First-principles study of point defects in LiGaO$_2$

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The native point defects are studied in LiGaO$_2$ using hybrid functional calculations. We find that the relative energy of formation of the cation vacancies and the cation antisite defects depends strongly on the chemical potential conditions. The lowest energy defect is found to be the Ga$_{Li}^{2+}$ donor. It is compensated mostly by V$_{Ga}^{-1}$ and in part by Li$^{2-}$ in the more Li-rich conditions. The equilibrium carrier concentrations are found to be negligible because the Fermi level is pinned deep in the gap and this is consistent with insulating behavior in pure LiGaO$_2$. The V$_{Ga}$ has high energy under all reasonable conditions. Both the Ga$_{Li}$ and the V$_{O}$ are found to be negative $U$ centers with deep 2+/0 transition levels.

I. INTRODUCTION

Recently, there has been an interest in ultra-wide-band-gap semiconductors such as β-Ga$_2$O$_3$ because of their potential in pushing high-power transitions to the next level of performance. An important figure of merit for such applications is the breakdown field and the latter is directly correlated with the band gap. Here we draw attention to an even higher band gap material, LiGaO$_2$. LiGaO$_2$ has a wurtzite-derived crystal structure and band gap of ∼5.3-5.6 eV (at room temperature) based on optical absorption but potentially even as large as 6.25 eV (at T = 0) based on quasi-particle self-consistent GW calculations with G the one-particle Green’s function and W the screened Coulomb potential. It can be thought of as a I-III-VI$_2$ ternary analog of wurtzite ZnO, in which each group II Zn atom is replaced by either a group-I Li or a group III-Ga in a specific ordered pattern with the Pbn$_2$1 spacegroup. In this structure the octetrule is satisfied because each O is surrounded tetrahedrally by two Li and two Ga. The prototype for this crystal structure is β-NaFeO$_2$. LiGaO$_2$ can be grown in bulk form by the Czochralsky method and because of its good lattice match has been explored as a substrate for GaN. It can also be grown by epitaxial methods on ZnO and vice versa. Mixed ZnO-LiGaO$_2$ alloys have been reported. It has been considered for piezoelectric properties and is naturally considered as a wide gap insulator. However, Boonchun and Lambrecht suggested it might be worthwhile considering as a semiconductor electronic material and showed in particular that it could possibly be n-type doped by Ge. That study only used the 16 atom primitive unit cell of LiGaO$_2$ and thus considered rather high (25 %) Ge$_{Ga}$ doping or Mg$_{Ga}$ doping. It did not study the site competition or native defect compensation issues. Here we study the native point defects by means of hybrid functional supercell calculations.

II. COMPUTATIONAL METHOD

Our study is based on density functional calculations using the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional. The calculations are performed using the Vienna Ab-Initio Simulation Package (VASP). The electron ion interactions are described by means of the Projector Augmented Wave (PAW) method. We use a well-converged energy cut-off of 500 eV for the projector augmented plane waves. We performed the calculations with a supercell size of 128 atoms (which corresponds to $2 \times 2 \times 2$ the primitive unit cell) and a single k-point shifted away from Γ is employed for the Brillouin zone integration. The valence configurations used were 2$s^1$ for Li, 3$d^{10}$ for Ga and 2$s^2$2$p^4$ for O. In the HSE functional, the Coulomb potential in the exchange energy is divided into short-range and long-range parts with a screening length of 10 Å and only the short-range part of the exact Hartree-Fock non-local exchange is included by mixing it with the generalized gradient Perdew-Burke-Ernzerhof (PBE) potential with a mixing fraction $\alpha = 0.25$. The band gap obtained in this way ($E_g = 5.10$ eV) is still slightly lower than the experimental value.

III. RESULTS

The energy of formation of the defect $D^q$ in charge state $q$ is given by

$$E_f(D^q) = E_{tot}(C : D^q) - E_{tot}(C) - \sum_i \Delta n_i \mu_i + q(\epsilon_v + \epsilon_F + V_{align}) + E_{cor}$$

where $E_{tot}(C : D^q)$ is the total energy of the supercell containing the defect and $E_{tot}(C)$ is the total energy of the perfect crystal supercell. The chemical potentials $\mu_i$ represent the energy for adding or removing atoms from the crystal to a reservoir in the process of making the defect. The $\Delta n_i$ is the change in number of atoms of species.
Likewise the chemical potential of the electron determining its charge state is $\epsilon_F + \epsilon_e + V_{\text{align}}$ with $\epsilon_e$ the energy of an electron at the valence band maximum (VBM) relative to the average electrostatic potential in bulk and $\epsilon_F$ the Fermi energy in the gap measured from the VBM. The alignment potential $V_{\text{align}}$ represents the alignment of the average electrostatic potential in the supercell far away from the defect relative to that in the bulk. This is calculated using the Freysoldt et al. approach.\textsuperscript{22,23} The final term is the image charge correction term which corrects for the Madelung energy of the periodic array of net defect point charges in the uniform background that is added to ensure overall charge neutrality when considering a locally charged defect state. It is closely related to the alignment potential and including these corrections allows one to extrapolate the energy of formation to the dilute limit of an infinitely large supercell.

