OPTICAL AND ELECTRONIC PROPERTIES OF TRANSITION METAL OXIDE BASED COMPOSITE MATERIALS

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree

of

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by

MONIKA



DISCIPLINE OF PHYSICS

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "OPTICAL AND ELECTRONIC PROPERTIES OF TRANSITION METAL OXIDE BASED COMPOSITE MATERIALS" in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2017 to June 2019 under the supervision of Dr. P. R. Sagdeo. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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Dedicated to

My Family, Teachers

And Friends

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ABSTRACT

Transition metal oxides (TMO) is an interesting group of oxides with a wide variety surface structures which affect the surface energy of these compounds and influence the chemical, optical, electrical and magnetic properties. Many of these properties strongly depends on materials defects like vacancies, dislocations, stacking faults and grain boundaries. The unusual properties of these oxides are due to the unique nature of outermost d-band configuration.

In the present studies we define the mixture of two TMO in any ratio as a composite material. Such composite materials have been studies from last few decades due to their intriguing properties and technological importance. In order to introduce multi-functionality, the composite materials appear to be one of the simple and widely adopted choices of various research groups. Recently the composite materials have been used for hydrogen production using water splitting and solar cell applications and appear to be most successful as compared with that of other counterparts.

Even though lots of successful experimental evidences are available in the literature on the potentials of composite materials but the scientific origin and the understanding of physics of composite materials is still unclear. It is believed that the formation of interfacial junction plays a very crucial role.

In case the junction is getting formed the signature of the same is easily found out using UV visible spectroscopy. Keeping this in view; the project is aimed to understand the effect of mixing various transition metal oxides by different methodology and to check the signature of junction formation if any and to investigate structural and optical properties.

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Chapter 1

1. Transition Metal Oxides: An Introduction

1.1 Transition Metals

Metals, semiconductors or oxide nanoparticles are of particular interest for their mechanical, electrical, magnetic, optical, chemical and other physical properties. Among these, oxides of transition metals are an important class of semiconductors that have wider applications such as magnetic storage media, solar energy transformation, electronics and catalysis. In periodic table d-block elements called transition metals because these elements have partially filled d orbitals. The d-block elements in group 3-11 are transition metals.[1] The d-orbitals completely filled up to Cu family and next family Zn (group 12) are technically not transition elements but these are included in transition metals as these show similar properties. d-block elements are divided into first transition series (from Sc to Cu), second transition series (from Y to Ag) and third transition series (from La to Hf). Ac is the first member of fourth transition series which also includes Rf through Rg.[2]

Transition metals have a wide range of chemical properties. Some transition metals are strong reducing agents while other has very less reactivity. The ability to resist oxidation makes them useful materials for constructing circuits and jewelry.

1.2 Transition Metal Oxides

Transition Metal Oxides (TMO) show a broad structural variety due to their ability to form phases of varying metal to oxygen ratios reflecting multiple oxidation states of the metal ions. Interesting properties shown by TMO are due to unique nature of outermost d- electrons.[3] General formulas for TMO are MO, M_2O , M_2O_3 and MO_2 . e.g.- ZnO, CuO, TiO₂ .We have used ZnO, CuO to prepare composite materials of (x)ZnO+(1-x)CuO series and also CuO and TiO₂ to

prepare the (x)CuO+(1-x)TiO₂ series. A brief review of the properties of all these compounds is shown below.

• ZnO

ZnO is an inorganic compound whose powder form has white colour and it is insoluble in water. It is a very cheap powder which is used in paints and UV blocking paste. It has a stable hexagonal Wurtzite structure with unique electronic, photonic and piezoelectric properties. It is a semiconductor with wide direct band gap of 3.37 eV[4] at room temperature. ZnO can be doped to have different defect structure exhibiting UV, green, blue or red emission. Along with the above described properties; ZnO has antibacterial and disordering properties also.



Figure 1.1: ZnO Hexagonal structure from ref. [3]

• TiO_2

It has a bulk band gap energy of about 3.2 eV but electrons can be placed in (3d) gap states which are about 0.7 eV below the fermi level created by Vacuum annealing. It is also available in form of nanocrystals and Nano rods having a large surface area. It also has magnetic properties. TiO_2 nanoparticles are also

known for their ability to inhibit bacterial growth and prevent future formation of cell structure. It has a good photocatalytic which can be used in antiseptic and antibacterial compositions. It can be used as a UV resistant material.[5] At room temperature it is very less reactive and does not react with Oxygen, Hydrogen etc.



Figure 1.2: Titanium Oxide Rutile and Anatase Structure from ref. [7]

• CuO

It is a black colored powder which is a p-type semiconductor having good importance in photocatalytic process. It has a narrow band gap of 1.2 eV.[6] It belongs to the monoclinic crystal system. Cupric oxide is used as a pigment in ceramics to produce blue, red, and green, and sometimes gray, pink, or black glazes. Cupric oxide can be used to safely dispose of hazardous materials such as cyanide, hydrocarbons, halogenated hydrocarbons and dioxins, through oxidation. It has attracted greater attention since it is used for photoconductive and photo-thermal applications. An improved understanding of nanoparticles and biological cell interactions leads to the development of new sensing, diagnostic, and treatment capabilities, such as improved targeted drug delivery, gene therapy, magnetic resonance imaging (MRI) contrast agents, and biological warfare agent detection.



Figure 1.3: CuO Monoclinic Structure from ref. [6]

1.3 Necessity of Composites

Interfaces between p- and n-type semiconductors have great technological importance at the heart of micro-electronics. Interfaces also play a significant role in other domains of materials research, such as solid state ionic. Semiconductor ZnO with broad-band-gap (3.2eV) has been extensively investigated as semiconductor photo catalysts for the contaminant remediation. However, ZnO can only absorb a small portion of solar spectrum in the UV region, which means that they do not allow the efficient utilization of visible light. Compared with those broad-band-gap semiconductors, the photo response of semiconductors with narrow-band-gap extends much more into the visible wavelength range. Nevertheless, the narrow-band-gap semiconductors exhibit low photocatalytic efficiency due to fast recombination rate for electron-hole pair photo generated on the semiconductors. The reports in the literature indicated that coupling of a narrow-band-gap semiconductor with another having broad-band-gap results in a more efficient separation and consequently, a higher visible light induced photocatalytic activity compared with the single narrow-band-gap semiconductor. In the past several years, composite semiconductors of ZnO coupled with narrowband-gap semiconductor, including Fe₂O₃,WO₃, CdS, Cu₂O and CuO, have been reported.[7] Similarly p-type CuO and n-type TiO_2 has great advantages in photocatalytic water splitting.

