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Advances in Applied Science Research, 2013, 4(6):13-20

ISSN: 0976-8610
CODEN (USA): AASRFC

Growth of thin films of ZnO by induction heated liquid phase epitaxy

G. Sankar[c], A. Claude[a]*, S. Sathya[b] and A. Poiyamozhi[c]

[c]Post Graduate and Research Department of Physics, Government Arts College, Dharmapuri, Tamil Nadu, India
[b]Department of Physics, Pachamuthu College of Arts and Science for Women, Dharmapuri, Tamil Nadu, India
[a]Post Graduate and Research Department of Physics, Arignar Anna Government Arts College, Villupuram, Tamil Nadu, India

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ABSTRACT

"Thin films" in today's science and technology scenario plays an important role scientifically and also in the high-tech industries. Thin films as a two dimensional system are of great importance's to many real world problems. Their material costs are small when compared to the bulk materials but they perform the same functions technically. Thus knowledge and determination of the nature, functions and new properties of thin films can be used for the development of new technology for future applications. Thin films have very interesting properties that are quite different from those of the bulk materials which they are made up. This is because of the fact that their properties depend on a number of inter related parameters and also on the technique employed for the fabrication. The charge is taken as a supersaturated solution with an optimal texture and so that crystallization evolves easily else there is a possibility of accumulation and multiple nucleation which will prevent the film formation. Homogeneous combinations of single layered and multiple layered thin films are grown after arranging for a thin film coating using Liquid Phase Epitaxy method. Zinc Oxide thin films in pure form was coated on suitable substrates. The thin films grown by this process will be subjected to structural, functional and optical characterizations.

Keywords: LPE, induction heating, crystalline, amorphous, homogenous films, heterogenous films

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INTRODUCTION

Thin films can be grown from various methods by using various materials. Different type of methods can be used to produce useful coatings of thin films [1,2]. These processes exploit the creation of solid materials directly from chemical reactions in gas and/or liquid compositions or with the substrate material. The solid material is usually not the only product formed by the reaction. Byproducts can include gases, liquids and even other solids. Common for all these processes are that the material deposited is physically moved on to the substrate. In other words, there is no chemical reaction which forms the material on the substrate [3]. This is not completely correct for casting processes, though it is more convenient to think of them that way. This is by no means an exhaustive list since technologies evolve continuously day by day.

EPITAXIAL THIN FILM GROWTH

Thin film growth by epitaxial method is one of the most promising methods adopted currently to obtain coated substrates. This method requires only a fraction of the charge required for thin bulk material growth. This technology is quite similar to what happens in CVD processes, however, if the substrate is an ordered semiconductor crystal (i.e. silicon, gallium arsenide), it is possible with this process to continue building on the substrate with the same crystallographic orientation with the substrate acting as a seed for the deposition [4]. If an amorphous/polycrystalline substrate surface is used, the film will also be amorphous or polycrystalline.

There are several technologies for creating the conditions inside a reactor needed to support epitaxial growth, of which the most important is Liquid Phase Epitaxial (LPE). In this process, a number of substrates are introduced into an induction heated reactor where only the substrate is heated [5]. The temperature of the substrate typically must be at least 50% of the melting point of the material to be deposited. An advantage of epitaxy is the high growth rate of material, which allows the formation of films with considerable thickness (>100µm). Epitaxy is also widely used technology for producing silicon on insulator (SOI) substrates.

INDUCTION HEATING

Induction heating is a process which is used to bond, harden or soften metals or other conductive materials. For many modern manufacturing processes, induction heating offers an attractive combination of speed, consistency and control. The basic principles of induction heating have been understood and applied to manufacturing since the 1920s. During World War II, the technology developed rapidly to meet urgent wartime requirements for a fast, reliable process to harden metal engine parts. More recently, the focus on lean manufacturing techniques and emphasis on improved quality control have led to a rediscovery of induction technology, along with the development of precisely controlled, all solid state induction power supplies where heat is actually "induced" within the part itself by circulating electrical currents.

Induction heating relies on the unique characteristics of *radio frequency (RF) energy* - that portion of the electromagnetic spectrum below infrared and microwave energy. Since heat is transferred to the product via electromagnetic waves, the part never comes into direct contact with any flame, the inductor itself does not get hot, and there is no product contamination observed. When properly set up, the process becomes very repeatable and controllable [6 -9].