The chemical potentials $\mu_i = \mu_i^0 + \tilde{\mu}_i$, where $\mu_i^0$ are the chemical potentials of each species in its reference state, namely the phase it occurs in at standard pressure and room temperature, and $\tilde{\mu}_i$ are the excess chemical potentials. The latter are viewed as a tunable parameter reflecting the growth conditions but must obey certain restrictions based on thermodynamic equilibrium. These include

$$\tilde{\mu}_{\text{Li}} + \tilde{\mu}_{\text{Ga}} + 2\tilde{\mu}_O = \tilde{\mu}_{\text{LiGaO}}$$

where $\tilde{\mu}_{\text{LiGaO}}$ is the energy of formation of LiGaO$_2$, which we calculated to be $-8.55$ eV. Each of the excess chemical potentials $\tilde{\mu}_i \leq 0$ on the left must be less than zero in order to avoid precipitation of the bulk elements Li and Ga or evolving O$_2$ gas. For example, $\tilde{\mu}_{\text{Li}}$ corresponds to metallic body-centered-cubic Li and thus $\tilde{\mu}_{\text{Li}} = 0$ corresponds to the assumption that the crystal with the defect is in equilibrium with bulk metallic Li as reservoir. Similarly $\tilde{\mu}_{\text{Ga}} = 0$ corresponds to equilibrium with metallic bulk Ga and $\tilde{\mu}_O$ corresponds to O in the O$_2$ molecule. However, we need to also consider further restrictions imposed by competing binary compounds Ga$_2$O$_3$ and Li$_2$O.

$$2\tilde{\mu}_{\text{Li}} + \tilde{\mu}_O \leq \tilde{\mu}_{\text{Li}_{2}O},$$

$$2\tilde{\mu}_{\text{Ga}} + 3\tilde{\mu}_O \leq \tilde{\mu}_{\text{Ga}_{2}O_{3}}.$$  \hspace{1cm} (3)

These restrictions determine the region of chemical potentials in which LiGaO$_2$ is stable relative to the competing binaries and elements. They are bounded by

$$\tilde{\mu}_{\text{Li}} \geq \frac{1}{3} \tilde{\mu}_{\text{Ga}} + \left[\tilde{\mu}_{\text{LiGaO}} - \frac{2}{3} \tilde{\mu}_{\text{Ga}_{2}O_{3}}\right],$$

$$\tilde{\mu}_{\text{Li}} \leq \frac{1}{3} \tilde{\mu}_{\text{Ga}} + \frac{1}{3} \left[2\tilde{\mu}_{\text{Li}_{2}O} - \tilde{\mu}_{\text{LiGaO}}\right].$$

with $\tilde{\mu}_{\text{LiGaO}} - \frac{2}{3} \tilde{\mu}_{\text{Ga}_{2}O_{3}} = -4.32$ eV and $\frac{1}{3} [2\tilde{\mu}_{\text{Li}_{2}O} - \tilde{\mu}_{\text{LiGaO}}] = -1.00$ eV.

It is represented in the phase diagram shown in Fig. 1. The points A, B, C, D correspond respectively to (A) Li-rich, Ga-poor, (B) Li-poor as well as relative Ga-poor, (C) Ga-rich, Li-poor and (D) Ga-rich and Li-rich but O-poor. The shading of the color is darker the higher the chemical potential of O and the line AB corresponds to the O-rich limit $\tilde{\mu}_O = 0$. In addition to the extreme chemical potential conditions (Ga-rich and Li-rich), we consider an intermediate oxygen chemical potential corresponding to a realistic growth condition during the annealing of LiGaO$_2$. The oxygen chemical potential is a function of temperature and oxygen partial pressure, as described by Reuter et al.\textsuperscript{23}

$$\tilde{\mu}_O(T, p) = \tilde{\mu}_O(T, p_0) + \frac{1}{2} k_B T \ln(p/p_0), \hspace{1cm} (5)$$

where $\tilde{\mu}_O(T, p_0)$ is the oxygen chemical potential at the standard pressure $p_0 = 1$ atm, $k_B$ is Boltzmann’s constant, and $T$ is the temperature in Kelvin. In the growth experiment of Ref.\textsuperscript{8} the mixed Li$_2$CO$_3$ and Ga$_2$O$_3$ powders were compressed into tablets and then calcined at 1200 °C for 20 h in air.\textsuperscript{25} We therefore choose an annealing temperature of 1200°C and an oxygen partial pressure of 0.21 atm which represents the ratio of oxygen gas in ambient environment. The growth conditions at annealing temperature of 1200 °C and oxygen partial pressure of 0.21 atm is represented by the dashed line EF in Fig. 1.

