

First-principle calculation of refractive indices of BAlN and B GaN

Feras AlQatari, Kuang-Hui Li, Kaikai Liu, and Xiaohang Li*

Computer, Electrical and Mathematical Science & Engineering Division,

King Abdullah University of Science and Technology, Thuwal, Makkah, Saudi Arabia

*Corresponding author: xiaohang.li@kaust.edu.sa

Abstract

The refractive indices of BAlN and B GaN ternary alloys are being investigated using first-principle calculation. The hybrid density functional theory is applied to determine the refractive indices of different alloys. A peculiar bowing effect in the static refractive indices and crossovers of different refractive index curves are found. We speculate that the explanation to these phenomena lies in the interband transitions of electrons where each band bows at a different rate from the other. An average of these bowing effects may result in the bowing of refractive indices.

Introduction

Wurtzite III-nitride (AlN, GaN and InN) materials have many applications in optical and high-power devices¹. Optoelectronics made of III-nitride materials can operate over a wide spectrum of wavelengths from infrared (IR) to ultraviolet (UV)^{1,2}. These materials owe this property to their highly tunable bandgaps from around 0.7 to 6 eV³. Due to their interesting optical properties, distributed Bragg reflectors (DBRs), which are useful for Vertical-Cavity Surface-Emitting Lasers (VCSELs), have also been investigated as possible applications for III-nitrides⁴. The search for materials with larger bandgaps and different refractive indices, motivated by the rising interest in optical devices in the UV range, has inspired multiple studies of BN-based materials and their alloys with traditional III-nitrides^{5,6,7,8,9,10,11}. Additionally, alloying III-nitrides with boron can reduce their lattice parameters giving a new option for strain engineering¹².

Knowing the refractive index of B III-nitride alloys allows for design and simulation of optoelectronic devices. It has been experimentally shown that a small incorporation of boron into GaN and AlN can cause a significant change in the refractive index of the material^{4,5}. Given these experimental studies, it seems clear that boron incorporation has the potential for allowing high tunability of the refractive indices of BAlN and B GaN alloys. However, no experimental study has investigated the effect on the refractive index for an unstrained single crystal of B III-nitride as far as we know. Additionally, the predicted large miscibility gap in wurtzite B III-nitride as has been shown in zinc-blende structures, prevents further studies on the experimental front¹³. The effect of alloying on the refractive index has also been theoretically investigated

over the full range of compositions and a large range of energies for BGaN alloys by Said et al⁷. However, it is unclear if the results they found are accurate based on the limitations of the local density approximation (LDA) used in their study.

In this work we investigate the refractive indices of BAlN and BGaN over the entire compositional range theoretically using hybrid density functional theory (DFT). Additionally, we confirm our model by calculating the refractive indices of the well-known AlGaN alloys and comparing them to experimental values as will be reported.

Computational method

All reported calculations were carried using the software MedeA-VASP (Vienna ab initio Simulation Package)^{14,15,16}. Before calculating the refractive indices the structure was optimized using DFT general gradient approximation (GGA-PBEsol) exchange-correlation. The energy cutoff was set to 520 eV for the plane-wave basis set. The structure optimization was performed on primitive cells for the binary systems and on 16-atom supercells for the ternary systems with chalcopyrite (CH) and luzonitelike (LZ) structures for the 50%, and 25% / 75% alloys, respectively, as reported in our previous study⁹. All structures were relaxed to Hellman-Feynman force less than 0.02 eVÅ⁻¹. The Monkhorst-Pack k-point mesh was set to 6 × 6 × 6 for the structural optimizations.

To calculate the optical properties, the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE) was used¹⁷. Similar to structure optimization, 520 eV was used as the energy cutoff for the plane-wave basis set. Because HSE calculations are computationally demanding, a k-mesh of 4 × 4 × 4 was used for the non-local exchange.

Results and discussion

Table 1: Lattice parameters of different alloys

<i>Alloy</i>		<i>a</i> (Å)	<i>c</i> (Å)
AlN	This work	3.113	4.981
	Experiment ¹⁸	3.11	4.98
<i>B_{0.125}Al_{0.875}N</i>	This work	3.063	4.959
<i>B_{0.25}Al_{0.75}N</i>	This work	2.984	4.783
<i>B_{0.5}Al_{0.5}N</i>	This work	2.876	4.556
<i>B_{0.75}Al_{0.75}N</i>	This work	2.713	4.372
GaN	This work	3.182	5.180
	Experiment ¹⁸	3.180	5.166
<i>B_{0.125}Ga_{0.875}N</i>	This work	3.107	5.049
<i>B_{0.25}Ga_{0.75}N</i>	This work	3.020	4.943
<i>B_{0.5}Ga_{0.5}N</i>	This work	2.898	4.673
<i>B_{0.75}Ga_{0.25}N</i>	This work	2.722	4.431
BN	This work	2.543	4.205
	Experiment ¹⁸	2.55	4.21

