ROLE OF TITANIUM DOPING IN
UV SENSING STUDY OF
COPPER OXIDE
CuO [$Cu_{1-x}Ti_xO$]

Submitted By

ASHMITA PANDA

Under the Guidance of

DR. SOMADITYA SEN

Associate Professor

Physics Metallurgical Engeneering And Material Sciences

Indian Institute of Technology Indore

PhD Scholar

PRASHANT KUMAR MISHRA

Research Scholar (JRF)

Department of Physics

Smart Lab Group

Indian Instipite of Technology Indore

ACKNOWLEDGEMENT

I would like to express my deep and sincere gratitude to my guide **DR. SOMADITYA SEN**. It is an honour for me work on a project under his guidance. I hereby take the oppurtunity to thank **Mr. Prashant Kumar Mishra (PhD Scholar)** for his extensive help and for providing valuable information regarding my work. I would like to express by sincere gratitude to **all lab members** for their help and support.

Contents

Introduction

Transition Metals are metals having incompletely filled d-orbitals in neutral or ionic state. As Cu^{2+} ion has the [Ar]d^9 configuration, copper belongs to the family of Transition Metals. These metal oxides have been of great interest to scientists, as they exhibit a variety of structures and properties.They are generally semi-conductors and possess an electronic structure characterised by two distinct bands : **Valence Band** and **Conduction Band**. The energy difference between the top of the valence band and bottom of the conduction band is termed as **Band Gap**. The nature of metal-oxygen bonding varies from metallic or highly covalent to nearly ionic. The unusual properties of transition metal oxides arise dure to the unique nature of outer d-electrons.

Copper Oxide is a unique transition element monoxide exhibiting low symmetry ***Monoclinic Structure***. It is a low dimensional antiferromagnetic compound with a Neel Temperature(T_N) of 230K. CuO has a band gap ranging from 1.2 eV to 2.1 eV. CuO quantum dots have been reported to exhibit greater band gaps of $\sim$5.3 eV. It behaves like a " "-type semiconductor.
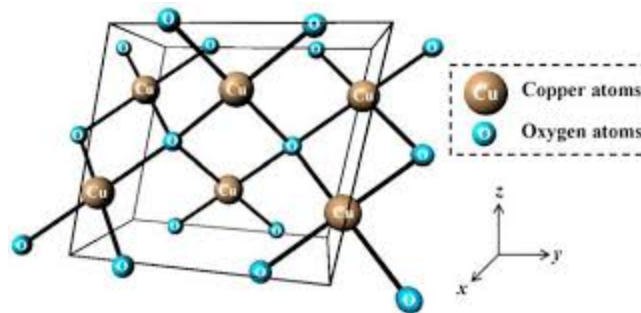

Fig. CuO Monoclinic Structure

It has lattice parameters **a=4.6837(5), b=3.4226(5)** and **c=5.1288(6)**, with **α= 90°, β= 99.54(1)°** and **γ= 90°**. Cu^{2+} ions are coordinated to oxygen atoms by fourfold symmetry, situated at the corners of a rectangular parallelogram. Four copper atoms situated at the corners of a distorted tetrahedron coordinate the O^{2-} ions. **4c (1/4, 1/4, 0) Wykoff's positions** are occupied by Cu^{2+} ions, and O^{2-} ions occupy **4e (0, y, 1/4) Wynkoff's positions**.There are no phase transitions observed in the CuO structure upto 3000K

3

temperature and 700kbar of pressure. CuO has three acoustic modes ($A_\nu + 2B_\nu$), six IR-active modes ($3A_\nu + 3_Bu$) and three Raman active modes ($A_g + 2B_g$). CuO belongs to C^6_{2h} space group with two molecules per primitive cell.

There is an increasing interest in copper oxide because its applications look promising in the field of catalysis, superconductivity, ceramics and biology. It is used as a burning rate catalyst in rocket fuel, in ceramics to produce blue, red and green glazes, sensors, torage devices and superconductors. It is also supposed to have biological application as an efficient antimicrobial agent.

Experimental

Sol Gel Method

It is the method of producing solid materials by fabricating the small molecules. The monomers are converted into a collodial solution *(sol)* which then acts as a precursor for the integrated network *(gel)* of either discrete particles or network polymers. Metal Alkaloids act as typical precursors. The gel like diphasic system contains both a liquid phase and a solid phase whose morphologies range from discrete particles to continuous polymer networks.
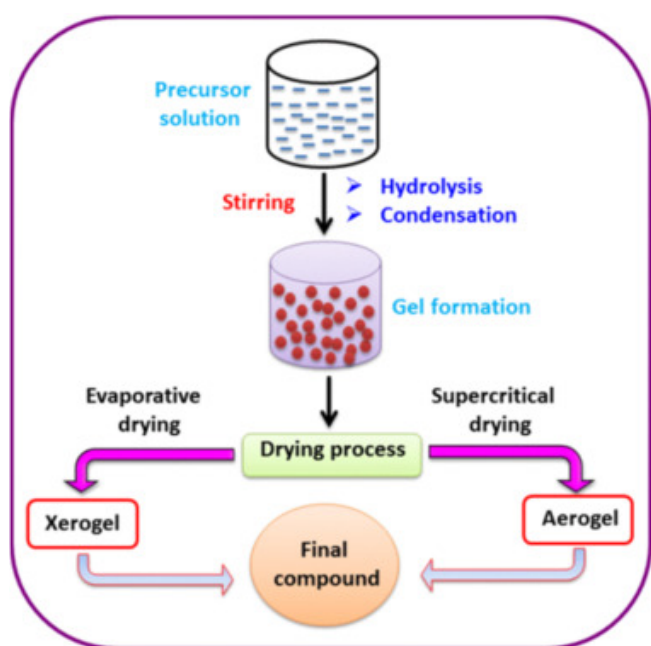
In colloids, a significant amount of fluid may need to be removed to increase the volume fraction of particles so that gel like characteristics may be visible. The remaining of the solution is subjectedto a **drying process** to remove the remaining solvent phase. The gel becomes significantly shrunken and dense after that. Sol Gel technique is a cheap and low temperature process that allows the fine control of the product's chemical composition. Materials prepared by this process can be used in ceramics processing. Thin films of metal oxides can be prepared by this method. Materials produced by sol gel technique have diverse applications in optics, electronics, energy, space, sensors, medicine, reactive material and separation technology.

