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Cr doped ZnO nanostructures: synthesis, electronic structures and magnetic properties

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Abstract

We report an experiment in which we have attempted to dope Cr into ZnO nanostructure as a function of dopant concentration using sol-gel method, followed by controlled thermal annealing with some success. We have also examined the samples thus prepared with scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Near Edge X-ray Absorption Fine Structure (NEXAFS), both theory and experiments, and magnetic measurements. We found that low concentration of Cr can indeed be doped in ZnO and is substitutional, occupying the tetrahedral site. However, upon increasing dopant concentration and annealing temperature, a secondary phase with Cr occupying an octahedral site precipitates out as evident from SEM, XRD and NEXAFS. Ferromagnetism at room temperature was not observed in any samples although at low Cr concentration and 400 °C processing temperature antiferromagnetism can be seen but at higher concentrations or processing temperatures the samples show only paramagnetism.

Keywords

Dilute magnetic semiconductor, doped zinc oxide, XAFS, NEXAFS, spintronics

Introduction

In the age of rapidly advancing information technology, it is becoming clear that new devices must be developed to handle high volume data for information storage and processing. Increasing the capabilities of these new devices has become crucial to their development. More specifically, one of the areas of development is spintronics, and dilute magnetic semiconductor (DMS) materials that nominally are semiconductors, but can exhibit ferromagnetism at room temperature. DMS offer a route to integrating information and processing into a single material since DMS are able to make use of both the spin and charge of electrons.¹⁻³ Adding the spin degree of freedom to conventional charge-based electronics will allow for many advantages including non-volatility, increased data processing speed, decreased electric power consumption and increased integration densities.⁴ The cultivation of these materials will be of utmost importance in minimizing the size of magnetic domains to allow for spin polarized current to be transferred throughout spintronic devices to achieve both reading and writing capabilities.

The interest in studying zinc oxide for spintronics applications was motivated by the work of Dietl et. al. and others who show that transition metal doped ZnO could result in materials with abnormally high (above room temperature) Curie temperature T_C .⁵ Below the T_C of a DMS, the spin of unpaired electrons from the transition metal will align and magnetization will persist resulting in ferromagnetism.⁶

While there has been considerable work conducted on transition metal such as Co or Mn doped

ZnO,⁷ results on Cr doped ZnO is relatively lacking, there has been intriguing evidence suggesting that Cr-doping may result in a ferromagnetic state which is more stable than a spin glass state.⁸

To understand the phenomenon of ferromagnetism in DMS further, we must consider how the spin populations become different. The best way to do this is to track the densities of states of a ferromagnetic oxide containing 3d impurities. A projected density of states (DOS) diagram of chromium doped zinc oxide is expected to be asymmetric which means that one spin state will be more populated than the other. It can be shown that both a spin split impurity band and unpaired electrons from the 3d ions contribute to the spin imbalance and ultimately the overall magnetic behavior of the material.¹⁻⁶

Debate remains over whether or not DMS have the potential to be integrated into practical technological applications. While some groups have reported observing room temperature ferromagnetism in Cr:ZnO materials,⁹⁻¹⁴ others have refuted such evidence.^{15,16} This controversy currently impedes the development of Cr:ZnO materials and debate will continue until we can show and explain why certain DMS display different Curie temperatures and magnetic properties. Previous work by Leedahl et al. has looked at Cr:ZnO with NEXAFS but only at a single concentration and processing temperature.¹⁷ In this work, we focus on a series of Cr:ZnO samples prepared by a sol-gel method and their characterization in an effort to provide a link between morphology, secondary phase formation, defects and magnetic properties. Changes in the electronic structure can be directly influenced by nanoparticle size. These effects are known as size-dependant quantum effects.¹⁸ In this work, the effect of Cr concentration and particle size

on the electronic and magnetic properties of chromium-doped zinc oxide will be studied via controlled synthesis.

