Study of the electronic properties of $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ ($0.05 \leq x \leq 0.09$) by X-ray absorption and photoemission spectroscopy

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Abstract

The electronic structure of $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ ($0.05 \leq x \leq 0.09$) was investigated using X-ray absorption near edge structure (XANES) and X-ray photoelectron spectroscopy (XPS). Samples were prepared by the solid state reaction method. Using X-ray absorption spectroscopy, the investigation of $M_{4,5}$ absorption edge of Ho revealed that the electronic structure was directly influenced by the Ho concentration in the $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ sample whereas the crystal structure properties showed little/no correlation to the substitution of Ho. The electronic structure differs substantially from those of the reference ZnO. The O K-edge spectra suggest that the combination of the Ho with ZnO enhances the effective charge of the O ions. A systematic study on the composition from lower to higher value of Ho dopant showed the blue shift in band gaps and is discussed in the view of the electronic structure of the $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ samples. The inverse susceptibility ($1/\chi$) against temperature curves is plotted to identify the magnetic contribution. Those curves indicate that the substitution of Ho into the ZnO compound causes a weaker antiferromagnetic (AFM) interaction.

Keywords: Holmium, Surface Morphology, X-ray absorption spectroscopy, XANES, ZnO, AC-inverse susceptibility.

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1. Introduction

Among the transition metal oxides that are of increasing interest is zinc oxide (ZnO). ZnO is a II-VI compound semiconductor with a wide band gap of about 3.4 eV which has attractive properties for applications in optical devices such as wavelength tunable lasers, light emitting materials, bio-imaging, gas sensors and solar cells [1,2]. However, it is well known that dopants can strongly influence the optical behavior. The rare earth (RE) ion doped ZnO has the potential to be a highly multifunctional material with coexisting semiconducting, electromechanical and optical properties [3-6]. Rare earth doped ZnO systems also possess intrinsic ferromagnetism due to magnetic moments of the 4f electrons [7,8]. It is well known that doping of ZnO by optically active ions often exhibits high luminescence efficiency at room temperature [9]. RE elements are recognized as excellent candidates for luminescence centers due to their partially filled 4f energy level. Therefore RE doping of ZnO appears to increase optical properties and have been the focus of numerous studies because of their unique optical properties and promising potential applications in optoelectronic [10,11]. Recently, many important results for rare earth doped ZnO systems have been reported in the literature [12-14]. Furthermore, a recent study of magnetic and structural properties for the incorporation of Ho ions in the ZnO host has been conducted [15]. The electronic structure of the ZnO: Ho system has not been reported yet. A comprehensive understanding of the role of Ho ions in ZnO is of great importance to further material applications.

In this work, we present results of X-ray absorption spectroscopy, photoemission spectroscopy and magnetic properties of Ho ions embedded into the ZnO host. The effect of Ho concentration on the electronic structure of the ZnO: Ho system is studied. The XANES and XPS experimental results presented here will shed light on the origin of the functional properties of this relatively new family of materials. To the best of our knowledge, this is the first report of XANES of Ho incorporated into the ZnO matrix. XANES spectra at oxygen *K*, Zn *L* and holmium *M* edges have been used for the first time to give information on the role of Ho in the ZnO:Ho system.

2. Experimental method

The polycrystalline samples of $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ (for $x = 0.05, 0.06, 0.07, 0.08$ and 0.09) were synthesized from ZnO and HoO powders by the standard solid state reaction method. The raw materials were pure ZnO and HoO powders, which are known to be non-ferromagnetic or antiferromagnetic. In the solid state reaction route, appropriate amounts of ZnO and HoO were mixed and grinded in an agate mortar. The resulting powders were calcined at 350°C for 4 h in air, and thereafter they were left to cool in the furnace. After cooling, the resulting materials were grinded and palletized using a cylindrical die of 10 mm in diameter, under a pressure of 2×10^6 Pa (20 bar). Finally all the pellets were heat treated at 950°C in air for 24 h, following which the furnace was cooled to room temperature.

XANES and XPS measurements were performed on beamline 8.2 at the Stanford Synchrotron Radiation Lightsource (SSRL) in the SLAC National Accelerator Laboratory. The base pressure of the experimental chamber during the experiment was $\sim 2.0 \times 10^{-7}$ Pa. The total electron yield (TEY) mode was used by measuring the sample current. The current measurements were done using a low noise preamplifier Stanford Research System Model SR570. The incoming synchrotron beam flux (I_0) signal from a gold grid was utilized to normalize the spectra. The AC-magnetic properties of the films were explored by measuring the in-phase components of their AC-susceptibilities. The AC-susceptibility apparatus was a Quantum Design PPMS with a closed cycle helium cryostat, from 10 K to 300 K, and the measurements were carried out in a field of 10 Oe at 1 kHz.