Sol-Gel Method can be distinguished into two types based on the nature of the solvent used.

Aqueous Sol-Gel Method :   Water is used as a reaction meduim.

Nonaqueous Sol-Gel Method :   Organic Solvents are used as reaction medium.

The nature of the metal precursors and solvent plays a very important role in the synthesis of metal oxide nanoparticles using solgel technique.

Synthesis

The aqueous sol-gel method has been followed by us for the preparation of titanium doped copper oxide. The chemicals used for the preparation of the nanostructure were copper oxide, nitric acid, ethylene glycol, citric acid and TALH[Titanium(IV)bis(ammonium lactato)dihydroxide] and double distilled water.

We synthesised pure and Ti doped CuO at different doping concentrations (x=0.0078, 0.0156, 0.1234, 0.0312).
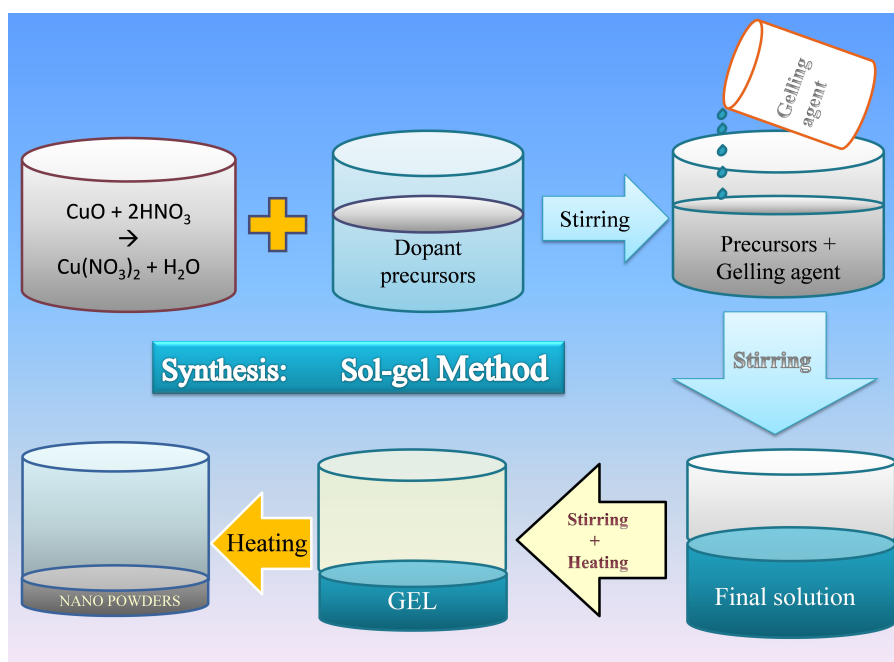

Fig. Method of producing Nanoparticles using Sol-Gel Technique

For doped phases, precursors are produced by dissolving copper oxide and TALH in double distilled water in approproate amounts. The solution is then stirred and nitric acid is added to it dropwise with continuous stirring. After 2 hours citric acid and ethylene glycol are added to the solution in 1:2 ratio. Gel formation takes place after that. Heating at high temperatures gives the final product. Annealing the material at 450°C and 600°C gives the nanocrytalling $Cu_{1-x}Ti_xO$.

For pure phase, the same procedure is repeated without TALH.

Characterisation Techniques

X-Ray Diffraction

X-Ray Powder Diffraction is a rapid analytical technique used for phase identification of a crystalline material and provide information on unit cell dimension.
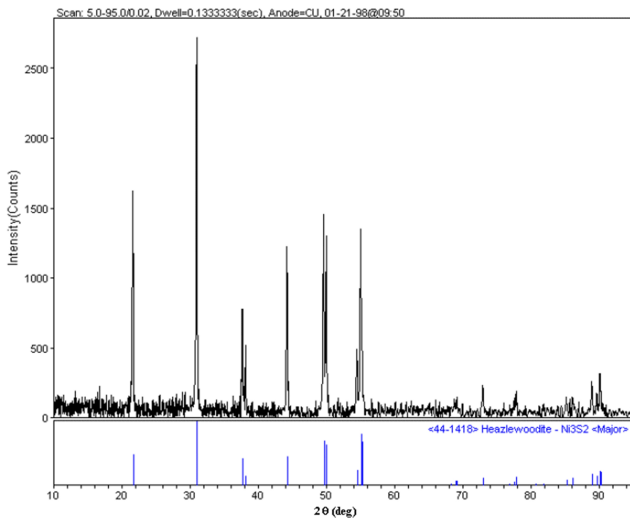