The term sol-gel synthesis quite literally describes itself. Starting with a dispersion of colloidal particles in a liquid (sol), synthesis ends with a nano-porous, interconnected, rigid network of polymeric chains (gel). Initial gel formation (gelation) is usually preceded by several steps, which include aging, drying and densification.¹⁹ These steps are designed to tailor the final nanostructure of the product. The use of sol-gel synthesis is extremely attractive in this work as it enables temperature dependent control over nano-particle size. This will allow for the study of particle size-dependent effects on electronic and magnetic properties.

The samples thus obtained have been characterized with X-ray Absorption Fine structure spectroscopy (XAFS), especially, the Near Edge X-ray Absorption Fine Structure (NEXAFS) technique and magnetic measurements. The interpretation is supported by band structure calculations and NEXAFS simulation using the Wien2k package.²⁰

XAFS is the study of X-ray absorption by atoms in a given chemical environment, in terms of absorption coefficient from below to above an elemental specific absorption edge (electron excitation threshold of a given core level). Beer's Law (Equation 1.1) describes the photon energy dependent absorption of x-rays by a material at normal incidence:

$$I = I_0 e^{-\mu t} \quad (1),$$

where I_0 is the x-ray intensity incident on a sample, $\mu(h\nu)$ is the photon energy dependent absorption coefficient, t is the sample thickness and I is the intensity transmitted through the sample. Tunable X-ray is provided by a synchrotron, the Canadian Light Source.^{21,22}

XAFS spectra are typically divided into two regimes: near edge x-ray absorption near-edge fine structure (NEXAFS) and extended x-ray absorption fine structure (EXAFS).²² For our purposes, we use NEXAFS data for characterization. When an incident X-ray possesses energy equal or greater than the binding energy of a core electron, a sharp rise in absorption is observed. In a free atom, there are often sharp transitions below the ionization threshold call Rydberg transitions and above the threshold (edge) the absorption coefficient is monotonic as photon energy increases above the threshold. When the atom is in a chemical environment however, be it molecule or condensed matters, molecular orbits and bands are formed; transition to the unoccupied states, such as LUMO and LUMO plus in molecules or the conduction bands in semiconductor or band states just above the Fermi level in metals, will result in resonances characteristic of the environment. These are dipole transition ($\Delta l = \pm 1$, $\Delta j = 0, \pm 1$); thus the K-edge (1s) probes unoccupied state of p character and $L_{3,2}$ -edge ($2p_{3/2,1/2}$) probe d and s characters; further increase in photon energy above the threshold will result in photoelectron with low kinetic energy which will propagate away from the absorbing atom, undergoes multiple scattering by the surrounding atoms, bring the information of the neighborhood via backscattering to the absorbing atom. This results in the so called multiple scattering resonance in the near edge region (up to ~ 30 eV above the threshold), beyond that, the kinetic energy of the photoelectrons increases sufficiently and single scattering become dominant, this is the EXAFS region.⁷

Clearly, the measurement of XAFS requires a tunable X-ray source, the synchrotron. NEXAFS are strongly sensitive to the oxidation state and local chemical environment. This will allow us to determine how the chromium atoms interact with the zinc oxide host lattice enabling the determination of whether the chromium atoms are substitutional or interstitial in nature. NEXAFS is also sensitive to coordination chemistry. Any secondary phase will be detected and the lattice type will be evident from analyzing the spectra.⁹

X-ray powder diffraction helps examine the crystal structure of a material. The crystal structure and size of nano-particles can be determined from XRD experiments. XRD is based on Bragg Diffraction;¹⁰ the particle size can be estimated from the width of the diffraction peak from the Scherrer equation.