Structure First we confirm that the optimized wurtzite structures are within a reasonable range. Table 1 shows our calculated lattice parameters in comparison to experimental. Values for the binary alloys show good agreement with experimental results. Ternary alloys are compared to other theoretical results as well as to the Vagard’s law. There is also good agreement in these values with the linear behavior of the Vagard’s law with a small bowing parameter. The structure was discussed more in depth in our previous study⁹.

Refractive indices Before discussing the results of interest for BAlN and BGaN alloys, we first confirm our model by comparing the refractive indices of AlGaN alloys with the reported experimental results. We chose AlGaN alloys for two reasons; the first is that AlGaN alloys are well studied semiconductors, and the second is that AlGaN belongs to the same III-nitride family of semiconductors. In Fig. 1, we show our calculated refractive indices of AlGaN as well as BAlN and BGaN values. The calculated values of AlGaN fall well within a reasonable range of the refractive indices with a small but consistent underestimation of these values^{19,20}.

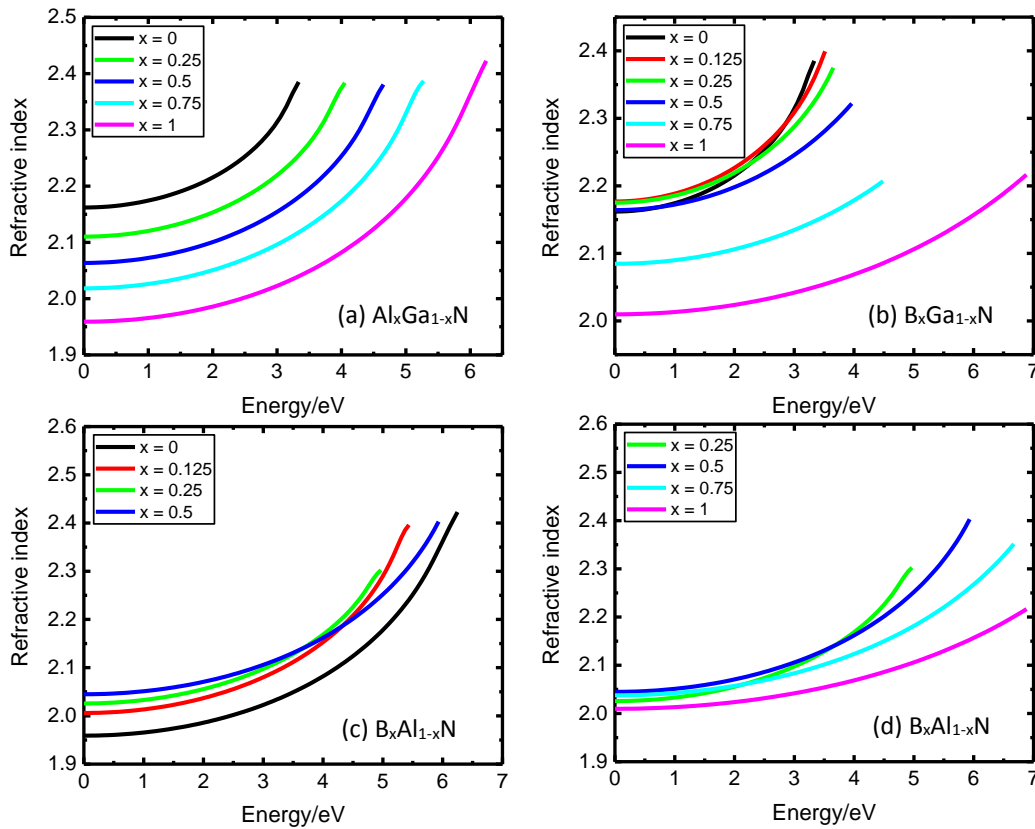


Figure 1: Refractive indices of $Al_xGa_{1-x}N$ (a), B_xGa_xN (b), $B_xAl_{1-x}N$ (c)&(d) as a function of photon energy. $B_xAl_{1-x}N$ figures were separated for clarity. The data is cutoff near the bandgap value of each material.