Fig. XRD Graph

It was discovered by monVon Laue in 1912, that crystalline substances ct as three-dimensional diffraction gratings for X-Ray wavelengths similar to te spacing of planes in a crystalline lattice. It is based on the consructive interference of monochromatic X-Rays and a crystalline sample. The interaction of the incident rays with the sample produces cinstructive interference and a diffracted ray when Bragg's law is satisfied ($n\lambda = 2d\sin\theta$). The diffracted rays are then detected, processed and counted. We can get all possible diffraction directions of the lattice by scanning the sample through a range of 2θ angles, because of the random orientation of the powdered material. Each mineral has a set of unique d-spacing. If we convert diffraction peaks of the material to d-spacing we can identify the mineral with ease.
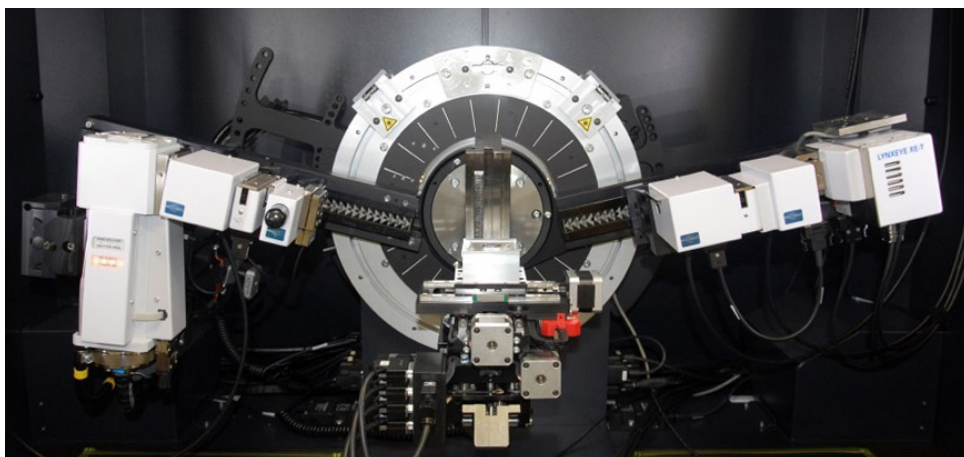

Fig. X-Ray Diffraction Device

The difffractometers contain three essential components :

- X-Ray Tube

- Sample Holder

- X-Ray Detector

The cathode ray heats a filament to generate electrons, applies a voltage to accelerate the electrons and then bombards the target material with them. At some point electrons gain suffiecient energy to dislogde inner shell electrons of the target material. Then characteristic X-Rays are produced. K_α and K_β are the more common components of the X-Ray spectra. K_α consists of two parts, $K_{\alpha1}$ and $K_{\alpha2}$. $K_{\alpha1}$ has slightly shorter wavelength and twice the intensity as $K\alpha2$. The specific wavelengths are characteristics of the target material. Copper acts as the most common target material for simple crystal diffraction.

CuK_α radiation = 1.542 Angstroms

The collimated X-ray beam is targeted towards the material. An instrument called the **goniometer** maintains the angle and rotates the sample. The intensity of the reflected X-rays is recorded. Constructive interference occurs when thegeometry of the sample satisfies Bragg's law and we observe a peak in the intensity. The X-ray signal is recorded, processed, and converted to a count rate. The sample rotates in the path of the X-ray beam at an angle θ and the detector rotates at an angle 2θ. For a typical powder sample, data is collected at 2θ from ~5° to 70°.

For performing X-ray Diffraction on a material it must be thoroughly grinded into a fine powder. The powder is then placed on special glass holders and the top os smoothed out with a glass plate. It provides a uniform surface and ensures better results.

Fig. CuO Powder

The data is obtained in the form of a graph of intensity (y-axis) vs 2θ (x-axis). X-Ray Diffraction of a sample is carried out at multiple temperatures like 450°C, 600°C, 850°C, etc to detect the phase changes occuing (if any) in the sample and to conclude if the sample has a pure phase or not.