2 Experimental Procedures

SOL-GEL SYNTHESIS

The first step in the synthesis of zinc oxide nano-particles was to prepare the sol. First, 2.00 g of zinc-acetate was mixed with one molar equivalent of citric acid and 30 mL of water in a 250 mL beaker. This leads to hydrolysis of the zinc acetate to form zinc hydroxide:

Next, 80 mL of 30% (v:v) ammonium hydroxide was added to the solution. As the pH of the solution rises, the equilibrium starts to heavily favor the formation of $[\text{Zn}(\text{OH})_4]^{2-}$

In many cases, zinc atoms could exist as $\text{Zn}(\text{OR})_4^{2-}$ where R is a citrate ion, acetate ion or a hydroxide ion. In the pursuit of creating high quality nano-particles, attention to particle size distribution is important.¹⁸ If we are to observe quantum size effects, particle size distribution must be kept to a minimum to produce precise findings. To achieve this, effective control of agglomeration must be employed. The sol gel method is an outstanding route for nano-particle synthesis since particle size and agglomeration can be controlled effectively by altering different variables of the synthesis. One way to inhibit rapid growth of particles is to add ligands that competitively bind to the zinc decreasing their functionality and inhibiting further hydrolysis. In this case, the citrate ions in solution can bind to the zinc atoms. The citrate ion is less hydrolysable than the acetate ion and effectively “blocks” nucleophilic substitution wherever it happens to be binding. This slows down the rates of both hydrolysis and condensation reactions that act to form the zinc oxide oxo-polymers.¹¹

This solution is stirred for six hours to allow for the formation of sufficient colloidal particles. After six hours stirring, we heat the solution to 90°C for 18 hours. During this stage, condensation reactions continue and the gel is formed. Another very important factor that affects the size of nano-particles is the final processing temperature. To study the effect of temperature on the size of nanoparticles, three different temperatures were used; 400, 600 and 800°C. As the gels are heated up, all of the organic materials and solvents occupying the nano-porous structure of the gels are evacuated and significant “cracking” occurs. The end product is a nano-powder.

Samples processed at 400°C are expected to contain the smallest nanoparticles. As the processing temperature is increased to 600°C, severed bonds are expected to anneal, increasing

crystallinity, and resulting in agglomeration leading to larger nanoparticles. Therefore, it is expected that powders processed at 800°C will have the highest crystallinity and largest particle size. Having samples with varying processing temperatures will enable the study of particle size and its effect on crystal structure, secondary phase formation and the resultant magnetic properties.¹²

DOPING

An important factor to consider when studying magnetism is the concentration of the dopant (chromium). Three different chromium concentrations were used; 1, 5 and 10% to study effects on the morphology and electronic properties of the DMS. The dopant was added as chromium acetate with zinc acetate in the first step. The molarity of transition metals was kept equivalent for each samples resulting in molar ratios of $\text{Zn}_{0.9}\text{Cr}_{0.1}\text{O}$, $\text{Zn}_{0.95}\text{Cr}_{0.05}\text{O}$ and $\text{Zn}_{0.99}\text{Cr}_{0.01}\text{O}$. Varying the dopant concentration will provide the opportunity to study how dopant concentration affects particle size, magnetic properties and the structural (substitutional or interstitial) nature of the dopant.

CHARACTERIZATION

All SEM images were taken at the University of Western Ontario Nanofabrication Facility using a LEO 1530 Field Emission Scanning Electron Microscope operating at 1 keV. All XRD data was collected using an Inel x-ray generator ($\text{Cu } K\alpha$ 1.54056 Å). All scans were performed using 30 kV and 20 mA. Match software and results collected by the International Centre for Diffraction Data were used for phase identification.

NEXAFS experiments reported in this paper were conducted on the high resolution spherical grating monochromator (SGM) beamline (11ID-1) at CLS in Saskatoon, Saskatchewan. The SGM beamline is capable of probing energies ranging between 250 and 2000 eV ($E/\Delta E > 5000$). Oxygen *K*-edge spectra were obtained from 520 – 570 eV, the chromium *L*-edge spectra were obtained from 570 – 595 eV and zinc *L*-edge spectra were obtained by scanning from 1000 – 1080 eV with a spot size of 1000 μm x 100 μm . The NEXAFS signal was recorded in total electron yield.

