

Supporting information

Theoretical and Experimental Investigations on Effects of Native Point Defects and Nitrogen Doping on Optical Band Structure of Spinel ZnGa₂O₄

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Experimental Section

Preparation of ZnGa₂O₄ precursor.

All chemical reagents were of analytic grade and were used as received without any further purification. The ZnGa₂O₄ nanoparticles were prepared through a sol-gel process as in reference 11. Typically, 2 mmol Zn(CH₃COO)₂·2H₂O and 4 mmol Ga(NO₃)₃·xH₂O were dissolved into 36 mL Mill-Q water (18.2 MΩ·cm) followed by adding NH₄OH dropwise under stirring until the pH was between 7 and 8. The solution was then stirred magnetically for 6h. The precipitate was obtained after centrifugal separation and washed with water. The above wet precipitate was dried overnight at 70 °C 80 °C in a convection oven.

Preparation of ZGO_Ns, ZGO_xN, ZGO_Ov and ZGO_NsOv samples

As-prepared ZnGa₂O₄ precursor (0.5g) powder was separately nitridated at 550°C under NH₃/Ar flow (NH₃/Ar, v/v% =10%, rate 100 mL/min), under pure NH₃ flow (rate 100 mL/min). After 3h of nitridation, the samples were cooled to room temperature under above atmosphere, and named as ZGO_Ns and ZGO_xN, respectively. The oxygen vacancy was imported by mixing ZnGa₂O₄ (1mmol) with carbon black (C/ZGO, w/w%=10%), followed by sintered at 800°C under H₂/Ar flow (H₂/Ar, v/v% =50%, rate,100 mL/min) for 2h and air condition for 2h, the sample was collected as named as ZGO_Ov. Partial ZGO_Ov sample was further nitridated at 550°C under pure NH₃ flow (rate 100 mL/min) for 3h, the sample was cooled to room temperature under pure NH₃ flow, and named as ZGO_NO.

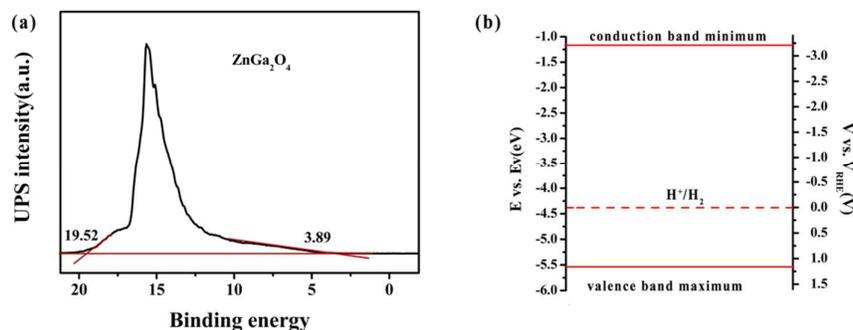
Physicochemical characterization.

The phases of as-synthesized products were identified using powder X-ray diffraction patterns obtained on a Rigaku D/Max 2200-PC diffractometer with the tube electric voltage and current of 40 kV and 20 mA for Cu Kα radiation (λ= 0.15418 nm) at a scan rate of 2° min⁻¹. Morphological analysis was performed using a field emission scanning electron microscope (Hitachi SU8010) with an accelerating voltage of 10 kV coupled with energy-disperse X-ray spectrometry (EDX). The X-ray photoelectron spectrum (XPS) was recorded on a PHI-5300 ESCA spectrometer

(Perkin Elmer) with its energy analyzer working in the pass energy mode at 35.75 eV, and the Mg K α line was used as the excitation source. The binding energy reference was taken at 284.7 eV for the C 1s peak arising from surface hydrocarbons. UV-vis diffuse reflectance spectroscopy (DRS) was recorded using an Agilent Cary-100 ultraviolet and visible spectrophotometer, using analytical BaSO₄ as reference.

