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## ZnGa<sub>2-x</sub>Al<sub>x</sub>O<sub>4</sub> ( $x = 0 \leq 2$ ) spinel for persistent light emission and HER/OER bi-functional catalysis†

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Spinel materials have demonstrated diverse applications in various fields, especially in the energy sector. Since the pure spinel structure has the limitations of poor inherent activity and low conductivity, defect engineering through octahedral B-site modulation is expected to enhance various properties. Here in this work, we have synthesized ZnGa<sub>2-x</sub>Al<sub>x</sub>O<sub>4</sub> ( $x = 0 \leq 2$ ) spinel and moved from one terminal (ZnGa<sub>2</sub>O<sub>4</sub>) to the other (ZnAl<sub>2</sub>O<sub>4</sub>) by varying the Ga/Al ratio using solvent-free solid-state reaction. Dopant and rare earth element-free (RE) ZnGa<sub>2</sub>O<sub>4</sub> spinel showed excellent blue luminescence with photoluminescent quantum yields (PLQY) of 13% while exhibiting persistent light emission close to 60 min. The Al<sup>3+</sup> incorporation at Ga<sup>3+</sup> site doesn't yield any improvement in persistent luminescence lifetime owing to quenching of shallow traps as suggested by thermoluminescence (TL) studies. Moreover our materials have demonstrated bifunctional electrocatalytic activity towards both oxygen evolution (OER) and hydrogen evolution reaction (HER) which has never been reported for ZnGa<sub>2-x</sub>Al<sub>x</sub>O<sub>4</sub>. X-ray photoelectron spectroscopy (XPS) and positron annihilation lifetime spectroscopy (PALS) suggested that mixed Al/Ga-containing spinels possessed enhanced oxygen vacancies/defects. This makes them better electrocatalyst towards OER and HER compare to ZnGa<sub>2</sub>O<sub>4</sub> and ZnAl<sub>2</sub>O<sub>4</sub>. The ZnGa<sub>1.75</sub>Al<sub>0.25</sub>O<sub>4</sub> composition by virtue of enhanced oxygen vacancies and less charge transfer resistance (47.3 ohms) demonstrated best electrocatalytic activity for OER compared to the other synthesized catalysts at the same applied potential (1.6 V). On the other hand, the ZnGa<sub>1</sub>Al<sub>1</sub>O<sub>4</sub> composition demonstrated excellent faradaic efficiency of ~ 90% towards HER. From this work we can achieve multifunctional applications towards optoelectronics and electrocatalysis just by modulating Al/Ga ratio in ZnGa<sub>2-x</sub>Al<sub>x</sub>O<sub>4</sub>.

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### 1. Introduction

A multifunctional material can be a boon towards a sustainable and developing economy, particularly in the area of energy, health, and environment.<sup>1,2</sup> The two most important priorities in the area of the energy sector are designing an (a) inexpensive and efficient persistent luminescent materials and (b) efficient electrocatalysts for green hydrogen generation.<sup>3,4</sup> Moreover, such a development will be pragmatic if it can be achieved

without any involvement of rare earth elements and noble metals (e.g., Pt, Ir or Ru).

For the development of a carbon-neutral society, the use of hydrogen as a fuel is inevitable since it produces benign water vapor and heat as byproducts. Currently, majority of the hydrogen production is executed by following steam methane reformation and coal gasification. However, these processes produce a copious amount of undesirable CO<sub>2</sub>.<sup>5,6</sup> In this context, green hydrogen production *via* electrolysis emerges as a reliable carbon footprint-free technology.<sup>7</sup> The electrochemical process typically has a high activation energy barrier for the reaction, where the presence of an electrocatalyst becomes essential to enhance the overall electrocatalytic energy efficiency.

The water-splitting process involves two reactions: hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode. The relative energies of chemical adsorption of H-atoms on the electrode surface and their subsequent electrochemical or chemical desorption regulates the electrocatalytic HER.<sup>8</sup> The OER reaction is kinetically a sluggish reaction that proceeds *via* 4-electron transfer.<sup>9</sup> Pt/C

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and Ru/IrO<sub>2</sub> are considered as the benchmark electrocatalytic material for HER and OER, respectively.<sup>10</sup> As large-scale productions of these materials are not suitable owing to their expensive and rare nature, the scientific community is actively exploring other abundant and low-cost electrocatalysts. Spinel oxides have been a popular choice in this regard due to their stable structure, adjustable valency, environmental safety and low cost.<sup>11</sup> Spinel is an important class of compounds having the formula AB<sub>2</sub>O<sub>4</sub> where A and B are divalent and trivalent cations, respectively. The spinel can be either normal or inverse depending upon the arrangement of A or B cations in the tetrahedral or octahedral site. For a normal spinel structure, A<sup>2+</sup> occupies the tetrahedral whereas B<sup>3+</sup> occupies the octahedral site. In the inverse spinel structure half of the B<sup>3+</sup> ions occupy the tetrahedral and half of them occupy octahedral site, and A<sup>2+</sup> ions cover the octahedral site.<sup>12</sup> But pure spinel is not a good candidate for catalysis owing to their many limitations, such as poor inherent activity and low conductivity.<sup>13</sup> So the defect engineering plays a crucial role in modulating the catalytic activity of spinels.

Defect engineering is one of the booming areas and a promising field for material chemists to synthesize various materials with enhanced catalytic, electrical, thermal, magnetic, and optical properties.<sup>14–17</sup> This area is acquiring more importance recently due to its many applications in the various technological fields in the area of phosphors,<sup>18</sup> scintillator,<sup>19</sup> batteries,<sup>20</sup> energy storage,<sup>21</sup> electrocatalysis,<sup>16,17,22</sup> thermoelectricity,<sup>23</sup> and photocatalysis.<sup>24</sup> The defects may be cationic vacancy, anionic vacancy (oxygen vacancy), and vacancy associates.<sup>25</sup> There are many strategies employed for defect creation, which include aliovalent doping, annealing in a reduced atmosphere, electrochemical reduction, plasma irradiation, and amorphization.<sup>26,27</sup>

Persistent luminescence is a phenomenon in which the luminescence persists for a longer time, even after the stoppage of excitation. This phenomenon has many applications in fields like bioimaging, cancer therapy, night vision materials, and anti-counterfeiting.<sup>28</sup> Traps play a vital role in persistent luminescence since these are the centers for storing the excitation energy, which is then transferred to emission center to initiate emission.<sup>29</sup> The persistent intensity, as well as the emission time, depends on the trap structure and trap depth that is directly linked to lattice defects.<sup>30,31</sup> This unique feature of the spinels was utilized in designing bright and long duration persistent light emitting materials (PLEMs).<sup>19,28,32</sup> The tactical addition of dopant ions is primarily applied to invoke significant lattice distortion and strain, which affects the light emitting properties of the phosphor. Furthermore, there are lots of studies on the afterglow materials which employ rare earth (RE) ions that are not only expensive but also associated with health hazards. Proper processing of original RE ions is also very laborious and expensive, which are available only in limited geographical locations.<sup>33,34</sup> In this context, RE-free materials delivering photo and persistent luminescence could be a great addition to a cost-effective phosphor library.