MAGNETIZATION MEASUREMENTS

Magnetic susceptibility measurements were performed on a Quantum Design Physical Property Measurement System (PPMS) over the temperature range of 2-300 K. The sample chamber was purged and sealed at 1-2 Torr. Samples were transferred to a polycarbonate capsule using a straw (cut in half and lengthwise and then washed to ensure no metallic traces are present). Since the powders are very light, it was compressed in the capsule with a PTFE cylinder. This was done so that 1) the sample does not move during measurements and 2) to ensure the maximum sample for the highest response.

Once the capsule was filled, it was capped and taped (with non-magnetic tape from 3M) and inserted into a straw to the approximate desired position. The sample was then inserted in the instrument and the sample center was located and repositioned as necessary until the sample center was nearest to 0.0 cm (with an applied field of 10000 Oe). At that point (centered), the hysteresis curve from 1T to -1T and back to 1T was taken at 300K, with a concentration of data points between 2000 and -2000 Oe. After this, the field was set to 0 Oe and the sample was zero-

field cooled to 2K where the sample center was located once more and a second hysteresis curve was recorded using the same parameters as the one at 300K. Then the field was set to 10000 Oe and the temperature was scanned in 75K increments, the reason being to locate the center as the holder length will change due to thermal expansion.¹⁴

THEORETICAL CALCULATION of DOS and NEXAFS

The Wien2k software package²⁰ was used to calculate the densities of states of Cr₂O₃, Cr doped ZnO with Cr in both octahedral and tetrahedral sites and simulate the NEXAFS at the Cr L-edge and the O K-edge. The calculation is based on the Density Functional Theory^{23,24} with the Generalized Gradient Approximation²⁵. Starting with a crystal symmetry, the WIEN program calculates the ground state of the crystals using the linearized augmented plane wave (LAPW) method. The valence states relativistic effects can be included in a scalar relativistic treatment. Core states are treated fully relativistically. The calculations were performed with the self-consistent cycles until the minimum energy of the states had reached. The NEXAFS spectra were then obtained by the transitions between the states following the selection rule of $\Delta l = \pm 1$. The models of the crystals are shown in Table 1.

3. Results and Discussion

SEM IMAGES

The SEM images (Figure 2) show a clear variation in particle size ranging from approximately 5 – 50 nm. This variation in particle size is shown to be temperature dependent rather than dopant dependant. The dopant appears to affect the structure of the nanoparticles rather than the size. The Cr:ZnO samples that were processed at 400°C have a very small particle size; roughly 5 – 10

nm. No distinguishable difference between image a) and image b) is noted. The dopant concentration has no noticeable effect on the nano-particle size. By looking at images c) and d), it is apparent that nano-particle size is a temperature dependent property. The size of nano-particles changes drastically when raising the annealing temperature to 800°C from 400°C. Although the dopant concentration does not affect the size of the nano-particle, images c) and d) clearly demonstrate a change in morphology from a more hexagonal crystal shape in image c, to a more cubic crystal shape in image d).

The sample containing 10% Cr (d) displays a more crystalline structure with what looks to be a cubic type lattice. This could indicate secondary phase formation as zinc oxide typically displays a hexagonal Wurtzite structure.

XRD DATA

Selected XRD data obtained for various Cr:ZnO specimens are summarized in Figure 3.

From analyzing of the XRD the spectra obtained from all of the Cr:ZnO samples, we can determine the structure of each phase detected and relate specific peaks to their corresponding planes in the crystal structure of whatever phase is detected using the *hkl* coordinate system.