UV-Sensing

Ultraviolet is a band of the electromagnetic spectrum with wavelength from 10nm to 400 nm, shorter than visible light but longer than X-rays. UV sensor is a device used for detecting the intensity of incident UV Radiation. It works on the principle of Photoelectric Effect.
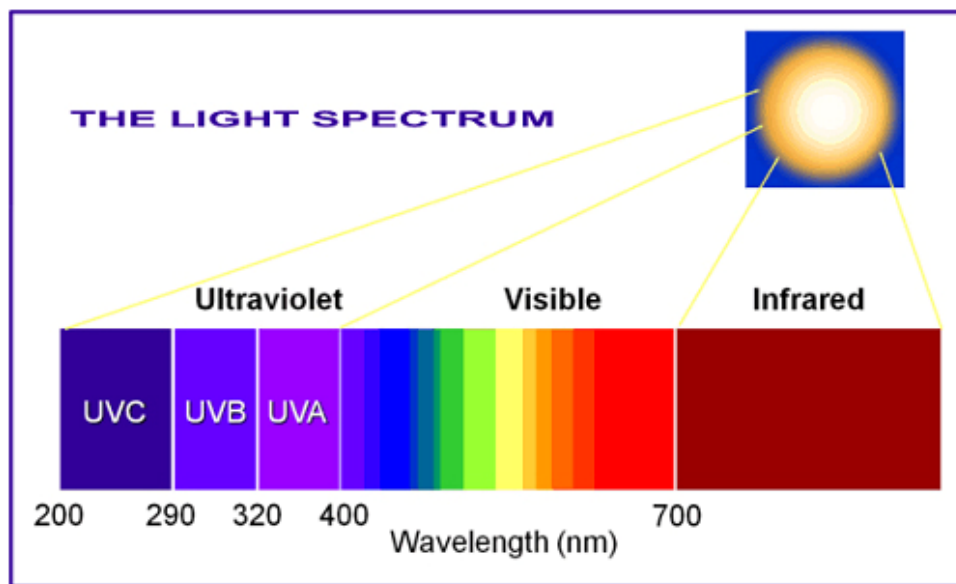

Fig. Light Spectrum

Photoelectric Effect is the emission of electrons or other free carriers when light hits a target material. The electricity generated is called photoelectric current.

We perform UV-Sensing of our material (Titanium doped Copper Oxide) to know if it responds to UV light, i.e., whether or not it produces electricity when UV light is shined on it. First we heat the powder to a suitable temperature, say 600°C (if it has not been heated before) for a duration of a few hours. We then make pellets of the material with the help of a binder (PVA). The pellets are then properly labeled and subjected to heating at 600°C again for a duration of 6 hours.

After this, the pellets are sufficiently hardened and the binder also
evaporates. The pellets are then `pasted', using silver and isoamyl acetate
solution. In this process, the pellet is painted with silver and isoamyl
acetate solution, except for a uniform strip at the center. Care must
be taken to make the surface area painted is almost the same for better
results. The pellets are subsequently heated for another 30 mins to fix
the paste and then put into the UV Sensing Machine.

Fig. CuO Pellet
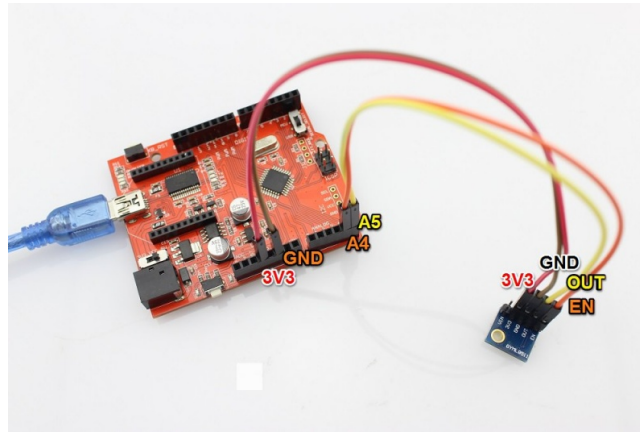
Fig. UV Sensor

The output is recieved in the form of raw data of time, current and voltage(remains almost
constant). The graph between current and time is plotted with time on the x-axis and current
on the y-axis. The graph gives us an insight about the current generated, growth and decay
time, and sensitivity of the material.

IV-Test

The IV-Test is performed on a material to obtain an idea about its resistance and its nature.
The samples are prepared in the same way as for the UV-Sensing. The output is obtained in
the form of raw data giving values of voltage and corresponsing current. The data is plotted
in the form of a graph with current on y-axis and voltage on x-axis. Sometimes the graph is
converted to a logarithmic one for ease of understanding.

Results and Discussion

X-Ray Diffraction

We performed X-Ray Diffraction on our sample which had been heated at a temperature of $600°C$ for 2 hours. Monoclinic single crystalline phase is revealed for all synthesised samples (x=0.0058, 0.0156, 0.0234, 0.0312).
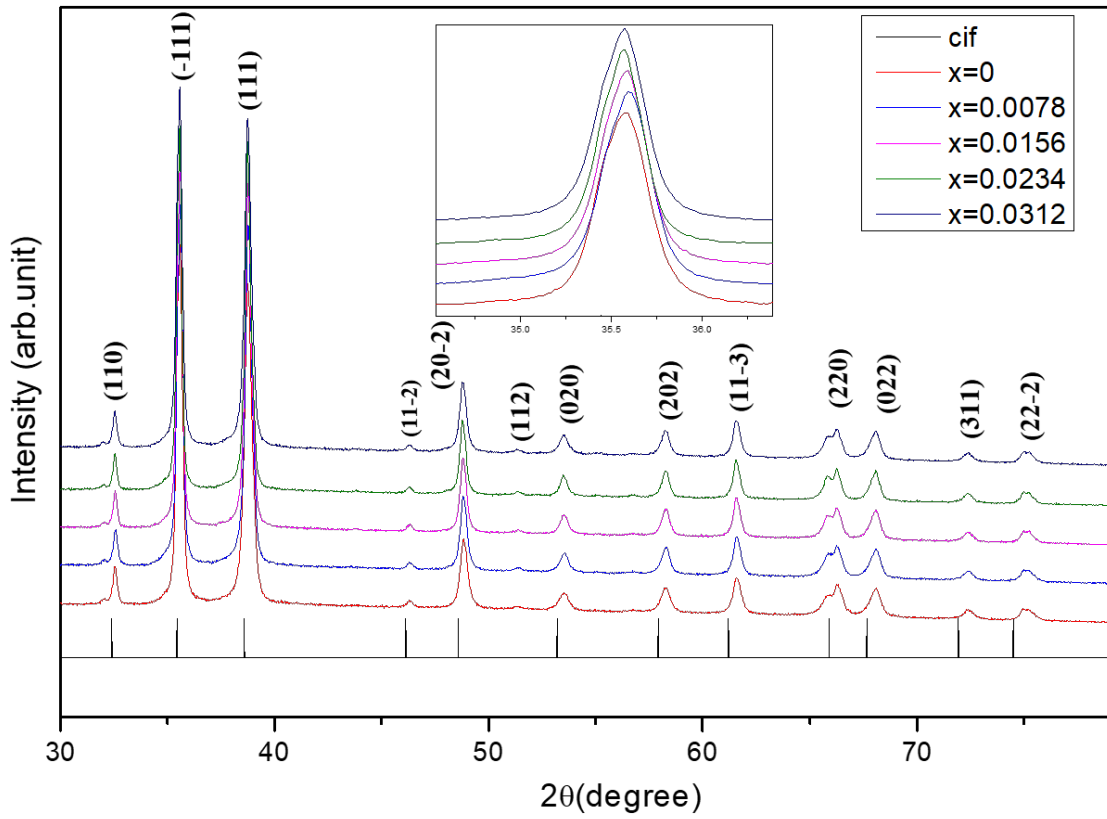

