Hole conductivity through a defect band in ZnGa$_2$O$_4$

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Semiconductors with wide band gap (> 3.0 eV), high dielectric constant (> 10), good thermal dissipation, and capable of $n$ and $p$-type doping are highly desirable for high-energy power electronic devices. Recent studies indicate that ZnGa$_2$O$_4$ may be suitable for these applications, standing out as an alternative to Ga$_2$O$_3$. The simple face centered cubic spinel structure of ZnGa$_2$O$_4$ results in isotropic electronic and optical properties, in contrast to the large anisotropic properties of the $\beta$-monoclinic Ga$_2$O$_3$. In addition, ZnGa$_2$O$_4$ has shown, on average, better thermal dissipation and potential for $n$- and $p$-type conductivity. Here we use density functional theory and hybrid functional calculations to investigate the electronic, optical, and point defect properties of ZnGa$_2$O$_4$, focusing on the possibility for $p$- and $n$-type conductivity. We find that the cation antosite Ga$_{2n}$ is the lowest energy donor defect that can lead to unintentional $n$-type conductivity. The stability of self-trapped holes (small hole polarons) and the high formation energy of acceptor defects make it difficult to achieve $p$-type conductivity. However, with excess of Zn, forming Zn$_{(1+2x)}$Ga$_{2(1-x)}$O$_4$ alloys display an intermediate valence band, facilitating $p$-type conductivity. Due to the localized nature of this intermediate valence band, $p$-type conductivity by polaron hopping is expected, explaining the low mobility and low hole density observed in recent experiments.

Keywords: Wide band gap oxide, defects, electronic conductivity, transparent conducting oxide

I. INTRODUCTION

Ultra-wide band gap semiconductors (WBS) have attracted great attention in recent years for their application in high-power transistors for energy conversion and solar-blind UV detectors, combining high critical electric field strength, transparency in the visible spectrum, and high conductivity through doping [1–5]. Among the promising semiconductor materials, Ga$_2$O$_3$ stands out with band gap in the range of 4.6-5.0 eV and a large electric breakdown field, resulting in Baills’ figure of merit (BFOM) just smaller than diamond and with capability that goes beyond existent technologies based on SiC and GaN [1, 6]. However, the low thermal conductivity and the complicated monoclinic crystal structure of $\beta$-Ga$_2$O$_3$ lead to low heat dissipation and anisotropic electronic and optical properties, which, in addition to the inherent difficulties in making the material $p$-type or even reliably semi-insulating, pose serious obstacles to device design and implementation [6–17].

Recent studies have focused on ZnGa$_2$O$_4$ as a ultra-wide band gap semiconductor for devices [2,5]. With a band gap of 5.0 eV, room-temperature electron mobility of $10^2$ cm$^2$/V.s, and high dielectric constant of 10.4, ZnGa$_2$O$_4$ has been considered as an alternative or, at least, as a complement to Ga$_2$O$_3$ [3,5]. Thin films of spinel ZnGa$_2$O$_4$ have been grown epitaxially on sapphire substrate [5]. Considering an average in all directions, experimental results indicate that the thermal dissipation in ZnGa$_2$O$_4$ thin films is about 10% more efficient than in Ga$_2$O$_3$ [3, 8].

Reported unintentional $n$-type conductivity in ZnGa$_2$O$_4$ with carrier density of $9\times10^{19}$ cm$^{-3}$ is three orders of magnitude higher than that in undoped Ga$_2$O$_3$ and one order of magnitude higher than in Si- or Sn-doped Ga$_2$O$_3$ [4–9]. The possible source of this unintentional $n$-type doping in ZnGa$_2$O$_4$ is still under debate, being attributed to oxygen vacancies (V$_O$), antises such as Ga on Zn site (Ga$_{2n}$), or a combination of both [4, 5]. The oxygen vacancy was predicted to be a shallow donor in some oxides, such as TiO$_2$ and In$_2$O$_3$, for example [10, 11]. However, in oxides with wider band gaps, such Ga$_2$O$_3$ or ZnO, the oxygen vacancy was predicted to behave as a deep donor, and could not contribute to the observed unintentional $n$-type conductivity [12, 13]. Similarly, it is expected that the unintentional conductivity observed in ZnGa$_2$O$_4$ cannot be explained by the presence of V$_O$.

Recent experimental results also indicate that ZnGa$_2$O$_4$ shows $p$-type conductivity when grown in O-rich flux condition [4, 5], with hole concentrations reaching $10^{15}$ cm$^{-3}$ at 800 K [4], and an extracted activation energy of 0.93 eV. Such high thermal activation energy was attributed to intraband conduction according to E. Chikoidze et al. [4]. This is an intriguing result considering the very low valence band (high workfunction) of ZnGa$_2$O$_4$. If both $p$ and $n$-type conductivity could be achieved in the wide band gap ZnGa$_2$O$_4$, this material would become a potential candidate for solid-state deep UV LED (light emitting diode), with photon energies in the window of 254-207 nm that is appropriate for eliminating virus and bacteria, including SARS-COV [14].

Although ZnGa$_2$O$_4$ is already being used as a transparent conducting oxide, the role of native point defects in their electronic and optical properties is still subject of debate. Using first principles calculations based on density functional theory (DFT) and hybrid functional, calculate the formation energies and transition levels for native point defects in ZnGa$_2$O$_4$. We find that the Ga$_{2n}$...
antisite is a shallow donor and likely the main source of unintentional n-type conductivity in ZnGa$_2$O$_4$. On the other hand, none of the native point defects are shallow acceptors, and cannot lead to p-type conductivity. Moreover, holes tend to become self-trapped, forming small polarons.