An interesting behavior of the refractive index appears as boron content is increased in the alloys. For both B GaN and B AlN, the refractive index goes up as we incorporate more boron up to a certain limit then it goes down. This is visualized as a ‘bowing’ effect in the static refractive index (the index at 0 eV) in Fig. 2. We believe explaining this would require an extensive study of the electronic structure and how it relates to the refractive index. The reason we focus on the static refractive index is that it captures the effect of alloying without having to consider the energy of any incoming photons. Our hypothesis is that this behavior can be explained due to at least 2 different well-known phenomena. The first is that when the atomic weight is increased, a rise in the refractive index is found. This is typically paired with a decrease in the bandgap²¹. This is obeyed in the AlGaN alloys as well as InGaN and InAlN. It is important to note that Said et al. found B GaN, unlike our results, to obey this behavior⁷.

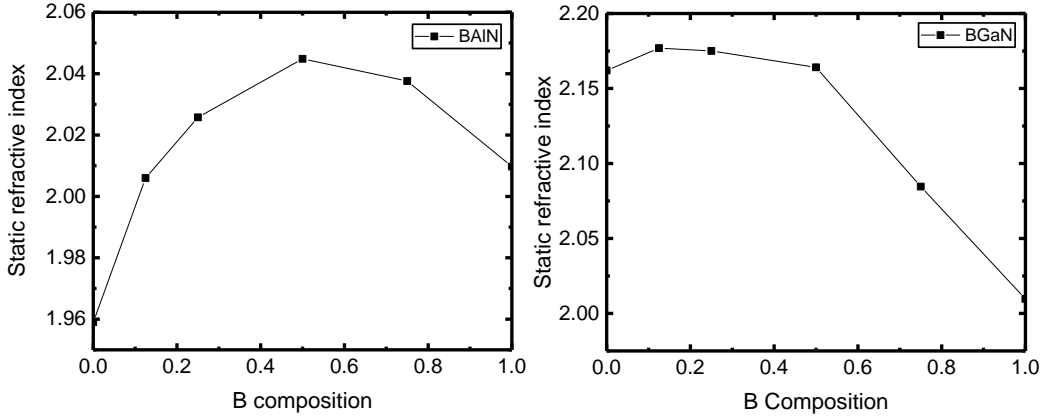


Figure 2: Static refractive indices of BAlN (left) and B GaN (right) as a function of boron composition.

$$n(\omega) = 1 + \frac{Nq_e^2}{2\epsilon_0 m} \sum_k \frac{f_k}{\omega_k^2 - \omega^2 - i\gamma_k \omega} \quad (1)$$

N is the electron density, q_e is the electron charge, ϵ_0 is the vacuum permittivity constant, m is electron mass, ω_k is the frequency for each electron transition, ω is the frequency of light, γ_k is the damping rate for each electron, f_k is oscillator strength of each electron.

The second phenomena likely is a consequence of the classical model of light propagation inside materials. Equation 1 suggests that we find a jump in the refractive index near the natural oscillation frequency of each oscillation mode. These oscillation modes are associated with electron transitions in the band structure²². The first electron transition occurs near the fundamental bandgap. Zhang et al. reported bowing found in two of the bandgaps of BAlN using DFT with LDA exchange correlation⁶. Shen et al. reported a smaller bowing in BAlN using the HSE hybrid functional²³.

At 0 eV, Equation 1 becomes:

$$n(0) = 1 + \frac{Nq_e^2}{2\epsilon_0 m} \sum_k \frac{f_k}{\omega_k^2} \quad (2)$$

Equation 2 indicates that the static refractive index is inversely proportional to the square of the natural frequency of each oscillation mode. The bowing in the electron transition energy associated with each mode may be very different. This approach is used by Shen et al. where they defined a different bowing parameter for each of two electron transitions²³. We hypothesize that the ‘bowing’ in the static refractive index may be the result of an average effect of the behavior of multiple electron transitions. A similar consideration was made by Linnik et al. to develop a model describing III-V semiconductors that have the cubic zinc-blende structure where they used the Interband Transition Contributions (ITC) model to describe the dielectric function²². The dielectric function is the square of the refractive index of a given material.

Another observation can be made by going back to Fig. 1. We can observe a crossing in the refractive indices of different alloys. This occurs only for low boron content B_xGaN alloys (x = 0, 0.125, and 0.25). In BAlN, this effect is clearer and occurs over many alloy concentrations.

