Structure correlated opto-electronic/mechanical properties of Fe/Si modified doped and co-doped

Synthesis and structure correlated opto-electronic and mechanical properties of Fe/Si modified doped and co-doped ZnO

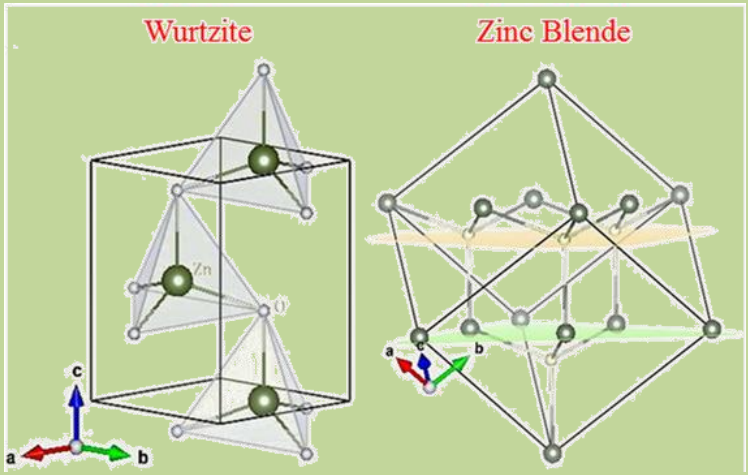
1. Introduction:

Zinc oxide (molecular formula: ZnO), is a multifunctional material having physical/chemical properties. High electrochemical coupling coefficient, high photo stability, high chemical stability, and broad range of radiation absorption[1,2]. Its wide band gap (~3.3 eV) and high exciton binding energy (~60 meV)[3] recognises it as a potential II–VI photonic semiconductor material. ZnO is used in optoelectronic devices, UV lasers, LEDs, electrodes in solar cells, gas/bio sensors etc. Research in the field have witnessed tremendous efforts in last few years for exploring the physical/optical properties of ZnO, particularly on fabrication and device applications[4]. To obtain high quality nano/micro structured ZnO material[5], synthesis processes like sol-gel, hydrothermal, co-precipitation and wet chemical method is used. It is known that optoelectronic properties of ZnO strongly vary depending on defect structure and based on synthesis techniques.

1.1 Crystal Structure:

ZnO generally crystallizes in two forms: hexagonal wurtzite and cubic zinc blende. It has been found theoretically using first principle periodic Hartree-Fock linear combination of atomic orbitals, the hexagonal ZnO wurtzite structure is thermodynamically the most stable form[6] with $P6_3mc$[6,7] symmetry and lattice parameters: a= 3.25 Å and c= 5.20 Å. Two superimposed sub lattices of Zn^{2+} and O^{2-} are observed separated by a distance. A tetrahedron with four cations located at four corners is found around each anion. The cation and anions form bonds of *sp3* covalent hybridization. This arrangement actually leads to a structure with a number of

alternating O^{2-} and Zn^{2+} ions planes stacked on top of the other separated by a distance (Figure.1). A positively charged (0001)-Zn plane as well as a negatively charged (0001)-O plane constitutes polar surfaces. A weak spontaneous polarization and a normal dipole moment along the c-axis results, along with a divergence in surface energy[7]. The zinc and oxygen atoms form a tetrahedral cage in the wurtzite ZnO. This tetrahedral symmetry causes polarity of ZnO. The direct consequences of polar symmetry of ZnO result in piezoelectricity and pyroelectricity along its c-axis. ZnO is an example of n-type semiconductor. The vacancies and interstitials (structural point defects) and threading/planar dislocations (extended defects) are responsible for the n-type behavior. The n-type conductivity occurs due to the oxygen vacancies presence in the ZnO lattice.



1.1.1 Physical property:

Pure ZnO is white in color and on heating it turns yellow. The molecular weight of ZnO is 81.37 g/mol and relative density is 5.607. The melting point of ZnO is 1900ºC and heat capacity is 9.62cal/deg/mole at 25ºC under high pressure. In water ZnO is not soluble. However, in acid ZnO can be made soluble.