Working Principle

With elaborating the principle and working of induction heating, It helps to have a basic understanding of the principles of electricity. When an alternating electrical current is applied to the primary of a transformer, an alternating magnetic field is created. According to **Faraday's Law**, if the secondary of the transformer is located within the magnetic field, an electric current will be induced.

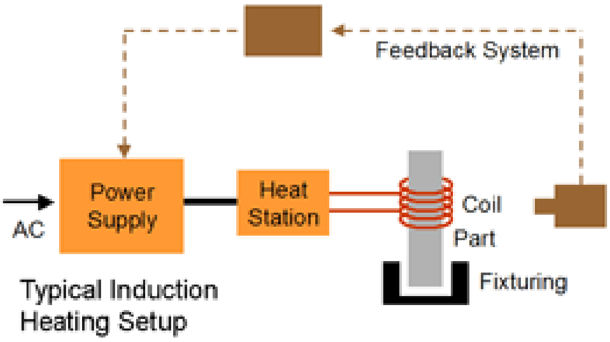

Fig. 1: Schematic of Induction Heating

In a basic induction heating setup (Fig.1) shown above, a solid state RF power supply sends an AC current through an inductor (often a copper coil),and the part to be heated (the workpiece) is placed inside the inductor. The inductor serves as the transformer primary and the part to be heated becomes a short circuit secondary. When a metal part is placed within the inductor and enters the magnetic field, circulating eddy currents are induced within the part.

As shown in the second diagram (Fig.2), these eddy currents flow against the electrical resistivity of the metal, generating precise and localized heat without any direct contact between the part and the inductor. This heating occurs with both magnetic and non-magnetic parts, and is often referred to as the "**Joule effect**", referring to Joule's first law – a scientific formula expressing the relationship between heat produced by electrical current passed through a conductor.

Secondarily, additional heat is produced within magnetic parts through **hysteresis** – internal friction that is created when magnetic parts pass through the inductor. Magnetic materials naturally offer electrical resistance to the rapidly changing magnetic fields within the inductor. This resistance produces internal friction which in turn produces heat.
In the process of heating the material, there is therefore no contact between the inductor and the part, and neither are there any combustion gases. The material to be heated can be located in a setting isolated from the power supply; submerged in a liquid, covered by isolated substances, in gaseous atmospheres or even in a vacuum.

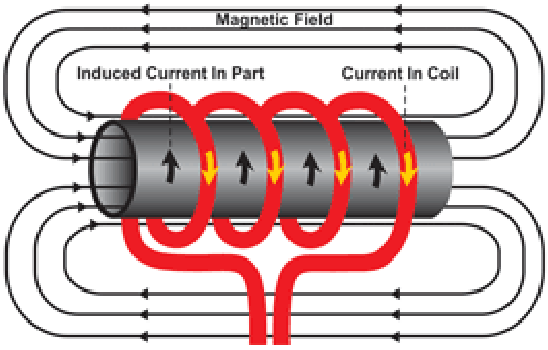

Fig. 2: Induction heating by Eddy current flow

MATERIALS AND METHODS

Magnesium, Cobalt, and Copper were doped on thin films of Zinc Oxide. The starting materials Zinc Nitrate $ZnNO_3$ (base material to form ZnO thin film) was taken as lab grade (AR) chemicals in fine powdered form of 98% purity. The chemical was finely grounded using pestle-mortar and taken for experimentation [10]. Suitable substrates are taken as thin plates of either Glass, Zinc, Aluminium or Stainless Steel. Thin films are grown on these substrates by induction heating method. ZnO thin films were grown by the following procedure. Initially 30gm of colourless odourless $ZnNO_3$ salt was taken, 10ml pure distilled water was added and make a standard saturated solution. Then an optimal supersaturated solution was attained by adding a little more of the salt while elevating the temperature by around 5 to 10°C. A stainless steel plate of length 4.7cm and thickness 0.2mm is taken and placed on the induction stove and switched on. When the steel plate is heated at temperature as high as 80°C, the plate is ready to absorb any coating by quenching. One layer of ZnO coating was achieved by applying the supersaturated solution of Zinc Nitrate which gets converts into Zinc Oxide while under evaporation and adsorption [11]. Four levels of coatings were continuously applied simultaneously and dried. We get a thin film of the type and nature shown below in Figure. 3.

