Investigation of Structural and Optical Properties of Zinc Oxide (ZnO) Powder by Co-Precipitation Method

Amy Aung[1], May Kalayar Kyaing[2], Ohn Mar Swe[3], Zin Mar Win[4]

Abstract

In this study, the wurtzite structure of ZnO powders was synthesized via the co-precipitation method at various temperatures 300°C, 400°C, 500°C and 600°C. The annealed ZnO powders were studied by Scanning Electron Microscope (SEM), X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), and UV-Vis Spectroscopy to get the results of the structural and optical properties. The average crystallite size of ZnO increased with increasing annealing temperatures. The full width at half maximum (FWHM) of ZnO particle decreases with increasing annealing temperatures assuming an increase in particle growth. The grain sizes were also studied to be increased with an increase in annealing temperatures. The SEM images illustrated that the shape of ZnO was an irregular spherical shape and agglomerated. The variations in size and shape of ZnO are due to the difference in precursor and annealing temperature. The various functional groups for synthesized ZnO were detected by FT-IR spectroscopy analysis. The FT-IR peaks exactly to the vibrational phonons of ZnO also verify the successful making of ZnO particles. The optical properties of the samples were investigated by measuring the UV-Visible Spectroscopy. The data from UV-vis examined the ZnO samples be influenced by different annealing temperatures.

Keywords: *ZnO, XRD, SEM, FTIR, UV-vis*

Introduction

Zinc oxide is among the most promising semiconductors of group II-VI for manufacturing technological devices on a nanometric scale. ZnO is a broad energy band gap (~3.3 eV) n-type semiconductor that has received much attention over the past few years. It has a wide band range of useful properties added in electrical, optical, chemical and magnetic properties. This property has made ZnO one of the smartest photocatalysts in the treatment of wastes and contaminants present in air and water by photo degradation mechanism. Therefore, ZnO can be applied in many applications such as a catalyst, gas sensors, piezoelectric devices, semiconductors, photocatalysts degradation of wastewater pollutants, field-emission displays and UV-shielding material. Nowadays, research on ZnO powders has focused on their preparation using various methods including a solid-state reaction, a microwave-assisted method, a sonochemical route, sol-gel, hydrothermal and co-precipitation methods. Every method has different pros and cons. However, the selected method should produce and reproduce the required powders for mass production. Furthermore, the cost of the apparatus and equipment should be inexpensive to reduce the production cost when it was to be used in the industry.

In this work, the co-precipitation method was determined to examine the effects of the various temperatures on the morphology and size of the powders on their properties. The morphology can be controlled by this synthetic condition and the preparation of the powders can be easily scaled up the structure and surface morphology of the ZnO powders. All ZnO samples were characterized by using x-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectrometer (FT-IR). The measurement of the optical properties is investigated by using a UV-visible absorption spectrometer. The structural and optical properties study reveals important differences in these properties of particles with respect to annealing temperature.

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Experimental Procedure

The phase identification and crystallite sizes of the samples were determined using XRD patterns recorded with an X-Ray diffractometer (Smart Lab) Cu Kα radiation (λ = 1.54056 Å) in terms of 2θ ranging from 10˚ to 70˚. The morphology of the various structures of ZnO powders was examined using Scanning Electron Microscopy (JEOL-JSM 5610LV). The formation of ZnO was confirmed the from FTIR spectrum (Model: Perkin Elmer Spectrum-2) recorded in the wavenumber region 4000 - 400 cm^{-1}. Optical absorption of the samples was recorded using Shimadzu UV–visible (UV–Vis) spectrophotometer (UV-1800) in the wavelength region 200 - 1100 nm.