Here, we have explored the possibility of deploying the spinel template for invoking multifunctionality, lighting, and

catalysis. We have probed pure spinels along with doped derivatives where Al<sup>3+</sup> ions are incorporated at Ga<sup>3+</sup> sites of the ZnGa<sub>2</sub>O<sub>4</sub> spinel. The present work comprises synthesizing a series of samples starting from ZnGa<sub>2</sub>O<sub>4</sub> to ZnAl<sub>2</sub>O<sub>4</sub> by modulating Ga/Al ratio, and probing their luminescence and electrocatalytic properties. Since the octahedral B site is susceptible to easy modulation and leads to intriguing properties, it is expected to see similar changes in both luminescence and electrocatalytic studies. The synthesized materials were characterized by using powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy. For determining the Ga/Al ratio, EDAX has been performed. In order to explore the emission as well as persistent luminescence characteristics with different Ga/Al ratios, photoluminescence (PL) was also carried out. The defect-related studies have been correlated using X-ray photoelectron spectroscopy (XPS), thermoluminescence (TL) and positron annihilation lifetime spectroscopy (PALS). Electrocatalytic activity, which includes both HER and OER of all materials, has also been performed.

## 2. Experimental

### 2.1. Synthesis

The spinel ZnGa<sub>2-x</sub>Al<sub>x</sub>O<sub>4</sub> ( $x = 0 \leq 2$ ) were synthesized by conventional solid state reaction route. The precursors used are ZnO of SPEX Pure (99.999%), Al<sub>2</sub>O<sub>3</sub> from Alfa Aesar (99.95%) and Ga<sub>2</sub>O<sub>3</sub> of SPEX Pure (99.999%). Then in order to prepare the series of samples with different Ga/Al ratio the required amount of the precursors were weighed and grinded in a mortar and pestle for the complete mixing of precursors. Then it is calcined at 900 °C for 15 h with ramp temperature of 10 °C per minute in a tubular furnace. It was allowed to cool to room temperature followed by re-grinding. The second stage heating included sintering at 1200 °C for 15 h. The final grinding was carried out for 30 minutes to obtain the phase pure spinel compound. The schematic of the same has been shown in Fig. S1.†

### 2.2. Instrumentation

To evaluate the phase purity of the synthesized material XRD has been carried out by using a benchtop proto X-ray diffractometer equipped with the monochromatic X-ray source as Cu K $\alpha$  (1.5405 Å). The XRD pattern recorded with a  $2\theta$  range from 15 to 80° with a scan rate of 2° min<sup>-1</sup>. All the measurements were done at an accelerating voltage of 30 kV and tube current at 20 mA. FTIR spectra were recorded on a Bruker Alpha FTIR spectrometer in pellet mode by making the pellet with KBr crystals. Raman spectral studies are carried out using a micro-Raman spectrometer (STR-300, SEKI Technotron, Japan). A 532 nm CW diode pumped solid state laser (DPSS, gem 532, laser quantum) is used as an excitation source. The spectrograph is calibrated using the 520.5 cm<sup>-1</sup> line from silicon wafer. SEM-EDS analysis has done on a Tescan VEGA MV 2300 T SEM-EDS instrument. Photo physical studies have been carried out using Edinburg make fluorescence instrument of series FLS 1000 in which xenon lamp is the source. All



thermoluminescence measurements are done using a commercial Risø TL/OSL-DA-20 reader. The XPS measurements were carried out on a SPECS instrument with a PHOBIOS 100/150 delay line detector (DLD). PALS measurements were carried out under ambient conditions where Na-22 encapsulated in 8 micron polyimide films was immersed in the powder sample. The resolution of the positron lifetime spectrometer was 185 ps. The spectra were analyzed using PALSFit software<sup>35</sup> taking into account the resolution of the spectrometer and fraction of positrons annihilating in the polyimide films. Scanning Electron Microscopy (SEM) has been carried out on a SNE4500 Mini SEM instrument. All the ICP-AES analyses were carried out using a Spectro-Arcos SOP Unit, Ametek, Germany. The spectrometer is augmented with a detector set consisting of thermally stabilized linear arrays of CCD detectors (3648 pixels per array). High purity argon was used as the plasma gas, carrier gas and auxiliary gas as well. The non-LTE plasma was sustained with a constant RF supply of 40 MHz and 1.3 kW of forward power. To establish the standardization, four point calibration curves were established using 1, 10, 100 and 500 ppm of multi elemental standards which were prepared from the stock of Merck-IV ICP solution standard. All measurements were done in triplicate. High pure Ar gas (total flow rate of 15 liters per minute) was also used for flushing of the detector before all the measurements to minimize the background. All the electrochemical characterizations were performed using Metrohm Auto Lab PGSTAT 201 potentiostat with three electrode systems at room temperature (298 K). The pH of the electrolyte used was adjusted using ORION STAR A111 pH Meter (Thermo Scientific) or LMPH-9 (Labman Scientific). A spiral platinum electrode (Pt) and silver chloride electrode (Ag/AgCl in 3 M KCl) were taken as the counter and reference electrodes, respectively.

### 3. Results and discussions

#### 3.1. Phase, vibrational spectroscopy and elemental analysis

Fig. 1a shows the XRD pattern of the synthesized samples. The pattern matches with the standard pattern of both  $\text{ZnGa}_2\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$  with JCPDS no. 00-038-1240 and 01-070-8182, respectively which implies the formation of phase pure material. There are no peaks of the starting precursors used. The major diffraction peaks of  $\text{ZnGa}_2\text{O}_4$  are present at  $2\theta$  values of 18.7, 30.6, 36.0, 37.6, 43.7, 54.1, 57.7, 63.3, 71.8, 74.9 and 75.9 corresponding to (311), (220), (111), (222), (400), (422), (511), (440), (620), (533) and (622) crystal planes respectively. Likewise, for  $\text{ZnAl}_2\text{O}_4$  the  $2\theta$  values are at 31.3, 36.9, 44.8, 49.1, 55.7, 59.4, 65.3, 74.1 and 77.3 corresponding to (220), (311), (400), (331), (422), (511), (440), (620) and (533) planes respectively. On increasing the Al ratio in the spinel, a shift in the diffraction peaks to higher angle is observed suggesting that there is a decrease in the  $d$ -spacing.

The FTIR spectrum is shown in Fig. 1b. In the spinel system the Al might coordinate to oxygen in two different ways, either it coordinates to 4 oxygen atoms ( $\text{AlO}_4$ ) forming a tetrahedral network or it can coordinate to 6 oxygen atoms ( $\text{AlO}_6$ ) forming an octahedron network. There are mainly 3 absorption peaks in the FTIR spectrum of  $\text{ZnAl}_2\text{O}_4$ ; they are at 663, 554 and 515  $\text{cm}^{-1}$

which represents the symmetric stretching vibration of Al-O bond, symmetric bending vibration of Al-O bond and asymmetric stretching vibration of Al-O bond respectively. Along with these peaks there is also a shoulder peak at 849  $\text{cm}^{-1}$  which is due to the stretching vibration of Al-O bond in the  $\text{AlO}_4$  unit. This implies that some of the Al is occupying as  $\text{AlO}_4$  unit also,<sup>36,37</sup> whereas in the FTIR spectrum of  $\text{ZnGa}_2\text{O}_4$ , there are mainly 2 peaks at 580 and 498 which represents the vibration of Ga-O-Zn and Zn-O bond.<sup>38</sup> On moving from zinc gallate to zinc aluminate, evolution of new vibrational peak above 600  $\text{cm}^{-1}$  is observed which represents the symmetric stretching of Al-O bond.