The goal of any absorption spectroscopy (FTIR, ultraviolet-visible ("UV-Vis") spectroscopy, etc.) is to measure how well a sample absorbs light at each wavelength. The most straightforward way to do this, the "dispersive spectroscopy" technique, is to shine a monochromatic light beam at a sample, measure how much of the light is absorbed, and repeat for each different wavelength.

Fourier transform spectroscopy is a less intuitive way to obtain the same information. Rather than shining a *monochromatic* beam of light at the sample, this technique shines a beam containing many different frequencies of light at once, and measures how much of that beam is absorbed by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is repeated many times. Afterwards, a computer takes all these data and works backwards to infer what the absorption is at each wavelength [12].

The beam described above is generated by starting with a broadband light source—one containing the full spectrum of wavelengths to be measured. The light shines into a certain configuration of mirrors, called a Michelson interferometer, that allows some wavelengths to pass through but blocks others (due to wave interference). The beam is modified for each new data point by moving one of the mirrors; this changes the set of wavelengths that pass through.

As mentioned, computer processing is required to turn the raw data (light absorption for each mirror position) into the desired result (light absorption for each wavelength). The processing required turns out to be a common algorithm called the Fourier transform (hence the name, "Fourier transform spectroscopy"). The raw data is sometimes called an "interferrogram".

Figure 3: Zinc Oxide thin film

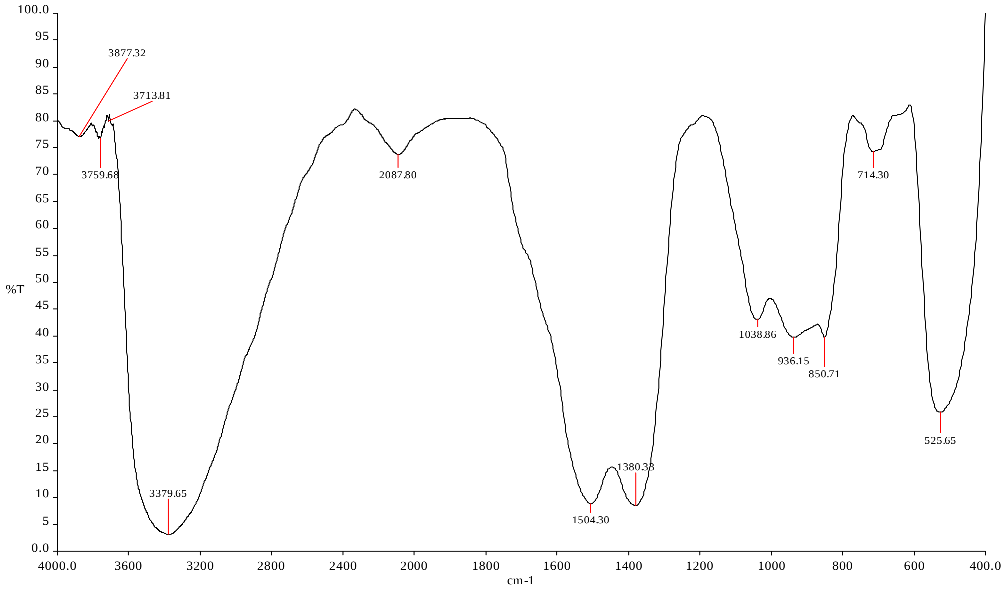

Fig.4: FTIR of ZnO thin film

The characteristic parts of the FT-IR spectra of pure and doped samples of ZnO. The IR bands in the spectrum of sample ZN1 can be assigned to $Zn_5(OH)_8(NO_3)_2 \cdot (H_2O)_2$ in accordance with XRD; however, the IR bands of a small amount of ZnO present in this sample, as shown by XRD, are not visible. The spectrum of ZnO sample is characterized with very broad IR bands centered at 502 and 406 cm^{-1} with shoulders at 553 and 376 cm^{-1}, as well as with the peak of very small relative intensity at 471 cm^{-1}. The characteristic IR band at around 3500 cm^{-1} is due to the structural OH^- group, whereas the IR bands in the range 3408 to 3500 cm^{-1} belong to the superposition of vibrations of crystalline and adsorbed H_2O. FT-IR spectrum of sample ZnO: Cu showed a sharp band at 3576 cm^{-1}, an intense band with a shoulders at 3481 and 3445 cm^{-1}, as well as a broad shoulder at 3298 cm^{-1}. For example, the spectrum of ZnO sample showed two IR bands at 564 and 423 cm^{-1}, with a shoulders at 388 cm^{-1}. The changes observed in the FT-IR spectrum of ZnO particles can be related with the changes in geometrical shape and size of these particles, as shown in journals compared the recorded and calculated spectra of ZnO (table 1). ZnO particles showed three distinct absorption peaks located between the bulk TO-phonon frequency ($\omega_{T\perp}$) and the LO-phonon frequency ($\omega_{L\parallel}$). These absorption peaks shifted towards lower frequencies when the permittivity of the surrounding medium was increased [13, 14].

