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PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0062059

Zinc-hydrogen and zinc-iridium pairs in β-Ga_2O_3

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Abstract

Zinc-doped monoclinic gallium oxide (β-Ga_2O_3:Zn) has semi-insulating properties that could make it a preferred material as a substrate for power devices. Infrared and UV/Visible spectroscopy were used to investigate the defect properties of bulk β-Ga_2O_3:Zn crystals. As-grown crystals contain a single O-H stretching mode at 3487.6 cm^{-1} due to a neutral ZnH complex. A deuterium-annealed sample displays the corresponding O-D stretching mode at 2582.9 cm^{-1}, confirming the O-H assignment. A strong Ir^{4+} electronic transition at 5147.6 cm^{-1} is also observed, along with sidebands attributed to ZnIr pairs. These sidebands show distinct differences compared with Mg-doped samples; most importantly, several peaks are attributed to Ir^{4+} paired with a Zn on the tetrahedral Ga(I) site. Annealing under an oxygen atmosphere produced insulating material with a resistance above 1 TΩ.

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β-Ga_2O_3 shows potential as an ultra-wide bandgap semiconductor for high-voltage/high-power devices with properties that rival or exceed those of wide bandgap semiconductors such as SiC or GaN. Frequently mentioned in this context are its bandgap (4.5 – 4.8 eV), electron mobility (up to 200 cm^2/Vs), and large breakdown field (~8 MV/cm).[1–3] Perhaps more importantly, large high-quality single crystals can be grown with relative ease and for reasonable expense.[4–7] Although *p*-type Ga_2O_3 is not likely with typical dopants[8,9], acceptor doping is the preferred method for producing semi-insulating substrates. Currently, Fe and Mg are commonly used as acceptors for this purpose.[10–14] The iron acceptor level is 0.7 eV below the conduction band,[10] while calculations indicate group-II acceptors have acceptor binding energies of 1.0-1.5 eV (Zn has 1.4 eV).[15] In the present work, Zn doping was explored as a potential alternative to Fe and Mg.

Zn-doped β-Ga_2O_3 single crystals with 0.25 at.% Zn were grown via the Czochralski (CZ) technique, similar to methods previously published.[16–18] As reported by Jesenovec et al.,[18] Zn doping stabilizes growth from the melt and enables faster pull rates than for undoped crystals. CZ growth was conducted at a 2 mm/hr pull rate and 2 rpm rotation. A mixture of 5N (i.e., 99.999%) purity Ga_2O_3 and 3N ZnO powder was used to achieve the desired doping. Crystals were grown in a 70 mm height × 70 mm diameter iridium crucible, with an Ar + O_2 gas mixture. The O_2 concentration was varied to suppress evaporation from the melt during growth based on gas flow scheme described elsewhere.[4] The cylindrical CZ boule had a diameter of ~36 mm and a height of ~28 mm. Glow discharge mass spectroscopy (GDMS) and secondary ion mass spectroscopy (SIMS) have revealed Zn incorporation to be ~10^{18} atoms/cm^3 (see supplementary material in Ref. 18). Other impurities determined from GDMS include Mg (~10^{17} cm^{-3}),

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Ir (~10^{17} cm^{-3}), and Si (~10^{18} cm^{-3}). However, the lack of a MgH IR peak (or MgD after deuteration) suggests that the actual Mg concentration may be lower than the GDMS estimate.

For the optical measurements, light was incident perpendicular to the (100) surface. Infrared measurements were performed with a Bomem DA8 vacuum Fourier transform infrared (FTIR) spectrometer using a SiC source, KBr beamsplitter, and InSb detector. Spectra were collected at 10 K with a resolution of 0.5 cm^{-1}. UV/Visible transmission measurements were performed under ambient conditions using a Perkin Elmer Lambda 900 Series UV/Vis/NIR spectrometer.

Electrical measurements were performed with a Keithley 6487 picoammeter using pressed indium contacts. The high resistances (10^{10}-10^{12} Ω) precluded Hall-effect measurements. Instead, two-point measurements were performed to provide order-of-magnitude resistance values. The thicknesses of the samples used in this work were very similar, 2.05 mm and 2.12 mm for the as-grown (subsequently oxygenated) and deuterated samples respectively.