Fig. 1c represents the Raman spectra of synthesized samples [ $\text{ZnGa}_{2-x}\text{Al}_x\text{O}_4$  ( $x = 0 \leq 2$ )]. According to group theory,  $\text{ZnGa}_2\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$  are expected to possess 5 Raman active modes ( $\text{A}_{1g} + \text{E}_g + 3\text{T}_{2g}$ ). These 5 modes are known as first order Raman active modes which are basically due to the motion of the  $\text{Zn}^{2+}$  in the tetrahedral site and not due to the motion of  $\text{Ga}^{3+}$  in the octahedral site. The Raman spectra of  $\text{ZnGa}_2\text{O}_4$  show mainly three peaks at 466, 608 and 711  $\text{cm}^{-1}$  which are two  $\text{T}_{2g}$  and  $\text{A}_{1g}$  modes respectively.<sup>38</sup> The Raman spectra of  $\text{ZnAl}_2\text{O}_4$  contains mainly 2 Raman peaks at 418 and 657  $\text{cm}^{-1}$  which represents the  $\text{E}_{1g}$  and  $\text{T}_{2g}$  modes which correspond to asymmetric bending motion of oxygen in tetrahedral and octahedral site respectively. Due to the high intensity of  $\text{E}_{1g}$  and  $\text{T}_{2g}$  modes, other modes are not visible here.<sup>39</sup> The intermittent compositions wherein  $x < 1$  display the feature typical of  $\text{ZnGa}_2\text{O}_4$  where as the one wherein  $x \geq 1$  are on line with spectra of  $\text{ZnAl}_2\text{O}_4$ .

The Ga/Al ratio has been calculated from the counts obtained in the EDAX spectra which have been given in Table 1 and the pictorial representation of the same can be seen in the Fig. 1d. In the elemental mapping results of one of the representative spinels  $\text{ZnGa}_1\text{Al}_1\text{O}_4$  (Fig. 1e), homogeneous distribution of all the elements could be clearly seen. Fig. S2† represents the EDAX mapping of all the other samples, which gives the information on elemental compositions. It shows the uniform distribution of elements throughout the sample. The elemental compositional analysis of the representative samples  $\text{ZnGa}_2\text{O}_4$ ,  $\text{ZnGa}_1\text{Al}_1\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$  has done by using ICP-AES. The procedure and the results are shown in ESI (Table S1).†

#### 3.2. Defect characterization: XPS and PALS

The survey scans of the representative samples ( $\text{ZnGa}_2\text{O}_4$ ,  $\text{ZnGa}_1\text{Al}_1\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$ ) are shown in Fig. S3† which confirms the surface composition of the materials. Fig. 2a represents the XPS core level spectra of oxygen which is deconvoluted into 2 peaks. The one with lower binding energy (~529–530 eV, red curve) corresponds to the lattice oxygen and the other with higher binding energy (~531 eV, green curve) corresponds to the oxygen vacancy.<sup>40</sup> The atomic percentage of oxygen vacancies in different spinel phases are listed in Table 2. It can be seen that the highest concentration of oxygen vacancy is present in  $\text{ZnGa}_{1.75}\text{Al}_{0.25}\text{O}_4$ . The core level XPS spectra of Zn, Al, Ga of the representative samples  $\text{ZnGa}_2\text{O}_4$ ,  $\text{ZnGa}_1\text{Al}_1\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$  are also shown in Fig. S4.† The two characteristic peaks of Zn 2p are located at 1021.8 and 1044.8 eV which corresponds to a peak



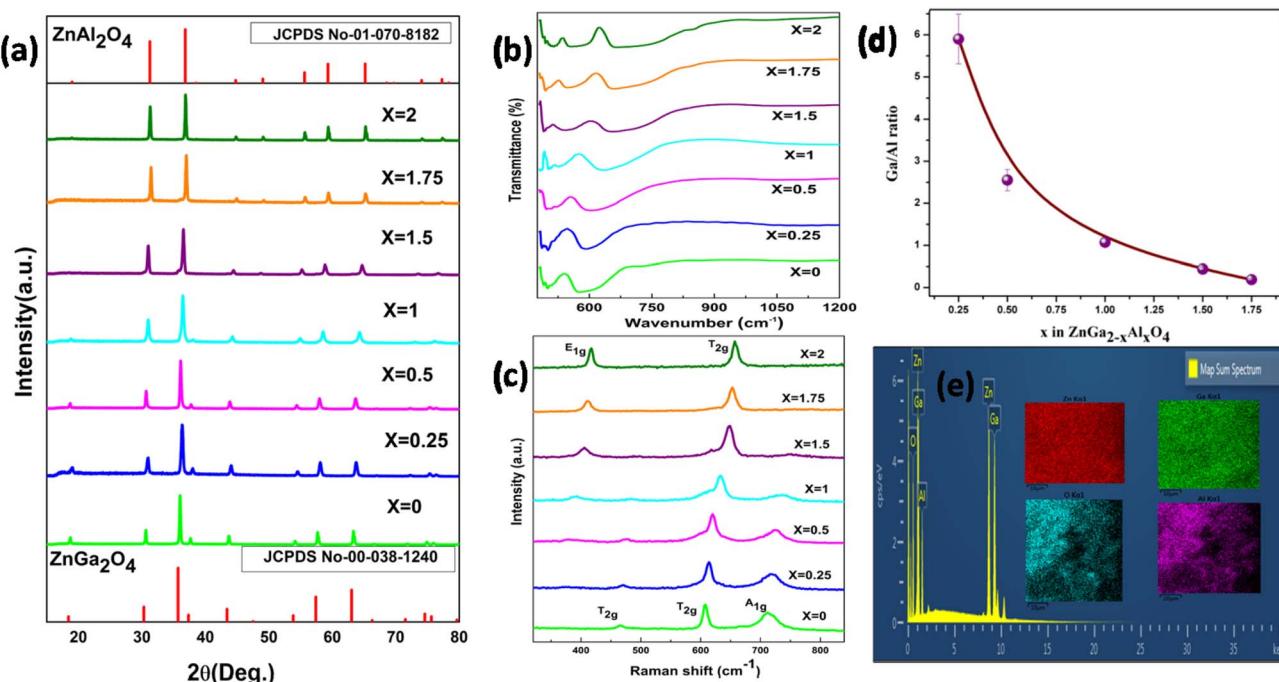


Fig. 1 (a) Powder XRD pattern (b) FTIR spectra (c) Raman spectra of  $\text{ZnGa}_{2-x}\text{Al}_x\text{O}_4$  ( $x = 0, 0.25, 0.5, 1, 1.5, 1.75, 2$ ) (d) Plot of Ga/Al ratio of  $\text{ZnGa}_{2-x}\text{Al}_x\text{O}_4$  ( $x = 0, 0.25, 0.5, 1, 1.5, 1.75, 2$ ) and (e) element mapping results of O, Al, Ga, and Zn elements in the  $\text{ZnGa}_1\text{Al}_1\text{O}_4$ .