Supplementary Figures

Fig. S1. UPS spectra (a) and band structure diagram (b) of ZnGa_2O_4 (black curve). The red lines mark the baseline and the tangents of the curve. The intersections of the tangents with the baseline give the edges of the UPS spectra from which the UPS width is determined.



The ionization potential of ZnGa_2O_4 is determined by ultraviolet photoelectron spectroscopy (UPS), which is calculated to be 5.57 eV by subtracting the width of the He I UPS spectra (Fig.S2a) from the excitation energy (21.20 eV). The conduction band energy E_c is thus estimated at 1.17eV from $E_v - E_g$, and E_c values of ZnGa_2O_4 in electron volts are converted to electrochemical energy potentials in volts according to the reference standard for which 0 V versus RHE (reversible hydrogen electrode) equals -4.44 eV versus vacuum level as shown in Fig. S2b.

Fig. S2. Structure of primitive bulk ZnGa_2O_4 (a) and high-symmetry points connected with red solid line (b). Balls in red, yellow and green represent O, Ga and Zn, respectively.

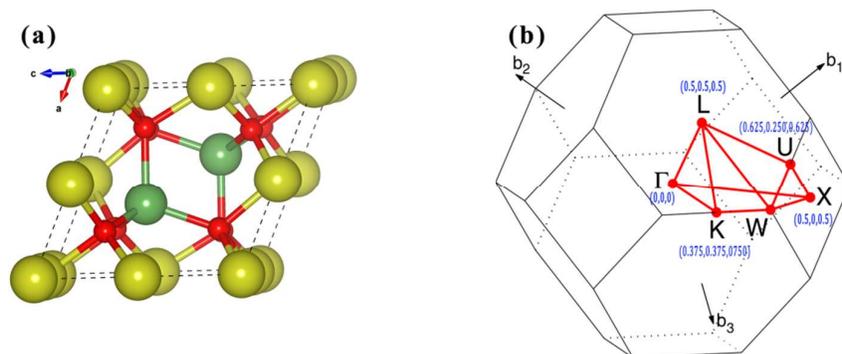


Fig. S3. Region magnified band structure of ZnGa_2O_4 for K-path search to calculate the effective masses of electron and hole.

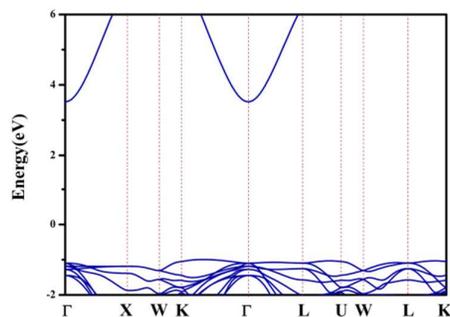


Fig. S4. Possible geometries of native and N-related point defects in ZnGa_2O_4 involve interstitial N (a-c), substitutional atom Ga_{Zn} (d) and Zn_{Ga} (e), atomic antisite $\text{Zn}_{\text{Ga}}\text{-Ga}_{\text{Zn}}$ (f), double substitutional N (h-j), N substitution in O site (k), O vacancy (l) and coexist of N substitution and O vacancy (m). Defect sites are labeled by arrows.