1.1.2 Opto-electronic property:

The exciton binding energy in ZnO is considerably large ~60 meV at room temperature and can persist also at higher temperatures [8] which makes it perfect for optical devices. Some transitions occur between discrete electronic states inside the band gap[8]. These states are related to dopants or defects. There are many reports on green photoluminescence of ZnO. The intensity

of green emission increases with decrease in particle size [9]. The reduced size results in quantum size effect [9]. Increase of bandgap also happens due to such reduced size [9].

1.1.3 Optical properties:

The optical band gap of ZnO is ~3.44eV at 10-50K and 3.37eV at room temperature[9]. The energy ~3.37eV corresponds to a wavelength of 368Å. Thus, ZnO shows transparency in visible light but strongly absorbs ultra violet light below 368Å. Hence, ZnO is used in various optoelectronic applications like light emitting diode (LED's), solar cells, photo detectors etc.[6,10–12]. Photoluminescence (PL) is observed in ZnO. PL shows a comparatively sharp emission peak at 380nm (due to band to band transitions) [10] and a wider yellow-green emission band (due to presence of oxygen vacancies and other related defects) [11].

1.1.4 Electrical Properties:

A wide band gap in ZnO of 3.37 eV at room temperature has many advantages such as the ability to sustain large electrical fields [12], high breakdown voltage [12], low electronic noise [12], high temperature and high-power operation [12]. This makes ZnO fit for a wide variety of electrical applications. The electron mobility of ZnO differs with temperature and has a maximum of ~2000 cm2/ (V•s) at 50K but ~ 205 cm2/ (V•s) at 300K [13].

1.1.1 Mechanical and Thermal Properties:

ZnO is a relatively soft material with approximate hardness (~ 5GPa). Its elastic constants are smaller in comparison to oxides of other transition metal elements [13]. High heat conductivity, low thermal expansion and high melting point are some of the basic characteristics of ZnO. It is added in rubber to increase the thermal conductivity of tires and is useful in space or at high altitude13,14 due to its high radiation hardness property [14].

1.1.2 Magnetic property:

Dilute magnetism is observed in Fe, Ni, Co etc. doped ZnO. However, there is a lot of controversy regarding FM actually occurring due to an intrinsic property of the doped materials. Researchers have argued on the origin of such dilute magnetism and have often assigned it to

some impurity phase. In certain cases, it is explained due to segregation of metallic clusters[15]. A true FM from an intrinsic structure has sometimes been reported due to a proper double exchange phenomenon[16,17] between ions of different oxidation states. Yet, room temperature ferromagnetism is still a challenge.

1.2 ZnO nanostructures:

ZnO nanostructures can be prepared by a variety of methods to form a range of different morphologies (as shown in Fig. 1.5). Growth methods are mostly solution-based that are simple, inexpensive, scalable and requires low temperature for synthesis.