Fig. XRD Graph

The graph shows peaks belonging to various planes in the monoclinic crystal structure. No peak belonging to impurity phases is detected, so all samples are in pure phase. This emphasizes that Titanium was successfully incorporated in monoclinic structure of CuO. The shifting of (111) diffraction peaks to lower angles hints towards the increase in lattice parameters. When we perform RietVeld Refinement on the X-Ray Diffraction data, we obtain the near perfect values of the lattice parameters a, b and c.
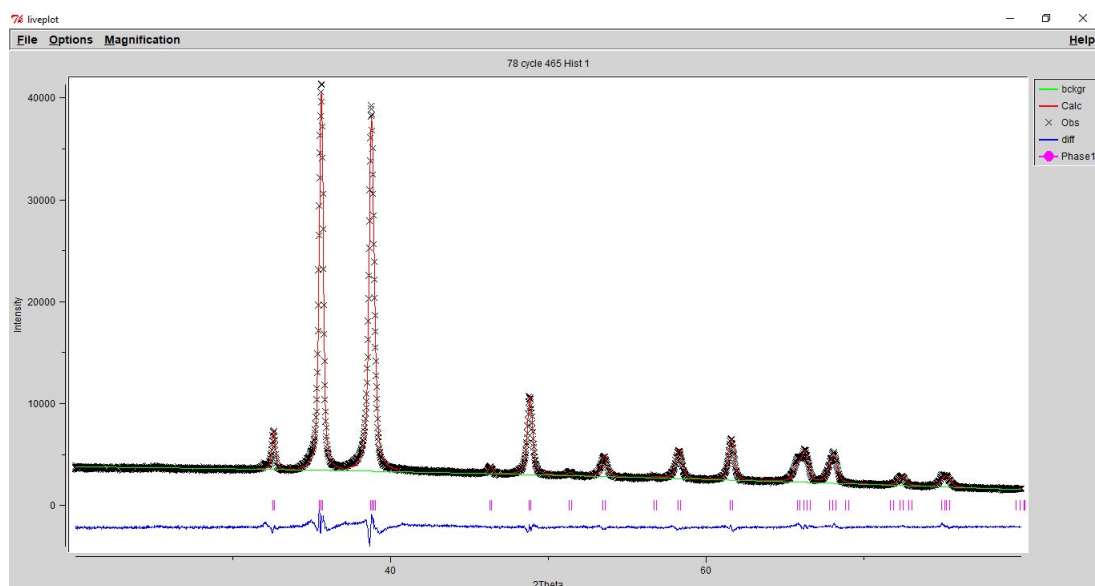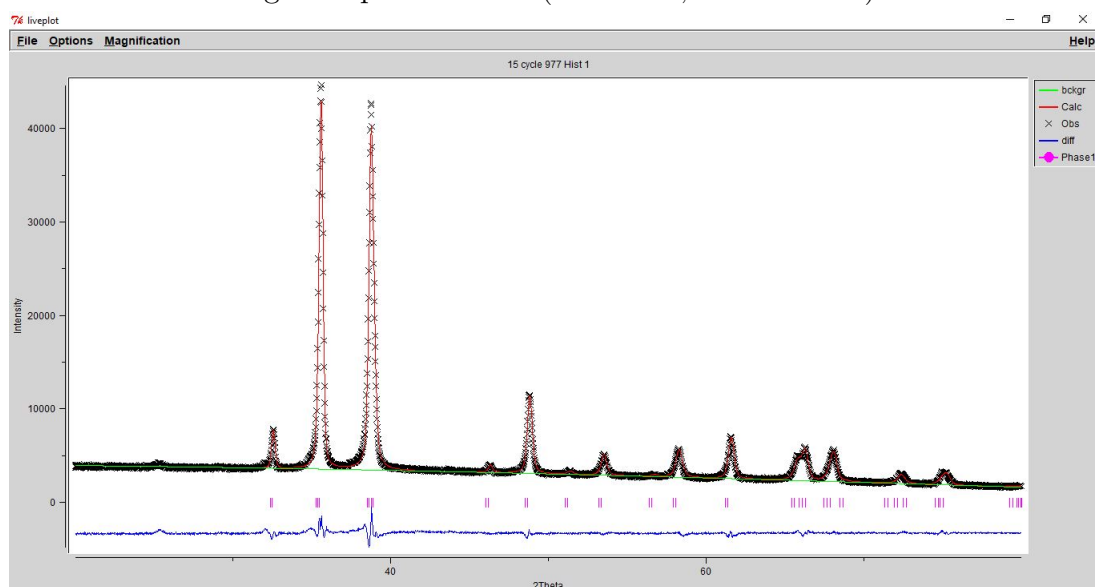
11