Distinctive to all spectra obtained for Cr:ZnO are the three large peaks between 2θ values of 30° and 40° . These peaks are characteristic of the zinc oxide hexagonal structure (Figure 4b). The first peak at approximately 31.7° corresponds to the plane represented by (100). The second peak at 34.5° corresponds to the (002). The third and largest peak shown in all spectra at 36.2° corresponds to the (101) plane. The peaks characteristic to planes in the Al

Sample holder are labelled as such. The spectra of samples processed at 400°C show only the spectral properties of zinc oxide. Figure 3 shows the emergence of new peaks (Δ) in samples processed at higher temperature, most notably a peak at approximately 30° and a shoulder at 36°. These (Δ) peaks correspond to the spinel structure of $\text{Zn}(\text{Cr}_2\text{O}_4)$ (a cubic arrangement) shown in Figure 4 together with the hexagonal ZnO structure and that of Cr_2O_3 . In both Cr compounds the Cr occupies the octahedral site whereas in $\text{Cr}:\text{ZnO}$, the Cr is substitutional in low concentration. This data supports the formation of a cubic secondary phase as suggested from the SEM images (Figure 2). Peaks corresponding to this proposed secondary phase are more prominent in samples with high processing temperature and high Cr concentration.

Comparing the XRD spectra of material processed at 400, 600 and 800°C to one another, it is immediately noticeable that the peak sharpness drastically increases for samples of higher processing temperature. This gives us information regarding the morphology of the material. This type of peak broadening is a common effect of particle size. Scherrer's equation relates particle size to line broadening:

$$\beta = K\lambda / (L \cos \theta/2) \quad (2)$$

where λ is the wavelength of the incident x-rays, β is the half value breadth of the diffraction beam and $\theta/2$ is the Bragg angle, L is the linear dimension of the particle and K is a numerical constant that Scherrer determined to be 0.93.²⁶ Due to the peak broadening that occurs for samples of lower processing temperatures, we can infer that the particle size is related to processing temperature. As we increase the processing temperature, we are seeing an increase in

particle size (in agreement with the SEM images). This is due to the agglomeration that occurs between the small particles formed at 400°C as the temperature rises to 600 and 800°C.

NEXAFS

NEXAFS reveal the densities of states characteristics governed by the dipole transition and local symmetry.²² The NEXAFS at the Zn L-edge, Cr L-edge and O K-edge are shown in Figures 5 (a), (b) and (c) respectively below. Figure 5 (a) shows the zinc *L*-edge spectra, the absorption edge at approximately 1020 eV is the *L*₃-edge which corresponds to the threshold energy of a $2p_{3/2} \rightarrow 4s, 3d_{5/2} 3d_{3/2}$ dipole transitions with the d channel being the dominant one in transition metals with unoccupied d states due to higher cross-section and occupancy. The other sharp rise at 1030 eV is the *L*₂-edge corresponding to the energy of a $2p_{1/2} \rightarrow 4s, 3d_{3/2}$ transition. Since the Zn 3d states are full so the absorption is largely due to transition to the unoccupied densities of states with s character in the conduction band. The zinc *L*_{3,2}-edge NEXAFS are very similar in all Cr:ZnO samples as the intensity and shape of each spectrum is nearly identical. As we have seen from the SEM and XRD, secondary phase formation involving Zn(Cr₂O₄) appears possible, it appears at first glance as though any secondary phase would not contain zinc atoms. If zinc was involved in any secondary phase formation, we would expect to see a change in the spectra as processing temperature and dopant concentration was varied. However, the possibility of Zn(Cr₂O₄) cannot be ruled out entirely as Zn would retain a 2+ oxidation state and the same tetrahedral coordination to oxygen as in wurzite ZnO in a spinel type structure. It is expected that Zn in a ZnO lattice would display the same absorption profile as a zinc atom in the similar chemical environment of a Zn(Cr₂O₄) phase.