1.4 CuO-TiO₂ composite

The modern world has been searching for alternative paths and technologies for fossil fuels due to its depletion, energy crisis, increasing energy needs and environmental effects. For the above needs, hydrogen has been prominently selected as an alternative fuel for future energy supply because of its high energy yield, 120 MJ/Kg, as compared to other sources. The use of solar energy for photocatalytic water splitting has been noted as a promising energy source which does not cause any environmental problems. Semiconductor-based metal oxides have been widely used as catalysts for the photocatalytic splitting of H₂ O to H₂ and O₂. Amongst semiconductors, primarily TiO₂ has been selected as an ideal catalyst because of its attractive properties like low cost, cheap, high chemical stability, good safety, non-toxic and good photo-oxidation potential. The disadvantage of TiO_2 is: it shows active absorption UV-irradiation in a photocatalytic reaction which contributes to low absorption of solar energy. Due to this, the rate of electron/hole (e^{-}/h^{+}) separation of TiO₂ is very low in visible region which causes less quantum efficiency for photo catalysis. There is a pressing need to modify the band gap of TiO₂ to enhance the rate of e^{-/h^+} separation results in good quantum efficiency.[8] Amongst metal oxides; CuO ptype semiconductor had proven to be a good co-catalyst in photocatalytic water splitting and also absorbs light in the visible region. CuO-TiO₂ has acknowledged as the cost-effective catalyst for photocatalytic water splitting. Zhengmin et al[9]have prepared CuO and CF-TiO₂ nanocomposite catalyst and recorded hydrogen production~1500 μ molg⁻¹h⁻¹. Takuya et al[10] have synthesized CuO/Al₂O₃/TiO₂ nano-composite and recorded maximum hydrogen production of about 1200µmolg⁻¹h⁻¹ catalyst in the presence of aqueous methanol solution. Khemthong et al have reported the synthesis of CuO-TiO₂ nanorod and highest photocatalytic hydrogen production recorded was 139.03µmolg-1catalyst in the presence of methanol as a sacrificial agent under solar irradiation. Yi-Hsien et al have been synthesized CuO deposited TiO₂ rods using microwave-assisted solvothermal method. They have observed good photocatalytic performance for 1 wt.% CuO deposited TiO₂ rods with H₂ production 3508.7 μ mol h⁻¹g⁻¹. Siew and

group have fabricated CuO/TiO2 nanofibers and then the prepared samples have been progressively heated to various temperatures. All the obtained samples have tested for photochemical H₂ production and found 6 mol% Cu doped TiO₂ as the best photo catalyst. Magesan and co-workers have been prepared TiO₂ composites doped with Al₂O₃, Bi₂O₃, CuO and ZrO₂ via sono chemical method. The prepared composite materials have been used as photo catalysts for the degradation of various organic pollutants such as methylene blue, methyl orange and rhodamine-B and also checked antibacterial activity. Karunakaran et al have synthesized CuO-TiO₂ core/shells through sol-gel method and tested for photochemical degradation of methylene blue and rhodamine-B dyes. From the obtained results, they have concluded that $CuO-TiO_2$ core/shell have not showed significant photo catalytic activity. Athanasia et al have prepared $(x)CuO+(1-x)TiO_2$ composite by adding various wt. % of Cu (0.01-2.8 wt. %) and used as a photo catalysts for the detection of H_2 production in the presence of glycerol as a sacrificial agent. They have observed fluctuations in the rate of H_2 production due to slow and reversible modifications of Cu oxidation states.[11] Wan-Ting et al have synthesized CuO loadings (up to 15 wt. %) on TiO_2 and studied its role on photochemical H₂ production with the assistance of ethanol as sacrificial agent using UV-light source. Praveen and his group have prepared CuO deposited TiO₂ nanotubes and has been tested the composite material for the production of hydrogen under the irradiation of sunlight using glycerol as sacrificial agent.

1.5 ZnO-CuO composite

ZnO material can be activated by UV and visible light to form the electron-hole pairs. These holes can split the H₂O molecule (from suspension from ZnO) to OH⁻ and H⁺. Dissolved oxygen molecules on could be converted to superoxide radical anions (•O2⁻) which react with H⁺ to produce (HO₂ •) radicals. The collisions of (HO₂ •) with electrons produce the hydrogen peroxide anion (HO₂⁻). These species react with hydrogen ions to produce H₂O₂ molecules that can penetrate the cell membranes and kill the bacteria.

The advantage of ZnO is their photocatalytic ability that can produce radical compounds. This material can be used as an antibacterial agent.[12] However, the ZnO material has large band gap which can decrease the photocatalytic properties. The addition of CuO to ZnO could form the CuO-ZnO composite that increased particle size and decrease the band gap energy.[13] The higher concentration of CuO in composites, the smaller band gap energy could be obtained.[14]As an important p-type narrow bandgap semiconductor, CuO has been applied to improve the photocatalytic efficiency of some wide bandgap semiconductors.[15] Therefore, ZnO-CuO nanocomposite was selected as a target material to synthesize by using a simple co-precipitation method, and further to investigate the photocatalytic activity of the multicomponent semiconductor system. The coupled ZnO-CuO nanocomposite showed an enhanced photocatalytic activity compared to the mono component CuO, ZnO nano catalysts because of the formation of nano heterojunctions leading to a modification of optical and electronic properties.[4]

Chapter 2

2. Sample preparation and characterization techniques

2.1 Sample Preparation process

Composites of (x)ZnO+(1-x)CuO and $(x)CuO+(1-x)TiO_2$ has been prepared by physical mixing of finely powdered form of these materials. To synthesize the series of (x)ZnO+(1-x)CuO and of $(x)CuO+(1-x)TiO_2$ with step size of 20% following steps were taken in consideration.