Fig. Liveplot of XRD (x=0.0078, CHI^2=4.762)
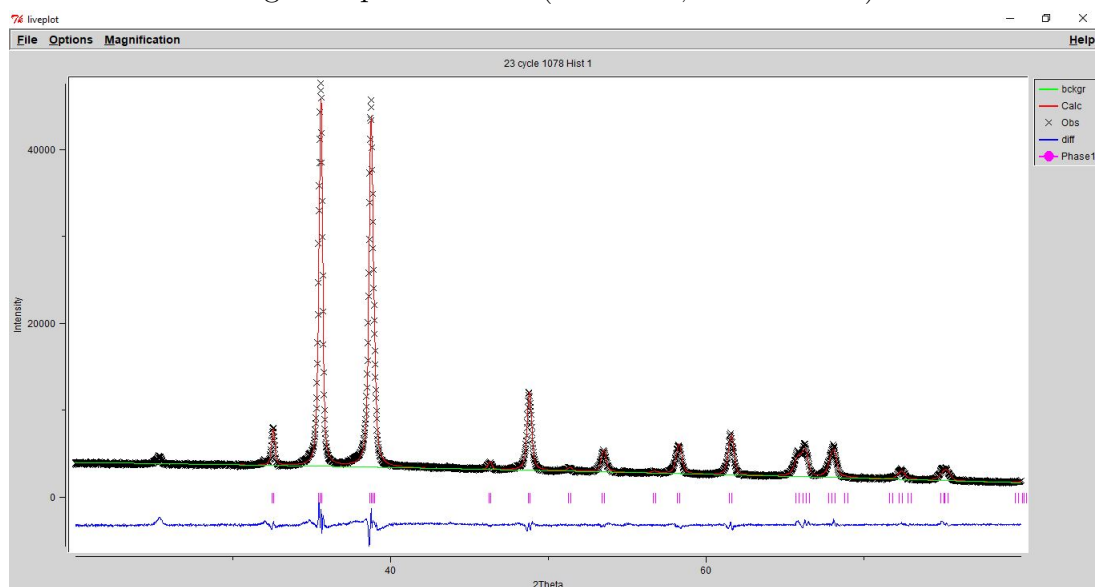

Fig. Liveplot of XRD (x=0.0156, CHI^2=4.220)

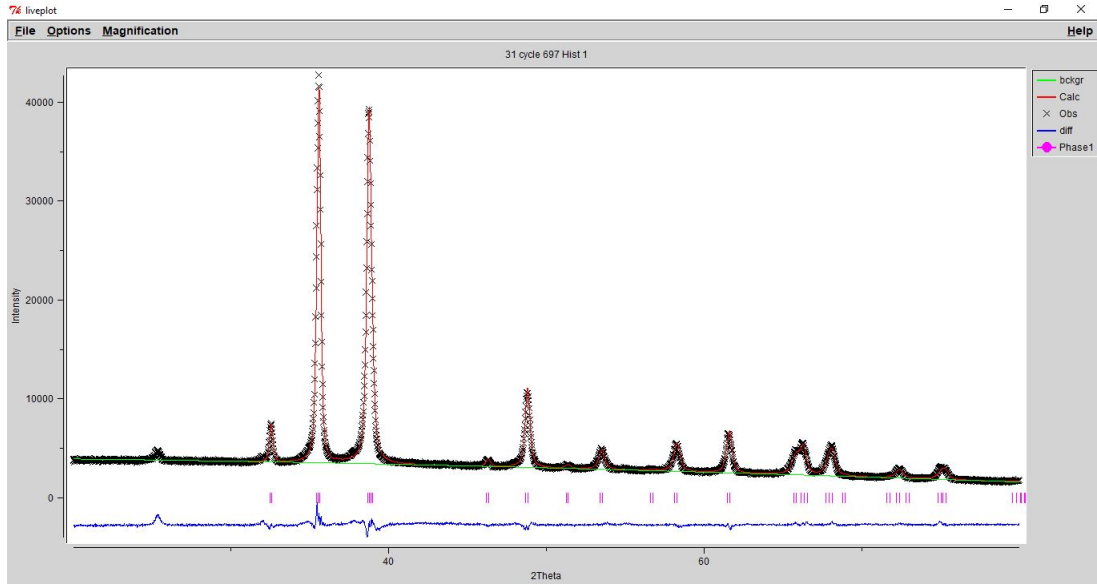Fig. Liveplot of XRD (x=0.0234, CHI^2=5.197)