On the other hand, if a large excess of Zn is incorporated in ZnGa$_2$O$_4$, forming Zn$_{(1+2x)}$Ga$_{(2-1-3x)}$O$_4$ alloys, the extra Zn occupying the Ga sites lead to a partially occupied intermediate valence band, within which holes existing as small polarons move by hopping, possibly explaining the observed p-type conductivity\[14, 15]. We also construct configuration coordinate diagrams to determine the energy of the optical emission peaks associated with each defect to help their identification, with special attention to the oxygen vacancy, the self-trapped hole, and the Ga$_{rm Zn}$ antisite.

II. THEORETICAL APPROACH AND COMPUTATIONAL DETAILS

Our first principles calculations are based on density functional theory (DFT)\[15, 16] and the HSE hybrid functional\[17, 18] as implemented in the Vienna Ab-Initio Simulation Package (VASP)\[19, 20]. The interaction between the valence electrons and the ionic cores was treated using projected augmented wave (PAW) potentials\[21, 22], considering the following valence configurations: O(2s$^2$2p$^4$), Ga(3d$^{10}$4s$^2$4p$^1$) and Zn(4d$^{10}$5s$^2$). In the HSE functional, the exchange is separated in two regions, long and short range, by a screening parameter $\omega = 0.20$\[17, 18]. In the default configuration, the short range region is composed of 25% of non-local Hartree-Fock exchange, and the remaining 75% derives from the Perdew-Burke-Ernzerhof (PBE) functional. All the correlation and the exchange for the long-range region are derived from the PBE functional\[17, 18]. However, the default value for the amount of Hartree-Fock exchange is not enough to correct the band gap for both Ga$_2$O$_3$ and ZnO, and we expect the same behavior for ZnGa$_2$O$_4$. Points A and B represent the condition of O-rich and O-poor, respectively, and the chemical potentials for O, Zn, and Ga are shown for both points.

Defect formation energies

The formation energy of a defect $D$ in the charge state $q$ was calculated according to the following expression:

\[ E_f(D, q) = E_{tot}(D, q) - E_{tot}(bulk) + \sum_i n_i \mu_i + qE_F + \Delta^q, \]

where $E_{tot}(D, q)$ is the total energy of the supercell containing a defect $D$ in charge state $q$, and $E_{tot}(bulk)$ is the total energy of perfect ZnGa$_2$O$_4$ in the same supercell. The chemical potential $\mu_i$ for the specie $i$ that was removed or added to the supercell for the defect is referenced to the total energy of the respective elemental phase. $E_F$ is the Fermi energy taking the valence-band maximum (VBM) as a reference, and $\Delta^q$ is the charge-state dependent correction due to the finite size of the supercell\[23, 24].

The chemical potentials are treated as variables in Eq. (1). To ensure the stability of ZnGa$_2$O$_4$, the chemical potentials should satisfy the following condition:

\[ \mu_{Zn} + 2\mu_{Ga} + 4\mu_{O} = \Delta H_f(ZnGa_2O_4), \]

where $\Delta H_f(ZnGa_2O_4)$ is the formation enthalpy of ZnGa$_2$O$_4$; we find $\Delta H_f(ZnGa_2O_4) = -13.79$ eV using HSE. To avoid the formation of competing phases, such as Ga$_2$O$_3$ and ZnO, the chemical potentials must also satisfy:

\[ 2\mu_{Ga} + 3\mu_{O} < \Delta H_f(Ga_2O_3), \]
\[ \mu_{Zn} + \mu_{O} < \Delta H_f(ZnO), \]

where $\Delta H_f(Ga_2O_3)$ and $\Delta H_f(ZnO)$ are the formation enthalpies of $\beta$-Ga$_2$O$_3$ and wurtzite ZnO. Following

![Phase diagram for ZnGa$_2$O$_4$](image-url)
these relations, we can determine the region of stability for ZnGa$_2$O$_4$ in the phase diagram as shown in Fig. 1. The blue and green areas show the regions where the oxides ZnO and Ga$_2$O$_3$ are stable, while the white area represents the region where ZnGa$_2$O$_4$ is stable. In the phase diagram, we choose two points, A and B, for which the defect formation energies are reported, representing O-rich and O-poor limit conditions, respectively.

The optical emission spectrum for point defects was determined based on calculated configuration coordinate diagrams, where it is assumed that the optical excitations occur at fixed atomic coordinates, as reported for In$_2$O$_3$ and Ga$_2$O$_3$ in the literature [11, 25].

III. RESULTS AND DISCUSSION

A. Crystal structure and electronic properties

ZnGa$_2$O$_4$ crystallizes in the face center cubic (FCC) spinel structure that belongs to $Fm\bar{3}m$ space group with an experimental equilibrium lattice parameter of $a_0 = 8.33$ Å [4] (the crystal structure is shown in the inset of Fig. 2). The calculated equilibrium lattice parameter of 8.36 Å is only 0.36% larger than the experimental value. In the spinel crystal structure, the oxygen atoms occupy a unique non-equivalent site with Wyckoff notation 32e, where each O is bound to four cations (three Ga and one Zn). On the other hand, there are two non-equivalent cation sites, with completely different chemical environments. One of these sites is surrounded by six oxygen atoms, forming perfect octahedral motifs (16d in the Wyckoff notation), while the second site forms a perfect tetrahedral chemical environment (8a in the Wyckoff notation). All the local chemical environments are shown in Fig. S1 in the Supplemental Material.