1. Weighing of the appropriate quantity of the high purity starting materials, fine grain powders, in stoichiometric proportions.

2. Mix them together in iso-Propyl alcohol (IPA) and grind them using agate mortar and pestle.

3. After making composite materials in powder form, we make pellet by using hydraulic pressure pelletizer in PVA.

2.2 X-Ray Diffraction (XRD)

X-rays are high energy electromagnetic radiation having energy 200eV to 1MeV. These rays lies between γ -rays and ultra-violet radiation in the electromagnetic spectrum. X-rays are produced by interactions between an external beam of electrons and the electrons in the shell of atom.

2.2.1 Generation of X-ray

X-rays are produced in an X-ray tube consisting two metal electrodes enclosed in a vacuum chamber. In this tube electrons are produced by heating tungsten filament cathode. The electrons are accelerated from high negative potential of cathode to anode which is at ground potential. The electrons, which have very high velocity collide with water cooled anode and loses some energy as X-ray.[16] When incident electron has sufficient energy to eject electron from target material then hole is left in inner shell. When this hole is filled by outer shell electron, an X-ray photon is produced. The total spectra of X-ray consist of K_{α} and K_{β} lines. K_{α} is consist of $K_{\alpha 1}$ and $K_{\alpha 2}$ line. $K_{\alpha 1}$ and $K_{\alpha 2}$ are sufficiently close in wavelength such that a weighted average of the two is used.

2.2.2 X-Ray Diffraction

X-ray diffraction (XRD) is the most important non-destructive technique to analyze wide range of materials including fluids, powders and crystal materials. X-ray diffraction technique is used to get information about crystal structure, crystallite size, lattice parameter, lattice strain, chemical composition, phase identification and inter planer distance between two planes of sample etc.

2.2.3 Principle

When X-rays incident on the Sample Surface that makes an angle θ with the planes of sample and some part of x-rays also diffracted at an angle θ . These diffracted X-rays are parallel to each other and gives constructive interference when Bragg's law satisfy.



Figure 2.1: Diffraction of X-ray by a Crystal from ref. [16]

Path difference = $2d\sin\theta$

For constructive interference path difference should be an integer multiple of wavelength λ . So the Bragg's law for constructive interference,

$$2d\sin\theta = n\lambda$$

Where d is inter planer spacing , θ is angle made by x-ray beam with that of plane , λ is wavelength of incident X-ray and n is an integer.

The spacing of the atoms in crystal lattices is the same order of the wavelength of X-ray (0.01 to 100 A°).

2.2.4 X-ray diffractometer

X-ray diffractometer mainly consists of three parts-

- 1. X-ray Source
- 2. Sample Stage
- 3. X-ray Detector.



Figure 2. 2: Schematic diagram of X-ray Diffractometer.

X-ray diffractometer can be arranged into two ways- first θ : θ arrangement in which sample is fixed and X-ray source and detector rotates with angle θ° per minute and other one is θ : 2θ arrangement in which X-ray source is fixed; sample rotates with angular speed θ° per minute while X-ray detector rotates with angle $2\theta^{\circ}$ per minute with respect to the beam source. The parameters

during the diffraction were as follows: Tube current-30 mA, Tube voltage- 40 kV, Range of scan- 20° to 80° (2 Θ), Wavelength used-1.5406 Å (Cu K α) Step size- 0.01 degree and scanning speed of 2 degree/minute.

2.2.5 Working

For monochromatic X-ray these produced X-ray passed through the Ni filter and after that fall on the sample surface. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector process this X-ray signal than output is recorded by computer device.

Intensities of diffracted X-rays depend on the density of electrons in different planes and also on the orientation of the planes of the crystal. Intensity of diffracted X-rays can be calculated by using structure factor S_G . Structure factor written as :

$$S_G = f_j e^{\left[-2\pi i \left(h x_j + k y_j + l z_j\right)\right]}$$

Where f_j is the atomic scattering factor. h, k and l are the miller indices of the reflection. x_j, y_j and z_j are positions of atoms in unit cell.

Intensity
$$I = |S_G|^2 = S_G * S_G^*$$

Reflection for which $|S_G|^2 = 0$ will have zero intensity and there is no diffraction pattern; these reflections are known as forbidden reflections.

2.3 UV- Visible Diffuse Reflectance Spectroscopy (DRS)

In this spectroscopy, we study the light absorb in UV-Visible region (200nm-800nm) of electromagnetic spectrum. It is known as electronic spectroscopy because it involves electronic transition from lower energy level to higher energy level. When an electromagnetic light falls on sample it gives two types of reflection:-

- 1. Specular Reflection
- 2. Diffuse Reflection



Figure 2. 3: Electromagnetic Spectra from ref. [13]

2.3.1 Specular Reflection

Specular reflection occurs on smooth surface, in this reflection incident light and reflected light makes same angle with normal. Reflected rays will be parallel if the incident rays are parallel. In this reflection the arrangement of the incident rays is retained by the reflected rays and this preservation of arrangement allows us to see images in mirrors.

2.3.2 Diffuse Reflection

Diffuse reflection occurs on rough surface. In this reflection, incident light reflected in different direction because of roughness of surface. In this reflection the incident angles for a set of parallel rays will not be the same and each reflected ray will have a different angle of reflection.[17]

For reflecting surface, reflectance(R) can be find using refractive index (n)-

$$R = \left(\frac{n-1}{n+1}\right)^2$$

Here R; reflectance can be measured accurately for perfectly smooth surface. For powder samples it cannot be measured because of its rough surface. When light falls on powder samples it diffracted in different direction. To converge these rays spherical mirrors are used by detector. For this type of samples diffuse reflectance spectroscopy can be used.



Figure 2. 4: Schematic diagram of Specular and Diffuse Reflection.

2.3.3 Principle of DRS

DRS is based on the principle of diffuse reflection. In diffuse reflection some part of light goes inside the sample under multiple scattering and fraction of this emitted back into the detector.





In order to estimate the optical band gap the diffuse reflectance spectra has been converted to equivalent absorption spectra using Kubelka–Munk equation : [17]

$$F(R_{\infty}) = \frac{K}{S} = \frac{(1-R_{\infty})^2}{2R_{\infty}}$$

 $R\infty = R$ (Sample)/R (Standard). R (Sample) is the diffuse reflectance of the sample and R(Standard) is that of the standard (BaSO4 in present case). K and S are the Kubelka–Munk absorption and scattering functions, respectively.