Table 1 EDAX based composition estimation of Ga/Al ratio in  $\text{ZnGa}_{2-x}\text{Al}_x\text{O}_4$  spinel

Sample	Atomic%	Ga/Al ratio
$\text{ZnGa}_{1.75}\text{Al}_{0.25}\text{O}_4$	Ga – 20.92 Al – 3.55	5.9
$\text{ZnGa}_{1.5}\text{Al}_{0.5}\text{O}_4$	Ga – 16.96 Al – 6.66	2.55
$\text{ZnGa}_1\text{Al}_1\text{O}_4$	Ga – 13.63 Al – 12.74	1.07
$\text{ZnGa}_{0.5}\text{Al}_{1.5}\text{O}_4$	Ga – 8.41 Al – 19.22	0.438
$\text{ZnGa}_{0.25}\text{Al}_{1.75}\text{O}_4$	Ga – 4.21 Al – 22.02	0.19

spacing of 23 eV that is characteristic for divalent Zn ion ( $\text{Zn}^{2+}$ ). In Ga 2p XPS spectra the two characteristic peaks are located at 1115.8 and 1142.7 eV with peak spacing of 26.9 eV which corresponds to trivalent gallium ion ( $\text{Ga}^{3+}$ ).<sup>41</sup> For Al 2p there is only one XPS peak at  $\sim$ 74 eV which represents the  $\text{Al}^{3+}$  in  $\text{AlO}_6$  octahedra.<sup>42</sup>

All the positron annihilation lifetime spectra could be fitted to sum of three exponentials. The three lifetimes obtained are numbered in the increasing order of the magnitude and the intensities corresponding to these lifetimes are referred to as  $I_1$ ,  $I_2$  and  $I_3$ , as is the convention. The longest-lived component of lifetime  $\sim$  1 ns and intensity ( $I_3$ )  $\sim$  0.6% was from positronium formation on the surface of the powder particles. Though this component was too small, inclusion of it in the fitting was necessary to obtain the best fit to the experimental spectra. The other two lifetimes ( $\tau_1$  and  $\tau_2$ ), their corresponding intensities

( $I_1$ ,  $I_2$  with  $I_1 + I_2 \sim$  constant) and the intensity weighted average positron lifetime in these samples is given in the Fig. 2b and c. The uncertainties on the values of the individual lifetimes and intensities is from the fitting of the spectra while uncertainty on the average lifetime is calculated from the uncertainties of individual lifetimes and intensities used in calculating the average.

The first positron lifetime is in the range of 150–170 ps and the second positron lifetime is in the range of 300–350 ps. The first positron lifetime is from the positron annihilations in the bulk with contribution from shallow positron traps while the second component is from the vacancy clusters. It is also noticed that in the solid solutions, the variation in the positron lifetimes is not monotonous. The positron lifetimes are higher in  $\text{ZnGa}_2\text{O}_4$  than  $\text{ZnAl}_2\text{O}_4$ . The intensity of the second lifetime is lower in Al rich samples when compared to Ga rich sample. The same is true of average positron lifetimes. The sample with  $x = 1$  shows nearly weighted average positron lifetime of in  $\text{ZnGa}_2\text{O}_4$  than  $\text{ZnAl}_2\text{O}_4$  where as others show deviations from this weighted average.

### 3.3. Optical measurements

Fig. 3a represents the excitation spectra of  $\text{ZnGa}_{2-x}\text{Al}_x\text{O}_4$  with a constant emission wavelength of 375 nm. It consists of a band near 254 nm which is due to the  $\text{O}^{2-} \rightarrow \text{Ga}^{3+}/\text{Al}^{3+}/\text{Zn}^{2+}$  charge transfer. Fig. 3b is the emission spectra which is excited at 254 nm. There are mainly two bands observed in the emission spectra which are in the blue and green region located at 400 and 500 nm respectively. Normally  $\text{ZnGa}_2\text{O}_4$  reported only have intrinsic blue emission due to the self activation of octahedral



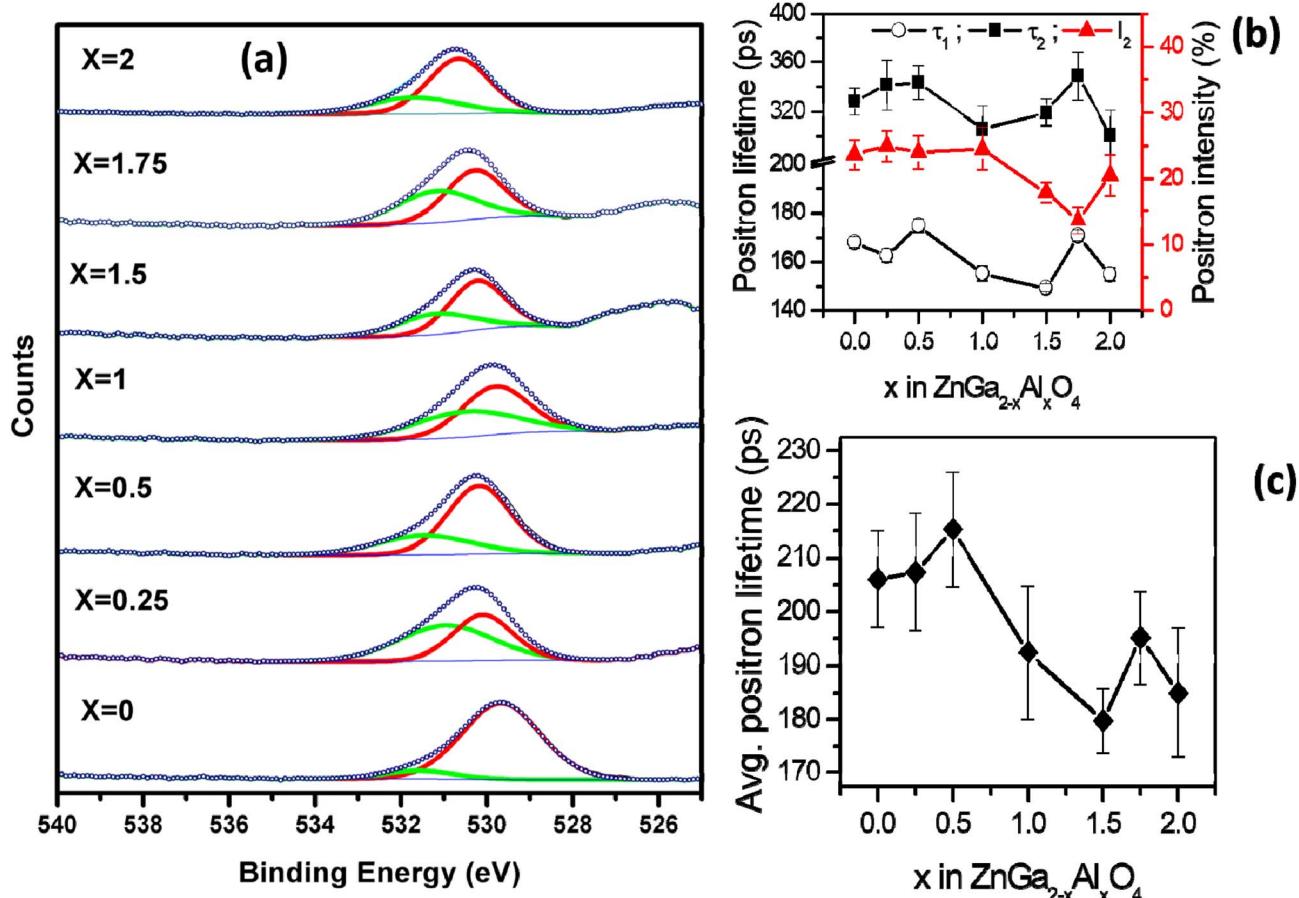


Fig. 2 (a) O 1s core level XPS spectra of  $\text{ZnGa}_{2-x}\text{Al}_x\text{O}_4$ . ( $x = 0, 0.25, 0.5, 1, 1.5, 1.75, 2$ ) (b) positron lifetime data (c) average positron lifetime.