Hydrogen contamination was significant in the as-grown sample (Fig. 1). A strong O-H stretching mode is observed as an absorption peak at 3486.7 cm^{-1} as well as a small, unassigned satellite at 3545.0 cm^{-1} (Fig. 1). This satellite was observed in β-Ga_2O_3:Mg as well and did not have a uniform intensity from sample to sample.[11] Therefore, this feature is independent of both Zn and Mg and is likely caused by a contaminant acceptor species complexing with hydrogen. From the integrated absorbance of the peak (supplementary material), we estimate the O-H density to be ~10^{17} cm^{-3}.

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The spectrum also contains a small peak at 3476.1 cm^{-1}. We attribute this to ^{18}O-H, since the frequency ratio 3486.7/3476.1 = 1.0030 is in good agreement with O-H complexes observed in GaAs.[19] In addition, the ratio of the integrated absorbances (~0.003) is close to the relative abundance of ^{18}O (0.002) compared to the most common ^{16}O. Similar to the case of Mg, there is no trace of the V_{Ga}2H peak (3437 cm^{-1}) that is dominant in other types of samples.[20]

Along with the hydrogen-related features, numerous peaks are observed in the 5000-5400 cm^{-1} region (Fig. 2). The dominant peak at 5147.6 cm^{-1} has been assigned to an internal electronic transition of an isolated Ir^{4+} atom on an octahedral Ga(II) site.[11,21–24] (Ir^{4+} has a charge of +1 relative to the Ga^{3+} host ion; i.e., it is a singly ionized donor). A smaller peak at 5406.3 cm^{-1} is assigned to isolated Ir^{4+} atom on a tetrahedral Ga(I) site. These peaks are also seen in the Mg-doped sample (Fig. 2) but the relative intensity of the 5406.3 cm^{-1} peak is lower than that for the Zn-doped samples. The difference may be due to different growth conditions such as temperature and oxygen pressure that affect the site preference.

Numerous sidebands are assigned to octahedral Ir^{4+} paired with a neighboring acceptor (Mg or Zn).[11,24] The Ir^{4+} sidebands observed here are stronger, more numerous, and spread over a wider spectral range than those in Mg-doped β-Ga_2O_3 (Fig. 2 and supplementary material). Given magnesium's known strong preference for the octahedral Ga(II) site,[14] these new peaks indicate potential evidence of zinc occupation of the tetrahedral Ga(I) site.[25] Specifically, we attribute the prominent sideband peaks at 4991.0, 5072.5, 5241.2, and 5245.0 cm^{-1} (numbered 1-4 in Fig. 2) to Ir^{4+} paired with Zn on a Ga(I) site.

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The polarization behavior of the ZnH and Ir^{4+} peaks was investigated by placing a linear polarizer in the IR beam path. Light was incident to the (100) surface (*a*-plane). The results (Fig. 3) are consistent with previous experiments on β-Ga_2O_3:Mg.[11] The ZnH peak grows in intensity as **E** rotates from the **b**-axis to the **c**-axis. This polarization dependence is consistent with an O-H dipole that is in the **a**-**c** plane, perpendicular the **b** axis (Fig. 1, inset). The behavior of the Ir^{4+} peak is exactly opposite, reaching maximum intensity when **E//b**.[11,25]

To test the effect of hydrogen annealing, an as-grown sample was sealed in a silica ampoule filled with 0.5 atm of D_2 (at room temperature), annealed in a horizontal tube furnace at 860°C for 3.5 hours, and quenched in water. The as-grown sample had a slight yellow coloration that disappeared following deuteration, leaving the annealed sample colorless. Two-point resistance measurements gave an electrical resistance of 0.3-0.6 TΩ for the as-grown crystal, which decreased to ~0.045 TΩ following deuteration. The decrease in resistance is consistent with the in-diffusion of deuterium donors, which raises the Fermi level.

Figure 4 shows a difference spectrum, with absorbance defined as

$$\text{Absorbance} = \log_{10}(I_0/I),$$

where I_0 is the transmission of the as-grown sample (the reference) and I is the transmission after deuteration. Deuteration introduced a large absorption peak at 2582.9 cm^{-1} and greatly decreased the intensity of the ZnH and Ir^{4+} peaks. The isotopic frequency ratio of the ZnH and ZnD lines is ~1.35, similar to results from β-Ga_2O_3:Mg[11] as well as O-H and O-D complexes in other materials.[26–29] The linewidths (FWHM) of the ZnH and ZnD peaks are 1.4 and 0.6 cm^{-1} respectively, sharper than those observed for

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MgH and MgD (2.5 and 1.5 cm^{-1})[11]. The reason for the narrower ZnH and ZnD lines may be due to a lower degree of coupling to lower-frequency vibrational modes, resulting in a longer vibrational lifetime.