Kubelka-Munk function is directly proportional to the absorption coefficient $(\alpha)as:$ -

$$F(R_{\infty}) \propto \alpha \propto \frac{\left(h\upsilon - E_g\right)^{1/n}}{h\upsilon}$$

 $(\alpha h\upsilon)^n = A(h\upsilon - E_g)$

For direct transition n=2, indirect transition n=1/2.

Tauc plot is a plot between $[F(R_{\infty}) \times hv]^n$ and *hv*, which yields an straight line and the intercept on the energy axis gives the value of band gap.

2.3.4 Instrumentation

UV-VIS diffuse reflectance spectrometer consist mainly following components-

- 1. Light Source
- 2. Integrating Sphere
- 3. Monochromators
- 4. Sample Holder
- 5. Detector

In this spectrometer mainly the Xe lamp is used as a light source which gives the electromagnetic radiation in uv-vis range. An integrating sphere is an optical device used to collect electromagnetic radiation and a monochromator i.e. grating and filter is used to get monochromatic light. In DRS, clip and jaw type sample holder is used to holding large and bulky samples and photomultiplier detector is used to detect diffused reflected electromagnetic radiation from sample. DRS setup is shown in figure.





Sample

Detector

Figure 2. 6: (a) Carry 60 UV-VIS Spectrometer

(b) Internal set up of UV-Vis spectrometer. [17]



Figure 2. 7: an integrating sphere attachment to detect diffuse reflectance.

2.3.5 Working

Diffuse reflectance has been measured by a setup of Carry 60 UV-VIS spectrometer. In this set up Xenon (Xe) flashed lamp is used to produce electromagnetic waves, these waves passes through different mono-chromators

for UV-VIS spectrum and after doing some optical arrangement, light is incident on sample by using optical fiber and diffuse reflected light is detected by the detector.

2.4 Raman Spectroscopy

Raman Spectroscopy is a non-destructive technique which provides information about vibrational, rotational and other low frequency transitions in molecules and more about chemical structure, phase and crystallinity of molecules. Raman Spectroscopy used to study soild (powders, pellets, thin films), liquid (gels, pastes) and gaseous samples.

2.4.1 Principle of Raman Spectroscopy

Raman Spectroscopy is based on inelastic scattering of monochromatic light. When a beam of monochromatic light is passed through the sample, a small amount of radiation energy is scattered, the scattered radiation having the almost same frequency of the incident radiation is called Rayleigh Scattering but in addition some discrete frequency will be scattered above and below that of the incident beam which is known as Raman scattering.



Figure 2. 8: Raman Principle.

In inelastic scattering molecule can gain or loss of energy ΔE i.e. its energy changes must be difference in energy between two allowed states. If molecule gain energy ΔE then photon will be scattered with energy hu- ΔE and frequency lower than that of incident beam is referred to as Stoke's radiation and if molecule loss energy ΔE , then photon will be scattered with energy hu+ ΔE and frequency higher than that of incident beam is called Anti-Stoke's radiation.[18]

Stoke's line occur due to excitation of the atoms from ground state to the excited state while Anti-Stoke's line occur due to the transition from excited state to ground state. Intensity of Stoke's line more than Anti-Stoke's line. The intensity of Stoke's line depend on the no. of atoms in ground state and the intensity of Anti-Stoke's line proportional to no. of atoms in excited state, so the no. of atoms in ground state is higher than excited state i.e. intensity of Stoke's line is higher than Anti-Stoke's line.

When a molecule put in the static electric field, separation of charge centers causes an induced dipole moment in the molecule. Direction of induced dipole moment is in the direction of static electric field.so dipole moment given as:

Where α is polarizability of the molecule, E is static electric field and p is dipole moment of induced dipole.

Condition for a molecule to be Raman active ,the vibrational mode of the molecule should be proceed with the change in the polarizability of the molecule.

2.4.2 Raman Spectrometer

A Raman spectrometer is including several main components:-

- 1. Laser excitation source
- 2. Sample

- 3. Focusing Mirror
- 4. A wavelength selector device(monochromater)
- 5. Detector
- 6. A recording device.

The instrumentation of Raman spectrometer is shown as:-



Figure 2. 9: experimental set up of Raman Spectrometer from ref. [18]

2.4.3 Working

The laser is an ideal source for Raman experiment because its gives a very narrow highly monochromatic coherent beam. The laser beam is passed through the beam expander, then go to the sample through microscope. Light scattered in different direction is collected by a lens in microscope after that focused by focusing mirror and passed into a grating monochromator. The signal is measured by a photomultiplier (detector) and after amplification it is recorded by a computer which plots the Raman spectra between wavelength and intensity. The schematic diagram is shown as:



Figure 2. 10: Schematic diagram of Raman spectrometer from ref. [18]

Chapter 3

3. Result and Discussion

(x)ZnO+(1-x)CuO and $(x)CuO+(1-x)TiO_2$ composite materials have been prepared by physical mixing of (x)ZnO,(1-x)CuO and $(x)CuO,(1-x)TiO_2$ powders such that no reaction take place between them. The samples in powder and pellet form; were annealed at different temperature and have been characterized by using experimental techniques discussed in chapter 2 and results are discussed in this chapter.

3.1 Results for (x)ZnO+(1-x)CuO Composites

3.1.1 Structural study (Xrd)

Composite materials were characterized by X-Ray Diffraction (XRD) in SIC Lab using Rigaku Ultima IV Diffractometer which is a Θ : Θ instrument. In these types of instruments, sample remains fixed while source and detector move at $\Theta^{\circ}/\text{min}$. The parameters during the diffraction were as follows: Tube current-30 mA, Tube voltage- 40 kV, Range of scan- 20 to 80 (2 Θ), Wavelength used-1.5406 Å (Cu Kα) Step size- 0.01 degree and Scanning speed of 2 degree/minute.High resolution XRD was done using Bruker D8 advanced diffractometer which is conceptually based on Θ : Θ geometry. Additionally this diffractometer has facility of rotating the sample uniformly. If sample is fixed then it may be possible that reflections from some planes would be forbidden, but rotation of sample make reflections from every plane family allowed. Parameters of the diffractometer during the diffraction were as follows: Tube current- 40 mA, Tube voltage- 40 kV, Rate of rotation- 20 rpm, Wavelength used- 1.5418 Å (Cu Ka), Range of scan- 20° to 90°, step size-0.02°, counting time-10 sec/step. The XRD analysis result of Pure ZnO, CuO, ZnO+CuO powder at room temperature, ZnO+CuO pellet and ZnO+CuO annealed at temperature 200°C and 400°C are shown in figure 3.1,3.2,3.3,3.4 and 3.5.