Table 2 Atomic% of oxygen vacancy in  $\text{ZnGa}_{2-x}\text{Al}_x\text{O}_4$  spinel

Sample	Peak 2	Atomic% of oxygen vacancy
$\text{ZnGa}_2\text{O}_4$	531.6	8
$\text{ZnGa}_{1.75}\text{Al}_{0.25}\text{O}_4$	531.0	55
$\text{ZnGa}_{1.5}\text{Al}_{0.5}\text{O}_4$	531.4	30
$\text{ZnGa}_{1.1}\text{Al}_1\text{O}_4$	531.1	45
$\text{ZnGa}_{0.5}\text{Al}_{1.5}\text{O}_4$	531.1	36
$\text{ZnGa}_{0.25}\text{Al}_{1.75}\text{O}_4$	531.2	47
$\text{ZnAl}_2\text{O}_4$	531.6	30

$\text{GaO}_6$  unit.<sup>43,44</sup> Appearance of bright blue PL around 400–460 nm in  $\text{ZnGa}_2\text{O}_4$  has been reported earlier as well and it is indeed ascribed to the self-activation of  $\text{GaO}_6$ .<sup>45–47</sup>  $\text{ZnGa}_2\text{O}_4$  nanocrystals PL peak with respect to its bulk counterpart is fairly narrower and blue-shifted by 35 nm.<sup>48</sup>

To tune the emission range in visible region, the normal way is to do the doping with different rare earth elements. But here the  $\text{ZnGa}_2\text{O}_4$  produced *via* solid-state reaction route is showing emission in green region in addition to the blue region. This is due to the formation of vacancies at higher annealing temperature which subsequently create different defect energy levels between the two bands, thus making the visible range emission

possible. The green emission is due to the presence of oxygen vacancies.<sup>49</sup> Noto *et al.*<sup>50</sup> have also reported similar kind of emission in  $\text{ZnGa}_2\text{O}_4$  prepared by microwave assisted solid state reaction in the range of 380 to 660 nm and 665–740 nm. Till date we couldn't find any report on afterglow PL from undoped  $\text{ZnGa}_2\text{O}_4$ .

From the CIE diagram which is shown in Fig. 3c it is clear that although the material has emission peaks in blue, green and red region, the overall emission profile occurs in the blue region. With different Al content there is color tunability in the blue region. The corresponding  $x, y$  coordinates are shown in the Table S2.† On increasing the Al content and gradually replacing  $\text{Ga}^{3+}$  ion in  $\text{ZnGa}_2\text{O}_4$  the photoluminescence quantum yield (PLQY) is getting reduced, the same trend is also observed in the emission intensity.  $\text{ZnGa}_2\text{O}_4$  is having a higher quantum yield of  $\sim 13\%$  as can be seen from Fig. 3d.

In order to study the afterglow decay processes, the curve of all the samples is shown in the Fig. 3e. The samples have been irradiated by 254 nm UV lamp for 5 min. It is clear from the figure that  $\text{ZnGa}_2\text{O}_4$  is showing a persistent luminescence of up to 55 minutes with appreciable counts. All the other samples are showing less persistent luminescence time. The presence of shallow traps in  $\text{ZnGa}_2\text{O}_4$  is responsible for the persistent luminescence. With increase in the Al content the persistent

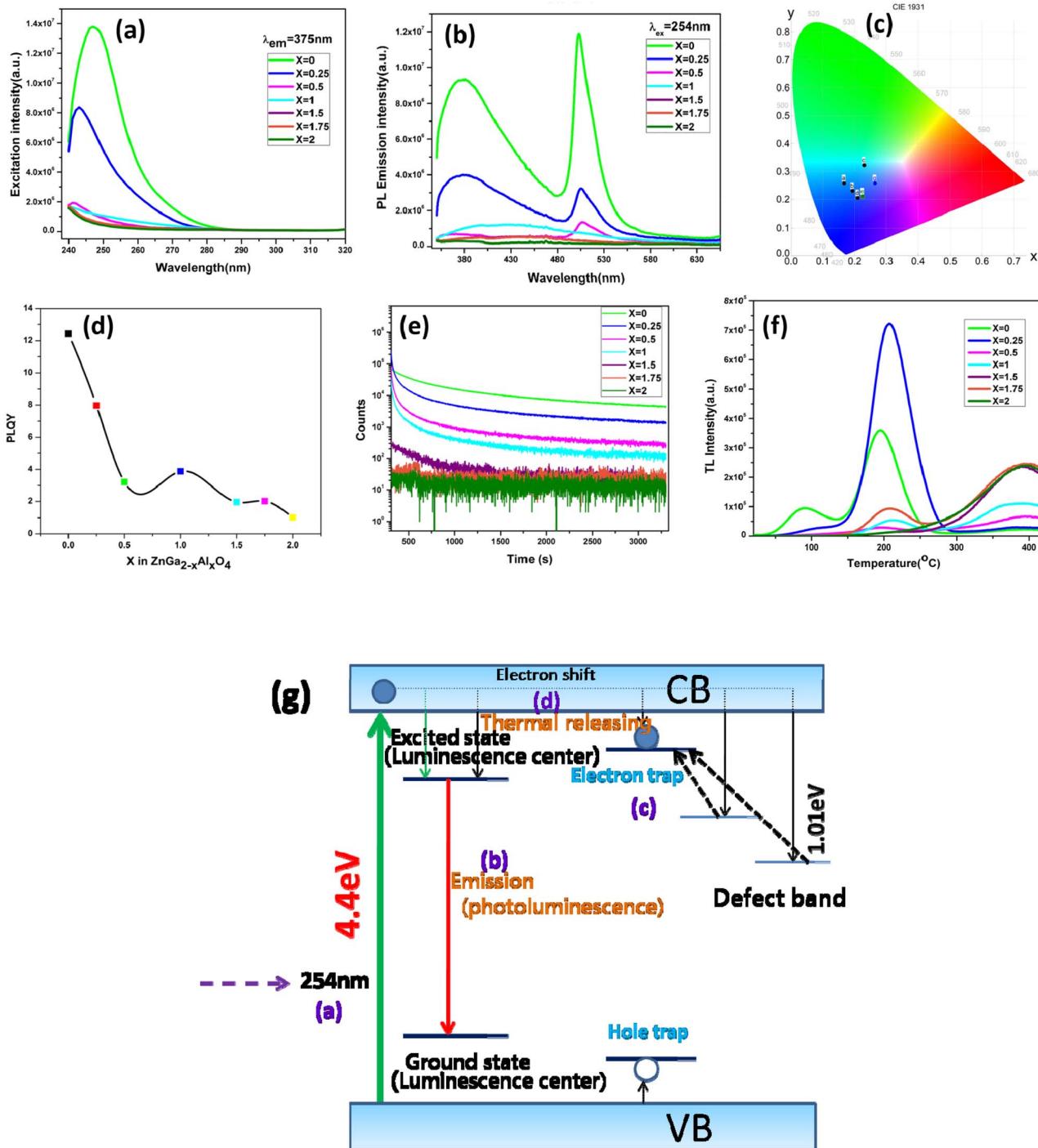


Fig. 3 (a) Excitation spectra (b) emission spectra (c) CIE diagram (d) plot of quantum yield against concentration (e) persistent lifetime spectra (f) thermoluminescence spectra of  $\text{ZnGa}_{2-x}\text{Al}_x\text{O}_4$  ( $x = 0, 0.25, 0.5, 1, 1.5, 1.75, 2$ ) (g) mechanism of the persistent luminescence.

luminescence has got degraded. From the decay curves it seen that the decay is a bi-exponential decay having a fast decaying and slow decaying component. The mechanism for the persistent luminescence is discussed in the later part of this section.