Preparation of Zinc Oxide solution

The ZnO samples were prepared by using a co-precipitation method using zinc chloride and sodium hydroxide as precursors. The concentration ratio between the zinc chloride and sodium hydroxide was determined using the chemical equation formula shown below:

$$ZnCl_2 + 2\,NaOH \rightarrow Zn(OH)_2 + NaCl$$

Then 0.2 M aqueous solution of zinc chloride was kept under constant stirring with a magnetic stirrer at room temperature to completely dissolve the zinc chloride for half an hour. After the zinc chloride was completely dissolution and the solution of sodium hydroxide with a concentration of 0.2 M was slowly dropped for 40 minutes. The mixture was stirred continuously and controlled at 80˚C for one hour. After the complete addition of sodium hydroxide, the mixture was heated for two hours without stirring. The proceeding took three hours, a milky white solution was obtained. The white precipitates were collected by filtration and rinsed with distilled water several times to make sure that the residual impurities were removed by-products that were bound with the zinc hydroxide and dried in an air atmosphere at 100˚C for 3 hours. The powders were annealed at various temperatures of 300˚C, 400˚C, 500˚C and 600 ˚C for one hour. The photograph of the sample preparation sequence for ZnO powder using the co-precipitation method was shown in Figure. The reaction equations are as follows;

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

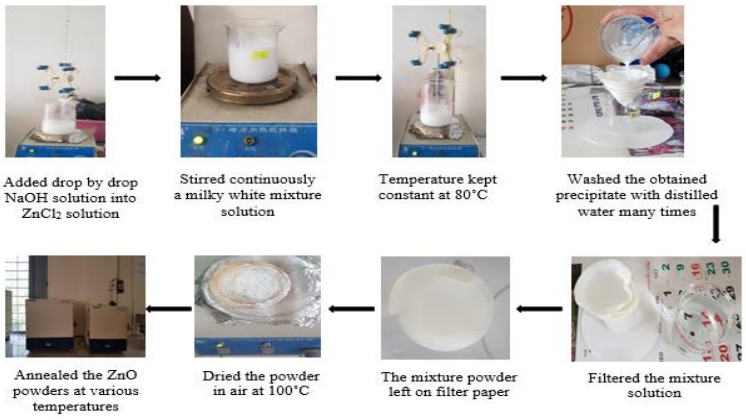


Figure 1 Sample preparation procedure for ZnO powders

Results and Discussions

XRD Analysis

The XRD patterns of the ZnO samples prepared with different annealing temperatures at 300˚C, 400˚C, 500˚C and 600˚C was shown in Figure 2. The peaks at scattering angles (2θ) of 31.7˚, 34.4˚, 36.3˚, 47.5˚, 56.6˚, 62.8˚, and 66.4˚ which corresponds to (100), (002), (101),

(102), (110), (103) and (200) crystal plane respectively. It also showed that the particle has a hexagonal phase (wurtzite structure). All the diffraction peaks of the ZnO samples can be well indexed to the ZnO reported. The XRD spectra revealed the influence of annealing treatments on the structural properties. The ZnO peak intensity was sharpened and increased with increasing the annealing temperature. The increase in the peak intensities was attributed to an increase in crystallinity and crystallite size.

The attribute peaks examined by ZnO samples were in beneficial agreement with that all accepted from the JCPDS card issues, a = 3.2484Å and c = 5.2060Å. With changes in temperatures, the sharpness of the diffraction peak got better with acceptance to the temperatures when the annealing temperatures increased the values of the full-width at half maximum (FWHM) were decreased. The pattern suggested that the ZnO samples with different temperatures are constituted in a hexagonal wurtzite structure with a perfect orientation of (101) diffraction plane. No additional peaks corresponding to the other impurities were detected in the XRD pattern, confirm that the high purity of the synthesis products. By increasing various temperatures (300°C, 400°C, 500°C and 600°C), the data approved an improvement in the crystallization of the ZnO. This improvement was due to the crystallization of ZnO particles by the supply of sufficient thermal energy. The average crystal size of all samples of powder was calculated using Debye-Scherrer's formula:

$$D = \frac{k\lambda}{\beta \text{Cos}\theta}$$

Where, θ is the Bragg angle of the X-ray diffraction peak, k ~ 1, λ = 1.5406Å, λ is the wavelength of Cu (Kα) radiation and β represents the corrected experimental full-width at half maximum of the diffraction peak in units in radians. The perfect peak was taken to calculate and the results were shown in Table 1. The average crystallite size was increased by increasing the annealing temperature.