Figure 3. 1: (a)XRD pattern of pure ZnO. (b) XRD pattern of pure CuO.

Figure 3.1 shows the XRD pattern of pure ZnO, which is well crystallized into hexagonal phase perfectly matching with JCPDS file no.89.1997 with the lattice parameters $a = b = 3.2408 \text{ A}^{\circ}$ and $c = 5.2362 \text{ A}^{\circ}$. Absence of any impure or extra peak confirms that ZnO is in single phase.

Composition and purity of CuO powder analyzed by XRD pattern of pure CuO which is crystallized into monoclinic phase perfectly matching with JCPDS file no.89.5899 with the lattice parameters $a = 4.6108 \text{ A}^\circ$, $b = 3.428 \text{ A}^\circ$ and $c = 5.0689 \text{ A}^\circ$. The XRD pattern reveals a high degree of purity and crystallinity of CuO powder.

Figure 3.3 shows the XRD pattern of ZNO+CuO powder at room temperature, which shows that all the diffracted peaks are matching with the peaks of pure ZnO and pure CuO. There are no extra peaks generated in ZnO+CuO composite which confirms that there is no structural change. So to encounter any structural change due to pressure, prepared powder was pelletized.



Figure 3. 2: (a) XRD pattern of ZnO+CuO powder (b) XRD pattern of ZnO+CuO pellet (without annealing).

XRD pattern of pellet of ZnO+CuO powder at room temperature is shown in figure 3.4, which shows the same XRD pattern of ZnO+CuO powder at room temperature. A comparative study of figure 3.3 and 3.4 suggest that pressure has no impressive effect on structural properties of composite.



Figure 3. 3: XRD pattern of ZnO+CuO powder, pellet and annealed at different temperature 200°C and 400°C.

In order to examine the effect of annealing temperature prepared sample of composite annealed at 200°C and 400°C. XRD pattern of ZnO+CuO powder annealed at different temperature 200°C and 400°C in figure 3.5 shows that all the diffracted peaks match with the XRD pattern of ZnO+CuO(without annelation) and there is no other peak generated at any angle. In case ZnO+CuO composite peaks of CuO are shifted towards lower angle, that will be investigated further. So a close observation of all XRD patterns (including pellet and annealed powder) indicates that there is no structural change as a result of change in pressure and annealing temperature.



3.1.2 Indexing pattern of ZnO

Figure 3. 4: Xrd pattern of ZnO indicating miller planes corresponding to each peak.

Indexing of XRD pattern has been done by following procedure.

Since ZnO has hexagonal structure, the relation between inter planer distance d and miller indices is given by:-

.....(2)

Using bragg's law, $2dsin\theta = n\lambda$

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} = \frac{4sin^2\theta}{\lambda^2}$$

Rearranging this,

Calculation of lattice parameter:

From the XRD pattern 2θ values were extracted to calculate sin θ . Value of interplanar distance d for different sin θ values was calculated using equation (2). Substitution of equation (1) into (2) gives a very nice relation in which value of sin θ can be used to calculate lattice parameter and miller indices. In equation (3) we will have only one variable (c) if we put h=k=0. By comparing the XRD pattern with standard JCPDS card one can find the peak corresponding to h=k= 0 value. By using that peak we can calculate c and similarly other two lattice parameter can be calculated. After calculate the value of sin² θ theoretically. Experimental values of sin² θ directly calculated from 2 θ values. Good agreement of theoretical and experimental value of sin² θ (as shown in table 3.1) indicates that h, k and l value.

20	θ	angle in radian	sin(θ)	d(Å)	Plane	Lattice paramet	sin^2(⊖) (measured)	h	k	Ι	sin^2⊖(cal culated)
						er	(,				
31.885	15.9425	0.278248	0.2746723	2.8066171	100	a=3.2408	0.0754448	1	0	0	0.0754399
34.249	17.1245	0.298878	0.2944487	2.6181125	2	c=5.2362	0.0867000	0	0	2	0.0865271
36.457	18.2285	0.318147	0.3128071	2.4644576			0.0978483	1	0	1	0.0970717
47.372	23.686	0.413398	0.4017237	1.9189806			0.1613819	1	0	2	0.1619671
56.359	28.1795	0.491824	0.4722350	1.6324497			0.2230059	1	1	0	0.2263199
63.014	31.507	0.549900	0.5226023	1.4751177			0.2731132	1	0	3	0.2701261
66.528	33.264	0.580565	0.5484971	1.4054767			0.3008491	2	0	0	0.3017599
68.021	34.0105	0.593594	0.5593444	1.3782206			0.3128661	1	1	2	0.3128471
68.612	34.306	0.598752	0.5636121	1.3677845			0.3176586	2	0	1	0.3233917
72.436	36.218	0.632122	0.5908587	1.3047112			0.3491140	0	0	4	0.3461086
77.163	38.5815	0.673373	0.6236267	1.2361560			0.3889103	2	0	2	0.3882870

Table 3. 1: Calculation of lattice parameter and miller indices of ZnO.

3.1.3 Indexing pattern of CuO

Since CuO has monoclinic structure, the relation between interplaner distance d and miller indices is given by:-

Using bragg's law, $2dsin\theta = n\lambda$ (5)

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} = \frac{4sin^2\theta}{\lambda^2}$$

Rearranging this,



Figure 3. 5: Xrd pattern of CuO indicating miller planes corresponding to each peak.