As with β-Ga_2O_3:Mg, as-grown β-Ga_2O_3:Zn has an absorption threshold near 480 nm (~2.6 eV) in the UV/Visible transmission spectrum (Fig. 5). This is attributed to an optical excitation of a valence-band electron to the Ir^{4+} level. Deuteration suppresses the absorption feature, leaving only band-edge absorption beginning near 275 nm (4.5 eV). This phenomenon was seen in β-Ga_2O_3:Mg as well, where the added deuterium (hydrogen in the β-Ga_2O_3:Mg experiments) passivates the acceptor atoms. This passivation effectively returns an electron to an Ir donor, returning it to the IR-inactive 3+ charge state. Filling the donor level also eliminates the 2.6 eV optical absorption.

A second sample was treated with oxygen. Two anneals were performed in sequence in sealed silica ampoules under a 0.5 atm O_2 atmosphere (at room temperature). Each anneal was performed for 15 hours, the first at 1000°C and the second at 1200°C. The ampoules were quenched in water following each anneal. Two-point electrical measurements yielded resistances of 1.3-1.6 TΩ following the 1000°C anneal and 1.9-2.1 TΩ following the 1200°C anneal. This increase in electrical resistance may be due to activating Zn acceptors (by driving off H), filling oxygen vacancies, and/or creating Ga vacancies.[30] From a technological viewpoint, such a large resistance bodes well for semi-insulating β-Ga_2O_3:Zn substrates.

Optical changes were subtle following treatment with oxygen and changes between the pair of anneals were not significant. Thus, only the results of the final 1200°C anneal in oxygen are presented here. In the IR, the ZnH peak and the Ir-

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transition satellites decreased slightly in intensity while the main Ir^{4+} peak increased slightly (Fig. 6). The decrease in the ZnH peak is consistent with hydrogen leaving the sample under the oxygen-rich environment. The decrease in the Ir^{4+} sidebands, shown as dips in Fig. 6, is explained by the dissociation of IrZn pairs and corroborated by the subsequent increase in strength of the isolated Ir^{4+} peak (5147.6 cm^{-1}). A sideband at 5145 cm^{-1} appears as a dip in the difference spectrum, similar to what is observed for β-Ga_2O_3:Mg.[24] There was no appreciable change in the UV/Visible transmission spectra after either anneal.

In summary, the properties of Zn acceptors in β-Ga_2O_3 show similarities and some intriguing differences with Mg. The similarity between ZnH and MgH vibrational modes suggest that their microscopic structures are the same; namely, hydrogen attaches to a host oxygen with a dipole oriented roughly along the *a* axis (Fig. 1). Annealing in oxygen at 1200°C raises the resistance to the TΩ range but only slightly reduces the ZnH concentration. Annealing at higher temperatures may drive out the hydrogen and result in even higher electrical resistance.

Recent electron paramagnetic resonance (EPR) results provided evidence that, like Mg, Zn preferentially occupies the octahedral Ga(II) site.[25] A small fraction of Zn (estimated 5-10%) was on the tetrahedral Ga(I) site. However, only one ZnH (or ZnD) peak was observed in our sample. One possibility for the lack of a second ZnH peak is that tetrahedral Zn may not bind H as strongly as octahedral Zn. A second possibility is that the EPR signature for tetrahedral Zn is not from isolated Zn but rather a ZnIr pair, consistent with our model of ZnIr pairs with Zn on the tetrahedral site. Such acceptor-donor pairs would be electrically neutral and therefore not be expected to bind hydrogen.

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See supplementary material for absorbance values of the O-H and O-D peaks, and the frequencies and peak heights of the Ir^{4+} IR absorption peaks.

The data that support the findings of this study are available from the corresponding author upon reasonable request.

The authors acknowledge helpful discussions with L. Halliburton, M. Scarpulla, and J. Varley. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-07ER46386. Crystal growth (J.J. and J.S.M.) was supported by Air Force Office of Scientific Research under award number FA9550-18-1-0507 monitored by Dr. Ali Sayir. Any opinions, finding, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the United States Air Force.

