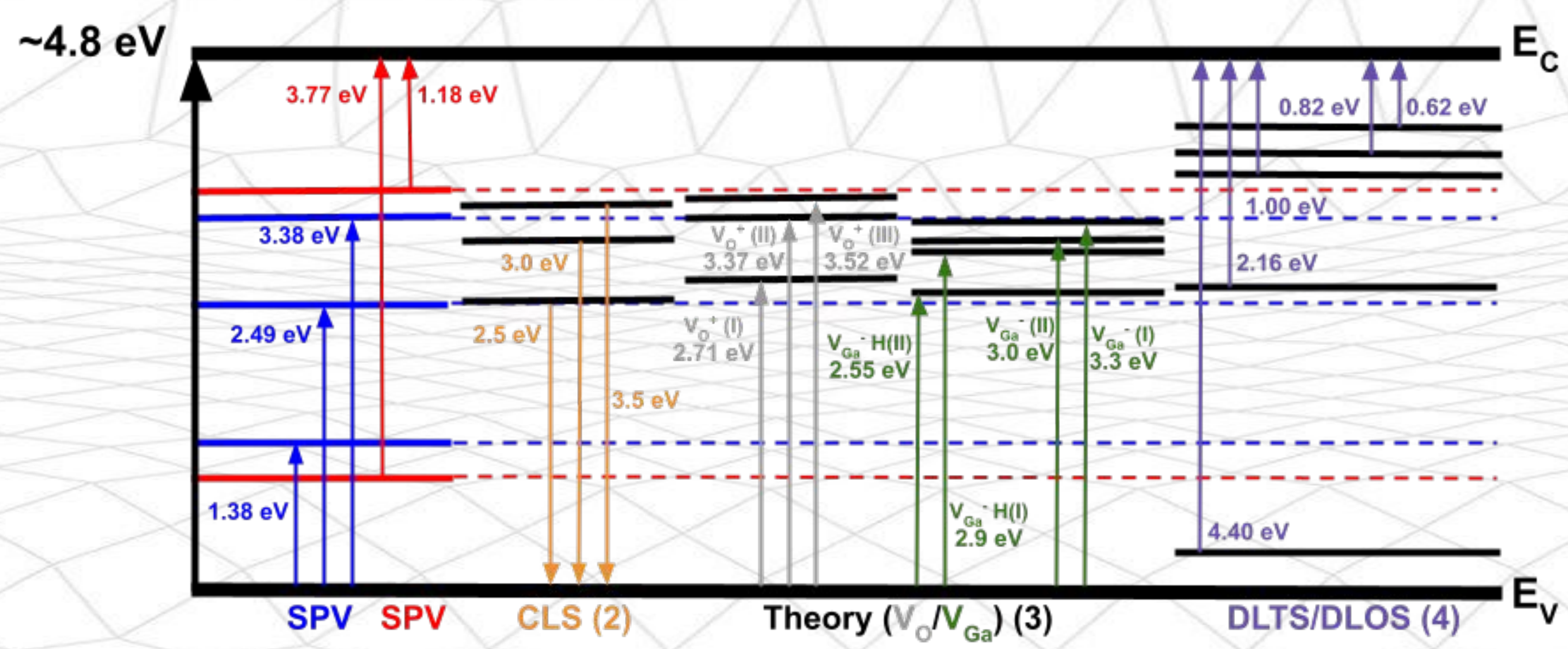
Defect Characterization



Raman spectra of α-GaOOH demonstrates growth pH sensitivity of crystal stress and bonding

