



Effect of pressure and doping on lattice structure of zinc oxide



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ABSTRACT

The semiconductor ZnO belongs to the IIb-VI binary compound. It has a high exciton binding energy of 60 meV. The bonding in these materials is covalent with some ionic character. Induced changes on the physical properties of Mn doped ZnO samples due to different dopant concentrations and pressure were evaluated. The results obtained showed higher solubility limit for Mn doped ZnO due to pressure. The trend of XRD results for higher Mn concentration (9 at%) as pressure increases, was towards doping improvement. The XRD, SEM and UV–vis study of the samples also revealed that there were variations in the lattice parameters, nanoparticle size and bandgap energy of the doped and pressurized doped samples. Further, the directions of variation of bandgap energy values and calculated particle size, as well as SEM values of the doped samples due to pressure variation were found to be the same i.e. all of them together either increase or decrease as pressure varies. However, these variations were found to be opposite to that of lattice constants (all *a* and most *c* values) variation for both Mn dopant concentrations (3 at% and 9 at%). These physical variations of unpressurized doped samples can be attributed to the change in the polar bonding of the elemental constitutions in the lattice. While for the pressurized doped samples, the variations attributed to repulsion of lone pairs as well as change in the electronegativity of the system.

1. Introduction

The semiconductor ZnO belongs to the group IIb-VI and has gained numerous interests [1–5]. Due to the substantial ionic character that exists in these materials, the bandgap increases beyond that expected from the covalent bonding. The ionic character of ZnO resides at the borderline between the covalent and ionic semiconductors.

In recent years, mixed transition-metal oxides with spinel structure have attracted much attention. Mn doped ZnO predicted to be a room-temperature diluted magnetic semiconductor [6]. Therefore, the Mn-Zn-O ternary systems belong to a class of interesting and useful materials in terms of their electrical and magnetic properties [7,8]. As one of the important mixed transition-metal oxides with spinel structure, ZnMn₂O₄ is a promising functional material and has become the focus of various researches owing to its potential applications [9–11].

The full-potential augmented plane wave plus local orbitals method is used to study the trends for structural, electronic and optical properties of the ZnB₂O₄ spinel oxides depending on the type of B element (B are Al, Ga and In). The calculated results show as pressure increases band gap (direct and indirect) increases almost linearly [12]. The role of d states in defining the electronic properties of the II-VI semiconductors has been discussed [13]. It has been reported that the p-d hybridization at Γ repels the valence without affecting the conduc-

tion band minimum.

The three crystal structures shared by ZnO are wurtzite, zinc blende, and rock salt (or Rochelle salt). The wurtzite structure of ZnO is the thermodynamically stable phase under ambient conditions; hence it is the most common. It consists of two interpenetrating hexagonal close-pack sublattices, each of which contains either Zn or O, they lie along the *c*-axis and are displaced by the amount of internal parameter $u=3/8$ in fractional coordinates [3]. The zinc–oxygen distance along the *c*-axis ($d_{\text{Zn-O}}=0.190$ nm) is slightly shorter than that of other Zn–O bonds ($d_{\text{Zn-O}}=0.198$ nm). The (0001)-Zn surface has been found to be chemically active, while the (0001̄)-O terminated surface is chemically inert [14,15]. These are the most common polar surfaces as they produce positively charged ions Zn-(0001) and negatively charged ions O-(0001̄) surfaces, resulting in a normal dipole moment and spontaneous polarization along the *c*-axis, as well as a divergence in surface energy. To maintain a stable structure, the polar surfaces generally have facets or exhibit massive surface reconstructions, but ZnO – ±(0001) are exceptions: they are atomically flat, stable and without reconstruction [16,17]. Efforts to understand the superior stability of the ZnO ±(0001) polar surfaces are at the forefront of recent research on surface physics [14,18–20]. The other two most commonly observed facets for ZnO are $\{2\bar{1}\bar{1}0\}$ and $\{01\bar{1}0\}$, which are non-polar surfaces and have lower energy than the $\{0001\}$ facets.