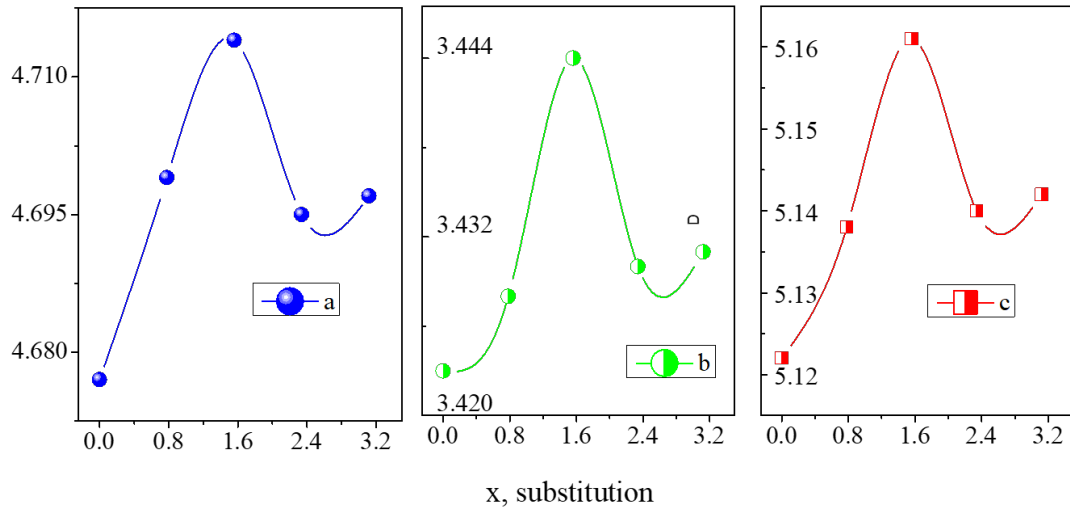Fig. Liveplot of XRD (x=0.0312, CHI^2=4.100)

x, substitution

Fig. Lattice Parameters

We observe that there is an increase in lattice parameters of the doped crystal. The graph peaks at x=0.0156, showing that the samples having 1.56% doping have the greatest lattice parameters. For x=0.0234 and x=0.0312, lattice parameters are significantly less than that of x=0.0156 but almost the same when compared to each other and x=0.0078 (except for a).

This pattern of lattiec parameters may indicate greater similarity in the crystal structure of 0.78%, 2.34% and 3.12% doped CuO. They deviate the least from the original structure while 1.56% deviates the most.

UV-Sensing

We performed UV-Sensing of our pure and doped samples (x=0.0078, 0.0156, 0.0234, 0.0312) which had been made into pellets and heated at 600°C for 6 hours. We combined all the results obtained into a single graph to facilitate our study.
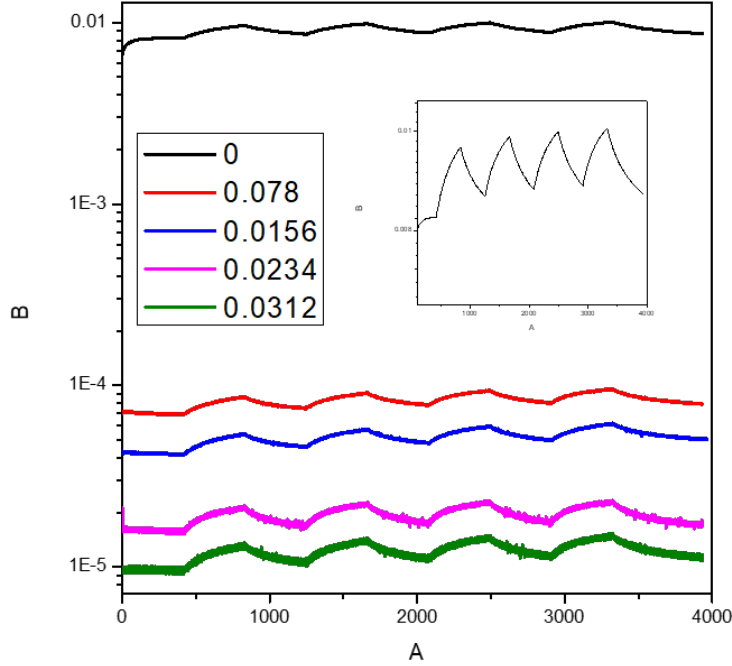

Fig. UV-Sensing

We can observe from the graph that there are no plateau regions between grwoth and decay. It indicates that the current never becomes stable with time. We can also observe that as the doping concentration increases, the value of current decreases. Thus we can conclude that the doped crystal is becoming increasingly resistant with increase in doping. Titanium contributes towards increasing the resistance of the crystal.