Table 1: Observed Modes of vibration of ZnO thin film

Description	Range	Observed for ZnO thin film
ν (C-H)	>3500 cm^{-1}	3877 cm^{-1} 3759 cm^{-1} 3713 cm^{-1}
NH_2 - ν (asym)	2500-3500 cm^{-1}	3379 cm^{-1}
N (R–N=C=N–R) asym	1500-2500 cm^{-1}	2087 cm^{-1} 1704 cm^{-1}
Metal $(CH = CH_2)_2$	1250-1500 cm^{-1}	1380 cm^{-1}
Metal (C = C)	1100-1250 cm^{-1}	1201 cm^{-1}
ν(P=O)	1000-1200 cm^{-1}	1038 cm^{-1}
ν(C–O)	1000-1050 cm^{-1}	1041 cm^{-1}
ν (C-X)	900-1000 cm^{-1}	934 cm^{-1}
ν (C–Hal) Hal = Cl, Br, I	800-900 cm^{-1}	850 cm^{-1}
ν (S=O)/ ν (S–O)	750-850 cm^{-1}	714 cm^{-1}
HOH bending	500-600 cm^{-1}	525 cm^{-1}

STRUCTURAL INVESTIGATIONS

X-ray diffraction pattern for ZnO films produced at different substrate temperatures. In Fig. 5 , according to JCPDS 65-3411 and International Centre for Diffraction Data (*ICDD*), *file number* 36-1451 for ZnO, all characteristics peaks of hexagonal ZnO wurtzite are present [14]. Furthermore, the peaks indicate that the ZnO films are polycrystalline. From Fig. 5 , at (002) a single maximum diffraction peak are observed in all films taken at five trials at various temperatures ranging from 50 to 250 ˚C at (100), (002), (101), (102), (110) and (103). These features indicate that the textured structure of these ZnO films grows with a preferential orientation along *c* axis perpendicular to the substrate surface.

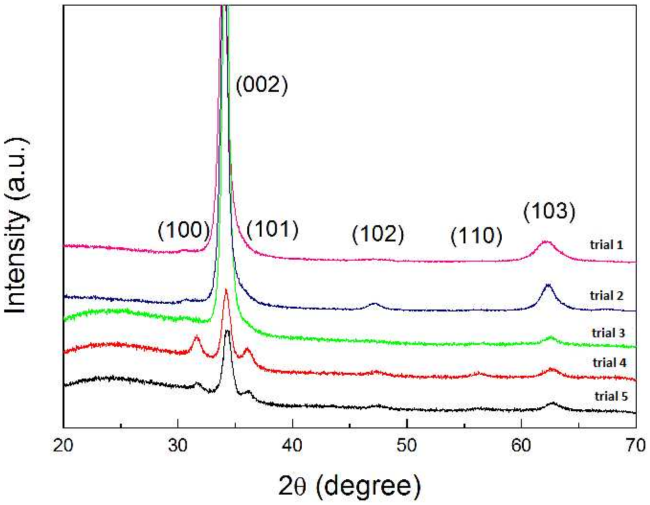

Fig. 5: XRD patterns of ZnO films deposited at different substrate temperatures

UV-VISIBLE ABSORPTION AND TRANSMISSION SPECTROSCOPY

Ultraviolet and visible spectrometers have been in general use for the last 35 years and over this period have become the most important analytical instrument in the modern day laboratory. In many applications other techniques could be employed but none rival UV-Visible spectrometry for its simplicity, versatility, speed, accuracy and cost-effectiveness [15, 16].

When white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown on the right. Here, complementary colors are diametrically opposite each other. Thus, absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red. Green is unique in that it can be created by absoption close to 400 nm as well as absorption near 800 nm.