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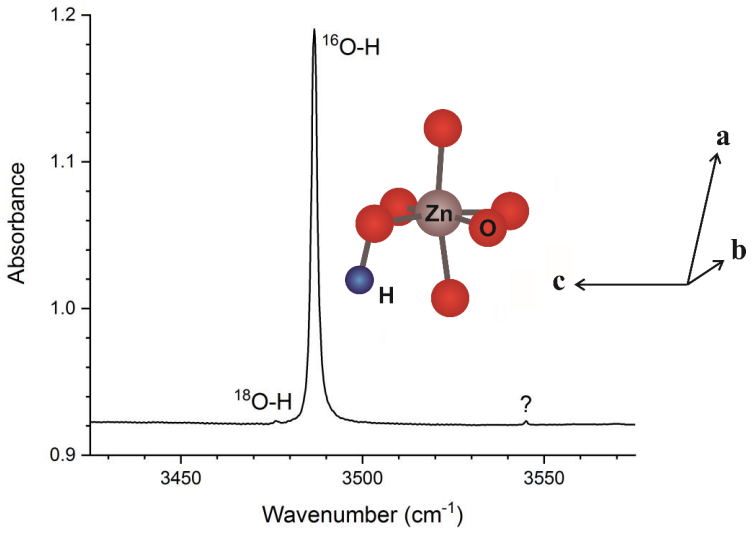

Figure 1. IR absForption spectrum of the ZnH complex in as-grown β-Ga_2O_3:Zn. The absorbance was calculated using a blank spectrum as the baseline. The peaks associated with ^{16}O and ^{18}O are labeled and the unassigned 3545.0 cm^{-1} peak is marked as '?'. Inset: Ball-and-stick model for the ZnH complex.

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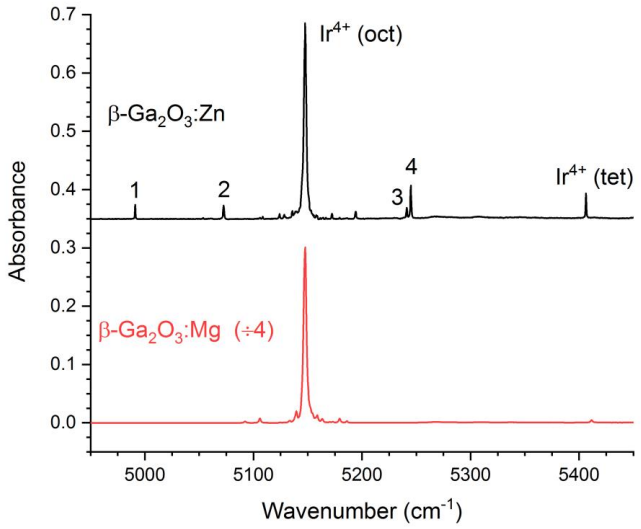

Figure 2. IR absorption spectra of Ir^{4+} electronic transitions in β-Ga_2O_3:Zn and β-Ga_2O_3:Mg. The absorbance was calculated using a blank spectrum as the reference. Data for the Mg-doped case were taken from Ritter *et al*.[11] The isolated Ir sites are labeled Ir^{4+} (oct) and Ir^{4+} (tet) corresponding to occupancy of the octahedral Ga(II) and tetrahedral Ga(I) sites respectively. Peaks numbered 1-4 are proposed to correspond to Ir^{4+} paired with a tetrahedrally-coordinated Zn.

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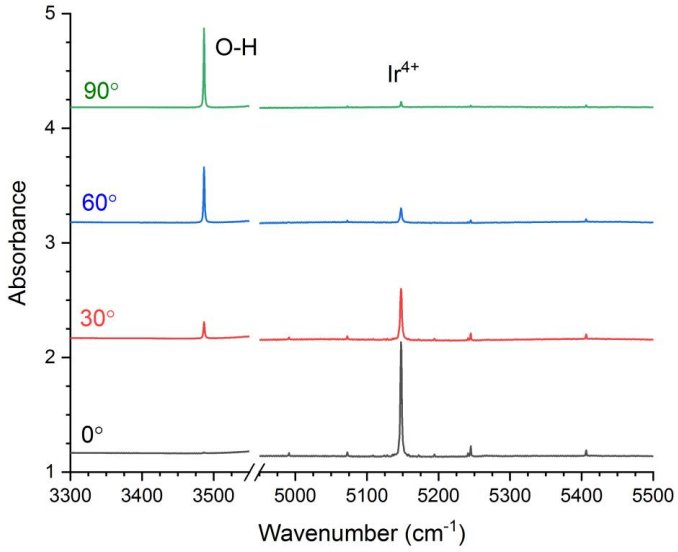