With the help of UV-Sensing data we can also study the sensitivity of the crystal and the effect of the doping on it. We plot the graphs of current (y-axis) vs x-substituion (x-axis) and Response Time/Recovery Time (y-axis) vs x-substituion (x-axis) to facilitate our study. From these we can also plot the graph of percentage sensitivity (y-axis) against x-substitution
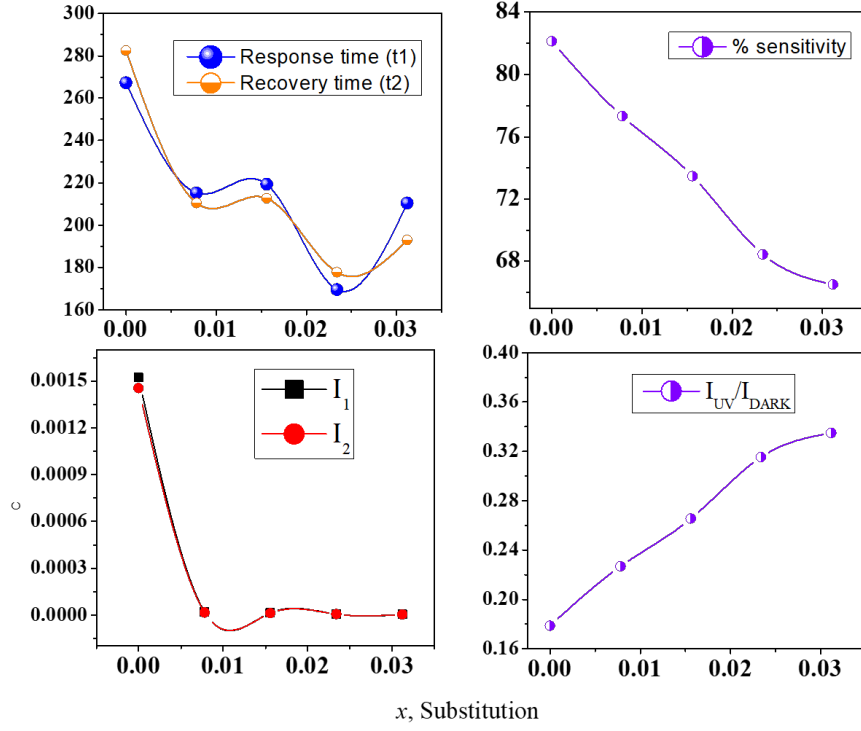
(x-axis) too.

Fig. Sensitivity

We observe that Response/Recovery Time of the doped crystal is significantly less than the pure crystal, though the decrease is not uniform. There are peks at every alternate point (x=0.0156, 0.0312). 2.34% doped CuO crystal has the least Response/Recovery Time.

We also observe that the growth and decay current of doped crystal is extremely less than that of the pure crystal. We fail to observe any more sharp declines. The growth and decay currents of all the doped crystals remain more or less the same, orrespective of their doping concentrations.

As a combined effect of the above results, we observe that the sensitivity of the crystal decreases uniformly with increase in doping concentration. Titanium reduces the sensitivity of CuO crystal.

IV-Test

We performed IV-Test of our pure and doped samples (x=0.0078, 0.0156, 0.0234, 0.0312) which had been made into pellets and heated at 600°C for 6 hours. We combined all the results obtained into a single graph to facilitate our study. The graph was then converted into a logarithmic graph.
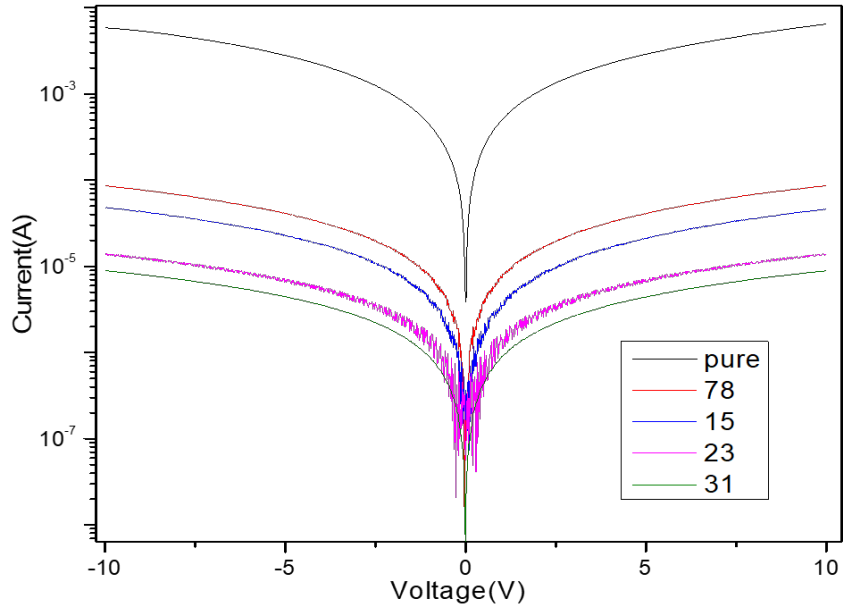

Fig. IV-Test Data

We can observe that the value of current staedily decreases with increase in doping concentration. This indicates that the resistance of the crystal increases with increase in doping concentration. The graph also indicates that the crystal is an Ohmic resistor by nature. The nature of the resistance remains constant throughout, i.e., it remains an Ohmic resistor at all doping concentrations.

Conclusion

This experiment was conducted to study the effects of Titanium doping on the structural properties and UV-Sensing of Copper Oxide crystal. From the results discussed above, we can conclude that titanium increases the lattice the lattice parameters of the CuO crystal.The increase is prominent but non-uniform. It also increases the resistance of the crystal without changing its inherent Ohmic nature. The increase is mostly uniform. The sensitivity of the crystal also decreases with increase in doping concentration. The decrease is smooth and uniform.