Table 1 Crystallite size of ZnO powders estimated using the XRD technique

Temperature (°C)	FWHM (radian)	Crystallite size D (nm)
300	0.225	32.25
400	0.219	38.15
500	0.202	41.38
600	0.181	41.17

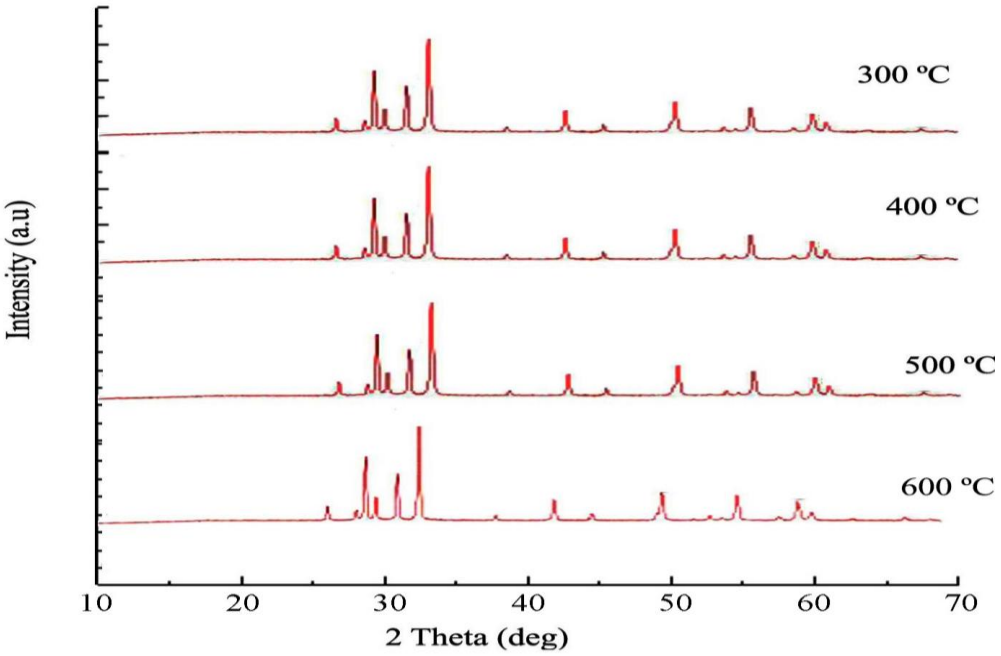
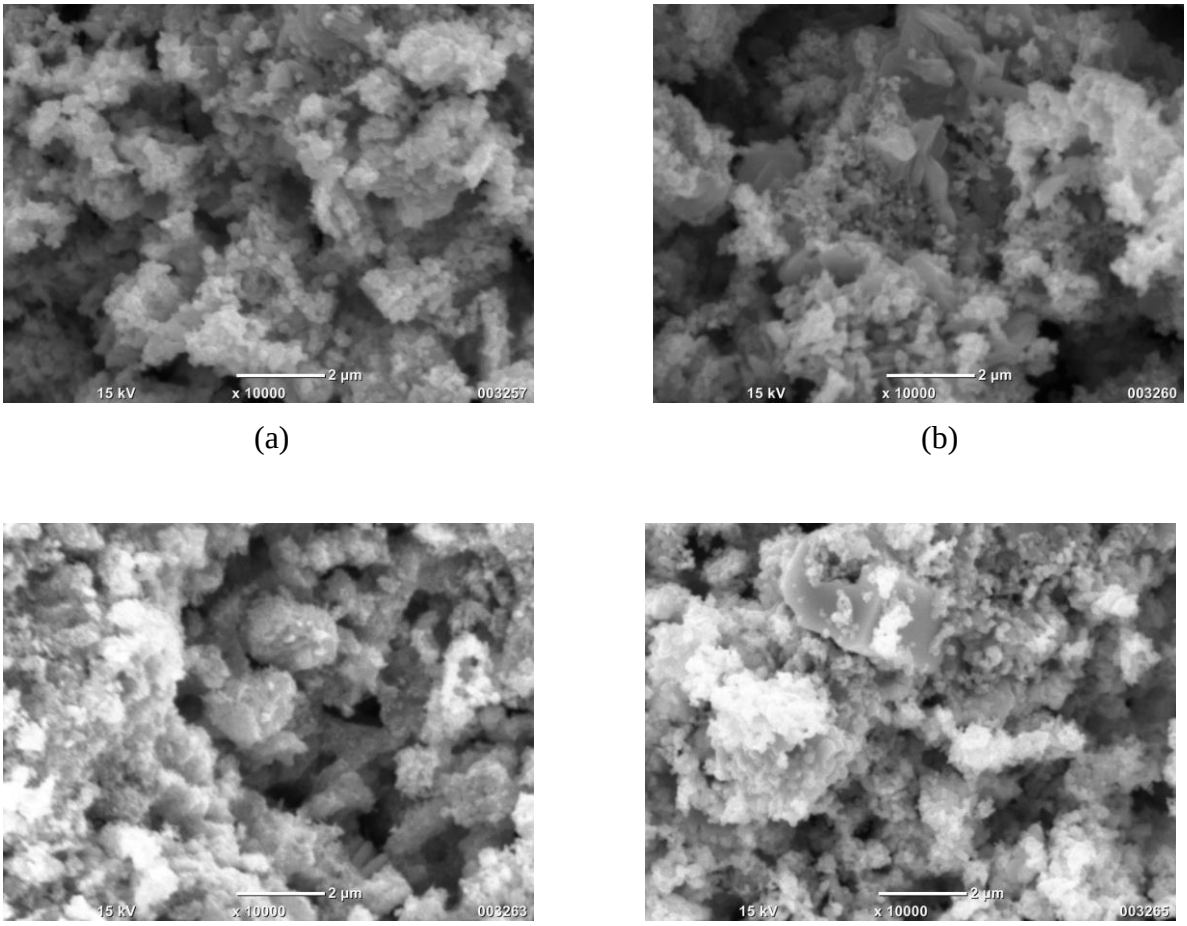