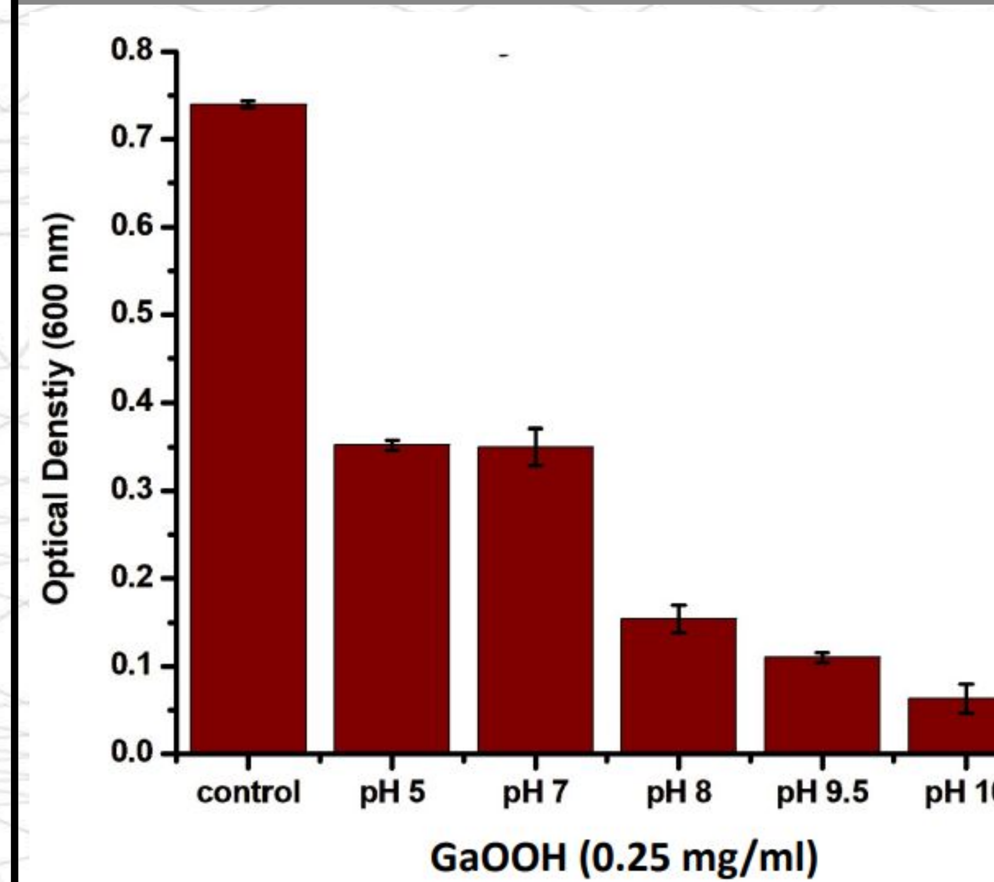


Relative intensities of defect to near band edge luminescence show abundance of optically active defects scales with increased growth pH



β-Ga_2O_3 band diagram with observed SPV sub-bandgap transitions for β-Ga_2O_3 microparticles following AR-RPT plotted against experimental and theoretical values reported in the literature for single crystal samples.

Impact on Applications - (Antibacterial)



- Lower synthesis pH of α-GaOOH particles results in increased bacterial growth inhibition
- Lower pH is also seen to result in increased defect abundance
- These crystalline defects are seen to be important sites for mediating antibacterial interactions and behaviors in related materials such as ZnO

Conclusions

- We successfully producing both α-GaOOH and β-Ga_2O_3 crystals of tuneable size and morphology via hydrothermal method
- We verified that the external morphology is preserved throughout the transition from the α-GaOOH to β-Ga_2O_3
- Characterized the surface defect structure of a β-Ga_2O_3 and show that it aligns with theoretical predictions
- Able to correlate synthesis conditions with surface level defects and link those to performance in antibacterial applications

We gratefully acknowledge support for this research from the National Science Foundation's Research Experience for Undergraduates program (PHY-2244258) and the Science & Engineering Research Center (SERC)

1. Marezio, M.; Remeika, J. P. (1 March 1967). "Bond Lengths in the α-Ga2O3 Structure and the High-Pressure Phase of Ga2−xFexO3". The Journal of Chemical Physics. 46 (5): 1862–1865. doi:10.1063/1.1840945..
2. Hantian Gao, Shreyas Muralidharan, Nicholas Pronin, Md Rezaul Karim, Susan M. White, Thaddeus Asel, Geoffrey Foster, Sriram Krishnamoorthy, Siddharth Rajan, Lei R. Cao, Masataka Higashiwaki, Holger von Wenckstern, Marius Grundmann, Hongping Zhao, David C. Look, Leonard J. Brillson; Optical signatures of deep level defects in Ga2O3. Appl. Phys. Lett. 11 June 2018; 112 (24): 242102. https://doi.org/10.1063/1.5026770
3. J. B. Varley, J. R. Weber, A. Janotti, and C. G. Van de Walle, "Oxygen vacancies and donor impurities in β-Ga2O3," Appl. Phys. Lett. 97, 142106 (2010).https://doi.org/10.1063/1.3499306
4. Z. Zhang, E. Farzana, A. R. Arehart, and S. A. Ringel, "Deep level defects throughout the bandgap of (010) β-Ga2O3 detected by optically and thermally stimulated defect spectroscopy," Appl. Phys. Lett. 108, 052105 (2016).https://doi.org/10.1063/1.4941429