The chromium $L_{3,2}$ -edge spectra, Figure 5(b) are plotted with the that of Cr_2O_3 as a reference. At the Cr L_3 -edge all of the Cr:ZnO samples (Supplemental Figure 1) show a very intense peak at approximately 577 eV preceded by a peak of about half the intensity around 576 eV corresponding to primarily $2p_{3/2} \rightarrow 3d$ transitions. The multiple peaks seen at the L_3 -edge (575 - 580 eV) are mainly due to crystal field splitting of the d orbitals into the e_g and t_{2g} set in a distorted octahedral field modified by spin orbit and exchange splitting. Another set of peaks appear at 585 eV corresponding to the L_2 edge. The sharpness of each spectra varies somewhat from sample to sample. This trend is primarily affected by the chromium concentration with the 10% samples showing the greatest intensity and sharpness followed by the samples with 5 %. All of the samples indicate Cr is in the Cr^{3+} oxidation state however, a striking difference between sample spectra is seen at 580 eV. The sample processed at 400°C, containing 1% Cr shows a strong peak while the sample processed at 800°C containing 10% Cr shows only a very slight shoulder. The other samples show a variation in peak intensity with stronger dopants and higher temperatures showing reduced peak intensity at 580 eV (Supplemental Figure 2). In fact, this multiple scattering peak at 580 eV confirms the presence of Substitutional Cr_{Zn} in the Cr:ZnO at low processing temperatures and low dopant concentration. A chromium atom in the zinc oxide lattice (Cr_{Zn}) should display a similar profile to a zinc atom in the zinc oxide lattice due to the tetrahedral coordination of both atoms. This is less apparent at the L-edge because the Zn d band is full and the Cr d band is less than half filled. We can however track this via the multiple scattering. The peak at 580 eV corresponds to a similar peak seen in figure 5(a) at approximately 1026 eV (about 6eV higher in energy from the L_3 -edge) which is a multiple scattering peak from

the tetrahedral surrounding, a strong indicator of a tetrahedral coordination environment. A sharpening of 577 eV and 578 eV peaks are seen for samples with 5% and 10% Cr content which likely contain Cr in both the ZnO matrix (substitutionally) and in a secondary phase similar to Cr_2O_3 . The tetrahedral Cr environment also shows a similar peak in Wien2k calculations albeit only semi-quantitatively, which is displayed in Figure 6, where the presence of the MS peak is observed in the calculation of Cr $L_{3,2}$ -edge NEXAFS in the T_d environment of Cr substituted Cr:ZnO (Figure 6, top right - CrZn_3O_4). Thus this dopant related trend once again points to secondary phase formation at high Cr concentrations and higher processing temperatures. The shape of the $\text{Zn}_{0.9}\text{Cr}_{0.1}\text{O}$ spectra is very similar to the spectra of Cr_2O_3 which indicates that the chromium participating in secondary phase formation is also Cr^{3+} in a similar octahedral environment. As the secondary phase forms in samples of higher dopant concentrations and processing temperatures, stronger Cr_2O_3 like character is shown. We are unable to determine if both Cr_2O_3 and $\text{Zn}(\text{Cr}_2\text{O}_4)$ exist as a secondary phase as both contains octahedral Cr although the latter is less distorted.

The O K-edge NEXAFS of the Cr:ZnO samples (Figure 5c) show very similar profiles but reveal several obvious differences that follow both temperature and dopant dependent trends. There is a small pre-edge feature from approximately 528-530 eV. This pre-edge peak appears most prominently in samples processed at 400°C and decreases in size as the processing temperature is raised. The dopant concentration also seems to influence the intensity of this pre-edge feature as samples containing 1% and 5% Cr display the most intense pre-edge peaks. The $\text{Zn}_{0.9}\text{Cr}_{0.1}\text{O}$ (800°C) sample reflects this trend, as it displays almost no pre-edge feature. It is also evident that the absorption edge at approximately 537 eV (O $2p_z$ state) is most strongly affected by dopant