Figure 3. Polarized IR absorption spectra of β-Ga_2O_3:Zn. The IR beam was polarized with respect to the **b**-axis, with 0° being parallel and 90° perpendicular. Spectra have been shifted vertically for clarity.

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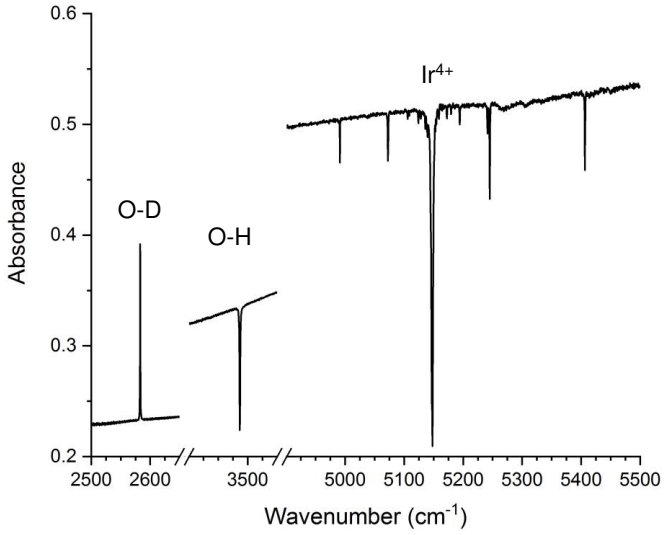

Figure 4. IR difference spectrum of deuterated β-Ga_2O_3:Zn, using the as-grown state as the reference. The main O-H peak as well as the Ir^{4+} peak and sidebands decreased greatly and an O-D peak emerged.

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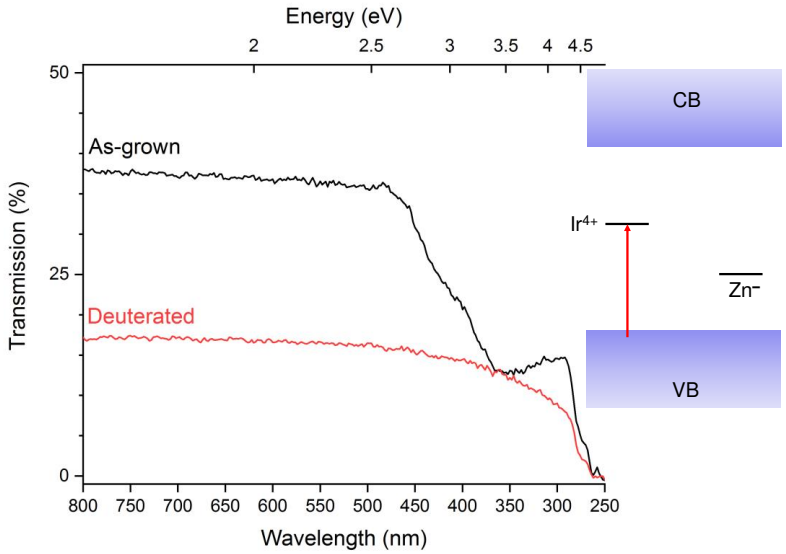

Figure 5. UV/Visible transmission spectra in the as-grown and deuterated states. The absorption threshold at 480 nm (2.6 eV) is due to Ir^{4+} (see diagram on the right). Upon deuteration, this absorption feature disappears as Ir^{4+} is converted to Ir^{3+}.