UV-Vis absorption was carried out on pure and doped samples of the thin films grown using a Lamda spectrophotometer from 100nm-1200nm. Absorption of light was observed till 200nm to 400nm and complete transmission was observed till 1200nm in samples of pure and doped Zinc Oxide. Absorption was more on the ultra-violet region than on the infra-red region [17].

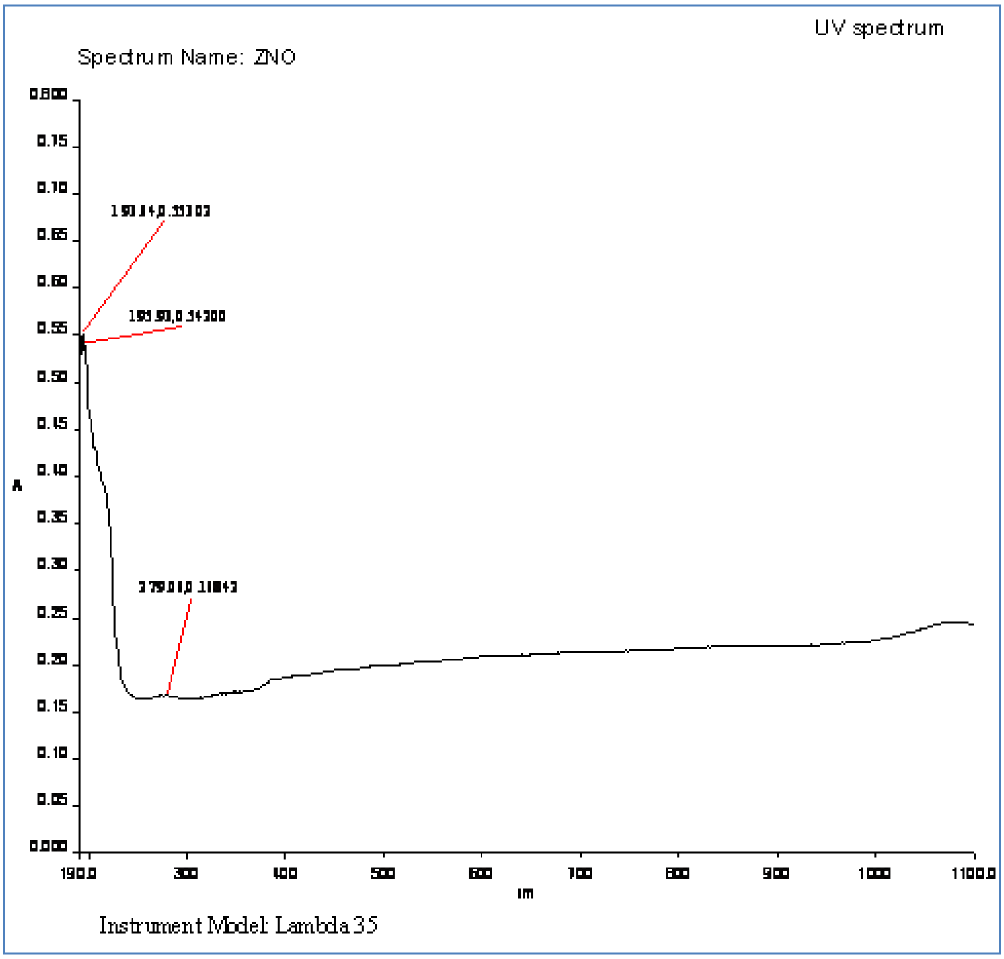

Fig. 6: UV Absorption Spectrum of Zinc Oxide thin film

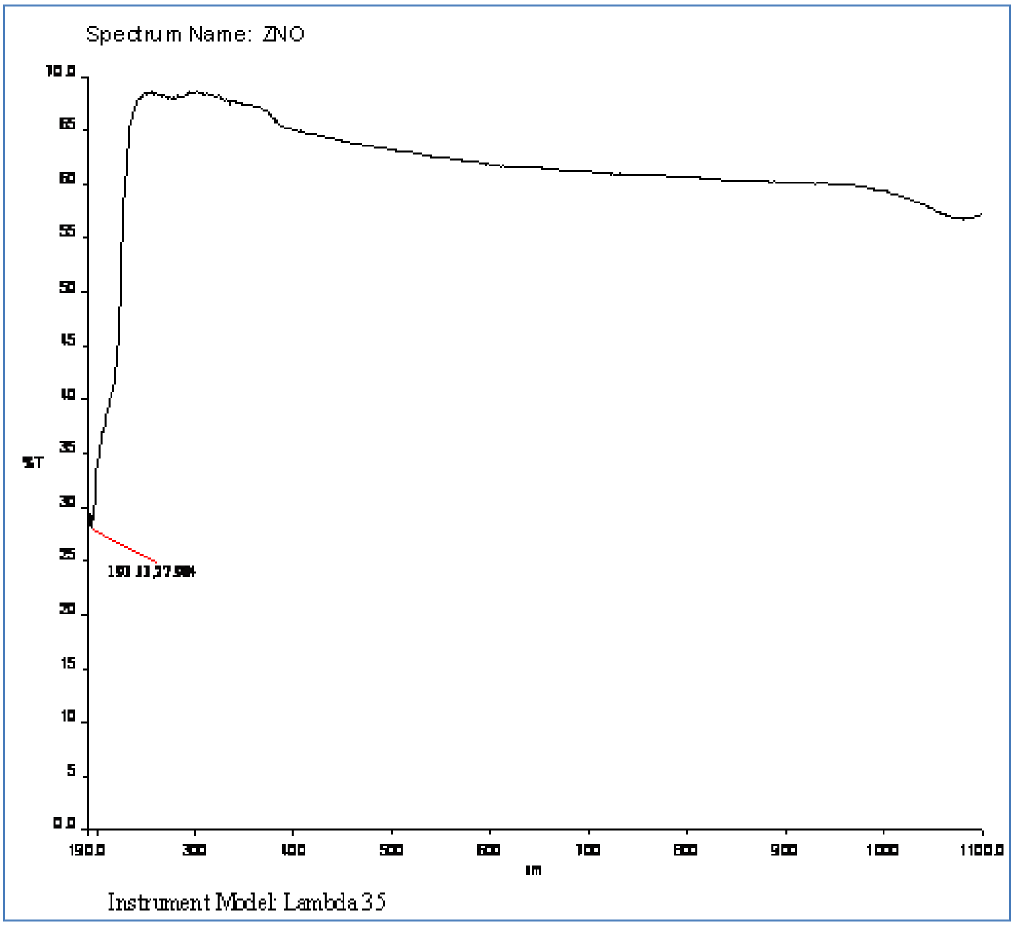

Fig. 7: UV Transmission Spectrum of Zinc Oxide thin film

RESULTS AND DISCUSSION

Thin films of pure Zinc Oxide and Zinc Oxide was grown using Liquid Phase Epitaxial Technique using a plate type ordinary induction heater used commonly for cooking. Thus we have achieved an important milestone in utilizing a commonly available heating source to execute a process which demanded much costly and sophisticated equipment [18].

There was a visible change in the colouration while it was doped and this can be seen visibly in the absorption spectra taken for each sample where the width and the intensity of each and every coloured sample was well distinct than that of the first pure and undoped thin film coating.

The thin films grown were characterized for their structural, optical and spectroscopic properties by appropriate studies [19]. The absorption and transmission spectra proves that the Zinc Oxide thin film in pure form had good transparency.

FTIR spectra are conveniently divided into sections according to the type of vibration in the structure. Thus bands were assigned to hydroxyl stretching, hydroxyl deformation, OH, O=O stretching and H_2O stretching modes. Combination bands are present in some cases. The observation of O=O and bands is significant as they are often hidden beneath vibrations arising from oxyanions in other basic dopant minerals [20]. The FTIR spectra elaborates the essential assignments for the bonds which are identified as symmetric, anti-symmetric or bending modes.

Acknowledgement
One of the authors AC thanks the respective Principals of Arignar Anna Government Arts college, Villupuram, Dr. Kanniga and Government Arts College, Dharmapuri, Dr. Anbarasan respectively for their encouragement and support. The authors also thank Prof. R. Muthulakshmi, HOD Physics at AAGAC, Villupuram and Prof. A. Poiyamozhi, HOD Physics at GAC, Dharmapuri for their goodwill and encouragement. The author also thanks all his colleagues and his friends for their encouragement. The author remembers with gratitude his guide Prof. P. Ramasamy, Dean, SSNCE and Dr. R. Gopalakrishnan, Dept. of Physics, Anna University, Chennai for initiating him into the area of research and development.

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