concentration. The sharpest, most intense peaks at this energy are samples with 1% chromium content and the least intense have a chromium concentration of 10% with intermediate intensities shown for samples containing 5% Cr. Processing temperature also affects the intensity of this peak, although to a lesser degree than the chromium concentration does. Dopant concentration being equal, the lower the processing temperature, the lower the peak intensity. The decrease in peak intensity at 537 eV for samples of high Cr content and high processing temperature seems to correspond to an increase in the shoulder seen from approximately 531-533 eV, to be distinguished from the peak at ~ 533 -534 eV in ZnO, which arises from 1s to $2p_x$, $2p_y$ transition (Supplemental Figure 2). Samples processed at 800°C show the largest shoulder in this energy range. A secondary effect correlates to the chromium content with the 10% sample displaying the largest shoulders for each respective processing temperature. The calculated spectra based on a model with significantly more concentrated Cr (similar local environment compared to experiment in the first shell only) show semi-quantitative agreement.

The strongest peak seen at approximately 537 eV is due to an oxygen 1s to $2p_z$ dipole transition. The pre-edge feature noted at 528-530 eV most likely indicates the presence of Cr^{3+} substituting into the zinc position in the ZnO (Cr:ZnO) lattice. This transition would be a 1s to 2p Cr:ZnO. The pre-edge peak is due to shake-down. As Cr^{3+} is incorporated into the ZnO lattice corresponding V_{Zn} (zinc vacancies) are required to maintain charge neutrality and result in states of O p character at lower binding energies. Additionally, the pre-edge peak could be associated with a transition involving hybridization of an O 2p state with an unoccupied Cr 3d state.²⁷ These transitions and are more prevalent in noncentrosymmetric (tetrahedral) environments such as when the Cr is substituting into the Zn position in ZnO. As we heat the sample up to 800°C this

pre-edge disappears which hints toward a more centrosymmetric (octahedral) secondary phase involving chromium (Cr^{3+}) similar to Cr_2O_3 forming and removing itself from the ZnO lattice.

The shoulder seen at 531-533 eV is very similar in energy to the peak seen in Cr_2O_3 which indicates that Cr^{3+} is likely involved in the secondary phase. Further supporting the case for secondary phase formation is the increase in this shoulder that is observed at higher processing temperatures. It is easy to accept the notion of secondary phase formation at higher temperatures due to increased diffusion rates of the Cr. As more and more chromium atoms are able to “meet” each other, they are able to form a secondary phase containing Cr^{3+} . This is just mass action. This explanation is also supported by the larger shoulder seen in samples with 10% Cr content as more Cr atoms would be available increasing the likelihood of such Cr-Cr encounters.

MAGNETIC MEASUREMENTS

From Figure 7, we see that the 10% Cr sample shows a linear trend at 2K. The lack of a response to the magnetic field implies that paramagnetism is prevalent. The shape of the magnetization curve at 1% chromium shows that there is some magnetic response. The absence of a hysteresis loop implies that the material is antiferromagnetic at low temperatures.²⁸ The formation of an octahedral Cr secondary phase is therefore detrimental to the magnetic properties of Cr:ZnO.

CONCLUSION

Effective control of nano-particle size is demonstrated by varying processing temperature in the attempt synthesis of Cr doped ZnO as magnetic semiconductors. In order to achieve larger nano-particles, higher processing temperatures must be used to increase annealing and allow for

agglomeration of smaller particles formed after the solvent evacuation step (heating to 400°C) of sol-gel synthesis. SEM data shows that a cubic structured secondary phase becomes noticeable at high processing temperatures of 800°C and a high chromium concentration of 10%. This observation is backed by the detection of a spinel structured $\text{Zn}(\text{Cr}_2\text{O}_4)$ using XRD and the detection of Cr^{3+} in an octahedral coordination to oxygen using NEXAFS for the same samples. XRD data suggest that chromium initially substitutes into the zinc oxide hexagonal wurtzite structure which is also supported by NEXAFS data showing the presence of tetrahedral chromium (Cr^{3+}) in samples with low dopant concentration and low processing temperature. Magnetic measurements show that paramagnetism is prevalent in samples with high dopant concentration and processing temperatures which indicates that $\text{Zn}(\text{Cr}_2\text{O}_4)$ might positively influence paramagnetism. To realize ferromagnetism, it would be advantageous to further investigate Cr:ZnO with low chromium concentration as well as moderate processing temperatures. It appears plausible that nanostructures may not be the best morphology to achieve room temperature ferromagnetism.