Fig. 3f shows the thermoluminescence (TSL) spectra of  $\text{ZnGa}_{2-x}\text{Al}_x\text{O}_4$  which is irradiated at 254 nm for 5 minutes then followed by heating the sample at a heating rate of  $2\text{ }^\circ\text{C s}^{-1}$ . The experiment has been performed without using the filter. Shape

of the glow curve determines the order of the kinetics. More precisely the term is defined as geometric shape factor or symmetry factor ( $\mu_g$ ) which is given by

$$\mu_g = \delta/\omega \quad (1)$$

where  $\delta = T_2 - T_M$  and  $\omega = T_2 - T_1$ .  $T_M$  represents the peak temperature at the maximum and  $T_1, T_2$  are temperatures on either side of the  $T_M$  corresponding to half intensity.<sup>51</sup>



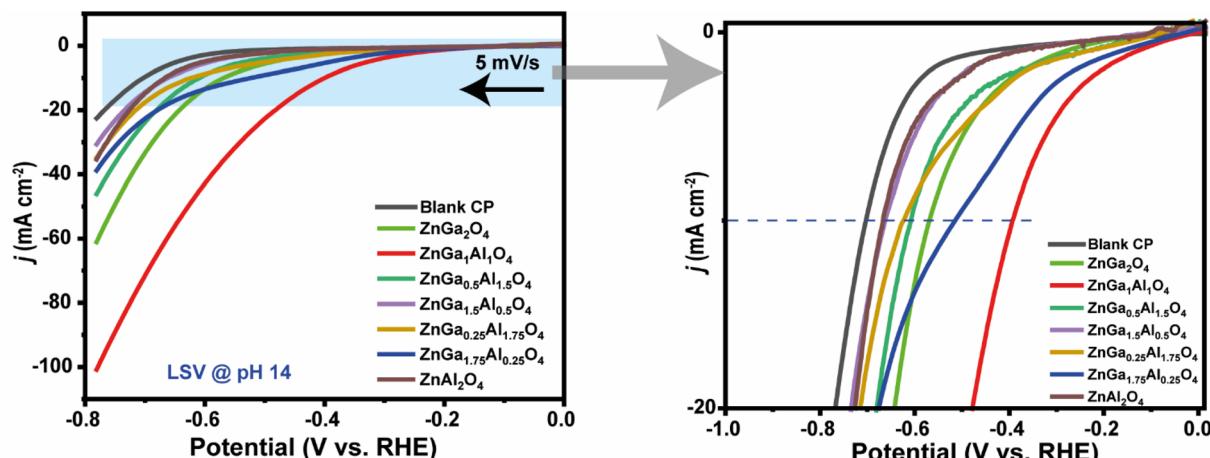


Fig. 4 The left figure highlights the linear sweep voltammetry plots (HER) recorded for all the catalysts probed in this study in 1.0 M KOH solution (scan rate 5 mV s<sup>-1</sup>). The horizontal black arrow indicates the initial scan direction. The right hand side picture depicts the onset potential region for the HER activity.

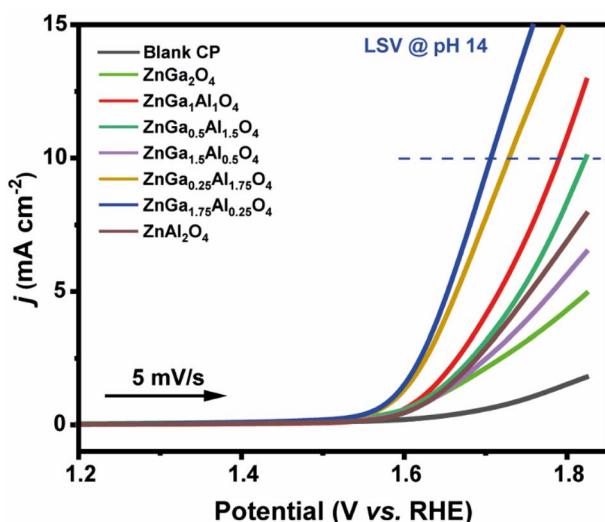


Fig. 5 Linear sweep voltammetry plots (OER) recorded for all the catalysts probed in this study in 1.0 M KOH solution (scan rate 5 mV s<sup>-1</sup>). The horizontal black arrow indicates the initial scan direction.

In the figure ZnGa<sub>2</sub>O<sub>4</sub> is having two different glow peaks which indicate that there are two types of traps present. Since the low temperature peak is overlapping with the higher temperature peak we are only calculating the trap parameters for the high temperature peak. The  $T_M$ ,  $T_1$  and  $T_2$  of the high temperature peak of ZnGa<sub>2</sub>O<sub>4</sub> are 195.7 °C, 167 °C and 225.3 °C respectively. Substituting the values to the above equation gives the value of  $\mu_g$  as 0.507, which suggest that the peak is obeying the second order kinetics, since the  $\mu_g$  value for a first order and second order kinetics have a value of 0.42 and 0.52 respectively.<sup>52</sup>

According to Chen's method, which is independent of the order of the kinetics, the trap parameters can be calculated by using the eqn (2).<sup>51</sup>

$$E = C_\alpha \left( \frac{KT_M^2}{\alpha} \right) - b_\alpha (2KT_M) \quad (2)$$

The corresponding activation energy is obtained as 1.013 eV. The frequency factor for a second order reaction has calculated by using the eqn (3).

$$\frac{\beta E}{KT_M^2} = S \exp\left(\frac{-E}{KT_M}\right) \left[ 1 + \frac{2KT_M}{E} \right] \quad (3)$$

where  $\beta$  is the heating rate and  $S$  is the frequency factor. The frequency factor for ZnGa<sub>2</sub>O<sub>4</sub> is  $7.13 \times 10^9$  s<sup>-1</sup>.