Calculation of lattice parameter

From the XRD pattern 2 θ values were extracted to calculate sin θ . Value of interplaner distance d for different sin θ values was calculated using equation (5). Substitution of equation (5) into (4) gives a very nice relation in which value of sin θ can be used to calculate lattice parameter and miller indices. In equation (6)

we will have only one variable (b) if we put h=l=0. By comparing the XRD pattern with standard JCPDS card one can find the peak corresponding to h=l= 0 value. By using that peak we can calculate b and similarly other two lattice parameter can be calculated. After calculation of lattice parameter their values were substituted in equation (6) to calculate the value of $\sin^2\theta$ theoretically.

2θ	θ	angle in	sin(θ)	d(Å)	Plane	Lattice	sin^2(Θ)	h	k	Ι	sin^2(⊖)
		radian				parameter	(measured)				(calculated)
32.551	16.2756	0.2840634	0.2802585	2.7506743	110	a=4.61084	0.0785448	1	1	0	0.0785222
35.425	17.7126	0.3091429	0.3042423	2.5338356			0.0925633	0	0	2	0.0925172
38.846	19.4232	0.3389994	0.3325436	2.3181924			0.1105852	1	1	1	0.1016515
46.168	23.0841	0.4028924	0.3920807	1.9661767			0.1537273	0	1	2	0.1430847
48.734	24.3671	0.4252849	0.4125803	1.8684847			0.1702225	1	1	2	0.1710397
53.455	26.7277	0.4664868	0.4497512	1.7140585	20	b=3.428	0.2022762	0	2	0	0.2022691
58.176	29.0884	0.5076888	0.4861588	1.5856957			0.2363504	1	2	1	0.2533532
61.632	30.8162	0.5378437	0.5122853	1.5048255			0.2624362	0	1	3	0.2587316
65.772	32.8861	0.5739702	0.5429703	1.4197829	22	c=5.06889	0.2948168	0	2	2	0.2947866
66.182	33.0914	0.5775525	0.5459751	1.4119692			0.2980887	3	1	0	0.3021616
68.064	34.0323	0.5939743	0.5596591	1.3774458			0.3132182	2	2	0	0.3140888
72.341	36.1706	0.6312955	0.5901911	1.3061871			0.3483255	3	1	1	0.3252911
74.941	37.4707	0.6539857	0.6083545	1.2671887			0.3700952	0	0	4	0.3700701

Table 3. 2: Calculation of lattice parameter and miller indices of CuO.

Experimental values of $\sin^2\theta$ directly calculated from 2 θ values. Good agreement of theoretical and experimental value of $\sin^2\theta$ (as shown in table 3.2) indicates that h, k and l value.

In order to encounter any change in electronic structure of composite material as a result of any change in annealing temperature and pressure diffuse reflectance spectroscopy was used.

3.1.4 Band gap by using DRS (Optical Properties)

The optical band gap of prepared (x)ZnO+(1-x)CuO has been measured using diffuse reflectivity measurements. These measurements have been performed in the 200 nm to 800 nm wavelength range using Cary-60 UV-VIZ-NIR spectrophotometer having Harrick Video-Barrelino diffuse reflectance probe. In order to estimate the optical band gap the diffuse reflectance spectra has been converted to equivalent absorption spectra using Kubelka–Munk equation:

$$F(R_{\infty}) = \frac{K}{S} = \frac{(1-R_{\infty})^2}{2R_{\infty}}$$

. .

 $R\infty = R$ (Sample)/R (Standard). R (Sample) is the diffuse reflectance of the sample and R (Standard) is that of the standard (BaSO4 in present case). K and S are the Kubelka–Munk absorption and scattering functions, respectively.

Tauc plot shows the quantity hv (the energy of the light) on the abscissa and the quantity $(\alpha hv)^n$ on the ordinate, where α is the absorption coefficient of the material. The value of the exponent n denotes the nature of the transition:

$$(\alpha hv)^{n} = B (hv - Eg) \dots(7)$$

Where n=1/2 (indirect allowed transition), n=2 for direct allowed transition.

Thus, a tauc plot gives the straight line and the intercept at energy axis gives the value of band gap.

Absorption spectra and Tauc plots of (x) ZnO+(1-x)CuO powder (without annealing) are shown in figure 3.8 and 3.9.



Figure 3. 6: Absorption spectra and Tauc plots of (x)ZnO+(1-X)CuO powder (Without annealing).

Band gap of (x)ZnO+(1-x)CuO series was determined using BaSO₄ as reference because BaSO₄ band gap does not lie in the spectroscopic region of spectrometer. The pure ZnO shows strong absorption in UV region with spectral wavelength between 200 & 400 nm and pure CuO sample has wide range absorption between 250-800 nm. In absorption spectra of ZnO-CuO composite, there are two prominent absorption bands which can be assigned to the characteristic absorption of ZnO and CuO component, respectively.[4]

Sample	B.G.1±0.01(eV)	B.G.2 ±0.01(eV)
ZnO		3.26
ZnO-CuO 20%	1.41	3.12
ZnO-CuO 40%	1.34	3.06
ZnO-CuO 60%	1.31	3.07
ZnO-CuO 80%	1.30	2.76
CuO	1.07	

Table 3. 3: Calculated band gap of (x)ZnO+(1-x)CuO powder.

The appearance of two kinds of characteristic absorption bands also confirms that ZnO-CuO sample is composite material composed of ZnO and CuO. Band gap of the(x)ZnO+(1-x)CuO series(table 3.9) calculated using equation (7) by using indirect band gap fitting and band gap of this series lies between that of pure ZnO and Pure CuO.[4] A gradual red shift in the band gap values was observed with the increase in CuO. The shifting of the band gap energies to lower values may be regarded as the consequences of the enhanced combined transition from $O^{2-}(2p)$ to $Zn^{2+}(3d^{10})$ and to $Cu^{2+}(3d^9)$.[19] Also there is no formation of junction.

To confirm this formation of composite does not change with temperature it was planned to anneal the prepared powder at higher temperatures. Also to understand the effect of pressure on so formed powder was pressed into pelletes and characterized.

A similar gradual red shift in the band gap values was observed with the increase in CuO (as shown in table 3.4). A comparative study of table 3.3 and 3.4 clearly indicates that there is no effect of annealing temperature on electronic structure of ZnO - CuO composite material.