The electronic band structure and density of states of ZnGa$_2$O$_4$, calculated using HSE, are shown in Fig. 2. The valence band is mainly derived from O 2p-orbitals, with the VBM located in between the K and Γ points; it shows low dispersion (high effective masses) and is low in energy (high ionization potential). In contrast, the conduction band is composed mainly of Zn and Ga s-orbitals, resulting in a large dispersion (CBM), with a minimum at Γ. The calculated indirect band gap is 4.90 eV. The local maximum in the valence band at Γ lies only 0.20 eV below the VBM, leading to a direct band gap of 5.10 eV.

The dispersion of the VBM in ZnGa$_2$O$_4$ is affected by the p-d coupling. In ZnO, the coupling between Zn d and O p orbitals shifts the position of the VBM to higher energies, increasing the dispersion in the vicinity of VBM [12]. The position of Ga d-orbitals in Ga$_2$O$_3$, on the other hand, is significantly lower than the VBM, resulting in a weaker p-d coupling and a low dispersion of the VBM [26, 27]. In ZnGa$_2$O$_4$, the p-d coupling has an intermediate intensity, lying between the cases of ZnO and Ga$_2$O$_3$, with contributions from both cations d-orbitals. Zn d orbitals are located around 4 eV below the VBM, as indicated by the red line in the orbital-resolved DOS in Fig. 2 while Ga 3d-orbitals lies 14 eV below the VBM (not shown in Fig. 2). Despite the moderated p-d coupling, the intensity is not sufficient to increase the dispersion of the VBM in ZnGa$_2$O$_4$. 

FIG. 2. Band structure and density of states for the FCC spinel structure of ZnGa$_2$O$_4$ taking the VBM as a reference. The band gap is indirect with the VBM located along the Γ-K direction, and the CBM occurs at Γ. The crystal structure of ZnGa$_2$O$_4$ where the Zn, Ga, and O are shown by the gray, green, and red spheres, respectively, is represented in the inset.
B. Intrinsic defects

We investigate all the possible intrinsic point defects in ZnGa$_2$O$_4$, i.e., vacancies (V$_O$, V$_{Zn}$ and V$_{Ga}$), antisites (Ga$_{Zn}$, Ga$_i$, Zn$_{Ga}$, Zn$_i$, O$_{Zn}$ and O$_{Ga}$), and interstitials (Zn$_i$, Ga$_i$ and O$_i$), as well as the self-trapped hole in the form of a small hole polaron. The defect formation energies as a function of Fermi level for O-rich (point A) and O-poor (point B) conditions are shown in Fig. 3.

For Fermi level near the valence band and for the O-rich condition, the most stable defects are Ga$_{Zn}$, Ga$_i$, Zn$_i$ and V$_O$; they are all donor defects. In contrast, for Fermi level near the conduction band, V$_{Zn}$, V$_{Ga}$ and Zn$_{Ga}$ are the lowest energy defects and act as acceptors. For the O-poor condition, the results are similar, however, the donors Ga$_O$ and Zn$_O$ are also low formation energy defects for Fermi level below the middle of the band gap.

It is important to mention that, in O-rich conditions, the acceptor defects are predominant in the region close to the CBM. The formation energy of these acceptor defects are significantly lower than any donor defect and, therefore, we expect $n$-type conductivity under O-rich condition to be very difficult to be achieved due to compensation. On the other hand, acceptor defects are high formation energy defects in the region near the VBM for O-poor condition, preventing, in principle, $p$-type conductivity. We also note that the lowest energy defects that can cause $n$-type ($p$-type) conductivity is Ga$_{Zn}$ (Zn$_{Ga}$), i.e. the cation antisites. This explains the observation of Ga (Zn) occupying the tetrahedral (octahedral) site in the spinel structure [3–5]. The most likely source of unintentional $n$-type conductivity in ZnGa$_2$O$_4$ is Ga$_{Zn}$, whereas V$_O$, often pointed as the source of unintentional $n$-type conductivity in many oxides, is a deep donor. In the following, we discuss the details of each defect in ZnGa$_2$O$_4$, separating the discussion on hole polaron, vacancies, antisites, and interstitial defects.

1. Small hole polaron

We find that a hole in the valence band of ZnGa$_2$O$_4$ spontaneously becomes self-trapped, forming a small hole polaron, as predicted for other oxides [28–30]. It is localized on one oxygen atom and accompanied by a local lattice distortion where one O-Ga bond length increased by 23%, transforming the tetrahedral environment around O to an almost trigonal planar configuration, with the wavefunction resembling that of an O 2$p_z$ orbital as shown in Fig. 4a. This effect is caused by the rather low dispersion and low energy of the valence band in ZnGa$_2$O$_4$. The calculated hole self-trapping energy of 0.44 eV is essentially defined as the difference between the total energy of the supercell containing one localized hole (by removing an electron from the supercell and letting the atomic positions to relax) and the supercell with a hole in the VBM. The relatively large self-trapping energy (much higher than $k_BT$ at room temperature) indicates that hole conductivity, if realized, will be given by small polaron hopping, with characteristic low mobility at room temperature.

2. Vacancies

Oxygen vacancy. When an oxygen vacancy is created in ZnGa$_2$O$_4$, four bonds are broken (three with Ga and one with Zn) leaving four dangling bonds. This electronic configuration reorganizes in a low energy single-particle state, and a higher energy threefold degenerate state. In the neutral charge state, the lower one fold degenerate state is occupied with two electrons and located in the band gap, 2.47 eV above the VBM, while the threefold state is unoccupied and lies resonant in the conduction band. Under this charge state, the atoms in the vicinity of V$_O$ relax inward by 14.51% of the equilibrium Zn-O bond length and the Ga atoms relax inward by 0.50% of the equilibrium Ga-O bond length, as indicated in Fig. 4b. Removing one electron from the gap state leads to 1+ charge state, V$_O^{1+}$; the gap state splits into spin-up occupied and spin-down unoccupied states, located at 2.90 eV and 4.53 eV above the VBM, respectively. The neighboring atoms relax outward from the vacancy by 6.21% and Ga by 5.90% of the respective equilibrium bond length. In the 2+ charge state, the lower state is also completely unoccupied and is shifted up to inside the conduction band. Under this charge state, the neighboring atoms further relax outward: the Zn by 30.05% and the three Ga 11.38%, as shown in Fig. 4c. The...
neighboring Zn atom around the V\(_{\text{O}}^{2+}\) forms an almost trigonal planar motif.