As it can be seen from the TSL data of the ZnGa<sub>2</sub>O<sub>4</sub> sample, with relatively shallow traps has most favorable conditions to be used as a persistent luminescent material. This is evidenced from the persistent luminescence study also. With increase in Al content in the samples a small shift in the TL glow peak towards higher  $T_M$  was observed which is attributed to the increase in the activation energy related to deeper traps. From the figure it is also clear that the TSL intensity of ZnGa<sub>1.75</sub>-Al<sub>0.25</sub>O<sub>4</sub> is high compared to other materials which suggest that the concentration of traps formed is higher in this. From the persistent luminescence and TSL study a possible mechanism has been proposed which has been shown in Fig. 3g. Initially upon irradiation with a UV light large number of electrons and holes are formed which is represented as process (a). Then the energy is transferred to the luminescence centre through the lattice thus producing the rapid luminescence which is the process (b). And for the delayed luminescence the two defect centres are responsible. In the process (c) the carriers are get trapped into the defect centres. After thermal treatment the carriers are get detrapped and producing the persistent luminescence by the process (d).<sup>53,54</sup>

### 3.4. Electro catalytic study

**3.4.1. Electrocatalytic HER performance.** A standard three-electrodes cell was used to perform both the HER and OER in an



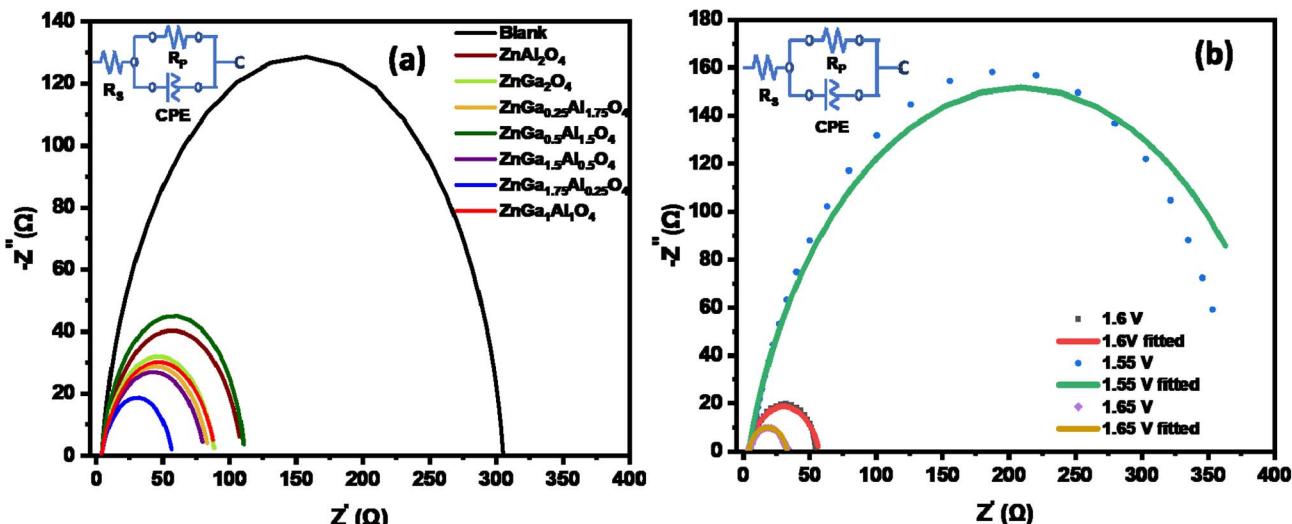


Fig. 6 Nyquist plot of (a) all synthesized catalysts at 1.6 V vs. RHE in 1.0 M KOH solution and (b)  $\text{ZnGa}_{1.75}\text{Al}_{0.25}\text{O}_4$  catalyst.

Table 3 EIS fitted data from the Nyquist plot

Electrodes	$R_S$ (ohm)	$R_P$ (ohm)	$R_{CT}$ (ohm)
Blank carbon paper	4.1	303.19	299.1
$\text{ZnGa}_2\text{O}_4$	4.12	84.97	80.85
$\text{ZnAl}_2\text{O}_4$	4.08	106	101.92
$\text{ZnGa}_{1.5}\text{Al}_{0.5}\text{O}_4$	4.16	79.5	75.34
$\text{ZnGa}_{0.5}\text{Al}_{1.5}\text{O}_4$	4.02	105.51	101.49
$\text{ZnGa}_1\text{Al}_1\text{O}_4$	4.06	84.29	80.23
$\text{ZnGa}_{0.25}\text{Al}_{1.75}\text{O}_4$	4.3	80.7	76.4
$\text{ZnGa}_{1.75}\text{Al}_{0.25}\text{O}_4$	3.97	51.2	47.23

alkaline medium (1.0 M KOH) of pH 14.0. Fig. 4 shows the LSV curves (HER) for all synthesized catalysts.  $\text{ZnGa}_1\text{Al}_1\text{O}_4$  exhibited higher HER activity compared to the other compositions with a minimal overpotential of 390 mV to achieve a current density of  $10 \text{ mA cm}^{-2}$  ( $j_{10}$ ), which is significantly lower than  $\text{ZnGa}_2\text{O}_4$  (570 mV/ $j_{10}$ ). The other electrocatalysts,  $\text{ZnGa}_{1.75}\text{Al}_{1.25}\text{O}_4$ ,  $\text{ZnGa}_{0.5}\text{Al}_{1.5}\text{O}_4$ ,  $\text{ZnGa}_{0.25}\text{Al}_{1.75}\text{O}_4$ ,  $\text{ZnGa}_{1.5}\text{Al}_{0.5}\text{O}_4$ ,  $\text{ZnAl}_2\text{O}_4$ , also

exhibited high overpotential values of 515 mV, 610 mV, 622 mV, 659 mV and 667 mV to achieve  $10 \text{ mA cm}^{-2}$  current density ( $j_{10}$ ). When both the Al & Ga were present at an equimolar ratio (1 : 1) in the spinel, it exhibited the most efficient HER activity. The corresponding Tafel plot is shown in Fig. S5† where we have observed the lowest Tafel slope for  $\text{ZnGa}_1\text{Al}_1\text{O}_4$  sample. This data clearly indicates the fastest electrocatalytic HER kinetics for this  $\text{ZnGa}_1\text{Al}_1\text{O}_4$  material.

**3.4.2. Electrocatalytic OER performance.** The OER properties of the prepared catalysts were also probed in 1.0 M KOH electrolyte *via* LSV studies. Fig. 5 represents the LSV curves for OER activity for all the synthesized catalysts.  $\text{ZnGa}_{1.75}\text{Al}_{0.25}\text{O}_4$  demonstrated the best OER activity compared to the other catalysts, as it operates at 460 mV overpotential to achieve  $10 \text{ mA cm}^{-2}$  anodic current density ( $j_{10}$ ). On the other hand,  $\text{ZnGa}_{0.25}\text{Al}_{1.75}\text{O}_4$ ,  $\text{ZnGa}_1\text{Al}_1\text{O}_4$ , and  $\text{ZnGa}_{0.5}\text{Al}_{1.5}\text{O}_4$  require 490 mV, 560 mV, and 590 mV of overpotential to achieve the same current density. The rest of the catalysts ( $\text{ZnGa}_2\text{O}_4$ ,  $\text{ZnGa}_{1.5}\text{Al}_{0.5}\text{O}_4$ ,  $\text{ZnAl}_2\text{O}_4$ ) exhibited poor OER

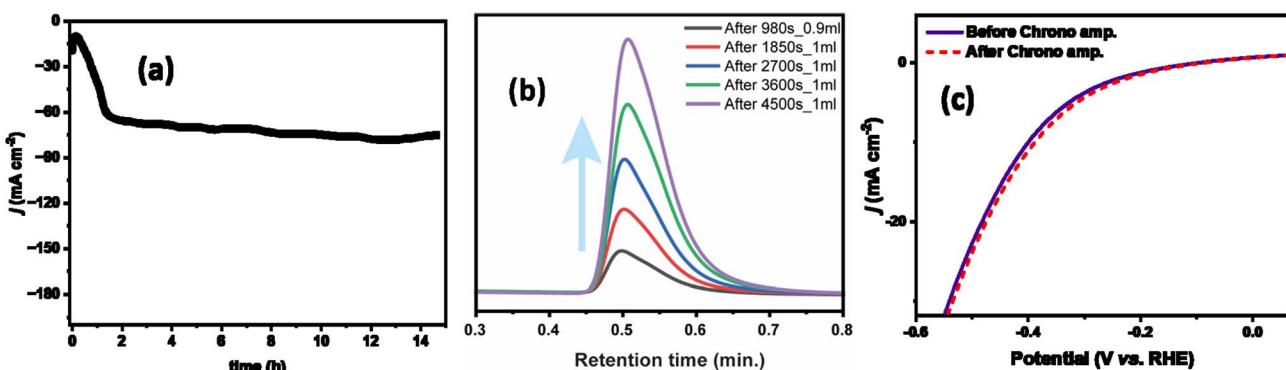


Fig. 7 (a) Time dependence of current density of  $\text{ZnGa}_1\text{Al}_1\text{O}_4$  catalyst under a constant potential of  $-1.45 \text{ V}$ , (b) volume of hydrogen gas measured during chronoamperometry test by gas chromatography, and (c) polarization curves, before and after chronoamperometry test of  $\text{ZnGa}_1\text{Al}_1\text{O}_4$  catalyst.



