

## Electronic and thermodynamic properties of $\beta$ -Ga<sub>2</sub>O<sub>3</sub>

Haiying He, Miguel A. Blanco,<sup>a)</sup> and Ravindra Pandey<sup>b)</sup>

Department of Physics, Michigan Technological University, Houghton, Michigan 49931

(Received 22 November 2005; accepted 25 May 2006; published online 27 June 2006)

Electronic and thermodynamic properties of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> are investigated in the framework of density functional theory. The equilibrium structural parameters and Debye temperature are obtained through fitting of the energy surface to the equation of state. Analysis of the band structure shows the valence band maximum to be degenerate at  $\Gamma$  and  $M$ , whereas the conduction band minimum is predicted to be at  $\Gamma$ . The valence band is almost flat, indicating a rather large effective mass for holes, whereas the calculated electron effective mass comes out to be about 0.12, expressed in units of the free electron mass. © 2006 American Institute of Physics. [DOI: 10.1063/1.2218046]

Thin films and single crystals of gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) have acquired an increasing importance in recent years because of their applications in various optoelectronic devices,<sup>1,2</sup> semiconducting lasers,<sup>3</sup> and ultrasensible gas detecting devices.<sup>4</sup> Optical absorption measurements<sup>5</sup> in single crystals of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> have revealed an absorption edge at 4.60 eV ( $\approx$ 2700 Å) at room temperature, suggesting it to be an intrinsic insulator, though it displays a semiconducting behavior when synthesized in reducing conditions.<sup>6</sup> Photoluminescence studies, on the other hand, reveal three dominant bands in the ultraviolet (UV), blue, and green regions.<sup>7</sup> It is suggested that the UV emission is an intrinsic phenomenon associated with the recombination of an electron and a self-trapped hole.<sup>8</sup> In spite of the availability of numerous experimental studies<sup>9–15</sup> investigating technological applications of Ga<sub>2</sub>O<sub>3</sub>, there are relatively fewer theoretical studies<sup>16,17</sup> on Ga<sub>2</sub>O<sub>3</sub>, even though first-principles calculations with proven predictive capabilities are now routinely performed on a wide variety of materials.

In this letter, our main interest lies in understanding the electronic and thermodynamic properties of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. We calculate the potential energy surface and fit an equation of state to it to obtain the equilibrium structural parameters including the lattice constants, bulk modulus and its pressure derivative, and Debye temperature. At the equilibrium volume, electronic properties including band structure, density of states, and charge density are calculated to determine interband transitions, electron effective mass, and the nature of chemical bonding in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>.

At ambient conditions, Ga<sub>2</sub>O<sub>3</sub> occurs in the monoclinic (i.e.,  $\beta$ ) phase, although it can be transformed into four other high-pressure and temperature polymorphs.<sup>18</sup> The monoclinic phase has  $C2/m$  symmetry, with 4 formula units per crystallographic cell (i.e., 8 Ga and 12 O atoms).<sup>19</sup> The calculated lattice parameters and internal coordinates refer to these four formula units per unit cell, but the calculated volumes and energies are given for 1 formula units (i.e., two Ga and three O) to facilitate the comparison with molar thermodynamic properties. The unit cell can be characterized by four lattice parameters:  $a$ ,  $b$ ,  $c$ , and  $\beta$ . In the unit cell, there are two crystallographically nonequivalent Ga atoms and

three nonequivalent O atoms located at  $4i(x, 0, z)$ . The local symmetry of the constituent atoms is  $C_s$ , and Ga atoms have tetrahedral- and octahedral-like coordinations.

The plane-wave pseudopotential approach within the generalized gradient approximation (GGA) (i.e., Becke for exchange and Perdew and Wang for correlation) of density functional theory (DFT) was employed to perform electronic structure calculations using VASP.<sup>20</sup> The energy cutoff for the plane wave expansion is 270 eV, and the cutoff for the augmented electron density is 554 eV. Under these computational conditions, the residual numerical uncertainty is estimated to be about 0.01 eV/atom.