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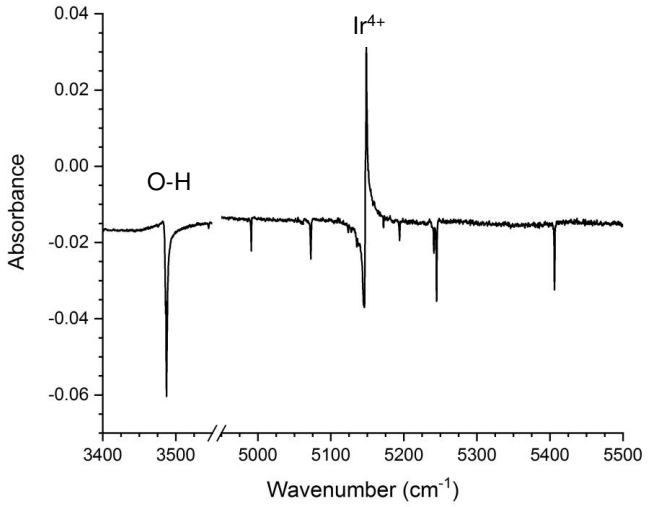

Figure 6. IR difference spectrum of oxygenated β-Ga_2O_3:Zn, baselined against the as-grown state. Changes are small, but intensities of the main O-H peak and the Ir^{4+} sidebands decreased while the isolated Ir^{4+} peak increased.

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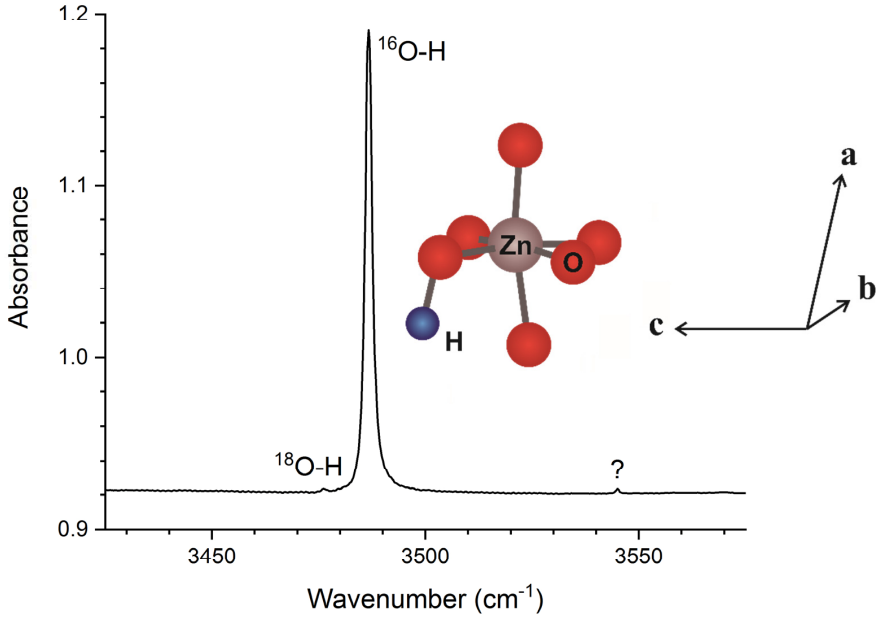

Figure 1. IR absorption spectrum of the ZnH complex in as-grown β-Ga_2O_3:Zn. The absorbance was calculated using a blank spectrum as the baseline. The peaks associated with ^{16}O and ^{18}O are labeled and the unassigned 3545.0 cm^{-1} peak is marked as '?'. Inset: Ball-and-stick model for the ZnH complex.

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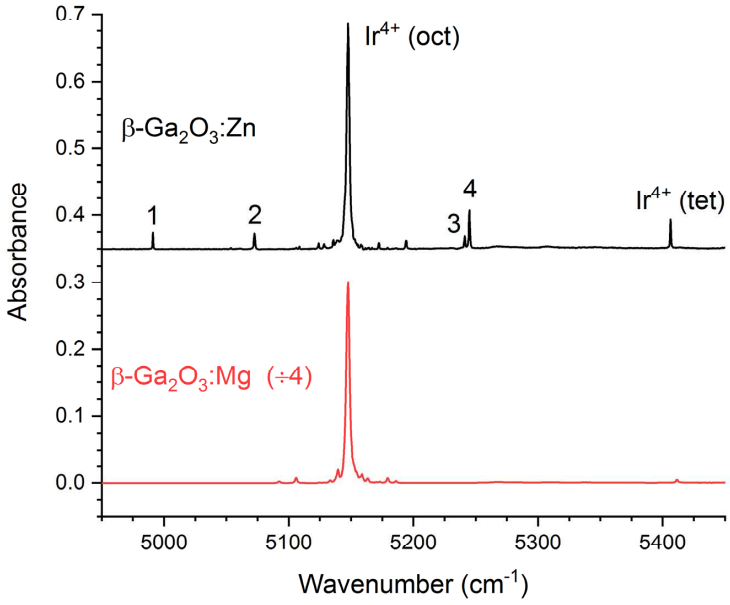