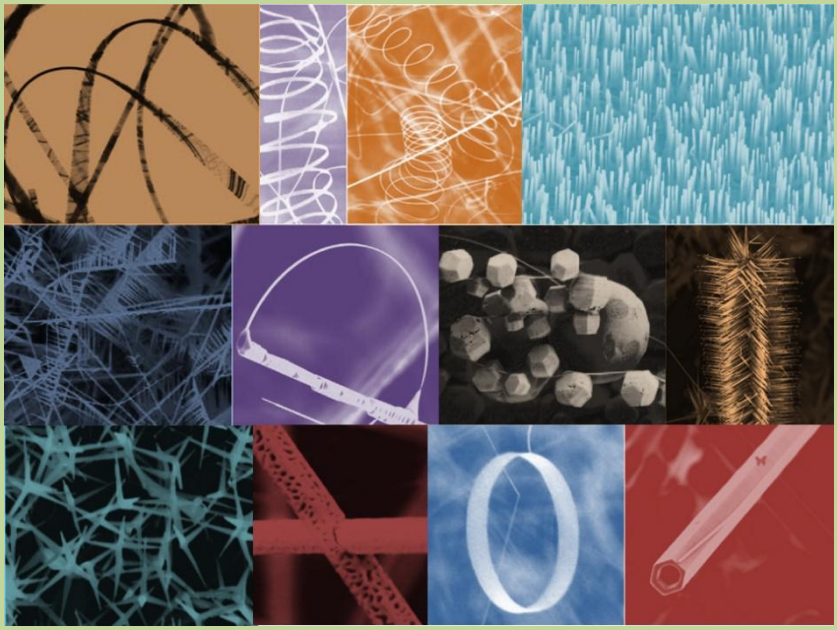


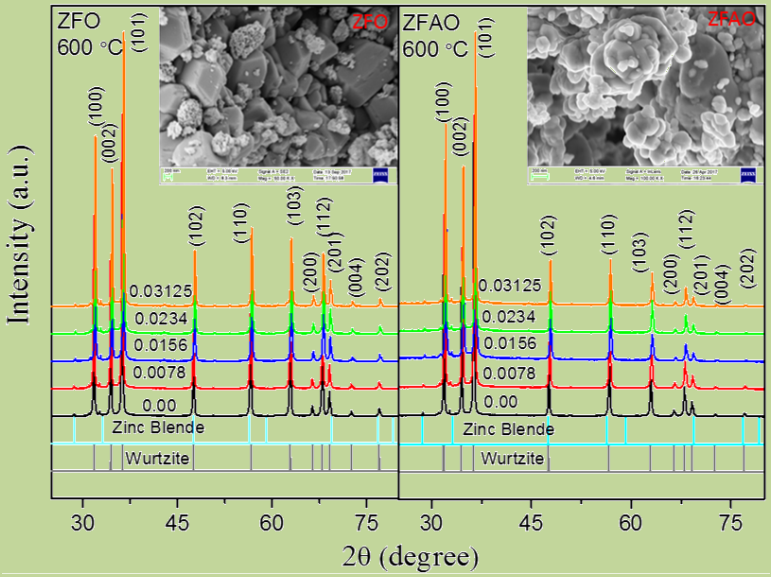
Figure 1.5: Various morphologies of ZnO Nanostructures

These ZnO nano-materials have a variety of practical applications in optoelectronic devices, energy harvesting devices, electronic devices, sensors, catalysts, active compounds in sunscreens, etc.

Projects:

Gaurav Bajpai is working on doped/substituted ZnO with single and multiple elements employing low temperature, sol-gel synthesis route followed by high temperature sintering. He has done structural studies using XRD. The valence state and other electronic properties have been studied using EXAFS/XANES, XPS, UV/Vis, PL etc. The molecular vibrational studies

have been studied using Raman, FTIR spectroscopy etc. Mechanical Properties like hardness have also been studied. By adding Fe to ZnO lattice, he has investigated the magnetic and electronic properties too. Photo sensing and Gas sensing, also is the subject of research. Co-doping with elements like Ag, Li, Na, K with Fe, he has explored the modifications of different functionalities due to size compensation and valence state compensation. Considering, the role of O, either deficit or excess he has investigated semiconductors in various lights.



XRD Pattern of ZFO & ZFAO ($0 \leq x \leq 0.03125$)