To obtain the equation of state for Ga<sub>2</sub>O<sub>3</sub>, a relationship between total energy and volume was determined from the fourteen-dimensional (14D) potential energy surface consisting of four lattice parameters and ten internal parameters. It involved the optimization of the lattice parameters as well as the internal coordinates at several fixed values of the crystallographic unit-cell volume. Figure 1 shows the calculated potential energy curve of Ga<sub>2</sub>O<sub>3</sub> which is fitted to the equation of state of Vinet *et al.*<sup>21</sup> It yields the equilibrium volume ( $V_0$ ) of 52.4 Å<sup>3</sup>/per formula unit, bulk modulus ( $B_0$ ) of 330 GPa, and its pressure derivative ( $B_0'$ ) of 1.7, at zero pressure. It is to be noted here that the lattice parameters  $b$ ,  $c$ , and  $\beta$  remain nearly the same for the range of unit-cell volume considered. However, the lattice parameter  $a$  shows a small variation of about 6% with respect to its equilibrium value. The lattice parameters corresponding to the equilibrium ge-

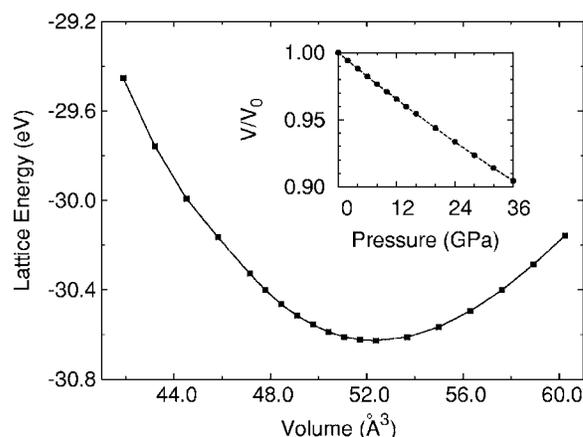


FIG. 1. Energy vs volume per formula unit of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>.  $V/V_0$  vs pressure is given in the inset, together with the fitted equation of state.

<sup>a)</sup>Permanent address: Departamento de Química Física y Analítica, Universidad de Oviedo, Oviedo 33006, Spain.

<sup>b)</sup>Author to whom correspondence should be addressed; electronic mail: pandey@mtu.edu

TABLE I. Equilibrium geometry of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. Experimental results are taken from Ref. 18.

Property	Expt.	Calc.
Lattice parameters		
$a$ (Å)	12.23	12.27
$b$ (Å)	3.04	3.03
$c$ (Å)	5.80	5.80
$\beta$ (deg)	103.7	103.7
Avg. nearest-neighbor distance		
Ga <sub>I</sub> - $R_{nn}$ (Å)	1.83	1.84
Ga <sub>II</sub> - $R_{nn}$ (Å)	2.01	2.00
O <sub>I</sub> - $R_{nn}$ (Å)	1.92	1.90
O <sub>II</sub> - $R_{nn}$ (Å)	1.87	1.86
O <sub>III</sub> - $R_{nn}$ (Å)	2.01	2.01
Fractional coordinates		
$x_{\text{Ga}_I}$	0.090	0.089
$z_{\text{Ga}_I}$	0.795	0.795
$x_{\text{Ga}_{II}}$	0.341	0.342
$z_{\text{Ga}_{II}}$	0.686	0.685
$x_{\text{O}_I}$	0.167	0.162
$z_{\text{O}_I}$	0.101	0.108
$x_{\text{O}_{II}}$	0.496	0.496
$z_{\text{O}_{II}}$	0.255	0.258
$x_{\text{O}_{III}}$	0.828	0.826
$z_{\text{O}_{III}}$	0.436	0.435

ometry are listed in Table I, showing an excellent agreement with the corresponding experimental values. The lattice constants, average nearest-neighbor distance, and internal parameters (i.e., fractional coordinates of atoms) are mostly within 1% of the respective experimental values. The calculated binding energy per formula unit of Ga<sub>2</sub>O<sub>3</sub> with respect to the constituent atoms is 30.6 eV. Assuming a quasiharmonic Debye-like model in which the Debye temperature depends only on the volume of the crystal,<sup>22</sup> the Debye temperature of Ga<sub>2</sub>O<sub>3</sub> is predicted to be 872 K.