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Table 1: Models of the crystals used in the Wien2K DOS calculations

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Figure 1. Schematic of the sol-gel process.

Figure 2. SEM of Cr doped ZnO (50 000x magnification): a) and c) $\text{Zn}_{0.99}\text{Cr}_{0.01}\text{O}$ processed at 400°C and 800°C, respectively; b) and d) $\text{Zn}_{0.9}\text{Cr}_{0.1}\text{O}$ processed at 400°C and 800°C, respectively.

Figure 3. XRD of Cr: ZnO. Location of small $\text{Zn}(\text{Cr}_2\text{O}_4)$ spinel peaks are denoted by a Δ

Figure 4. A spinel type crystal structure of ZnCr_2O_4 (left) where tetrahedral Zn atoms, octahedral Cr atoms with neighboring O atoms connected with solid lines are shown. A wurtzite crystal structure (middle) where Zn atoms and O atoms are shown. The local structure of Cr in Cr_2O_3 (distorted octahedral) is shown on the right.

Figure 5 (a) Zn $L_{3,2}$ -edge (b) Cr $L_{3,2}$ edge and (c) Oxygen K -edge NEXAFS of $\text{Zn}_{0.90}\text{Cr}_{0.10}\text{O}$ and $\text{Zn}_{0.99}\text{Cr}_{0.01}\text{O}$ at various temperature as noted together with ZnO and Cr_2O_3 reference spectra. The MS peaks are marked with an arrow.

Figure 6. Comparison of experimental NEXAFS with Wien theory. Top and bottom left depict the simulated spectrum of Cr in O_h , distorted O_h , top right Cr in T_d local environment, respectively, compared with experiment. The MS peak is reproduced by theory at slightly higher energy. The bottom right displays the experimental and calculated O K-edge NEXAFS in $Cr_{Zn}:ZnO$ (as $CrZn_3O_4$).

Figure 7 a and b; magnetization vs. field plots for the $Zn_{0.9}Cr_{0.01}O$ and $Zn_{0.99}Cr_{0.01}O$ samples.

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Model	Cr ₂ O ₃	CrZn ₃ O ₄	CrZnO ₄
Spatial Group Symmetry	Ia3	P3m1	Cmcm
Lattice Constant	a = b = c = 9.437 Å. ∠ = β = γ = 90 °.	a = b = c = 3.2498 Å. ∠ = β = 90 °, γ=120 °.	a = 5.5908Å b = 8.4537Å c = 6.3901Å ∠ = β = γ = 90 °.
Atomic Position:	Cr 1 at (0, 0.5, 0.5) Cr 2 at (0.25, 0.28837700, 0) O at (0.36045850, 0.86592550, 0.40740950).	Cr at (0.6667, 0.3333, 0.75) Zn 1 at (0, 0, 0) Zn 2 at (0.6667, 0.3333, 0.25) Zn 3 at (0, 0, 0.5) O 1 at (0, 0, 0.19125000). O 2 at (0.6667, 0.3333, 0.44125000) O 3 at (0, 0, 0.69125000) O 4 at (0.6667, 0.3333, 0.94125000)	Cr at (0, 0.358149, 0.75) Zn at (0, 0, 0.5) O 1 at (0. 0.2474675, 0.0275535, 0.25) O 2 at (0.5, 0.254419, 0.041682)

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10% Cr 800C

1% Cr 400C