Figure 2 XRD patterns of ZnO powders prepared at different annealing temperatures

Scanning Electron Microscopy Analysis

Microstructural characterization of integrated samples was studied by SEM analysis. In Figure 3 was shown the surface morphology of the ZnO samples analyzed from the different annealing temperatures. The ZnO powders worth a spherical shape and remain in large aggregation. When the annealing temperatures was increased the mean size and distribution of particles were increased. The large agglomeration of all samples during the annealing process may be because of the high surface energy of particles. In the annealing process, when the particles were formed, they collide and combined with one another to form a large particle. The annealing temperature was an important issue that influence the surface morphology of the particles as well as the particle size.

A particle size diagram for the sample powders annealed at different temperatures investigated the size distribution of the ZnO particles. The size of the particle of powders were very sensitive to the heating temperature. With growing temperature, the particle sizes were large with small surface area produce. The grain size of the samples was determined by counting a sufficiently large number of grains to ensure accuracy. The average grain size of the ZnO samples is in the range of 0.32 – 0.48 µm as indicated in Figure 3. The mean grain size of the films was observed to increase with increasing annealing temperature, which can be attributed to grain coalescence at higher annealing temperatures. The "image J" software was used to measure of scanning electron microscopy analysis.



(a) (b)

(c) (d)

Fig. 3 SEM images of ZnO powders annealing at different temperatures of (a) 300˚C, (b) 400˚C, (c) 500˚C, (d) 600˚C

FTIR Spectra Analysis

Chemical and structural changes that take place during heat treatment can be monitored by spectroscopic analysis. Figure 4 displayed the FTIR spectra of ZnO particles annealed at 300˚C, 400˚C, 500˚C and 600˚C. FTIR is used as a confirmatory technique for nanoparticle formation and offers an impression of the vibrational and rotational modes of the existing molecules involved in the reduction and stabilization of ZnO. The peak at ~3400 cm^{-1} represents the fundamental stretching vibration of the O–H bond of the hydroxide group or water moisture adsorbed at the surfaces. The H+ in the environment always absorb strongly by the O^{2-} anions of ZnO hexagonal to form an O–H bond, whereas the hydroxyl (OH^-) group residual in raw material tends to be absorbed the cations Zn^{2+} due to the electrostatic potential that leads to the formation of O-H functional group, therefore O–H band exists strongly in ZnO and other metal oxides nanoparticles.

The small peak between 2923 and 3494.71cm^{-1} is due to C–H and O–H stretching vibration. The wide peaks present at 3370.54 cm^{-1} reflect the presence of O–H stretching vibration. The medium intense band at 1633.98 cm^{-1} is due to the bending vibrations of H_2O molecules. The peak at the range of 723.7 - 718.89 cm^{-1} originated from the stretching vibration modes of Zn-O-Zn indicating the complete transformation from zinc chloride to zinc oxide. The ZnO sample annealed at 300°C and 400°C presents a typical infrared spectrum of the ZnO wurtzite phase identifiable by its characteristic band located at about 430 cm^{-1}.