Figure 3. 7: Absorption spectra and Tauc plot of (x)ZnO+(1-x)CuO powder annealed at 200°C.

Sample	B.G.1±0.001 (eV)	B.G.2±0.001 (eV)
ZnO		3.25
ZnO-CuO 20%	1.40	3.12
ZnO-CuO 40%	1.33	3.04
ZnO-CuO 60%	1.32	3.01
ZnO-CuO 80%	1.29	2.63
CuO	1.26	

Table 3. 4: Calculated band gap of (x)ZnO+(1-x)CuO powder annealed at 200°C.



Figure 3. 8: Absorption spectra and Tauc plot of(x) ZnO+(1-x)CuO pellet.

Sample	B.G.1±0.01 (eV)	B.G.2±0.01 (eV)
ZnO		3.11
ZnO-CuO 20%	1.03	2.24
ZnO-CuO 40%	1.01	1.78
ZnO-CuO 60%	0.99	1.75
ZnO-CuO 80%	0.86	1.17
CuO	0.90	

Further prepared sample were pelletized by applying ten ton pressure.

Table 3.4: Calculated band gap of (x)ZnO+(1-x)CuO pellet.

A close observation of table 3.4 reveals that there is significant change in band gap was observed which may be due to the interfacial diffusion between ZnO and CuO. Also in case of pellets band gap decreases as compared to that of powder i.e. conduction band and valance band are moving towards each other.

To justify the result that we got above; same experiment was done again for one sample of (0.9)ZnO+(0.1)CuO series with air (figure 3.11) and white paper baseline (figure 3.12). Result of the experiment with air baseline confirms the change in band gap on making pellet which is evident from table 3.5.



Figure 3. 9: Absorption spectra and Tauc plot of ZnO+CuO powder annealed at different temperature and ZnO+CuO pellet (Air Baseline).

It may be inferred that with application of pressure there is some movement in conduction and valence band towards each other. So pellet form of composite material can be potential candidate for low band gap photovoltaic solar cells.

Sample	Band Gap±0.01 (eV)
ZnO	3.24
ZnO+CuO (R.T.)	3.24
ZnO+CuO(200°C)	3.24
ZnO+CuO(400°C)	3.24
ZnO+CuO(pellet)	3.11
CuO	2.01

 Table 3. 5: Calculated band gap of ZnO+CuO powder annealed at different temperature and ZnO+CuO pellet.



Figure 3. 10: Absorption spectra and Tauc plot of ZnO+CuO powder annealed at different temperature and ZnO+CuO pellet (white paper baseline).

In this case, we got similar result as that of air baseline which enables us to say more firmly that pressure has significant effect on electronic structure of the composite materials. A probable reason for change in band gap (in case of pellet) is interfacial diffusion between grains.

Sample	Band Gap±0.01 (eV)
ZnO	3.24
ZnO+CuO (R.T.)	3.23
ZnO+CuO(200°C)	3.23
ZnO+CuO(400°C)	3.23
ZnO+CuO(pellet)	3.16
CuO	1.09

Table 3. 6: Calculated band gap of ZnO+CuO powder annealed at different temperature and ZnO+CuO pellet (white paper baseline).

Since application of pressure on material can activate some new mode of vibration and also suppress some modes. Keeping this in view; Raman spectroscopy was used to study the electron-phonon coupling of composite materials annealed at different temperatures and also of pelletized materials.

3.1.5 Raman Spectra

It is well known that a number of physical properties of materials depend on the interactions between vibrational modes of molecules or lattices. Raman Spectra of pure ZnO and pure CuO is shown in figure 3.11.



Figure 3. 11: Raman spectra of (a) pure ZnO and (b) CuO.

In case of ZnO; there are five peaks in the figure located at 99,204,333,381 and 439 cm⁻¹ which can be assigned to E_2 , A_1 , A_1 , A_1 and E_2 respectively. It can be seen that there are four peaks in case of CuO which are located at 83, 289, 339 and 439 cm⁻¹. Previous studies [Raman spectra of nanocrystals] have shown that the three Raman peaks in CuO arise from vibrations of the oxygen atoms only. Copper (II) oxide (CuO) belongs to the C⁶_{2h} space-group with two molecules per primitive cell. There are nine zone-center optical phonon modes with symmetries $4A_u+5B_u+Ag+2Bg$; only three Ag+ 2Bg modes are Raman active.

In case of Raman spectra of ZnO-CuO composite at room temperature shows peaks at 98,199,325 and 430 cm⁻¹. First two peaks are of ZnO while other two peaks have contribution from both the materials. It is evident from comparative study of Raman spectra of powder and pellet that there is red shift of 12cm⁻¹ in case of pellet with respect to that of powder. Also mode at 198 cm⁻¹ has been suppressed and a new peak is generated 524cm⁻¹ which is a possible origin of new vibrational mode. So it is confirmed by Raman spectroscopy also that in case of pellet there is some change in electron-phonon coupling and hence in electronic structure as verified by optical spectroscopy.



Figure 3. 12: Raman spectra of (a) ZnO+CuO powder and (b) ZnO+CuO (pellet).

Figure 3.15 shows that there is no change in Raman spectra of the samples annealed at 200° C and 400° C which firmly concludes that there is no effect of annealing temperature on Raman active modes. Possible reason of suppression and generation of new modes is strain induced due to application of pressure.



Figure 3. 13: Raman spectra of ZnO+CuO Powder annealed at (a) 200°C and (b) 400°C.

3.2 Results for (x)CuO+(1-x)TiO₂ Composites

3.2.1 Structural Study (Xrd)

Xrd pattern was used to analyze the crystal structure and phases of CuO powder and pellet, TiO_2 powder and pellet, $(x)CuO+(1-x)TiO_2$ composite.



Figure 3. 14: XRD pattern of CuO powder and pellet at(a) SIC and (b) RRCAT lab.



Figure 3. 15: XRD pattern of (a) TiO2 powder and pellet (b) (x)CuO+(1-x)TiO2 pellet.