The formation energies as a function of the Fermi level (\(E_F\)) for V\(_{\text{O}}\) in different charge states are shown in Fig. 3. We observe that V\(_{\text{O}}^{0+}\) is not stable for all possible values of \(E_F\) when compared to the neutral and 2+ charge states. This indicates that the gap state is either fully occupied with two electrons or empty resonant in the conduction band. The thermodynamic transition level from neutral to 2+ charge state occurs at 1.26 eV below the CBM, making V\(_{\text{O}}\) a deep donor and unlikely to contribute to n-type conductivity at room temperature. On the other hand, if the equilibrium Fermi level lies in the middle of the band gap (insulator) or close to the VBM (p-type), V\(_{\text{O}}\) acts as a compensation defect for holes. The low or negative formation energy of V\(_{\text{O}}\) in O-poor condition, second lower between all the intrinsic donor defects, make it very difficult to make ZnGa\(_2\)O\(_4\) p-type.

Therefore, in addition to the high stability of hole polaron discussed before, this is another controllable to realize p-type conductivity in ZnGa\(_2\)O\(_4\). In contrast, V\(_{\text{O}}\) also does not act as a source of free electrons when the Fermi level in ZnGa\(_2\)O\(_4\) is close to the CBM and the n-type conductivity is predominant. This behavior is in contradiction with that in In\(_2\)O\(_3\) or TiO\(_2\) [10, 11], but similar to that in ZnO [12] and Ga\(_2\)O\(_3\) [13].

**Zinc vacancy.** The removal of a Zn atom results in two holes in the valence band that tend to localize in the form of small hole polarons at the O 2p\(_\sigma\) orbital of two different O atoms neighboring the vacancy (V\(_{\text{Zn}}^{0+}\)). Because of the electrostatic repulsion of positive charges, the distance between these two hole polarons is maximized around the Zn vacancy; these small polarons are associated with unoccupied single-particle states in the gap, in opposite spin channels.

By adding one electron to V\(_{\text{Zn}}^{0+}\), one of the small hole polarons vanishes, resulting in the negatively charged state V\(_{\text{Zn}}^{-}\), with a (0/-) transition level at 1.51 eV above the VBM. Introducing a second electron fills the remaining single-particle level of V\(_{\text{Zn}}^{-}\) inside the band gap, resulting in V\(_{\text{Zn}}^{2-}\). The (-/2-) transition level is at 1.76 eV above the VBM. The local lattice configuration around V\(_{\text{Zn}}^{2-}\) is shown in Fig. S2 in the Supplemental Material.

The formation energy of V\(_{\text{Zn}}^{2-}\) is low, and even becomes negative in O-rich conditions when \(E_F\) is near the CBM. This indicates that V\(_{\text{Zn}}^{2-}\) is a likely source of electron compensation in n-type ZnGa\(_2\)O\(_4\). For \(E_F\) near the VBM, V\(_{\text{Zn}}^{2-}\) has high formation energy. The position of the (0/-) and (-/2-) transition levels well above the CBM indicates that V\(_{\text{Zn}}^{2-}\) is a deep acceptor and cannot serve as a source of p-type conductivity.

**Gallium vacancy.** The vacancy of Ga is similar to the Zn. Because of the 3+ oxidation state of Ga, three holes are generated in the system when a V\(_{\text{Ga}}\) is created. These three holes tend to localize in the form of small polarons and sit on three different O 2p\(_\sigma\) orbitals around the V\(_{\text{Ga}}\), maximizing the distance between them. Because the large electrostatic repulsion between these polarons, V\(_{\text{Ga}}^{0\text{-}}\) is less stable than V\(_{\text{Zn}}^{0+}\). When an electron is added to the system, one semi-occupied quasi-particle state that lies in the band gap (neutral charge state) become completely occupied and move toward the valence band. This condition represents the V\(_{\text{Ga}}^{1-}\) charge state and the transition from (0/1-) occur at 1.63 eV above the VBM. Similar behavior is observed for the other negative charge states, with transitions (1/-2-) and (2/-3-) lying at 2.40 eV and 2.53 eV above the VBM. All these transitions can be observed in the formation energy of Fig. 3 and the atomic configuration for V\(_{\text{Ga}}^{3-}\) is shown in Fig. S2 in the Supplemental Material.

In O-rich limit condition, the formation energy of V\(_{\text{Ga}}\) becomes low or negative for \(E_F\) in the upper part of the gap, while in O-poor condition this defect has very high formation energy. In the O-rich limit, the Ga vacancy is stable in the 3- charge state, V\(_{\text{Ga}}^{3-}\), acting as compensation center to n-type conductivity.

**3. Antisites**

As mentioned before, the antisites, especially Zn\(_{\text{Ga}}\) and Ga\(_{\text{Zn}}\), play an important role in the electronic conductivity of ZnGa\(_2\)O\(_4\). Both chemical environments are shown in . While Ga\(_{\text{Zn}}\) is the lowest energy donor defect and a likely source of unintentional n-type conductivity, Zn\(_{\text{Ga}}\) is the lowest energy acceptor defect that acts as an electron compensation center.