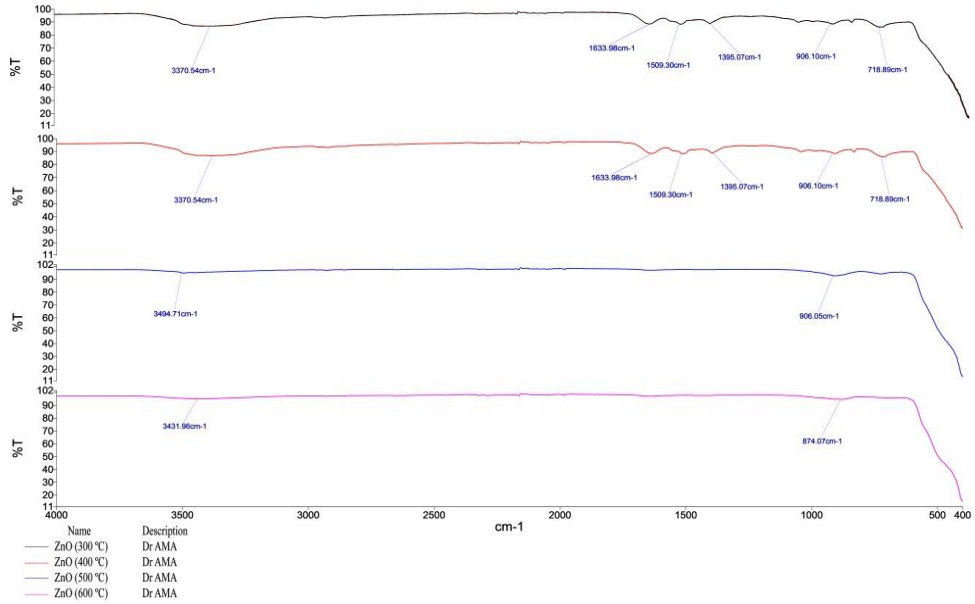


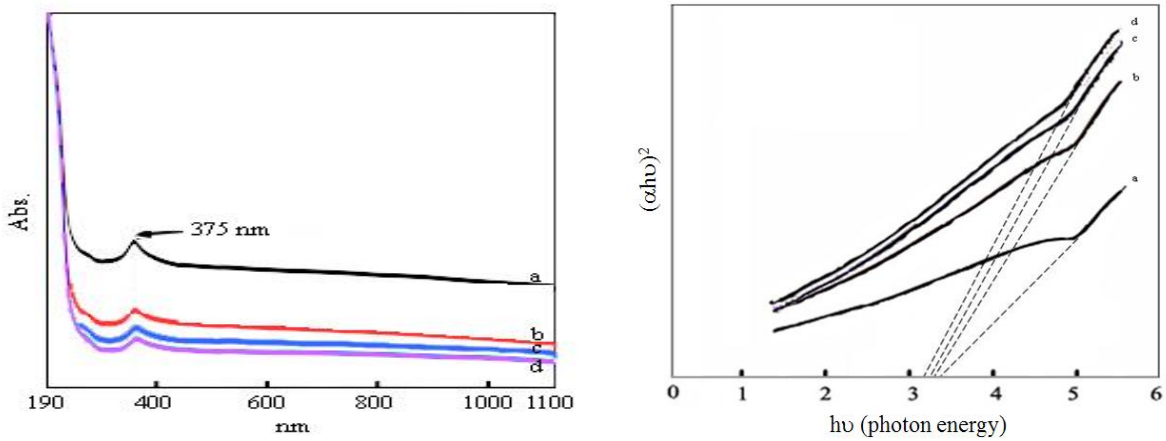
Figure 4 FT-IR spectra of ZnO powder annealing at different temperatures