3. Results and discussion

3.1. XANES results

X-ray absorption spectroscopy (XAS) is a powerful tool for chemically sensitive local structural determination. The use of XAS, or more specifically the XANES, indicates that the features that appear in the XAS are due to the photoabsorption cross section for electronic transitions from an atomic core level to final states. The XANES of ZnO at O K -edge probes the orbital character of the O $2p$ unoccupied states in the conduction band and their hybridization with Zn and Ho orbitals. In order to understand the role of O $2p$ in the samples, XANES measurements at the oxygen K , Zn L and Ho $M_{4,5}$ edges were performed. The O K edge

absorption spectra of $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ samples are displayed in Fig. 1. The spectra are normalized by subtracting a straight line fitted to the region before the peaks (below 530 eV), and adjusting the intensity of the spectra to 1 at 570 eV. The spectra were recorded in total electron yield (TEY) mode at room temperature.

For metal oxides, the absorption spectra at O *K* edge arise from the covalent mixing of the metal and the oxygen states. In the photon energy region of 530–539 eV, absorption spectra can be mainly assigned to the O 2*p* hybridized with Zn 4*s* states. In the region of 539–550 eV the spectrum is mainly attributed to O 2*p* hybridized with Zn 4*p* states. Above 550 eV, the contribution is mainly from O 2*p*-Zn 4*d* mixed states [16]. By comparing the ZnO absorption spectrum to Ho doped spectra in Fig. 1, the pre-edge peak at ~535 eV evolves with Ho concentration, which clearly suggests that Ho ions are incorporated in the system and affect the electronic structure of the samples. The pre-edge peak is mainly due to dipole transitions from O 1*s* to O 2*p* states that are hybridized with Zn 4*p* and Ho 5*d* 4*f* states [17,18]. The intensity of pre-edge and the main peak at ~538 eV decreases with increasing Ho concentrations as shown in the upper inset of Fig. 1. The decreasing of the main peak intensity with Ho doping shows that the number of O 2*p* unoccupied states decreases with the increase of Ho concentration in the samples. The intensity of the oxygen *K* edge absorption peak, which is proportional to the number of holes in the oxygen valence band, confirms that the oxygen occupation increased with Ho concentration. Thus, the significant decrease of the absorption intensity of the O *K* edge indicates an increase of the occupation of O 2*p* level by Ho doping. The increase of the effective charge on the O ions with Ho concentration can be explained by much lower electronegativity of Ho (1.23) than that of Zn (1.65), which decreases the average electronegativity of cations.

Fig. 2 shows the normalized XANES spectra of $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ samples at the Zn *L*-edge in TEY mode. The Zn *L*₃ edge is composed of three peaks at 1028, 1032 and 1037 eV. According to the dipole-transition selection rule, Zn *L*-edge XANES probes the unoccupied Zn *s* and *d*-derived states. The Zn 3*d* orbital is fully occupied with 10 electrons, so the lowest unoccupied orbital of the Zn ion is 4*s*, followed by Zn 4*p* and 4*d*. The first peak after 1020 eV can be mainly ascribed to the Zn-4*s* components, while the others, following the first peak, are mainly derived from the Zn 4*d* and O 2*p* hybridized band components [17,19]. The lower inset of Fig. 2 represents Zn *L*-edge XANES spectra of ZnO reference and two distinctive $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ ($x =$

0.09 and 0.05) samples to demonstrate the effect of Ho doping. One can notice that L -edge intensity first increases with holmium doping, but the intensity decreases as x continues to increase in the sample, which may be associated with the changes in the local environment. Fig. 3 shows the peak height of Zn L_3 , which is calculated from the integrated area under the Zn L_3 peak in Fig. 2. It can be observed that Zn L_3 -edge absorption intensity, is sensitive to the crystallization of ZnO by the clear decrease of the peak intensity of the $x = 0.09$ sample as compared to reference ZnO [15]. The higher the L_3 -edge absorption intensity, the larger the density of Zn $4s$ and $4d$ states due to the presence of defects caused by Ho / or a lower atomic Zn concentration in the sample [20]. It is understandable that XANES spectra of the Zn L_3 edge are attributed to the unoccupied Zn s and d derived states. Thus, the observed results represent that the number of unoccupied $4sp$ and $3d$ states and the number of neighbouring atoms are reduced with x value in the $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ samples.