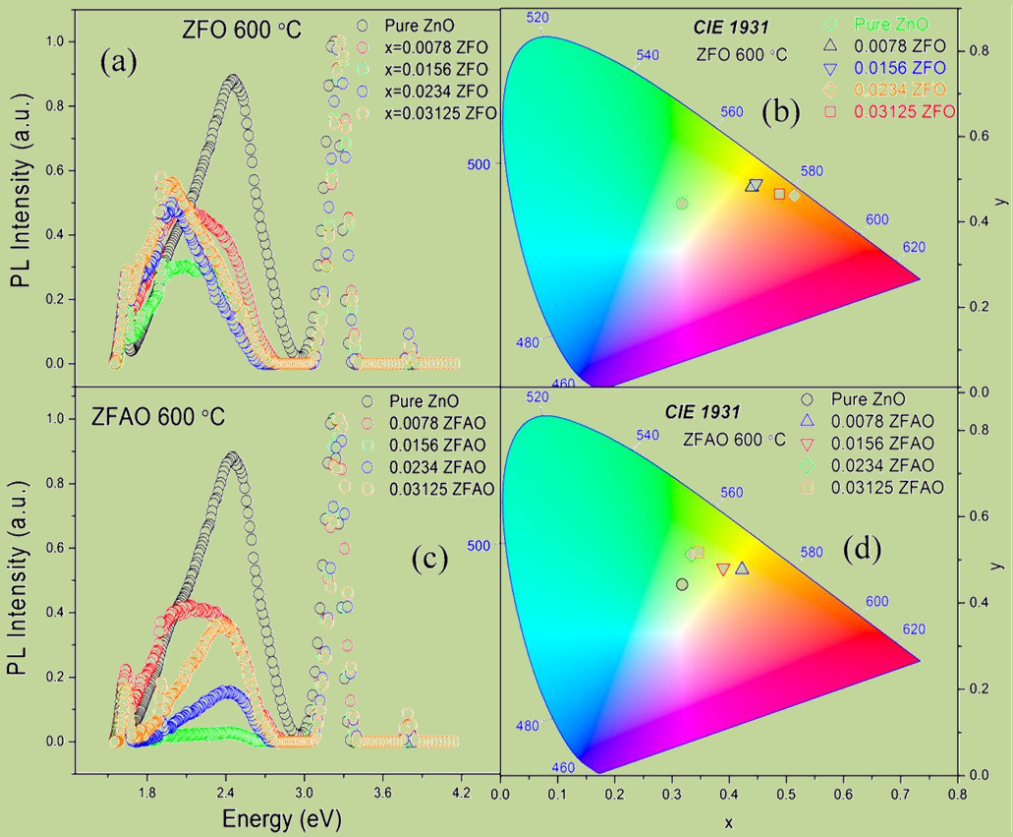


Fig (a) & (c) PL spectra of ZFO & ZFAO & Fig. (b) & (d) Chromaticity diagram

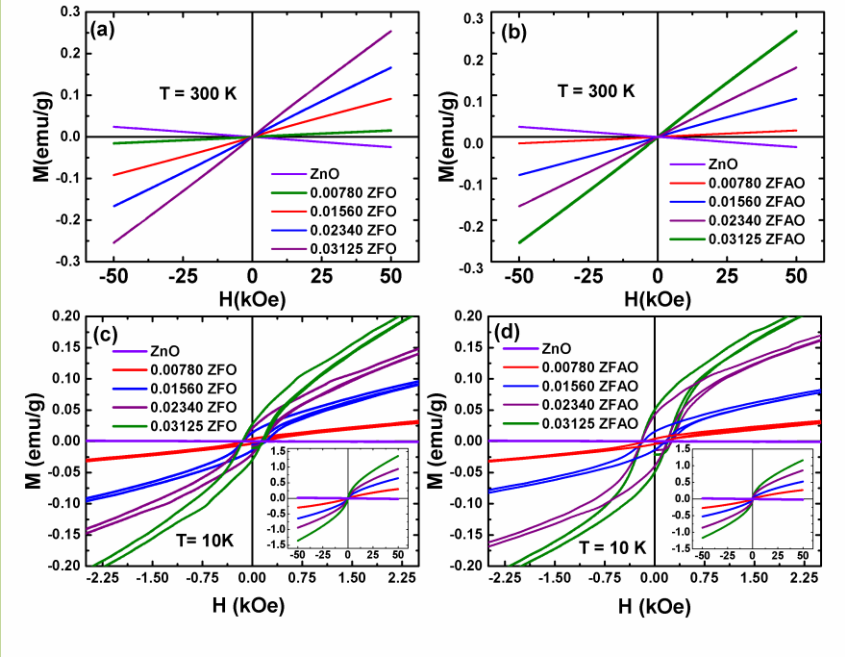
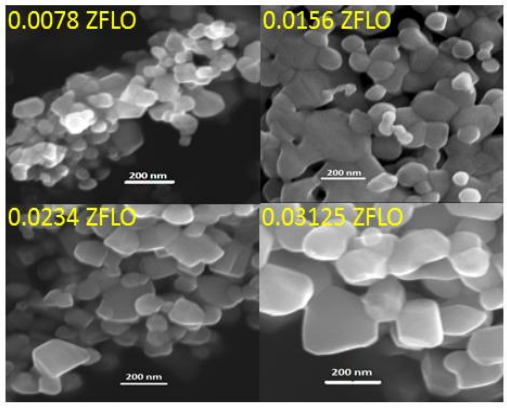


Fig. Hysteresis loops (M–H) of ZFO & ZFAO measured at 300 K and 10 K. The insets of Fig. (c) and (d) show the complete hysteresis loops measured between -50 kOe and 50 kOe.

FESEM Images of ZFLO



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