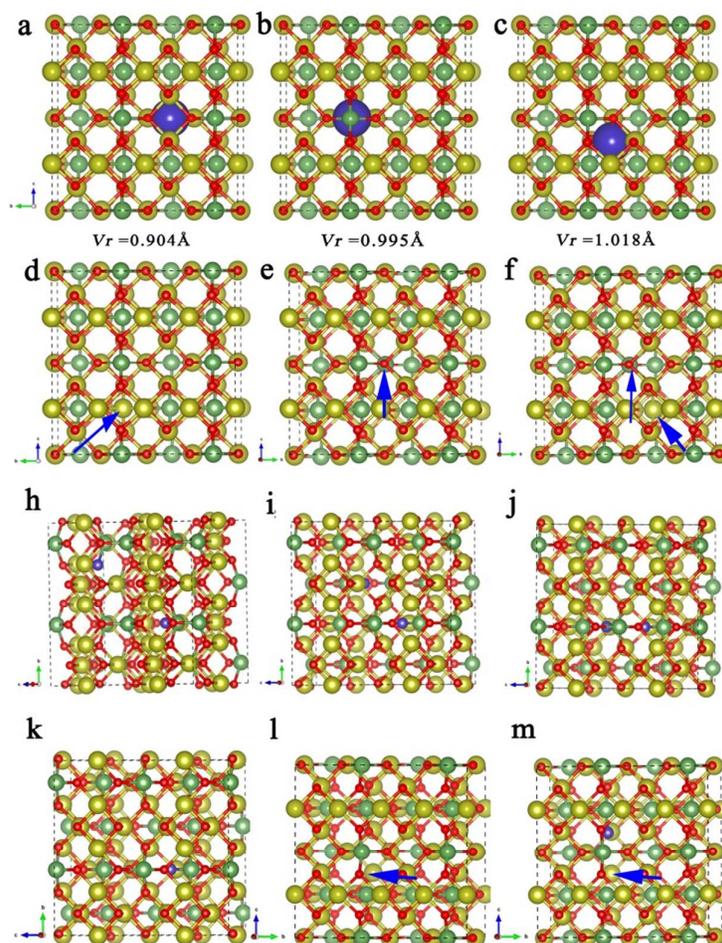


Fig. S5. Band structures for native point defects (a) substitutional atom Ga_{Zn} , (b) Zn_{Ga} , and (c) atomic antisite $\text{Zn}_{\text{Ga}}-\text{Ga}_{\text{Zn}}$.

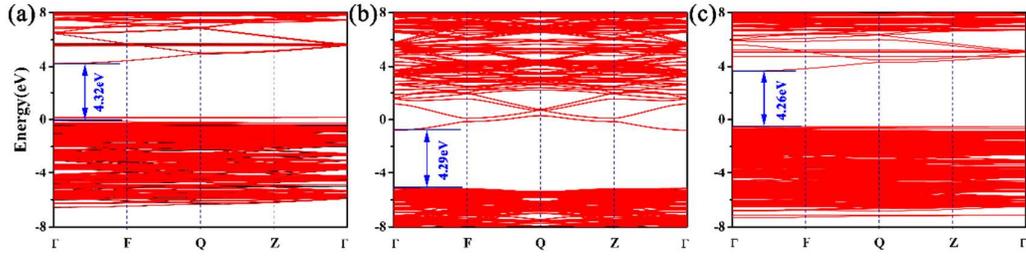


Fig. S6. Formation energy of N doping in ZGO_Ov with different charged states in various chemical conditions.

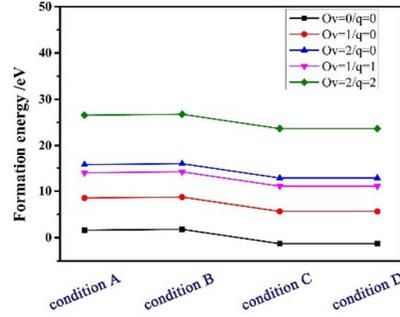
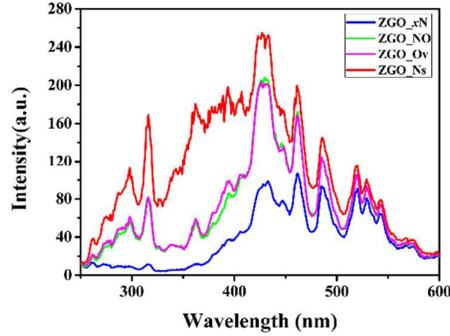


Fig. S7. Photoluminescence spectra of ZGO_xN, ZGO_NO, ZGO_Ov and ZGO_Ns.



Equation S1. Leslie and Gillan correction for effect of points charge in defected system.

$$E^{Md} = -\frac{\alpha Q^2}{2\epsilon L}$$

Where α is the Madelung constant (1.33), ϵ is the dielectric constant (10.4) and L is estimated from its supercell volume as $L = (\text{volume})^{1/3}$.