STUDY ON THE VARIOUS ANNEALING PROCESSES OF CUO-MNO$_2$-ZNO ELECTROLYTE FOR LOW-TEMPERATURE SOLID OXIDE FUEL CELLS

Nang Htoo[1], Than Than Win[2], Yin Maung Maung[3]

Abstract

CuO-MnO$_2$-ZnO (CMZO) mixed oxide was prepared by solid state reaction for the purpose of low temperature solid oxide fuel cell (LTSOFC) applications. Solid-oxide fuel cells (SOFCs) promise high efficiencies in a range of fuels. CuO–MnO$_2$–ZnO mixed oxides with different Cu : Mn : Zn atomic ratios were obtained at 200°C, 300°C, 400°C and 500°C in 1 h. The change in the annealing temperature had a significant influence on the structural, surface morphology and optical properties. Powder X-ray diffraction and scanning electron microscopy with energy dispersive X-ray diffraction spectroscopy confirm the phase purity and the particle size of CMZO mixed oxide. Based on optical absorbance measurements, it was shown that CMZO with higher annealing temperature were characterized by a higher cut-off wavelength and lower optical band gap energy.

Keywords: mixed oxide; solid state reaction; X-ray diffraction; surface morphology, optical properties

Introduction

A composite material (also called a composition material or shortened to composite, which is the common name) is a material made up of two or more constituent materials with major different physical or chemical properties, that combines to produce a material with different features from the individual components. The individual component remain separate and distinct within the finished structure, differentiation composites from mixtures and solid solutions [McEvoy.M.A.et.al (2015)]. Due to its strangeness, lightness or less expensiveness, it is favoured to traditional materials [Science.et.al (2015)]. ZnO has got an agreement of attention in the application of electronics and optoelectronics such as battery active materials, solar cells, gas sensors and light-emitting diodes due to its good electrochemical activity, well-known surface conductivity, high electron mobility, wide bandgap and eco-friendly nature [S.Zaman.et.al (2012)]. ZnO, a wide band gap (3.37eV) n-type semiconductor, have a large excition binding energy (60meV) and piezoelectric properties [Y.P.Gao.et.al (2007)]. CuO is an important narrow band gap (1.3eV) p-type semiconductor with many applications in sensors, catalysis, batteries, high temperature superconductors, solar cells and field emitters [R.Saravanan.et.al (2013)]. Among the available metal oxides, MnO$_2$ receives much attention due to its prospective application in the field of catalytic and electrochemical applications. Due to the low cost and plenty of MnO$_2$, it can compare to other metal oxides [Fanhui Meng.et.al (2013)]. Composite nanostructures of these two wide and narrow band gap semiconductors may offer united functionalities and open the way for new enhanced applications, such as photocatalysts [T.Chang.et.al (2013)], gas sensors [A.Zainelabdin.et.al(2012)], humidity sensors [T.Soejima. et.al (2013)], biosensors [M.H.Habibi.et.al (2013)] and solar cell [Jianmin Shen.et.al (2012)].

[1] Assistant Lecturer, Physic Department, Dangon University
[2] Physics Department, Panglong University
[3] Department of Physics, University of Yangon

Materials and Methods

The raw materials of CuO, MnO_2 and ZnO were chosen as starting materials. The purity of materials was characrterized by X-ray diffraction (XRD). ZnO (60mol%), CuO(20mol%) and MnO_2 (20mol%) were mixed according to the stoichometric ratio by solid state reaction method to form composite. Physical grinding method is adopted in this experiment for the size reduction of CMZO material. The CuO-MnO_2-ZnO material was put in a ball milling machine which having high speed rotator. It was grinded for 3h then annealed at 200˚C, 300˚C, 400˚C and 500˚C. In the present work, the preparation and characterization of CMZO composite by using solid state reaction method. The resultant samples obtained by this method were be measured by XRD, SEM and UV-visible absorption spectrum to calculate the effect of different temperature at the same time on the formation of crystalline structure, morphological features and optical properties of the resultant composite.