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Wide bandgap materials have several useful characteristics as compared to lower bandgap materials. The higher energy gap gives devices the ability to operate at higher temperatures, and for some applications, allows devices to switch larger voltages [21]. This characteristic brings the electronic transition energy into the range of the energy of visible light, hence devices such as light-emitting diodes (LEDs) and semiconductor lasers can be made to emit light in the visible spectrum, or even produce ultraviolet emission. Bandgaps can often be engineered by alloying, as well as externally applied stimuli such as pressure, temperature, electric field, etc.

In recent years, investigations on the effects of high pressure on semiconductor nanostructures, such as nanocrystals, nanowires, and nanotubes, have become a focus area in condensed matter physics and material science due to their tunable optical properties for applications in optoelectronics, quantum dot lasers, high density memory, bioengineering, etc. [22–25].

Experimentally, phase transition from wurtzite to the cubic [Rochelle salt (NaCl)] structure of zinc oxide, was obtained at a pressure of about 10 GPa, this was accompanied with a large decrease in volume of about 17% [26].

Lack of studies on moderate pressurized Mn doped ZnO, motivated us to investigate the effects of load pressure (in the range of 400–800 megapascals) on the electrical and optical properties of ZnO:Mn samples for different concentrations of Mn dopants. The bandgap energy depends on the crystal field or a sum of binding energies over the entire solid. While the binding energies or interatomic potential depends on the atomic distance and charge quantity of the atoms. Therefore, the energy gain by pressure can tune the bandgap energy. This indicates that it is possible to discover new sources for light emission with a desired wavelength by controlling the external stimuli. In simple oxides of fixed structure (ZnO) or highly symmetric structures, volume changes and metal-oxygen bond distances are closely related. Data can be compiled from sources on the expansion and compression of simple oxides [27]. Consequently, data on oxide compression provide important information on the variation of metal-oxygen distances with pressure and dopant.

2. Experimental procedure

Samples of different Mn concentrations (0.03, 0.05, 0.09 at%) doped ZnO, prepared by coprecipitation method (for details see Ref. [28]). The doped nanopowder thus obtained were mixed in proportion of 10% with polyvinyl alcohol. The different Mn doped ZnO samples then were hydraulically pressed uniaxially at load pressure 472, 629, 789 MPa to obtain s1, s3, s5, and s2, s4, s6 samples, for the Mn concentration of 3 at% and 9 at%, respectively, see Table 1. Finally the samples were calcinated in furnace at the temperature of 89 °C. The pressed samples have shape of tablet with diameter of ~1 cm and thickness of ~2 mm.

Table 1
Samples studied in this work.

Sample	Specification	Load pressure (MPa)
a	Pure ZnO	0
b	Mn (3%) doped ZnO	0
s1	Mn (3%) doped ZnO	472
s3	Mn (3%) doped ZnO	629
s5	Mn (3%) doped ZnO	789
c	Mn (9%) doped ZnO	0
s2	Mn (9%) doped ZnO	472
s4	Mn (9%) doped ZnO	629
s6	Mn (9%) doped ZnO	789