We can define the Fermi level pinning for n- and p-type conductivity, \(E_{\text{pin}}^n\) and \(E_{\text{pin}}^p\), respectively, as the maximum and minimum position for \(E_F\) in the gap, taking the VBM as a reference, before the intrinsic defect starts to compensate the prevalent conductivity in the material [31, 32]. For materials that are easy to dope n-type, \(E_{\text{pin}}^n\) lies near the edge or resonant in the conduction band. Conversely, for materials that can easily doped p-type, \(E_{\text{pin}}^p\) lies in the near or below the VBM. If the Fermi level pinning for n- and p-type doping lie near the middle of a wide band gap, the material tend to show insulating behavior. From Fig. 3, we can conclude that in O-rich limit, ZnGa\(_2\)O\(_4\) will tend to show insulating be-
havior, with Fermi level pinning near the middle of the gap, while in O-poor limit, it will tend to show n-type conductivity, with Fermi level pinning near the CBM, in both cases dictated by Ga\(_{2}\text{Zn}\) and Zn\(_{Ga}\).

In the following we discuss each antisite defect in detail; the local lattice relaxations associated with Zn\(_{Ga}\) and Ga\(_{Zn}\) are shown in Fig. 5 and the remain antsites, with less importance for this material, are shown in Fig. S2 in the Supplemental Material.

**Gallium on zinc site.** In the case of Ga\(_{Zn}\), Ga with 3+ formal oxidation state replaces Zn with 2+ formal oxidation state in the tetrahedral sites (8a in the Wyckoff notation). This aliovalent substitution creates one unpaired electron that is weakly bound to Ga. The neutral charge Ga\(_{Zn}^0\), therefore, unstable, making this defect a shallow donor, with Ga\(_{Zn}^{1+}\) being the lowest energy charge state for all values of Fermi level in the gap. In the tetrahedral chemical environment of Ga\(_{Zn}^{1+}\) (shown in Fig. 5b), Ga\(_{Zn}O\) bond length is 1.88 Å, i.e., 2.59% smaller than the original Zn-O bond length of 1.93 Å.

Among all the intrinsic donor defects, the formation energy of Ga\(_{Zn}^{1+}\) is the lowest in both O-rich and O-poor conditions. These results have two consequences: (i) if ZnGa\(_2\)O\(_4\) exhibits unintentional n-type conductivity or is semi-insulator, the main source of electrons in the conduction band or hole compensation is Ga\(_{Zn}^0\); (ii) the low formation energy of this defect indicates that Ga can incorporate in the tetrahedral sites in large concentrations, as observed in recent experiments [3, 5].

The formation energy of Ga\(_{Zn}^0\) also determines \(E^{\text{pin}}\), which is given by the point where the formation energy of Ga\(_{Zn}^{1+}\) is equal to zero in the O-rich condition with the richest Zn chemical potential, which is not exactly the A point used to plot the Fig. 3. If the Fermi level moves from \(E^{\text{pin}}\) towards the VBM, Ga\(_{Zn}^0\) will have negative formation energy, and it will form spontaneously. Under this condition, holes will be automatically compensated by the electrons from Ga\(_{Zn}^0\). Therefore, Fermi level pinning at \(~2\) eV above the VBM and the high stability of the small hole polaron makes it very difficult to realize p-type conductivity in Zn\(_{Ga}O_4\).

**Zinc on gallium site.** In this case, Zn substitutes on the octahedral Ga site (16d in Wyckoff notation). In the neutral charge state, Zn\(_{Ga}\) leaves an unpaired electron in the valence band that becomes a localized hole in the form of a small polaron sitting on a neighboring O atom. More precisely, the hole is derived from a hybridization of Zn \(d_{x^2−y^2}\) with O \(p\) orbitals, as shown in Fig. S3 in the Supplemental Material, and differ from the polaron previously discussed and shown in Fig. 3(a). The hole localization, in this case, is accompanied by a local lattice relaxation in which the Zn\(_{Ga}O\) bond length is shorter 4.3% than the original Ga-O bond length. By adding one electron to form Zn\(_{Ga}^{1−}\), the hole polaron vanishes, and the octahedral environment Zn\(_{Ga}\), shown in Fig. 5b), becomes more symmetric. The Zn\(_{Ga}O\) bond length of 2.10 Å is 3.96% longer than the original Ga-O bond length of 2.02 Å.

As shown in Fig. 3 neutral Zn\(_{Ga}^0\) is stable only for \(E_F\) near VBM. However, its formation energy is high in both O-rich and O-poor conditions. The negative charge state, Zn\(_{Ga}^{1−}\), is stable for \(E_F\) larger than 1.15 eV, marking the \((0/−)\) thermodynamic transition level. Zn\(_{Ga}^{1−}\) has the lowest formation energy among all the acceptor intrinsic defects in the O-poor condition and is comparable to V\(_{Zn}^{2−}\) and V\(_{Zn}^{3−}\) in the O-rich condition for \(E_F\) near the CBM. Therefore, we predict that Zn\(_{Ga}\) is one of the main sources of electron compensation in Zn\(_{Ga}O_4\), determining \(E^{\text{pin}}\). The pinning Fermi level for the electrons is calculated at the point where Zn\(_{Ga}^{1−}\) has its formation energy equal to zero in the O-poor with Ga richest chemical potential condition (which is not exactly the point B used to plot the Fig. 3), and it lies 0.23 eV above the CBM (inside the conduction band). In other words, for \(E_F > E^{\text{pin}}\), electrons added to the material will fill the holes associated with Zn\(_{Ga}\). Having \(E^{\text{pin}}\) near CBM indicates that Zn\(_{Ga}O_4\) can be easily doped n-type, and that if doped with impurities, high electron concentrations can eventually be attained, even compared to Ga\(_2O_3\), as reported by recent experiments [4].