Figure 2 displays the upper valence and lower conduction band structure of Ga<sub>2</sub>O<sub>3</sub>. Anionic and cationic states constitute the top of the valence and the bottom of the conduction band, respectively, as revealed by the total and partial density of states (DOS) shown in Fig. 3. The uppermost valence band is mainly formed by O 2*p* states, with a width

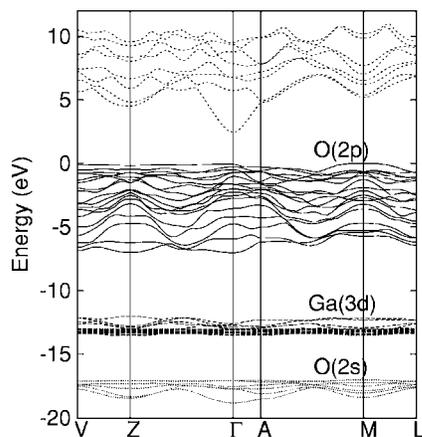


FIG. 2. Band structure of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. The Fermi energy is aligned to zero. The  $\mathbf{k}$  points are  $\Gamma=(000)$ ,  $A=(00\frac{1}{2})$ ,  $Z=(\frac{1}{2}0)$ ,  $M=(\frac{1}{2}\frac{1}{2})$ ,  $L=(0\frac{1}{2}0)$ , and  $V=(0\frac{1}{2}0)$ .

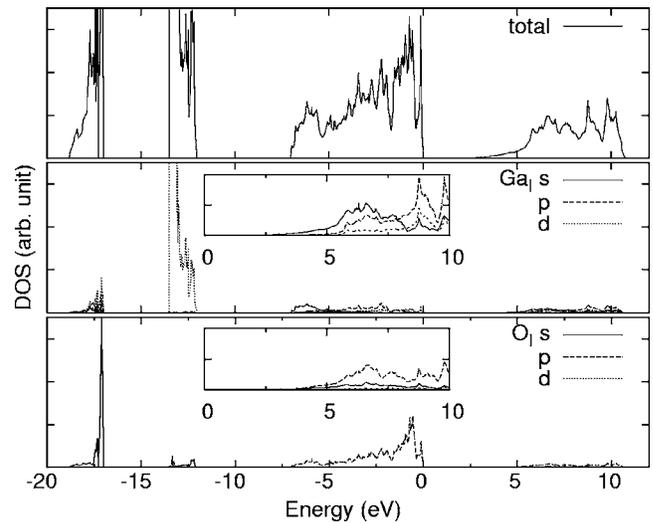


FIG. 3. Total and projected density of states of Ga<sub>2</sub>O<sub>3</sub> in the monoclinic phase. The PDOS associated with the conduction bands in the energy range of 0–10 eV is magnified in the inset. The Fermi energy is aligned to zero.

of about 7.0 eV. We note here that our GGA-DFT results do not agree with tight-binding calculations, which find the upper valence band to be composed of O 2*p*, Ga 4*p*, and Ga 4*s* bands.<sup>16</sup>

The valence band maximum appears to be almost degenerate at the  $\Gamma$  and  $M$  special points, the energy at  $\Gamma$  being 0.03 eV lower than that at  $M$ . On the other hand, the conduction band minimum occurs at  $\Gamma$ , so there is a direct gap at  $\Gamma$  and an indirect  $M$ - $\Gamma$  gap. It is well known that GGA DFT-based calculations underestimate the band gap, although this can be corrected using a semiempirical expression<sup>23</sup> which shifts the levels in the conduction band. Using the high-frequency dielectric constant value of 4.71 for Ga<sub>2</sub>O<sub>3</sub>, the semiempirical correction yields a direct gap of 4.40 eV at  $\Gamma$ , and an indirect  $M$ - $\Gamma$  gap of 4.37 eV, in good agreement with the value of 4.60 eV obtained by optical absorption measurements.<sup>5</sup> A recent experimental study<sup>1</sup> finds the absorption edges to be at 4.79 and 4.52 eV for light polarized along the  $\mathbf{b}$  and  $\mathbf{c}$  axes, respectively. Finally, our calculations do not predict the closing of the energy gap, at least up to 40 GPa, in the monoclinic Ga<sub>2</sub>O<sub>3</sub>. The calculated pressure coefficients of the energy gap at  $\Gamma$  and  $M$  are 0.025 and 0.027 eV/GPa, respectively.

