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ab initio Energetics and Thermoelectric Profiles of Gallium Pnictide Polytypes

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Trupti K. Gajaria[1], Shweta D. Dabhi[2] & Prafulla K. Jha[1]

The *state-of-the-art* Density Functional Theory (DFT) is utilized to investigate the structural, electronic, vibrational, thermal and thermoelectric properties of gallium pnictides GaX (X = P, As, Sb) in cubic zincblende (ZB) and hexagonal wurtzite (WZ) phases. The lattice parameters, bulk modulus, energy band nature and bandgap values, phonon, thermal and thermoelectric properties are revisited for ZB phase while for WZ phase they are predictive. Our results agree reasonably well with the experimental and theoretical data wherever they are available. The phonon dispersion curves are computed to validate the dynamic stability of these two polytypes and for further investigating the thermal and thermoelectric properties. Our computed thermoelectric figure of merit ZT gives consistent results with highest observed magnitude *of 0.72 and 0.56* for GaSb compound in ZB and WZ phases respectively. The first time calculated temperature variation of lattice thermal conductivity for WZ phase shows lower value than ZB phase and hence an important factor to enhance the figure of merit of considered gallium pnictides in WZ phase. Present results validate the importance of GaX in high temperature thermoelectric applications as the figure of merit ZT shows enhancement with significant reduction in thermal conductivity at higher temperature values.

Necessity to overcome the energy crises and desire to fulfill the energy demands of mankind, the researchers have been immensely studying various III-V compounds for developing green energy harvesting and storage devices[1–3]. This class of materials contribute to many cutting-edge technologies such as green energy harvesting photovoltaic (PV)[4–6], nanoelectronics[7], thermoelectric[8,9], optoelectronic[10], sensors[11], visible/IR emitters[12,13], and hybrid complementary metal oxide semiconductors (CMOS)[14] due to their moderate and direct energy gap, good mechanical strength and structural polytypic behavior. Three eminent Japanese scientists, Nakamura, Amano and Akasaki shared the Nobel prize in Physics-2014 and set up a benchmark for III-V group compounds through their groundbreaking novel research on gallium nitride (GaN) based heterostructures which led to the discovery of blue light emitting diode (blue-LED)[12]. One of the recent studies reported by Lumb *et al.*[15] demonstrates 44.5% efficient gallium antimonide (GaSb) based solar cells which are capable of absorbing IR photons from the sunlight. The revolutionary contributions of III-V compounds in major areas of technology have brought them in recent focus and their further investigations may open up new perspectives in developing suitable materials for device technologies. However, this demands a rigorous investigation to understand the potential outcomes of these compounds in different phases in which they exist under different conditions[16,17]. The zincblende (ZB) and wurtzite (WZ) are the two extensively studied III-V polytypes for their mechanical, electronic, optoelectronic and vibrational properties in bulk and nano regimes during the last few years[18–41].

Recently, the thermoelectric studies on variety of semiconductors including III-V compounds[8,9,42–50] have gained greater attention due to the importance of thermal management in devices especially when, the device sizes are continuously decreasing. The literature reveals many theoretical[21–25,30,39] and experimental[18–20,26–29,31,32,36,40,41] studies on the structural, mechanical, electronic and vibrational properties of gallium pnictides; (GaX; X = P, As, Sb). However, a lack of systematic study on thermoelectricity in GaX polytypes is observed. While there exist few scattered studies on lattice conductivity computations in ZB phase of bulk GaX, same is completely missing for WZ phase[51–53].

[1]Department of Physics, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, 390002, Gujarat, India. [2]P. D. Patel Institute of Applied Science, Charotar University of Science and Technology, CHARUSAT campus, Changa, 388421, Gujarat, India. Correspondence and requests for materials should be addressed to P.K.J. (email: prafullaj@yahoo.com)

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Exploring the hidden catalyst from boron pnictide family for HER and OER

Trupti K. Gajaria [a], *Basant Roondhe* [a], *Shweta D. Dabhi* [b], *Prafulla K. Jha* [a,*]

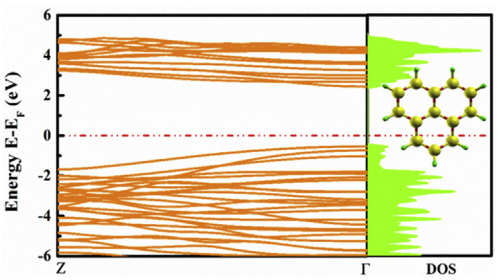
[a] *Department of Physics, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, 390002, Gujarat, India*

[b] *P. D. Patel Institute of Applied Science, Charotar University of Science and Technology, CHARUSAT Campus, Changa, 388421, Gujarat, India*

HIGHLIGHTS

- Nanostructured boron phosphide for HER and OER catalyst.
- Indirect to direct bandgap transition under confinement effect.
- Modulation of catalytic activity by means of substitutional doping.
- Toxic and expensive metal-free HER catalyst.