Figure 2. IR absorption spectra of Ir^{4+} electronic transitions in β-Ga_2O_3:Zn and β-Ga_2O_3:Mg. The absorbance was calculated using a blank spectrum as the reference. Data for the Mg-doped case were taken from Ritter *et al.*[11] The isolated Ir sites are labeled Ir^{4+} (oct) and Ir^{4+} (tet) corresponding to occupancy of the octahedral Ga(II) and tetrahedral Ga(I) sites respectively. Peaks numbered 1-4 are proposed to correspond to Ir^{4+} paired with a tetrahedrally-coordinated Zn.

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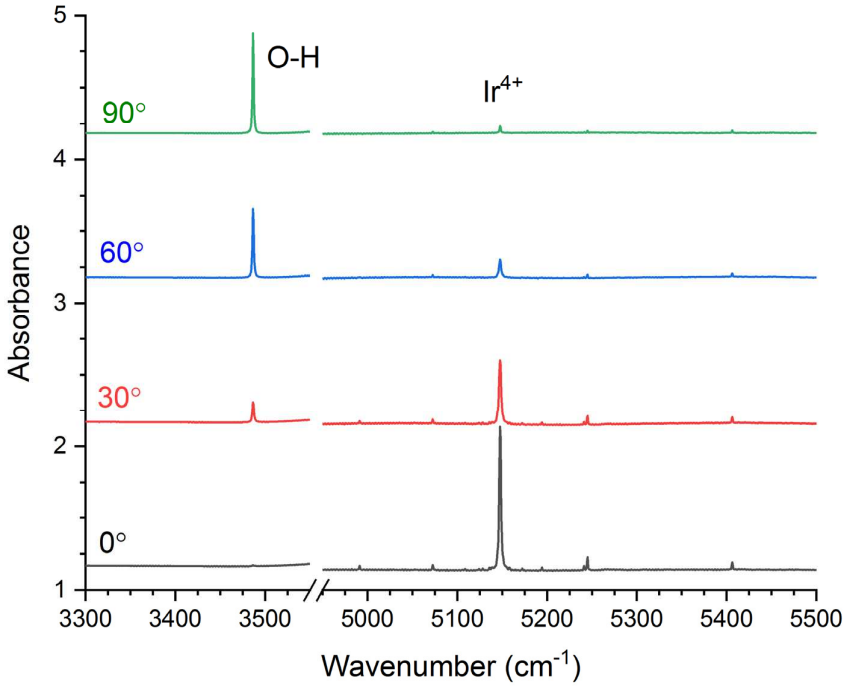

Figure 3. Polarized IR absorption spectra of β-Ga_2O_3:Zn. The IR beam was polarized with respect to the **b**-axis, with 0° being parallel and 90° perpendicular. Spectra have been shifted vertically for clarity.

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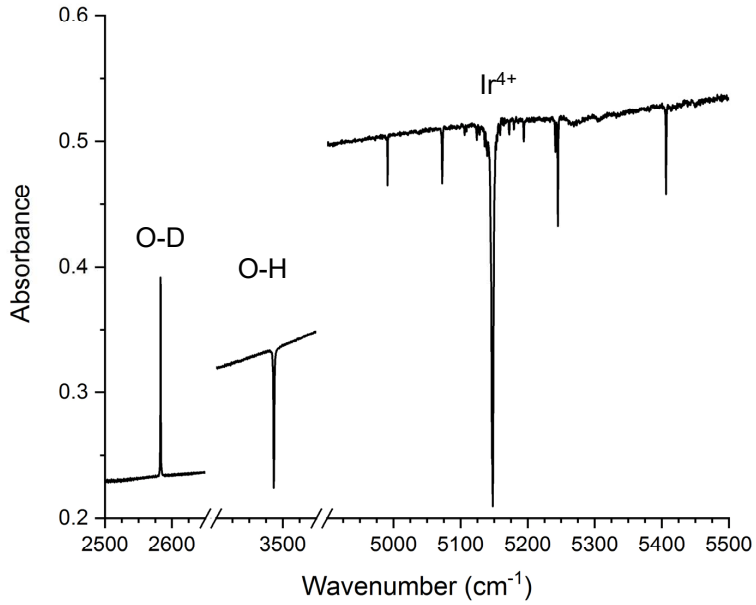

Figure 4. IR difference spectrum of deuterated β-Ga_2O_3:Zn, using the as-grown state as the reference. The main O-H peak as well as the Ir^{4+} peak and sidebands decreased greatly and an O-D peak emerged.