UV-Vis Spectroscopy Analysis

The absorption spectrum of ZnO powder at different annealing temperatures was shown in Figure 5. A broad absorption peak was observed in each spectrum at 370-382 nm which was a characteristic band for the pure ZnO. No other peak was observed in the spectrum confirming that the synthesis products were ZnO only. The absorption edge was examined for the samples annealed at different temperatures. This might due to changes in their morphologies, particle size and microstructures. Temperature 300˚C exhibits a strong absorption at 370 nm, temperature 400˚C at 373 nm, temperature 500˚C at 377 nm and temperature 600˚C at 382 nm. The ZnO particles which have absorption at an elevated wavelength in the UV-vis spectrum owed larger particle size. The UV-vis data were in good unity with the XRD data in ZnO particle size expectation. The energy band gap can be calculated from the UV-vis spectroscopy absorption peak at a given wavelength in the following equation:

$$E_g = h\upsilon_g = \frac{hc}{\lambda_g}$$

Where Energy (E_g) = Band gap, Plank's constant (h= 4.14 x 10^{-15} eVs), velocity of light (c) = 2.99 x 10^8 m/s and wavelength (λ_g) = absorption peak value (1eV = 1.6 x 10-^{19} J). The UV absorption spectra were shown an absorption peak centered at 375 nm at annealing temperatures (300˚C, 400˚C, 500˚C and 600˚C) in Figure 5 (a). It was known that the bulk ZnO has an absorption band edge at ~ 3.30 eV in the UV-visible spectrum. The absorption peak intensity at 375 nm decreased with increasing annealing temperature. The vacancy energy level plots of the $(\alpha h\upsilon)^2$ (where α is the absorption coefficient and hυ is the photon energy) as a function of hυ was shown in Figure 5 (b). ZnO powders annealed at 300˚C was an energy of 3.34 eV, annealed at 400˚C was an energy of 3.31 eV, annealed at 500˚C was an energy of 3.28 eV and annealed at 600˚C was an energy of 3.24 eV. This showed that an increase in the annealing temperature decreased the vacancy energy level. The decrease in the vacancy energy levels of ZnO as annealing temperature increases may be attributed to the defects that are in the ZnO powders. The outcomes from the UV-vis were in good agreement with the outcome of the XRD in ZnO grain size expectation.



(a) (b)

Figure 5 (a) Absorption spectra of ZnO powders annealed at different temperatures
(b) Plots of $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) at different temperatures

Conclusions

Zinc Oxide (ZnO) sample powders were combined by the co-precipitation method and annealed at various temperatures. The samples of ZnO powders annealed at different temperatures of the structural and optical properties were implemented by using XRD, SEM, FT-IR and UV-vis measurements. The wurtzite structure of Zinc oxide powders was confirmed from the diffraction patterns of the samples. The average particle sizes estimated from the XRD results were observed to be increased with increasing annealing temperatures for ZnO samples. By XRD measurement observed the structural properties of ZnO have hexagonal wurtzite structure. All the peaks' intensity improved by the increasing annealing temperature. The grain growth was further confirmed which revealed the formation of agglomerated particles. The SEM data exhibited the evolution of spherical-shaped agglomerated ZnO samples. The FT-IR confirmed the functional group of ZnO with FT-IR spectra broadband ranging from 4000 cm^{-1} to 400 cm^{-1} at Zn-O stretching mode. The UV-vis absorption exhibited an absorption peak at 375 nm which was shown to decrease with an increase in annealing temperature. The vacancy energy levels of the ZnO decreased with an increase in the annealing temperature. The optical band gap of the ZnO samples decreased from 3.34 eV to 3.24 eV with increasing annealing temperature indicating particle size growth, and the particle sizes estimated using effective mass approximation corroborated the same. The increase in the intensity of the UV emission peaks with the increase of annealing temperatures corroborated the XRD results.

Acknowledgment

The authors would like to thank Dr Tin Maung Tun, Rector and Dr Khin Chit Chit, Dr Cho Cho and Dr Thidar Aye, Pro-Rectors, University of Yangon for their kind permission to do this research paper.

We would like to express my special thanks to Professor Dr Yin Maung Maung, Head of the Department of Physics, University of Yangon for his kind permission and supporting this work. We also thank Dr Ye Chan, Professor and Head of Universities' Research Centre, Dr Min Maung Maung, Professor, Dr Cho Cho Thet, and Dr Nyein Thida, Professors, Department of Physics, University of Yangon for their valuable advice to carry out this work.

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