The spectra of the Ho ions in the $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ samples generally resemble the major contribution of the trivalent state to the electronic transitions at the Ho $3d$ edges. For the holmium, the $M_{4,5}$, white line will be a doublet representing $3d_{5/2}$ and $3d_{3/2}$ excitations to the partly filled $4f$ shell. X-ray absorption spectroscopy of the Ho $3d$ level yields sharp peaks at 1352.5 and 1390.7 eV (Fig. 4). The XAS measurements of Ho at the $M_{4,5}$ edge were performed in the total yield mode. Double peaks in the spectra were resulted from the $3d^9 4f^{n+1}$ spin-orbit splitting of the $3d$ hole, the strong Coulomb and exchange interaction of the $3d$ and $4f$ electrons. $M_{4,5}$ absorption spectra of Ho originate from $3d$ to $4f$ levels which are due to $3d^{10} 4f^{11} \rightarrow 3d^9 4f^{12}$ transitions. Transitions from $3d$ to the unoccupied $5p$ state are also allowed but have a negligible cross section compared to the $3d$ to $4f$ transitions [21]. It has been shown that the peak position of the M edge increases in energy from pure $4d$ metals to their metal oxides which is related to the oxidation states [22,23]. As observed the Ho M -edge absorption peak of ~ 1352 eV slightly shifts to high energy on the increasing Ho concentration as a result of the increasing oxidation states of oxygen.

In order to study the effect of Ho concentration in the sample more quantitatively, the full-width at half-maximum at the M_4 and M_5 edges as a function of the Ho concentration was examined (see Fig. 5). The change of FWHM in Fig. 5 cannot be explained by any change of $3d$ core levels, and it can only be related to the change in the unfilled states. The measured FWHM

of M_4 and M_5 decrease from 16.8 to 11.3 and 7.0 to 6.3 respectively due to a change in $4f$ level with the x value in the sample.

The reduction in FWHM correlated to a reduction in the width of the $4f$ band. The line width decreases with the increasing Ho ratio resulting in sharp peaks. However the intensity of M edge absorption is strongly dependent on $3d-4f$ transitions and the number of $4f$ final states available. When such $4f$ vacancies are present a strong and sharp peak is observed near the band edge. Therefore the lifetime is very sensitive to the band structure of the unfilled $4f$ band state. It has been shown that the measured white line width for any oxide is less than that of the corresponding metal [24]. Higher holmium concentration in the samples increases the oxidation states which results in a reduction of the FWHM in $M_{4,5}$ edges.

Fig. 6 presents the measured branching ratio (BR) intensity as a function of the Ho concentration in the sample. The area under the peaks of the M_4 and M_5 lines would be the correct measure of their intensity, which is proportional to the oscillator strength of the $3d-4f$ spin-orbit interaction. On the other hand, the normalized branching ratio $I(M_5) / I(M_5 + M_4)$ represents a high-spin state rather than a low-spin-state. It can be seen in Fig. 6 that the BR changed significantly from 0.6 to 0.7 as Ho concentration increased. The measured BR values were consistent with the values obtained from previous research for rare earth series, which were changed from 0.39 (in La) to 1 (in Yb) in the lanthanides [25]. The higher BR indicated stronger spin-orbit interaction of Ho $3d$ electrons as x value increased in the sample. However, all the samples have a lower branching ratio compared to the bulk Ho of 0.89 [26]. The plotted curve in Fig. 6 shows that the electronic structure changes little with increasing Ho concentration. The x value ($0.05 \leq x \leq 0.09$) dependency in the sample clearly indicates that the spectrum of Ho can be quite different than the bulk structure.

3.2 XPS results

Fig. 7 shows the valence band X-ray photoelectron spectra of ZnO:Ho samples. Normal XPS were recorded with 400 eV photon energy and all spectra calibrated by C 1s peak (284.6 eV) from surface contamination. Each spectrum referenced to Fermi edge at 0 eV and two characteristic peaks are observed.