**Cations on oxygen site.** The substitution of O for Zn or Ga (Zn\(_O\), Ga\(_O\)) in the tetrahedral environment (32e in Wyckoff notation), create an excess of electrons and a large Coulomb repulsion between the atoms around it. This repulsion is so strong that repels one Zn atom from the original lattice in the tetrahedral (8a) to the interstitial site (16c); the neighboring Zn atom relaxes from a tetrahedral motif to an octahedral environment as shown in Fig. S2 in the Supplemental Material. The displacement of the Zn atom is needed to accommodate the much larger Zn\(_O\) or Ga\(_O\) atoms, compared to the size of the original O atom.

In the formation energy plot shown in Fig. 3 Zn in O site is stable in the 2+ charge Zn\(_O^{2+}\). On the other hand, Ga\(_O\) is stable in three charge states, 3+, 1+ and 0, with transitions \((3+/1+)\) 0.64 eV and \((1+/0)\) 0.24 eV below...
the CBM. If we consider $E_F$ near the CBM ($n$-type conductivity), all of these defects have very high formation energy, regardless of the O chemical potential. This indicates that ZnO and GaO cannot be a possible source of electrons in $n$-type ZnGa$_2$O$_4$. The formation energy of ZnO and GaO is low or negative only for $E_F$ below the middle of the band gap. However, as noted before, $E_{F\text{pin}}$ does not allow $E_F$ to go to this region, and therefore, in general, we can conclude that the concentration of cations in the O site would be negligible in ZnGa$_2$O$_4$.

**Oxygen on cation site.** We tested the possibility of O substituting on Zn and Ga sites, namely O$_{Zn}$ and O$_{Ga}$, in ZnGa$_2$O$_4$. In the relaxed configuration, O$_{Ga}$ binds with neighboring O atom, forming a O$_{Ga}$-O split interstitial, with a bond length of 1.34 Å as shown in Fig. S2 in the Supplemental Material. For O$_{Zn}$, the O$_{Zn}$-O bond length is 1.41 Å. However, in this configuration, both O atoms bond to two Ga neighbors, likely due to the small internal volume of the 8a tetrahedral compared to the 16d octahedral.

As seen in Fig. [3], O$_{Zn}$ and O$_{Ga}$ can act as donors or acceptors. If $E_F$ lies close to the VBM (CBM) the most stable charge defect is the 2+ (2−), being amphoteric. Note that the neutral charge state is not stable for both defects, and a negative-U behavior is observed with a transition from 1− to 1+ at 2.07 eV and 1.95 eV above the VBM for O$_{Zn}$ or O$_{Ga}$, respectively. Similar to the cation on the O site, the formation energies of O$_{Zn}$ and O$_{Ga}$ are very high in the possible range of $E_F$ determined by $E_{F\text{pin}}$ and $E_{F\text{pin}}^p$. As consequence, we do not expect large concentrations of O$_{Zn}$ and O$_{Ga}$ in ZnGa$_2$O$_4$.

4. Interstitials

There are two non-equivalent interstitial sites in the spinel crystal structure, labeled 16c and 8b according to the Wyckoff notation. Both are shown in Fig. S1 in the Supplemental Material. The 16c interstitial site is surrounded by six equidistant O atoms at 2.16 Å, forming an octahedral motif. The 8b site is surrounded by four equidistant O at 1.67 Å and four Ga at 1.81 Å. We tested both 16c and 8b sites for Zn, Ga, and O, the formation energies are shown in Fig. S2. Because of the small volume of the 8b site, it is unlikely that Zn or Ga will occupy this interstitial site, leading to formation energies that are significantly higher than Zn or Ga occupying 16c site. The local lattice relaxation associated with the interstitial defects, for the most stable charge states, are shown in Fig. S2 in the Supplemental Material.

**Cations interstitial.** As noted, the most stable interstitial site for Ga$_{i}$ and Zn$_{i}$ is the 16c. In both cases, the interstitial cation is arranged in an octahedral environment with Ga-O bond length that ranges from 1.94 Å to 2.04 Å while for Zn-O, from 2.10 Å to 2.11 Å. In addition, Ga$_{i}$ and Zn$_{i}$ disturb the local chemical environment of the first Zn neighbors, moving them outward from the interstitial. This repulsion is stronger for Ga$_{i}$ and is observed in the local atomic environment shown in Fig. S2 in the Supplemental Material. The ionized defect composes the most stable configuration. In the case of Zn (Ga$_{i}$), 2 electrons of s-orbital (2 from s and 1 from p) are weekly bound, so that these interstitials are most stable in the 2+ and 3+ charge states, acting as donors.

In Fig. [3] for both O-rich and O-poor conditions, Ga$_{i}$ and Zn$_{i}$ have very high formation energies when $E_F$ is near the CBM; therefore, we do not expect that these defects contribute to the observed unintentional $n$-type conductivity. Only in the region with $E_F$ below the middle of the band gap, Ga$_{i}$ and Zn$_{i}$ have low formation energies, being a potential source of hole compensation in ZnGa$_2$O$_4$. This behavior is very similar to the cation on the O site, and especially in O-poor conditions, where their formation energies are very similar.