GRAPHICAL ABSTRACT



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ABSTRACT

A systematic investigation of catalytic activity of boron phosphide nanowire (BP NW) towards over-all water-splitting reaction has been performed by evaluating the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) activities. Intended to the mentioned aim, we have utilized Kohn-Sham formulated extensively popular ab initio method based on density functional theory (DFT). The structural and electronic properties of the BP NW are computed and compared with its bulk phase. We observe dramatic indirect to direct bandgap transition with pronounced energy gap after introducing two-dimensional confinement that is akin to the other reported III-V NWs. The calculated partial density of states with van Hove singularity also confirms the same. Owing to its moderate bandgap value, the applicability of the BP NW as an HER/OER catalyst is assessed by computing the site dependent HER/OER activities. Our computation on Gibbs free energy for the case of hydrogen adsorption with −1.19 eV magnitude gives better results; whereas in case of OER, the results with higher magnitude of Gibbs energy implicate over binding of oxygen with adsorbent thus revealing non-feasible desorption of oxygen from adsorbent. Significant perturbation in electronic states of NW under hydrogen adsorption confirms high sensitivity of BP NW for hydrogen adsorption. Further, the effect of substitutional doping on HER and OER activities suggests that the doped NW shows poor HER activity in

* *Corresponding author.*
E-mail address: prafullaj@yahoo.com (P.K. Jha).

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Hydrogen evolution reaction electrocatalysis trends of confined gallium phosphide with substitutional defects

Trupti K. Gajaria [a], *Basant Roondhe* [a], *Shweta D. Dabhi* [b], *Piotr Śpiewak* [c], *Krzysztof J. Kurzydłowski* [c,d], *Prafulla K. Jha* [a,*]

[a] *Department of Physics, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, 390002, Gujarat, India*

[b] *Department of Physical Sciences, P D Patel Institute of Applied Sciences, Charotar University of Science and Technology, CHARUSAT Campus, Changa, 388421, Gujarat, India*

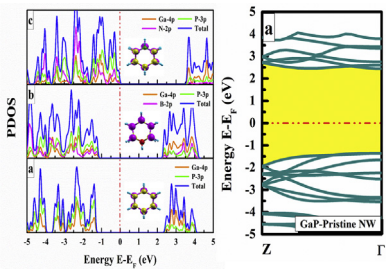
[c] *Materials Design Division, Faculty of Materials Science and Engineering, Warsaw University of Technology, 141 Wołoska Str., 02-507, Warsaw, Poland*

[d] *Faculty of Mechanical Engineering, Bialystok University of Technology, 45C Wiejska Str., 15–351, Bialystok, Poland*

HIGHLIGHTS

- First time predicted HER activity of Gallium Phosphide Nanowire.
- The effect of substitutional defect in GaP NW on HER.
- Defect engineering as a tool for tailoring the catalytic properties.

GRAPHICAL ABSTRACT



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ABSTRACT

The integration of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) gives better prediction of the system properties towards the applications like water-splitting and gas storage capacity/mechanism. The pursuit of generating low-cost and effective catalyst for such purposes has motivated the material scientists and researchers to design and study the novel nanostructured materials both theoretically and experimentally. We have utilized the well-established *state-of-the-art* density functional theory (DFT) for envisaging the HER activity of the two-dimensionally confined Gallium Phosphide (GaP). The effect of substitutional defect caused by foreign atoms like boron and nitrogen on the structural, electronic and adsorption properties of the GaP nanowire is analyzed by incorporating the van der Waals dispersion correction. The energy differences and the contributions of the individual atomic species to the electronic energy states have been

* *Corresponding author.*
E-mail address: prafullaj@yahoo.com (P.K. Jha).

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Diameter and strain dependent structural, electronic and optical properties of gallium phosphide nanowires

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Trupti K. Gajaria, Shweta D. Dabhi, and Prafulla K. Jha