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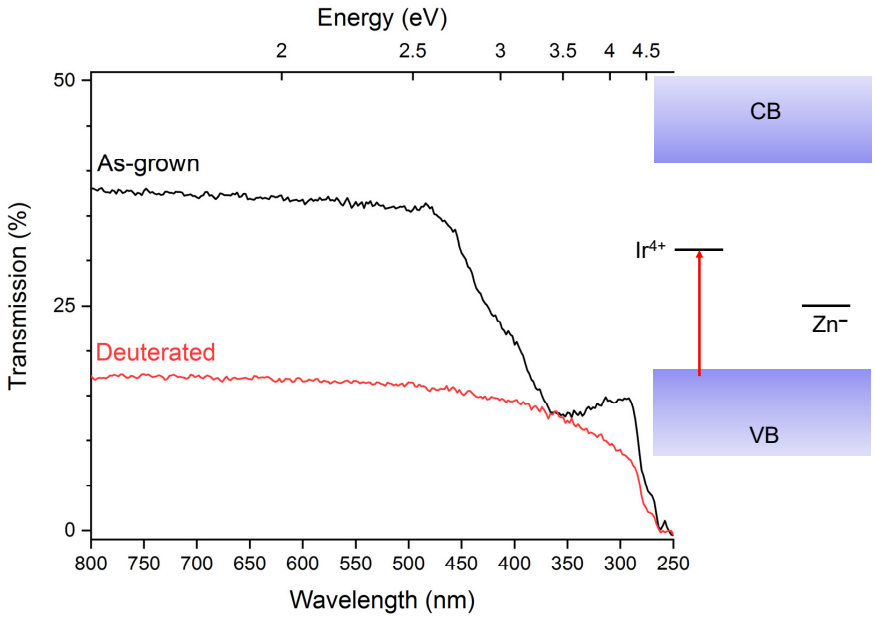

Figure 5. UV/Visible transmission spectra in the as-grown and deuterated states. The absorption threshold at 480 nm (2.6 eV) is due to Ir^{4+} (see diagram on the right). Upon deuteration, this absorption feature disappears as Ir^{4+} is converted to Ir^{3+}.

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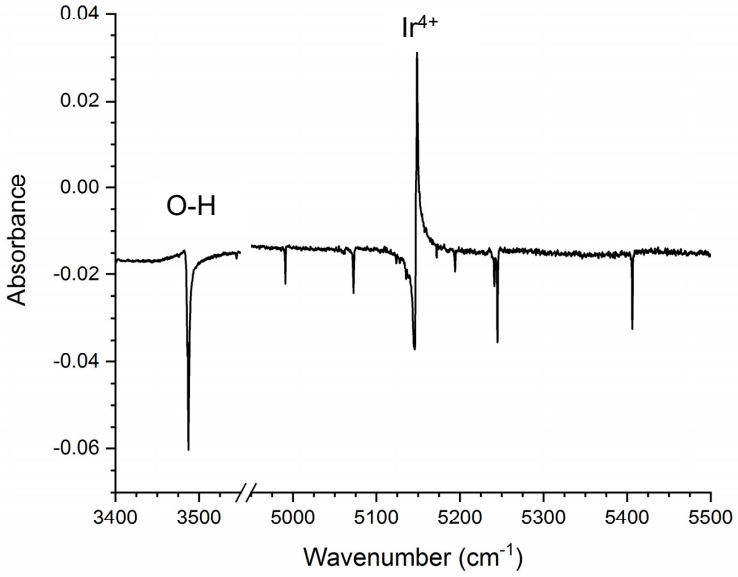

Figure 6. IR difference spectrum of oxygenated β-Ga_2O_3:Zn, baselined against the as-grown state. Changes are small, but intensities of the main O-H peak and the Ir^{4+} sidebands decreased while the isolated Ir^{4+} peak increased.