A close inspection of the density of states (see the insets of Fig. 3) and charge density associated with the lowest conduction band finds it to be associated with Ga 4*s*. Since Ga atoms have either tetrahedral coordination or octahedral coordination, a significantly different dispersive behavior of the bands associated with the tetrahedrally (Ga<sub>I</sub>) and octahedrally (Ga<sub>II</sub>) coordinated atoms is expected; the conduction band minimum at  $\Gamma$  is associated with the Ga<sub>II</sub> atoms, showing a large splitting of about 3.28 eV with respect to that associated with Ga<sub>I</sub> atoms. This large splitting can be related to a larger degree of covalency at the tetrahedral sites, which moves the Ga<sub>I</sub>-4*s* levels into antibonding states at higher energies.

Following the predicted value of 4.40 eV associated with the transition from the top of the valence band to the bottom of the conduction band at  $\Gamma$ , the interband transitions associated with  $Z$ ,  $A$ , and  $M$   $\mathbf{k}$  points are predicted to be at 6.61, 6.99, and 7.11 eV, respectively. This group is followed

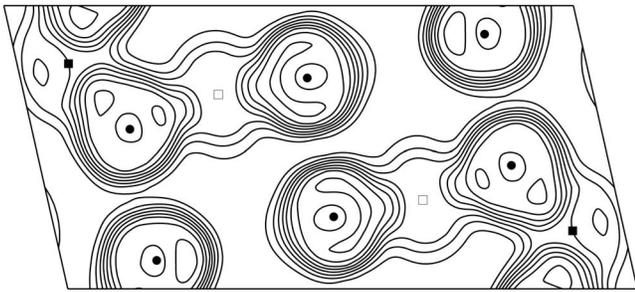


FIG. 4. ELF plot for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> in the plane perpendicular to the **b** axis with isolines from 0 to 1 with 0.1 spacing. Ga<sub>I</sub> atoms shown as filled squares, Ga<sub>II</sub> atoms as empty squares, and O atoms as circles.

by two peaks at 7.69 and 9.42 eV, associated with *V* and *L* **k** points. It is expected that the predicted values will assist the experimentalists in identifying the peaks in the optical spectra obtained by either reflectance or x-ray photoelectron spectroscopy.

The valence band is almost flat, indicating a rather large effective mass for holes. On the other hand, the calculated electron effective mass with  $m_e^*/m_0$  values of 0.123, 0.124, and 0.130 along **a**<sup>\*</sup>, **c**<sup>\*</sup> ( $\Gamma$ -A), and **b**<sup>\*</sup> ( $Z$ - $\Gamma$ ), respectively, is close to the effective mass of 0.15 $m_0$  of the wurtzite GaN as obtained by electron spin-resonance experiments.<sup>24</sup> For each **k** direction, we have fitted the energy dispersion of the conduction band minimum to a parabolic function in the vicinity of the  $\Gamma$  point.

We use the (valence) electron localization function<sup>25</sup> (ELF) to analyze bonding in the crystal. The ELF contour plot on the plane perpendicular to **b** is shown in Fig. 4. Electrons are localized in basins around the O atoms, and there is no bond localization region, suggesting a mainly ionic bonding, as expected considering the difference in electronegativity of Ga and O. However, small deviations from the spherical symmetry around the nuclei suggest the presence of some covalency in the crystal. On the basis of these deviations, a higher degree of covalency is seen to be associated with Ga<sub>I</sub>-O bonds as expected due to its lower coordination in the crystalline lattice.

In summary, we have calculated structural and electronic properties of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. A fitting of the equation of state to the energy surface yields lattice parameters at zero pressure which are in good agreement with the corresponding experimental values. The analysis of the band structure shows the

gap to be indirect, and no metallization of Ga<sub>2</sub>O<sub>3</sub> is predicted to occur for pressures up to 40 GPa. The valence band is almost flat, indicating a rather large effective mass for holes, whereas the calculated electron effective mass comes out to be about 0.12, expressed in units of the free electron mass.