The measured spectra are normalized with the photoelectron current measured by a gold mesh and the secondary electrons background of the spectra was subtracted using the Shirley method [27]. Based on the pure ZnO spectral properties the main peak at a binding energy of ~ 10.9 eV can be assigned to Zn $3d$ contribution, whereas the broad peak at ~ 5.3 eV binding energy can be attributed to O $2p$ and Zn $4sp$ -O $2p$ mixing contribution [28,29]. As the doping of Ho gradually increased, both peaks were suppressed, whereas a new peak become apparent at 6.5 eV binding energy. This peak mainly involves the Ho-O bonding and is formed through hybridization between Ho $5d$ $4f$ and the O $2p$ levels. In the region of the first peak just after E_F the valence band maximum (VBM) can be determined by linear fit as shown in the inset in Fig. 7. The VBM is located at the intersection point between the fitting line and the background. It is was found that the VBM of $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ samples shifted from 3.1 to 3.8 eV as the x value increased in the sample. A similar shift to the higher binding energy side is also observed for the Zn $3d$ peak. According to the Burstein–Moss effect [30], the bandgap change is in one direction with the increase of holmium (x) level in the sample, the bandgap is blue-shifted due to the increase of carrier concentration.

Zn $3p$ core level photoemission spectra were recoded to investigate how the electronic structure of ZnO modifies upon Ho doping. Fig. 8 shows the Zn $3p$ XPS spectra of $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ samples. The spectra consist of two Zn $3p_{3/2}$ and $3p_{1/2}$ doublets, located at 87.9 and 90.6 eV, respectively. Note that the binding energy of $3p$ doublets moves to the higher binding energy side by ~ 0.2 eV upon Ho doping, which is also seen for the Zn $3d$ peak. The intensity of the $3p_{3/2}$ and $3p_{1/2}$ peaks which was calculated from the area under each peak showed that it progressively decreased as the value of x increased in the sample.

3.4 Magnetic characterization

Ho^{+3} ions have the capacity to successfully substitute the Zn^{+2} ion in the ZnO lattice, which indicates the existence of the ZnHoO phase, and that the magnetic moments of doping Ho contribute as a source of magnetism in the samples.

The plots of the inverse AC magnetic susceptibility ($1/\chi$), as a function of temperature T , are shown in Fig. 9. The behavior presented there is a characteristic of all the TM-doped ZnO samples. The high temperature parts of the curves clearly display Curie-Weiss behavior [31]:

$$\frac{1}{\chi} = \frac{(T - \theta)}{C} \quad (1)$$

where, θ and C are the so called Curie-Weiss temperature and Curie constant respectively. Therefore, the data at higher temperatures could be fitted to some straight lines. These straight lines have been extrapolated towards the lowest temperatures to obtain the Curie-Weiss temperatures, θ , which are indicative of the nature and strength of couplings between the magnetic moments in the lattice. Fig. 9 indicates that all the θ , values are negative, hence the samples have antiferromagnetic interactions. For the $x = 0.09$ sample (having larger χ), θ is small and negative (≈ -24.84 K), but for the smaller values of the concentrations, the magnitudes are bigger indicating that the antiferromagnetic couplings increase with the decreasing concentrations of the magnetic ions in the ZnO lattice. The values of θ for the lower concentrations are for $x = 0.05, 0.06, 0.07$ and $0.08 \approx -27, -28, -31$ and -35 K, respectively.

The shape of AC magnetic susceptibility, $1/\chi$, indicates weak ferromagnetism in the samples. It is believed that ferromagnetic interactions arise in bulk samples due to substitution of the Ho^{3+} ions in the ZnO host lattice. The oxidation state of the Ho^{3+} ions, which is +3, was measured by XPS. There are a number of reports which show that ferromagnetic behavior in the (TM-RE) doped ZnO system is dependent on doping percentage, the less the doping quantity, the more ferromagnetic behavior [32]; the results shown in Fig. 9 support this. It is well known that Ho existing in the +2 oxidation state has no unpaired spins so there is no ferromagnetic contribution; while a Ho ion having +3 state has unpaired spins exhibiting net magnetic moment and can contribute to ferromagnetic behavior [33]. These findings indicate that there is a possible spin state transition when the temperature is close to zero K, clearly the orbital contribution to μ_{eff} in this temperature decreases. The O 1s core peak spectrum, also not shown here, exhibits asymmetrical trends in BE. The presence of multi-component oxygen species is the reason for asymmetry in oxygen BE values. In summary, a detailed XPS analysis of samples indicates different oxidation states of dopants, of which the dominant state is +3, which is the expected cause of ferromagnetic behavior in the samples.