response as all of them necessitate  $>800$  mV of overpotential for significant  $O_2$  evolution under analogous conditions. The higher concentration of oxygen vacancies formed in  $ZnGa_{1.75}Al_{0.25}O_4$  which is obtained from XPS data is responsible for the higher OER activity. The change in concentration of oxygen vacancies with addition of Al can be explained in terms of antisite defects. Antisite disorder where cations are exchanged between tetrahedral and octahedral sites and Zn and oxygen vacancies are commonly reported defects in these materials.<sup>55,56</sup> The antisite disorder is energetically more favorable in  $ZnGa_2O_4$  than  $ZnAl_2O_4$ .<sup>56</sup> Though the reasons are not clear at this juncture, the doping of Al in  $ZnGa_2O_4$  which hinder antisite disorder might be causing more oxygen vacancies for charge compensation if Zn occupies octahedral sites.

Some of the previously reported electrocatalyst and their overpotential values are listed in Table S3.<sup>†</sup> It can be seen from this table that our OER and HER catalyst is having low overpotential values compared to those electrocatalysts. But we are aware of the fact that there are many more electrocatalysts with much lower overpotential values. So we would like to emphasize here that in this work, our aim is to unveil the structure–function relationship for Ga and Al-consisting Zn-spinels. Here, we have figured out the optimal ratio of Ga and Al for anodic OER and cathodic HER activity. Hence, we can now utilize different variants of the Zn-spinels in an electrolyser to drive the complete water-splitting.

**3.4.3. Electrochemical impedance spectroscopy.** The electrochemical characterizations of all catalysts were further analyzed by Electrochemical Impedance Spectroscopy (EIS).<sup>57</sup> The Nyquist plots were measured by the application of a sinusoidal wave with AC amplitude of 10 mV from  $10^5$  Hz to 0.1 Hz operating frequency range. To understand the better activity of  $ZnGa_{1.75}Al_{0.25}O_4$  catalyst towards OER, EIS was measured with DC applied potential 1.55 V, 1.6 V, and 1.65 V w.r.t RHE. Here we have compared the charge transfer resistance of all catalysts at 1.6 V applied potential.

All data are fitted by using an  $R(RC)$  circuit. The total electrical equivalent model consists of a solution resistance ( $R_S$ ), in a series with a parallel connection of internal resistance ( $R_P$ ) and a double-layer capacitance ( $C_{dl}$ ).  $R_P = R_S + R_{ct}$  can be illustrated as the sum of bulk electrolyte resistance and charge transfer resistance. For solid electrodes, double-layer capacitance can be replaced by a constant phase element (CPE).<sup>57</sup> The fitted data based on Fig. 6a are summarized in Table 3. The less  $R_{ct}$  (47.3 ohms) of  $ZnGa_{1.75}Al_{0.25}O_4$  indicates better electrocatalytic activity for OER compared to the other synthesized catalysts at the same applied potential (1.6 V). Fig. 6b shows the Nyquist plot of  $ZnGa_{1.75}Al_{0.25}O_4$  at 1.55 V, 1.6 V, and 1.65 V vs. RHE. Dotted lines are original data and solid lines are fitted one. All the data are fitted by using an  $R(RC)$  circuit with a minimal error ( $\chi^2$ , 0.05 to 0.08).

**3.4.4. Durability test.** Besides the electrocatalytic performance, the durability test is one of the major parameters for understanding large industrial-scale applications. Polarization curves confirmed that  $ZnGa_1Al_1O_4$  showed less overpotential towards alkaline hydrogen evolution reaction among all other synthesized catalysts. Therefore, to measure the HER stability of

the  $ZnGa_1Al_1O_4$  catalyst, chronoamperometric tests were assessed under a constant potential of  $-1.45$  V (Fig. 7a). The cathodic current initially increased with time and then got stabilized at  $-76.5$  mA  $cm^{-2}$  which indicates the good stability behavior of the catalyst.

The current density was slightly changed after 15 hours of chronoamperometry due to the sluggish mass transfer of HER and the blockage of some active sites of the catalyst. However, this catalyst exhibited fascinating faradaic efficiency of 88.7%. During the chronoamperometry test, the volume of  $H_2$  increased concerning time (Fig. 7b).

As shown in Fig. 7c, before and after the stability test the  $ZnGa_1Al_1O_4$  catalyst exhibited almost the same polarization curve with a slightly smaller overpotential of 360 mV to attain  $j_{10}$ . Also we have varied the current density from 50 mA  $cm^{-2}$  to 250 mA  $cm^{-2}$ , and observed a regular change in the potential. This experiment was performed over a period of  $\sim 16$  hours, where the potential remains stable at a current density of 250 mA  $cm^{-2}$ . This has shown in Fig. S6.<sup>†</sup> The leaching of the aluminum is not observed in the electrolyte and it is below the detection limit of the instrument (<1 ppm). This suggests the good stability of the electrocatalysts. ICP results are shown in Table S4.<sup>†</sup>

## 4. Conclusion

The present work comprises the synthesis of solvent-free one pot synthesis of  $ZnGa_2O_4$  to  $ZnAl_2O_4$  by changing the Ga/Al ratio *via* solid state reaction. The materials have been characterized by using XRD, FTIR, Raman, XPS, PALS and EDAX.  $ZnGa_2O_4$  showed a persistent luminescence of about 60 min with appreciable counts and the mechanism for the same has been proposed by using thermoluminescence studies.  $Al^{3+}$  incorporation reduces both PL and persistent luminescence duration owing to reduction in shallow traps and increase in non-radiative channels. Optical characterization indicates that  $ZnGa_2O_4$  spinel displays excellent PL properties, with PLQY  $\sim$  13%. Moreover, due to synergistic effect of  $Al^{3+}$  incorporation and formation of oxygen vacancy, the resulting solid-state solution of  $ZnGa_2O_4$  and  $ZnAl_2O_4$  catalyst showed a bifunctional catalytic activity and superior stability for the OER and HER reaction with very low charge transfer resistance for the former and high faradaic efficiency of  $\sim$ 90% for the later. Apart from the use of  $ZnGa_1Al_1O_4$  as electrocatalysts for HER,  $ZnGa_{1.75}Al_{0.25}O_4$  for OER catalysts, the unique PL and afterglow properties of  $ZnGa_2O_4$  indicate a promising potential of these materials for energy and solid-state lighting applications.

## Conflicts of interest

There are no conflicts of interest to declare.

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