One of the authors (M.A.B.) acknowledges funding from Spanish DGICYT Grant No. BQU2003-06553.

- <sup>1</sup>N. Ueda, H. Hosono, R. Waseda, and H. Kawazoe, *Appl. Phys. Lett.* **71**, 933 (1997).
- <sup>2</sup>D. D. Edwards, T. O. Mason, F. Goutenoire, and K. R. Poeppelmeier, *Appl. Phys. Lett.* **70**, 1706 (1997).
- <sup>3</sup>M. Passlacki, M. Hong, and J. P. Mannaerts, *Appl. Phys. Lett.* **68**, 1099 (1996).
- <sup>4</sup>M. Fleischer and H. Meixner, *J. Appl. Phys.* **74**, 300 (1993).
- <sup>5</sup>H. H. Tippins, *Phys. Rev.* **140**, A316 (1965).
- <sup>6</sup>L. N. Cojocaru and A. Prodan, *Rev. Roum. Phys.* **19**, 209 (1974).
- <sup>7</sup>E. Vllora, T. Atou, T. Sekiguchi, T. Sugawara, M. Kikuchi, and T. Fukuda, *Solid State Commun.* **120**, 455 (2001).
- <sup>8</sup>T. Harwig, F. Kellendonk, and S. Slappendel, *J. Phys. Chem. Solids* **39**, 675 (1978).
- <sup>9</sup>X. Wu, W. Song, W. Huang, M. Pu, B. Zhao, Y. Sun, and J. Du, *Chem. Phys. Lett.* **328**, 5 (2000).
- <sup>10</sup>G. Park, W. Choi, J. Kim, Y. Choi, Y. Lee, and C. Lim, *J. Cryst. Growth* **220**, 494 (2000).
- <sup>11</sup>W. Han, P. Kohler-Redlich, F. Ernst, and M. Rühle, *Solid State Commun.* **115**, 527 (2000).
- <sup>12</sup>M. Orita, H. Ohta, and M. Hirano, *Appl. Phys. Lett.* **77**, 4166 (2000).
- <sup>13</sup>Z. W. Pan, Z. R. Dai, and Z. L. Wang, *Science* **291**, 1947 (2001).
- <sup>14</sup>C. Liang, G. Meng, G. Wang, Y. Wang, L. Zhang, and S. Zhang, *Appl. Phys. Lett.* **78**, 3202 (2001).
- <sup>15</sup>J. Li, X. Chen, Z. Qiao, M. He, and H. Li, *J. Phys.: Condens. Matter* **13**, L937 (2001).
- <sup>16</sup>E. A. Albanesi, S. J. Sferco, I. Lefebvre, G. Allan, and G. Hollinger, *Phys. Rev. B* **46**, 13260 (1992).
- <sup>17</sup>M. A. Blanco, M. B. Sahariah, H. Jiang, A. Costales, and R. Pandey, *Phys. Rev. B* **72**, 184103 (2005).
- <sup>18</sup>S. Geller, *J. Chem. Phys.* **33**, 676 (1960).
- <sup>19</sup>J. Åhman, G. Svensson, and J. Albertsson, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C52**, 1336 (1996).
- <sup>20</sup>G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996); Vienna *Ab Initio* Simulation Package, Technische Universität Wien, 1999.
- <sup>21</sup>P. Vinet, J. H. Rose, J. Ferrante, and J. R. Smith, *J. Phys.: Condens. Matter* **1**, 1941 (1989).
- <sup>22</sup>M. A. Blanco, E. Francisco, and V. Luaña, *Comput. Phys. Commun.* **158**, 57 (2004).
- <sup>23</sup>V. Fiorentini and A. Baldereschi, *J. Phys.: Condens. Matter* **4**, 5967 (1992).
- <sup>24</sup>M. Fanciulli, T. Lei, and T. D. Moustakas, *Phys. Rev. B* **48**, 15144 (1993).
- <sup>25</sup>A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.* **92**, 5397 (1990).