The defects considered are the vacancies $V_{\text{Ga}}$, $V_{\text{Li}}$ and $V_{\text{O}}$ and the antisites Li$_{\text{Ga}}$ and Ga$_{\text{Li}}$. The effects of spin polarization were included for cases with unpaired electrons in defect levels. Interstitial defects will be considered in the future but comparison with II-IV-N$_2$ semiconductors suggest that they would be of high energy.\textsuperscript{22,23,24} The defect energies of formation are shown for the six chemical potential points A, B, C, D, E and F in Fig. 2.

First we see that Ga$_{\text{Li}}$ is the lowest energy defect for $\epsilon_F = 0$ in all cases. It is a double donor, which is in the 2+ charge state over most of the gap. Still, it has a well-defined $2+/0$ transition making it a negative U system. In Fig. 2 we can see that while for the neutral charge state, the O around Ga$_{\text{Li}}$ move outward, they
FIG. 2. Energies of formation of various defects in LiGaO$_2$ for chemical potential conditions identified in Fig. 1.

move inward for the 2+ charge state with an in-between outward relaxation for the 1+ state. The additional stabilization by outward motion of the O when adding two electrons rather than one causes the negative $U$ behavior where the 1+ charge state is never the lowest energy one for any Fermi level position. It is thus not behaving like a simple shallow donor, consistent with the relatively deep donor binding energy of 0.74 eV below the conduction band minimum (CBM). We thus do not expect it to be an effective n-type dopant. We can see that this defect has negative energy of formation at $\epsilon_F = 0$ in most cases. This reflects that even in the most Ga-poor case, this defect is hard to avoid because we cannot make the system poor enough in Ga without reaching the stability limit imposed by Li$_2$O. On the other hand, a Fermi level $\epsilon_F = 0$ is not expected to be realistic as discussed later.

The Li$_{Ga}$ antisite on the other hand is a double acceptor which can occur in 0, −1, −2 charge states. It is the lowest energy defect in its 2− charge state near the CBM in cases A, D and E. These are the cases richest in Li.

As for the vacancies, $V_{Li}$ occurs in 0, −1, −2 charge states, while $V_{Ga}$ occurs in 0, −1, −2, −3 charge states. We can see that $V_{Ga}^0$ has a high energy of formation in all cases. Although its negative charge states have significantly lower energy for $\epsilon_F$ close to the CBM, it never becomes the lowest energy defect and therefore does not play a role in determining the Fermi level. The $V_{Li}$ is more interesting. Although it has high energy in the Li-rich case D (which is somewhat unrealistic and O-poor) it has low energy in the Li-poor cases, B, C, F. Even in case E, its intersection with the Ga$_{Li}^{2+}$ occurs close to that of the intersection of the latter with Li$_{Ga}^{2-}$. We thus expect that both these acceptors may play a role in compensating the Ga$_{Li}^{2+}$.

Turning now to the O-vacancies, there are two non-equivalent sites for the oxygen in LiGaO$_2$: on top of Li (O$_1$) or on top of Ga (O$_2$). We find that both $V_{O1}$ and $V_{O2}$ are only stable in the neutral and 2+ charge states (with $V_{O2}$ slightly lower in energy than $V_{O1}$) with the transition level (2+/0) at 2.48 eV above the VBM or 2.62 eV below the CBM. This is a quite deep donor level and indicates that the vacancy is also a negative $U$ center. In Fig. 4 one can see that also in this case the relaxations are strongly charge-state dependent. This figure shows the relaxations near a $V_{O2}$ but similar results hold for $V_{O1}$. In the neutral charge state, the Ga move inward, while the Li move outward. In the 2+ state both move strongly outward. This is similar to the $V_{O}$ in ZnO although the level is here even deeper and close to mid gap. We find that the $V_{O}^{2+}$ energy of formation is negative for Fermi levels close to the VBM for points C, D, E, F. They become positive for the O-rich limits (A, B). Its energy of formation is always higher than that of the Ga$_{Li}^{2+}$ and thus it is not expected to play a significant role in the charge balance.