In addition to the experimental measurements, we also performed XANES calculations to determine the distances of atomic species from a selected zinc atom. The theoretical treatment is implemented in the *ab initio* XANES and electronic structure code of FEFF 8.2 [34]. The

calculated radial structural function is shown in Fig. 10, which represents the atomic distribution around Ho. In the calculations, a Zn atom in the wurtzite ZnO cluster was selected as the absorber and a photoelectron emitter. Structure parameters for the starting models have been obtained by x-ray diffraction (XRD) analysis of the same samples (not shown here). All distances are determined from the Zn atom located at the origin. The nearest neighbor Ho atom from Zn is found at 2.75 and 3.31 Å for $x = 0.09$ and 0.05 respectively. The first neighbor atom from Zn should be O. The first peak in Fig. 10 shows the distances of Oxygen atoms (Zn-O) at 1.59 Å. The second and the third peak intensities are superposition of different signals from the atomic groups which are located closer to each other. These results confirm that all the Ho ions occupy the Zn sites in the ZnO lattice.

4. Conclusions

The $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ pellet samples ($x = 0.05, 0.06, 0.07, 0.08$ and 0.09) were synthesized and their electronic properties were studied by XANES and XPS. The band gap is found to increase with addition of Ho. The characteristics of the ZnO:Ho samples exhibited that Ho doping has a strong effect on structural and electronic properties, which could be shown in the significant increase in the band gap due to doping level and electron transfer from Ho to oxygen. There is a monotonic decrease in the Zn L_3 edge intensity with the increasing Ho concentration, which is partially substituted for Zn. This could be attributed to decrease of Zn $3d$ -O $2p$ hybridization with the decreasing ionic radius of Zn. The experimental results showed that the Ho doped ZnO samples had room temperature ferromagnetism. Ho ions were in trivalent state $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ samples. Ferromagnetism of the samples originates by the substitution of Zn^{2+} with Ho^{3+} in the ZnO. We have tried further increasing of holmium concentration up to $x=1.2$. However, the higher levels of the Ho doping did not improve the magnetic structure further. Our XRD measurements showed that the crystal structure of the sample degrades when the doping amount increased beyond $x=0.09$. All our experimental and theoretical results indicate that optimization of Ho concentration by substituting Zn sites in the ZnO matrix is an effective method to improve the magnetic and crystal structures. The Ho doped ZnO compounds could be suitable for applications such as sensors and optoelectronic devices and-magneto-optical device applications. The strong correlation between structural, optical, and magnetic properties was illustrated in the different properties of ZnO and Ho-substituted ZnO. Finally, enhancement of magnetism was

detected in Ho-substituted ZnO samples, which may lead to novel applications in spintronic devices.

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Figure captions:

Figure 1: Oxygen K-edge XANES spectra of ZnO and $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ samples for $x = 0.05, 0.06, 0.07, 0.08,$ and 0.09 . The upper inset shows the zoom-in region of main O 1s peak for comparison.

Figure 2: XANES spectra of $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ ($x = 0.05, 0.06, 0.07, 0.08$ and 0.09) samples and ZnO reference at the Zn $L_{3,2}$ edge region recorded at room temperature. The spectra normalized by subtracting a straight line fitted to zero before L_3 edge, and adjusting the intensity of the spectrum to 1 at 1100 eV. The lowest inset shows the spectra of ZnO reference and $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ ($x = 0.05$ and 0.09) samples for comparison.

Figure 3: Normalized peak intensity of Zn L_3 edge at 1033 eV as a function of Ho in $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ samples.

Figure 4: Normalized and the background-corrected total electron-yield (TEY) spectra of the $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ samples at Ho $M_{4,5}$ edges. Ho concentration (x) for each spectrum is indicated.

Figure 5: M_4 and M_5 main peak full-width at half-maximum (FWHM) in the total electron-yield (TEY) as a function of Ho concentration in the sample. The drawn line serves only to guide the eye.

Figure 6. Branching ratio of the background-corrected intensities at the $M_{4,5}$ edge as a function of Ho ratio. The drawn line serves only to guide the eye.

Figure 7: Valence band XPS spectra of $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ samples. X values in the sample shown on the each spectrum. The inset shows VBM determination by the fitted curve.

Figure 8: The Zn $3p$ XPS spectra of $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ samples. The numbers on the each spectrum show x value in the samples.

Figure 9: AC-susceptibility curves for the $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ compounds at 1 kHz in a field of $H = 10$ Oe.

Figure 10: The radial structural function of two distinctive $\text{Zn}_{0.8-4x}\text{Ho}_x\text{O}_y$ samples ($x = 0.05$ and 0.09) .

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