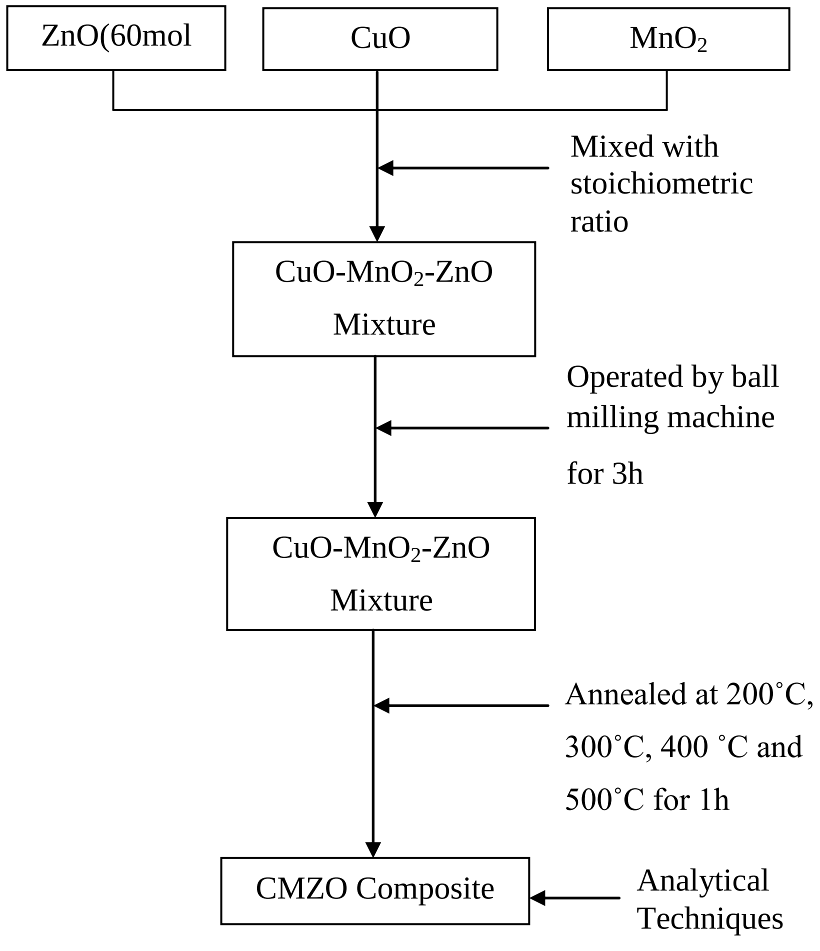

Figure 1 CuO-MnO_2-ZnO (CMZO) composite preparation sequence

Results and Discussion

The crystal structure was confirmed by XRD. The XRD diffraction patterns for CuO-MnO_2-ZnO(CMZO) nanoparticles after annealing at 200˚C, 300˚C, 400˚C and 500˚C was shown in figure 2(a-d). After annealing at given temperature, the composites was a mixture of the individual binary oxide phases co-existing in one material. Some reflection peaks were not matched with the standard peak. The intensity of XRD peaks of the sample reflects that the formed nanoparticles are crystalline and broad diffraction peaks indicate small size cryatallite. The CuO phase crystallized in the monoclinic crystal structure, MnO_2 in tetragonal and ZnO in hexagonal.

XRD technique is capable of gathering many useful information relating the crystal structure. In this research work, X-ray diffractrometer was used for the phase analysis of the films calcined at different temperatures using Cu-Kα_1 radiation (λ=1.54056Å) at an accelerating voltage of 40kVand a current of 50mA. The film samples were mounted on a flat XRD plate and scanned at room temperature in the range $10 \leq 2\theta \leq 70$. X-ray line broadening technique was used to determine crystallite size of the films calcined at different temperatures using Scherrer formula,

$$G = \frac{0.9 \times \lambda(Å)}{B(rad) \times \cos\theta_B}$$

Where G is the crystallite size, B is the full width at half-maximum XRD peak in radians, λ is the wavelength of the X-ray radiation and θ_B is the Bragg angle in radians. XRD data of CMZO composite was shown in table 1(a-c).

Table 1(a) XRD data of CMZO material for CuO

Temp (˚C)	cosθ	FWHM (rad)	Crystallize Size (nm)
200	0.94	0.005	34.76
300	0.95	0.005	42.93
400	0.94	0.004	41.10
500	0.95	0.006	29.72

Table 1(b) XRD data of CMZO material for ZnO

Temp (˚C)	cosθ	FWHM (rad)	Crystallize Size (nm)
200	0.93	0.002	78.96
300	0.92	0.002	65.92
400	0.92	0.004	42.83
500	0.93	0.004	57.09

Table 1(c) XRD data of CMZO material for MnO_2

Temp (˚C)	cosθ	FWHM (rad)	Crystallize Size (nm)
200	0.92	0.004	48.32
300	0.93	0.004	53.30
400	0.93	0.005	35.08
500	0.89	0.006	53.89