Using the charge neutrality condition between free electron concentration $n_e(T, \epsilon_F)$, free hole concentration...
\[ n_h(T, \epsilon_F) \] and the various defect concentrations,

\[ c(D^0; T, \epsilon_F) = N_D g(q) e^{-\left(E_f(D^0, \epsilon_F=0) + q\epsilon_F\right)/k_B T} \]  \hspace{1cm} \text{(6)}

where \( N_D \) is the number of available sites per cm\(^3\) and \( g(q) \) a degeneracy factor depending on the charge state, we can find the equilibrium Fermi level and the defect concentrations for a given temperature following the procedure of Ref[25]. For the electron and hole concentrations we use a parabolic band with effective density of states masses \( m_e^* \approx 0.4 \) and \( m_h^* \approx 1.8 \) (as obtained from the calculate hybrid functional band structure and averaging over directions.) For a temperature of \( T = 1500 \) K close to the growth temperature, we find that under chemical potential conditions \( C \), the equilibrium Fermi level is \( \epsilon_F = 3.815 \) eV, close to the intersection of the \( V_{Li}^{-1} \) and \( Ga_{Li}^{2+} \). The electron concentration \( n_e = 6 \times 10^{13} \) cm\(^{-3}\) but the \( [V_{Li}^{-1}] = 2[Ga_{Li}^{2+}] = 1.0 \times 10^{26} \) cm\(^{-3}\) are unrealistically high. This is related to the energies of formation of the main defects \( Ga_{Li} \) and \( V_{Li} \) being negative for the equilibrium Fermi level. For point \( E \), the equilibrium Fermi level position is closer to mid gap, \( \epsilon_F = 2.75 \) eV with \([Ga_{Li}^{2+}] = 3.7 \times 10^{14} \), \([V_{Li}^{-1}] = 7.22 \times 10^{14} \) and \([Li_{Ga}] = 1 \times 10^{13} \) cm\(^{-3}\), \([V_{O}^{2+}] = 5 \times 10^{12} \) cm\(^{-3}\). So, in this case the concentrations of defects are much smaller and the \( Ga_{Li}^{2+} \) is still mostly compensated by \( V_{Li}^{-1} \) but partially also by \( Li_{Ga}^{2+} \). The electron concentration \( n_e = 3.2 \times 10^{12} \) cm\(^{-3}\) is then only slightly higher than the hole concentration \( n_h = 1.6 \times 10^{11} \) cm\(^{-3}\) but both free carrier concentrations are in fact negligible under both chemical potential conditions considered. Even un-
under the most Ga-poor conditions (point A), Ga$_{\text{Li}}^{2+}$ is the dominant defect and is compensated mostly by V$_{\text{Li}}^{1-}$. In this case, $\epsilon_F = 1.92$ eV is closest to the VBM and the material would then be slightly p-type with $n_H = 9.7 \times 10^{13}$ cm$^{-3}$.

**TABLE I.** Transition levels $\epsilon(q, q')$ in eV relative to the VBM

| Defect | $q, q'$ | $\epsilon(q, q')$ |
|--------|---------|-----------------|
| V$_{\text{Li}}$ | (0/1-) | 1.0270 |
| V$_{\text{Ga}}$ | (0/1-) | 2.1843 |
| | (1/-2) | 3.0989 |
| | (2/-3) | 3.3088 |
| Li$_{\text{Ga}}$ | (0/1-) | 1.5464 |
| | (1/-2) | 2.1855 |
| Ga$_{\text{Li}}$ | (0/2+) | 4.3569 |
| V$_{\text{O}}$ | (0/2+) | 2.4831 |

It is instructive to compare the defect physics in this system to that in II-IV-N$_2$ semiconductors like ZnGeN$_2$. The similarity is that in both cases, the antisites play a crucial role. However, the dependence on chemical potentials of the elements is more important here because a wider region of stability occurs. Furthermore the Ga$_{\text{Li}}$ antisite is here not a shallow but a deep donor and is thus not expected to lead to unintentional n-type doping. This is consistent with the insulating behavior of LiGaO$_2$. However, it does not exclude the possibility of n-type doping by Si or Ge or Sn which will be studied separately.

The main defect transition levels in the gap are summarized in Table I and in Fig. 5.

**IV. CONCLUSIONS**

In this paper we have studied the native defects in LiGaO$_2$. We find that the relative energy of formation of vacancies and antisites depends strongly on the chemical potential conditions. The Ga$_{\text{Li}}$ antisite is a dominant donor defect. However, it has a rather deep 2+ /0 donor level and is a negative $U$ center. It is thus not expected to lead to significant n-type doping. It furthermore becomes compensated mostly by V$_{\text{Li}}^{1-}$ and in part by Li$^{2-}$ depending on how rich the system is in Li. The V$_{\text{O}}$ is found to be an even deeper double donor negative $U$ center. The defect transition levels are all relatively deep in to the gap with no truly shallow levels.

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