Figure 3.16 shows the XRD pattern of pure CuO powder and pellet which is well – crystallized into monoclinic phase perfectly matching with the JCPDS file no. 89.5899 with the lattice parameters $a= 4.6108 \text{ A}^\circ$, $b=3.428 \text{ A}^\circ$ and $c=5.0689 \text{ A}^\circ$. No peaks of other phases and impurity were detected. Intensity of diffracted peaks of CuO pellet is less comparison to CuO powder because pellet is behaving less like a polycrystalline sample. In case of pellet, number of planes available for a particular direction is less than that of in powder.

XRD pattern of TiO_2 powder and pellet (figure 3.17) has been crystallized into two phases anatase and rutile phase. All the diffracted peaks matched with JCPDS file.

Figure 3.18 shows the XRD pattern of CuO-TiO₂ composite pellet, which shows that all the diffracted peaks matching with the pure CuO and pure TiO₂ and there is no any other peak generated at any angle. So the XRD pattern indicates that there is no structural change in CuO-TiO₂ composite when we applying pressure.

3.2.2 Band gap by using DRS (Optical Properties)

Band gap of $(x)CuO+(1-x)TiO_2$ composites calculated using DRS. Linear region of Tauc plot of $(x)CuO+(1-x)TiO_2$ composites was fitted with straight line and the

intercept of this plot on energy axis gives the band gap of composites. Fitting is done by considering (x)CuO+(1-x)TiO₂ series having indirect band gap. Absorption spectra and tauc plot of(x)CuO+(1-x)TiO₂ powder (without annealing) are shown in figure 3.19.



Figure 3. 16: Absorption spectra and Tauc plot of (x)CuO+(1-x)TiO2 powder (without annealing).

The appearance of two kinds of characteristic absorption bands also confirms that $CuO-TiO_2$ sample is composite material composed of CuO and TiO₂ respectively. When we mix the TiO₂ in CuO, band gap of CuO-TiO₂ composite increase due to the enhanced transition of $O^{2-}(2p)$ to $Cu^{2+}(3d^9)$ and $Ti^{2+}(3d^2)$.

Sample	B.G.1±0.01 (eV)	B.G.2±0.01 (eV)
CuO	1.12	
CuO-TiO ₂ 20%	1.18	2.9
CuO-TiO ₂ 40%	1.20	3.11
CuO-TiO ₂ 60%	1.21	3.15
CuO-TiO ₂ 80%	1.24	3.17
TiO ₂		3.23

Table 3.7: Calculated band gap of $(x)CuO+(1-x)TiO_2$ powder (without annealing).

To confirm this formation of composite does not change with temperature it was planned to anneal the prepared powder at higher temperatures.



Figure 3. 17: Absorption spectra and Tauc plot of (x)CuO+(1-x)TiO2 powder annealed at 200°C.

A comparative study of table 3.7 and 3.8 clearly indicates that there is no effect of annealing temperature on electronic structure of CuO-TiO₂ composite material.

Sample	B.G.1±0.01 (eV)	B.G.2±0.01 (eV)
CuO	1.24	
CuO-TiO ₂ 20%	1.29	2.65
CuO-TiO ₂ 40%	1.30	3.01
CuO-TiO ₂ 60%	1.31	3.14
CuO-TiO ₂ 80%	1.39	3.19
TiO ₂		3.24

Table 3.8: (Calculated band	gap of(x)	$CuO+(1-x)TiO_2$	2powder	annealed at 200°C.
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To see the effect of pressure on $CuO-TiO_2$ composite we make a pellet and see the absorption spectra and calculate band gap of composite.



Figure 3. 18: Absorption spectra and Tauc plot of (x)CuO+(1-x)TiO2 pellet.

Sample	B.G.1±0.001 (eV)	B.G.2±0.001 (eV)
CuO	0.15	
CuO-TiO ₂ 20%	0.74	1.27
CuO-TiO ₂ 40%	0.94	1.55
CuO-TiO ₂ 60%	1.17	1.85
CuO-TiO ₂ 80%	1.23	2.60
TiO ₂		2.92

Table 3.9: Calculated band gap of $(x)CuO+(1-x)TiO_2$ pellet.

Absorption spectra of CuO-TiO₂ composite (pellet) shown in figure 3.21, there are two absorption bands which can be assigned to the characteristic absorption of CuO and TiO₂. Calculated band gap of composite in Table 3.9 shows that there is significant change in band gap, which may be due to the interfacial diffusion between CuO and TiO₂. It will be investigated further. Also in case of pellets band gap decreases as compared to that of powder i.e. conduction band and valance band are moving towards each other.

Chapter 4

4. Summary and Conclusion

(x)ZnO+(1-x)CuO and $(x)CuO+(1-x)TiO_2$ composite materials were prepared by physical mixing of pure ZnO, CuO and TiO₂ powder. Composite materials were characterized using XRD, UV-Vis and Raman spectroscopy. XRD pattern of (x)ZnO+(1-x)CuO composite materials shows that there are no extra peaks generated and all the samples in single phase. Similarly XRD pattern of $(x)CuO+(1-x)TiO_2$ composites show no extra peaks.

In DRS, absorption spectra of ZnO-CuO composite shows the two prominent absorption bands which can be assigned to the characteristic absorption of ZnO and CuO component, respectively. The appearance of two kinds of characteristic absorption bands confirms that ZnO-CuO sample is composite material composed of ZnO and CuO. In case of CuO-TiO₂ composite we get two absorption bands which clarify that CuO-TiO₂ composed of CuO and TiO₂.

DRS data of ZnO-CuO reveals that band gap of ZnO-CuO composites lies between pure ZnO and pure CuO and after annealing composite there is no significant change in band gap, while in case of pellet band gap change significantly which may be due to the interfacial diffusion between grains.

Raman spectra of ZnO –CuO composite pellet show some shifting as compared to powder which may be due to strain induced during pellet preparation or interfacial diffusion.

4.1 What I have learned from this project work

- Literature survey.
- Understanding of various Optical properties.
- Different characterization techniques.
- Understanding of how to handle sophisticated instruments.

4.2 Future Scope

- To study the temperature dependent band gap of composite materials.
- The photo luminescence experiment to confirm direct and indirect band gap.
- Hydrogen production using CuO-TiO₂ composite materials.
- To check the multi-ferocity of TMO composites.
- The correlation between the pellet and the powder samples of pure and composite material will be investigated further in greater details.

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