Conclusion

We have investigated the refractive index of BAlN and B_xGaN alloys using hybrid density functional theory. A bowing effect was found in the static refractive indices of different alloys. The bowing effect in the bandgaps of these alloys provides a clue. However, it does not seem to provide a full explanation. We suspect that the bowing in the refractive indices of one set of alloys to be the result of the bowing of multiple electronic bands. A more in-depth study of the electronic band structure is needed to prove such hypothesis. Furthermore, we believe that developing our model could pave the way for better understanding of optical properties of materials and a more accurate explanation of how refractive indices relate to band structures of materials.

References

- ¹ O. Ambacher, *J. Phys. D: Appl. Phys.* **31**, 2653 (1998).
- ² H. M. Kim, Y. H. Cho, H. Lee, S. I. Kim, S. R. Ryu, D. Y. Kim, T. W. Kang, and K. S. Chung, *Nano Lett.* **4**, 1059 (2004).
- ³ O. Ambacher, J. Smart, J.R. Shealy, N.G. Weimann, K. Chu, M. Murphy, W.J. Schaff, L.F. Eastman, R. Dimitrov, L. Wittmer, M. Stutzmann, W. Rieger, and J. Hilsenbeck, *J. Appl. Phys.* **85**, 3222 (1999).
- ⁴ M. Abid, T. Moudakir, G. Orsal, S. Gautier, A. En Naciri, Z. Djebbour, J. H. Ryou, G. Patriarche, L. Largeau, H. J. Kim, and Z. Lochner, *Appl. Phys. Lett.* **100**, 051101 (2012).
- ⁵ S. Watanabe, T. Takano, K. Jinen, J. Yamamoto, and H. Kawanishi, *Phys. Status Solidi C* **7**, 2691 (2003).
- ⁶ M. Zhang, and X. Li, *Phys. Status Solidi B* **254**, 1600749 (2017).
- ⁷ A. Said, M. Debbichi, and M. Said, *Optik* **127**, 9212 (2016).
- ⁸ H. Sun, F. Wu, Y. J. Park, T. M. Al tahtamouni, W. Guo, N. Alfaraj, K.-H. Li, D. H. Anjum, T. Detchprohm, R. D. Dupuis, and X. Li, *Appl. Phys. Express* **11**, 011001 (2018).
- ⁹ K. Liu, H. Sun, F. AlQatari, W. Guo, X. Liu, J. Li, C. G. T. Castanedo, and X. Li, *Appl. Phys. Lett.* **111**, 222106 (2017).
- ¹⁰ H. Sun, Y. Park, K.-H. Li, C. G. T. Castanedo, A. S. Alowayed, T. Detchprohm, R. D. Dupuis, and X. Li, *Appl. Phys. Lett.* **111** (12), 122106 (2017).
- ¹¹ X. Li, S. Wang, H. Liu, F. A. Ponce, T. Detchprohm, R. D. Dupuis, *Phys. Status Solidi B* **254** (8), 1600699 (2017).
- ¹² A. Ougazzaden, S. Gautier, T. Moudakir, Z. Dhebbour, Z. Lochner, S. Choi, H. J. Kim, J. H. Ryou, R. D. Dupuis, and A. A. Sirenko, *Appl. Phys. Lett.* **93**, 083118 (2008).
- ¹³ L. K. Teles, L. M. R. Scolfaro, J. R. Leite, J. Furthmuller, and F. Bechstedt, *Appl. Phys. Lett.* **80**, 1177 (2002).
- ¹⁴ MedeA1 2.20.1, Materials Design, Inc., Angel Fire, NM 87710, USA (2016).
- ¹⁵ G. Kresse, and J. Furthmuller, *Phys. Rev. B* **45**, 11169 (1996).
- ¹⁶ G. Kresse, and J. furthmuller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ¹⁷ J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **124**, 219906 (2006).
- ¹⁸ J. H. Edgar, *Properties of Group III Nitrides*, INSPEC, London (1994).
- ¹⁹ K. Takeuchi, S. Adachi, and K. Ohtsuka, *J. Appl. Phys.* **107**, 023306 (2010).
- ²⁰ J. F. Muth, J. D. Brown, M. A. L. Johnson, Z. Yu, R. M. Kolbas, J. W. Cook,
- ²¹ M. Anani, C. Mathieum S. Lebid, Y. Amar, Z. Chama, and H. Abid, *Computational Materials Science*, **41**, 570 (2008).
- ²² M. Linnik, and A. Christou, *Physica B* **318**, 140 (2002).
- ²³ J. X. Shen, D. Wickramaratne, and C. G. Van de Walle, *Phys. Rev. Mater.* **1**, 065001 (2017).