**Oxygen interstitial.** We tested the O interstitial in both 16c and 8b Wyckoff positions. For O$_{i}$ in the 8b position, we observed a special condition that we call O$_{\text{split}}$, i.e., the interstitial O binds to a native O, forming an O-O with a bond length of 1.41 Å, suggesting a formation of an O$_2$ molecule. This configuration is shown in Fig. S2 in the Supplemental Material. The antibonding $\pi^\ast$ of O$_{\text{split}}$ lies in the band gap of ZnGa$_2$O$_4$ and is completely occupied in the neutral charge state. A situation similar to that is observed in In$_2$O$_3$ and ZnO [11, 12]. Due to the occupation of $\pi^\ast$, the bond length of O$_2$ molecule in ZnGa$_2$O$_4$ is larger than the isolated O$_2$ one, and similar to the O$_2^\ast$ configuration. It is important to note that O$_{\text{split}}$ is stable only in the neutral charge state and has high formation energy. Therefore, even if O$_{\text{split}}$ is formed in ZnGa$_2$O$_4$, this defect will not contribute for $n$- or $p$-type conductivity.

The second configuration for O interstitial in the 16c site, O$_{i}$, has a linear bond with two Zn atoms, forming Zn-O-Zn structure with an angle of 179°. This configuration is stable in two charge states: neutral and 1−, with a transition level of 2.53 eV below the CBM. However, similar to O$_{\text{split}}$, the formation energy of O$_{i}$ is very high, and we do not expect a large concentration of this defect even in the O-rich condition. This is a good point for a $n$-type conductivity because O$_{i}$ act as a source of electron compensation in ZnGa$_2$O$_4$.

C. Source of $p$-type conductivity

According to our calculations, intrinsic $p$-type conductivity is unlikely in ZnGa$_2$O$_4$ due to three reasons: (i) the holes tend to localize in the form of small polarons due to the localized character of the valence band. These polarons are very stable; (ii) There are no intrinsic shallow acceptors with small formation energy in the vicinity of the valence band, which creates a problem for holes generation; and (iii) The Fermi level pinning for $p$-type, $E_{F\text{pin}}^p$, lies around 2 eV above the VBM, and therefore the Fermi level cannot be moved towards the VB without hole compensation by intrinsic donor defects. Despite
all these points, experimental results indicate a possible low \( p \)-type conductivity in high temperature, under O-rich conditions, with a hole density that does not exceed \( 10^{15} \, \text{cm}^{-3} \). [3, 5]

To investigate this condition, we suppose an alloy of ZnGa\(_2\)O\(_4\) with an excess of Zn, forming Zn\(_{1+2x}\)Ga\(_{2(1-x)}\)O\(_4\). These extra Zn atoms occupy the Ga site, forming ZnGa\(_x\). The calculations were performed for a concentration \( x = 0.25 \), i.e., an increase of 25% of the Zn atoms in the system. The excess of Zn atoms creates an intermediate band that is semi-occupied, assuming all ZnGa\(_x\) are in the neutral charge state. However, to determine the characteristic of the intermediate band, we suppose a completely unoccupied band with the Fermi energy at the top of host O 2p band. The detached band is composed by the hybridization of O 2p-orbitals and Zn 3d-orbitals (orbitals of the extra Zn in the system), forming a charge distribution similar to the polaron discussed previously in the point defect ZnGa\(_x\), and shown in Fig. S3. The calculated density of states of this system is shown in the Supplemental Material Fig. S4. Therefore, we can address the detached band to a polaronic nature.

The formation of a detached band is observed in other alloys of oxides, such as In\(_2\)O\(_3\) with Bi, even though in that case the nature of the detached band is not a polaronic one [35, 36]. Also, intermediate bands play important roles in anti-doping processes in quantum materials [37], and have also been proposed for the construction of high efficiency solar cells [38, 39].

As we can observe in Fig. 6, the polaronic band lies around 0.91 eV above the host valence band maximum and has a width of 1.81 eV. The pinning of Fermi level for \( p \)-type conductivity, \( E_{pin}^{p} \) lies inside this band. The possible Fermi level variation is shown in the gray area on the right side of Fig. 6. This means that is possible to shift down the Fermi level to create holes in the polaronic band before the intrinsic donor defects Ga\(_{2n}\) start to form spontaneously and start to compensate the holes. In other words, it is possible to have a \( p \)-type conductivity inside the polaronic band. Despite that, the conductivity should occur by hoping of the localized hole in O and Zn atoms, which can lead to low charge mobility. At the same time, if the concentration of Zn in the alloy Zn\(_{1+2x}\)Ga\(_{2(1-x)}\)O\(_4\) decreases, the width of the polaronic band also decreases and this creates a limit for holes density in the system [35, 36]. Thus, the width and the nature of the detached band in ZnGa\(_2\)O\(_4\), grown in O-rich condition, explains the low charge mobility and the high temperature to observe this conductivity. Therefore, we can say that the \( p \)-type conductivity occurs in the detached polaronic band formed by an excess of Zn atoms in the system and does not occur in the valence band as suggested previously [3, 4].

### D. Optical emission

In the optical measurement, the peaks in the photoluminescence spectrum could be a fingerprint of the defects states in the material. Considering that, we calculate the emission photon energy for the most stable defects in ZnGa\(_2\)O\(_4\): hole polaron, \( V_0 \), \( V_{Ga} \), \( V_{Zn} \), ZnGa\(_x\), Ga\(_{2n}\). It is important to mention that the emission spectrum was calculated according to the Franck-Condon approximation in the generalized coordination diagram, a procedure applied before for other oxides [11, 40]. According to the Fermi level pinning, \( E_{pin}^{n} \) and \( E_{pin}^{p} \), ZnGa\(_2\)O\(_4\) can have the Fermi levels between the middle of the band gap and the CBM, and we considered that range to calculate the optical emission spectrum for defects. In this range, only \( V_0 \) has two charge states with high stability: 2+ and 0, and therefore we considered both charge configurations. For all the remaining defects, \( V_{Ga} \), \( V_{Zn} \), ZnGa\(_x\), and Ga\(_{2n}\), we considered only the most stable charge state.