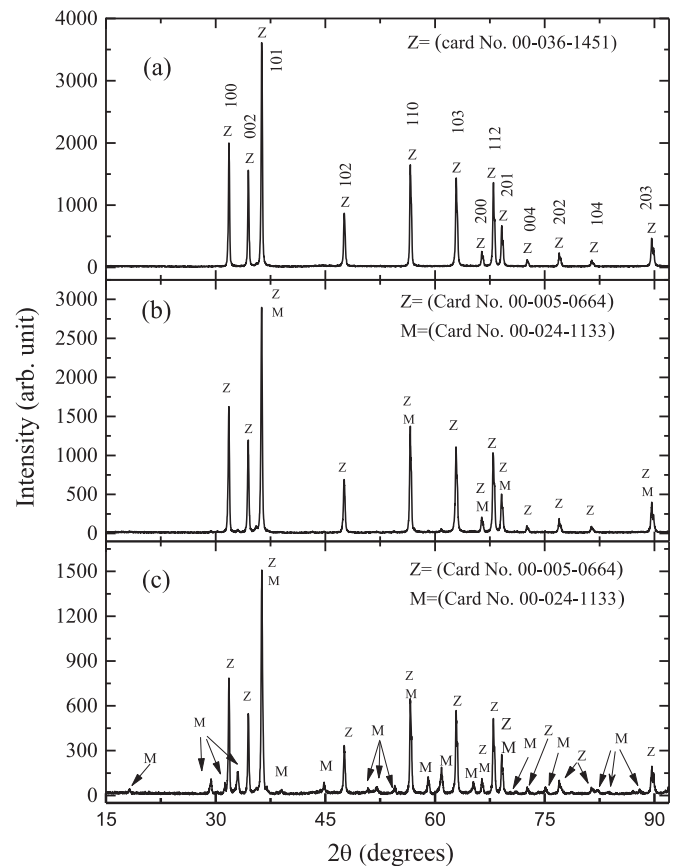


Fig. 1. The XRD patterns of the (a) pure ZnO, (b) Mn (3 at%) doped ZnO, and (c) Mn (9 at%) doped ZnO samples, respectively. Peaks due to ZnO alone is marked with letter Z and those of $\text{Mn}_2\text{O}_4\text{Zn}$ alone are represented with M and those peaks which are attributed to both ZnO and $\text{Mn}_2\text{O}_4\text{Zn}$ are represented with $\overset{Z}{M}$. Also are given the Miller indices of ZnO planes for the corresponding peaks in Fig. 1(a), along with matched Card number.

3. Results and discussion

Fig. 1(a)–(c) show the XRD patterns of pure ZnO, Mn (3 at%) doped ZnO and Mn (9 at%) doped ZnO samples, respectively. As shown in the figures, zinc oxide phase (Card No. 00-036-1451) and zinc white (Card No. 00-005-0664) are the predominate phase in all samples. The hexagonal structures of the undoped ZnO sample, as well as the doped ZnO samples were confirmed by the XRD study. As expected, without doping, no minor phase can be detected on the XRD pattern. As a result of doping, the peak intensities are damped and as dopant concentration increased from 3% to 9%, more damping was observed. None of the pure ZnO peak disappeared for the doped samples. These observations suggest that the Mn ions can be incorporated into the ZnO host lattice with no effect on the hexagonal structure of ZnO.

For all XRD patterns with X'Pert software calibration set: the minimum significance = 2.00, minimum tip width ($^{\circ}2\text{Th.}$) = 0.01, maximum tip width ($^{\circ}2\text{Th.}$) = 1.00 and peak base width ($^{\circ}2\text{Th.}$) = 2.00.

In Figs. 1–3, peaks due to ZnO alone are marked with letter Z, peaks of $\text{Mn}_2\text{O}_4\text{Zn}$ (hetaerolite, Card No. 00-024-1133, with tetragonal structure) alone are represented with M and those peaks attributed to both ZnO and $\text{Mn}_2\text{O}_4\text{Zn}$ are represented with $\overset{Z}{M}$.

As shown in Fig. 1(b), there is no extra peak due to Mn (3 at%) doped ZnO, but peaks which are attributed to hetaerolite ($\text{Mn}_2\text{O}_4\text{Zn}$, Card No. 00-024-1133) and zinc white (Card No. 00-005-0664) are matched ($\overset{Z}{M}$ -peaks). Increase in Mn dopant concentration from 3 at% to 9 at% causes minor peaks of the hetaerolite phase to be observed in the XRD patterns, and are marked with M in Fig. 1(c). These M-peaks

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