If a photon with energy larger than the band gap is inserted in the semiconductor, one electron from the valence band is promoted to the conduction band leaving a hole behind. Because of the high stability of small hole polaron in ZnGa\(_2\)O\(_4\), the atoms around one O relax to localize the hole in the form of a small polaron, resulting in a quasi-particle state inside the band gap. After atomic relaxation, a free electron in the conduction band...
can be attracted by the small polaron and recombine, emitting light. In ZnGa$_4$O$_4$, this recombination emits a photon with an energy of 3.18 eV, which corresponds to the edge of the visible spectrum, close to the ultra-violet region. This recombination process is shown in Fig. 7.

For V$_O$, two processes can occur according to the Fermi level position. First, if $E_F$ is deeper and lies in a region where V$_{O}^{2+}$ is the most stable charge state, the incidence of a photon can excite one electron from the valence band to the quasi-particle level of V$_{O}^{2+}$ that lies in resonance in the conduction band as discussed before. This procedure change the oxidation state from V$_{O}^{2+}$ to V$_{O}^{1+}$ according to the reaction: V$_{O}^{2+}$ + 1e $\rightarrow$ V$_{O}^{1+}$. After the atomic relaxation, V$_{O}^{1+}$ becomes unstable and tends to return to V$_{O}^{2+}$ configuration. This procedure occurs by recombination of one electron of V$_{O}^{1+}$ and one hole in the valence band, emitting a photon with energy equal to 2.47 eV. This energy lies in the visible spectrum and corresponds to the green color.

The second procedure that can occur with V$_O$ is when the $E_F$ is closer to the CBM. Under this configuration, the neutral oxygen vacancy is the most stable one, V$_{O}^{0}$. The incidence of photons in the material can promote one electron of V$_{O}^{0}$ to the conduction band, and promote the reaction: V$_{O}^{0}$ + 1h $\rightarrow$ V$_{O}^{1+}$. Again, the V$_{O}^{1+}$ configuration is not stable, and there is a tendency to capture one electron and return to the neutral charge state. This procedure leads to a photon emission with an energy of 2.45 eV, which is very similar to the condition before. Therefore, we expect that all the emissions associated with V$_O$ occur in the green color independent of the Fermi level position, with both conditions shown in Fig. 7. The green emission is observed by experimentalists with photon energy around 2.48 eV (499 nm).

Considering the other two vacancies, V$_{Zn}$ and V$_{Ga}$, the procedure is very similar to the second condition of V$_O$. A photon promotes one electron that lies in the defect state of V$_{Zn}^{2+}$ (V$_{Ga}^{3-}$) to the conduction band, and resulting in the reaction: V$_{Zn}^{2+}$ (V$_{Ga}^{3-}$) + 1h $\rightarrow$ V$_{Zn}^{1+}$ (V$_{Ga}^{2-}$). The excited state tends to return to the ground state and recombine with a free electron from the conduction band. This procedure emits a photon with energy equal to 1.75 eV for V$_{Zn}$ and 1.32 eV for V$_{Ga}$, which correspond to a spectrum with red color and at the infra-red region, respectively.

For antisite point defects, we observe different behavior. For Ga$_{Zn}$, when the photon promotes one electron from the valence band to the Ga$_{Zn}^{1+}$ defect level, the system relaxes to Ga$_{Zn}^{0}$ according to the reaction: Ga$_{Zn}^{1+}$ + 1e $\rightarrow$ Ga$_{Zn}^{0}$. The defect level in the neutral condition lies in resonance in the conduction band, and therefore this condition favors recombination through band-band emission. In other words, Ga$_{Zn}$ will not have a photoemission fingerprint because the band-band is the lowest energetic path.

For Zn$_{Ga}$, the incident light in ZnGa$_4$O$_4$ promotes one electron from Zn$_{Ga}^{1-}$ state to the conduction band by the process: Zn$_{Ga}^{1-}$ + 1h $\rightarrow$ Zn$_{Ga}^{0}$. If the Fermi level is close to the CBM, Zn$_{Ga}^{0}$ is unstable and tends to capture one free electron to return to the original charge state. A photon with energy equal to 3.10 eV, which is close to the UV spectrum, is emitted in this procedure. According to the emission spectrum fingerprint, we can say that hard to distinguish the hole polaron and Zn$_{Ga}$ defect.
IV. SUMMARY AND CONCLUSIONS

In summary, we calculate the electronic, optical, and defect properties in ZnGa₂O₄, a potential candidate for high-energy power electronics and UV-blight detectors. We observe that antisites play important role in the conductivity of ZnGa₂O₄. While GaZn is likely the main source of unintentional n-type conductivity, ZnGa₂O₄ is the most stable acceptor defect and the main source of electrons, either as self-trapped holes or bound to intrinsic defects. The p-type conductivity in the valence band is difficult to be achieved. There is a large tendency for hole localization in the form of small polaronic bands. The conductivity occurs by hopping, which explains the low mobility and low hole density observed in experimental results. In addition, we compute the emission spectrum of the lowest energy defects in ZnGa₂O₄. Most of the defects that are associated with polarons emit in the spectrum close to ultra-violet, while the oxygen vacancy emits in the green. The possibility for both types of conductivity, better thermal dissipation, and isotropic properties make ZnGa₂O₄ a potential candidate to replace Ga₂O₃, or at least complements it as an ultra-wide band gap material for electronic and optoelectronic applications.

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