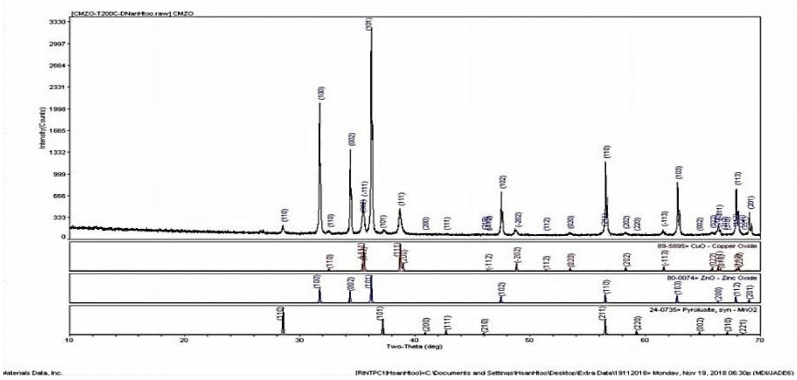

Figure 2(a) XRD pattern of CMZO material at annealing 200˚C

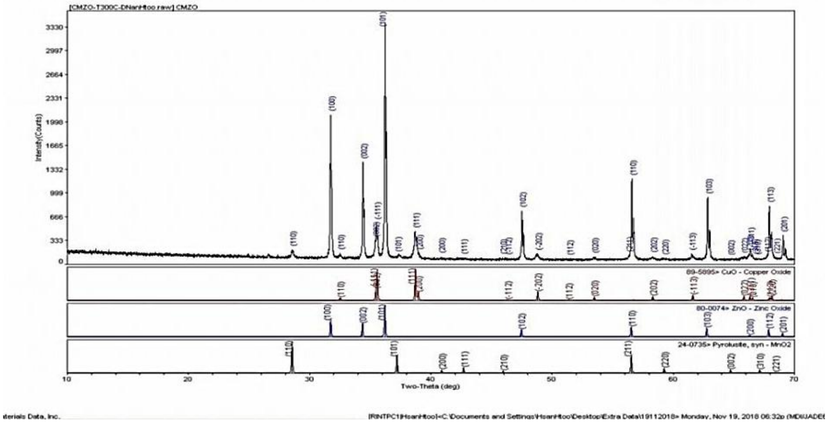

Figure 2(b) XRD pattern of CMZO material at annealing 300˚C

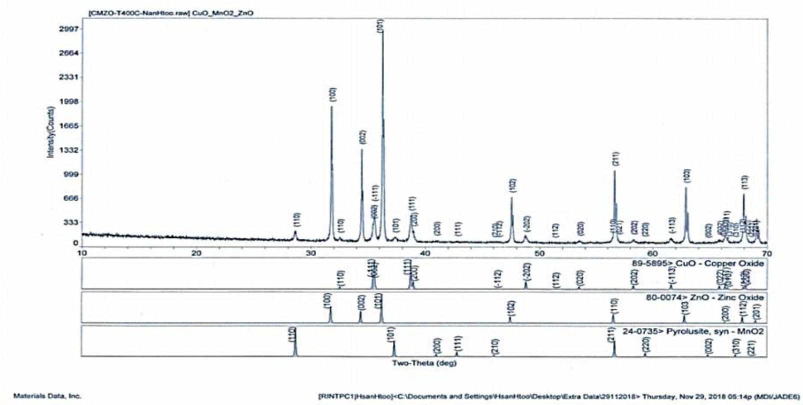

Figure 2(c) XRD pattern of CMZO material at annealing 400˚C

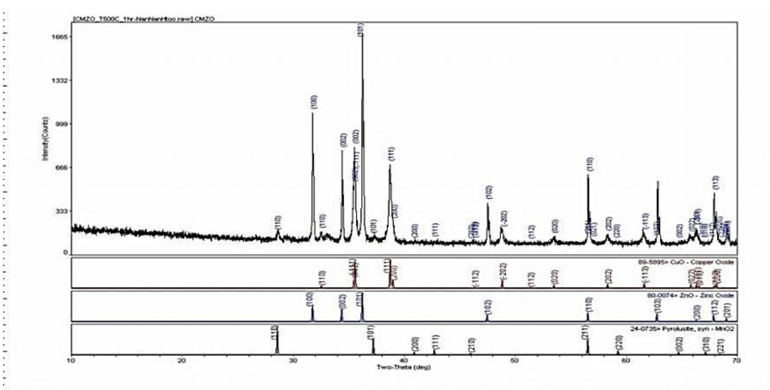

Figure 2(d) XRD pattern of CMZO material at annealing 500˚C

A Scanning Electron Microscope was used to chatacterize the morphological feature of the CMZO composite after calcination at 200˚C - 500˚C for 1h and showed in figure 3(a-d). To determine the elemental composition, EDX mapping as well as point analysis were used as a selected area. CMZO composite were composed of non-homogeneous mixed clusters with different elements. Table 2(a-d) showed elemental composition of CMZO composite

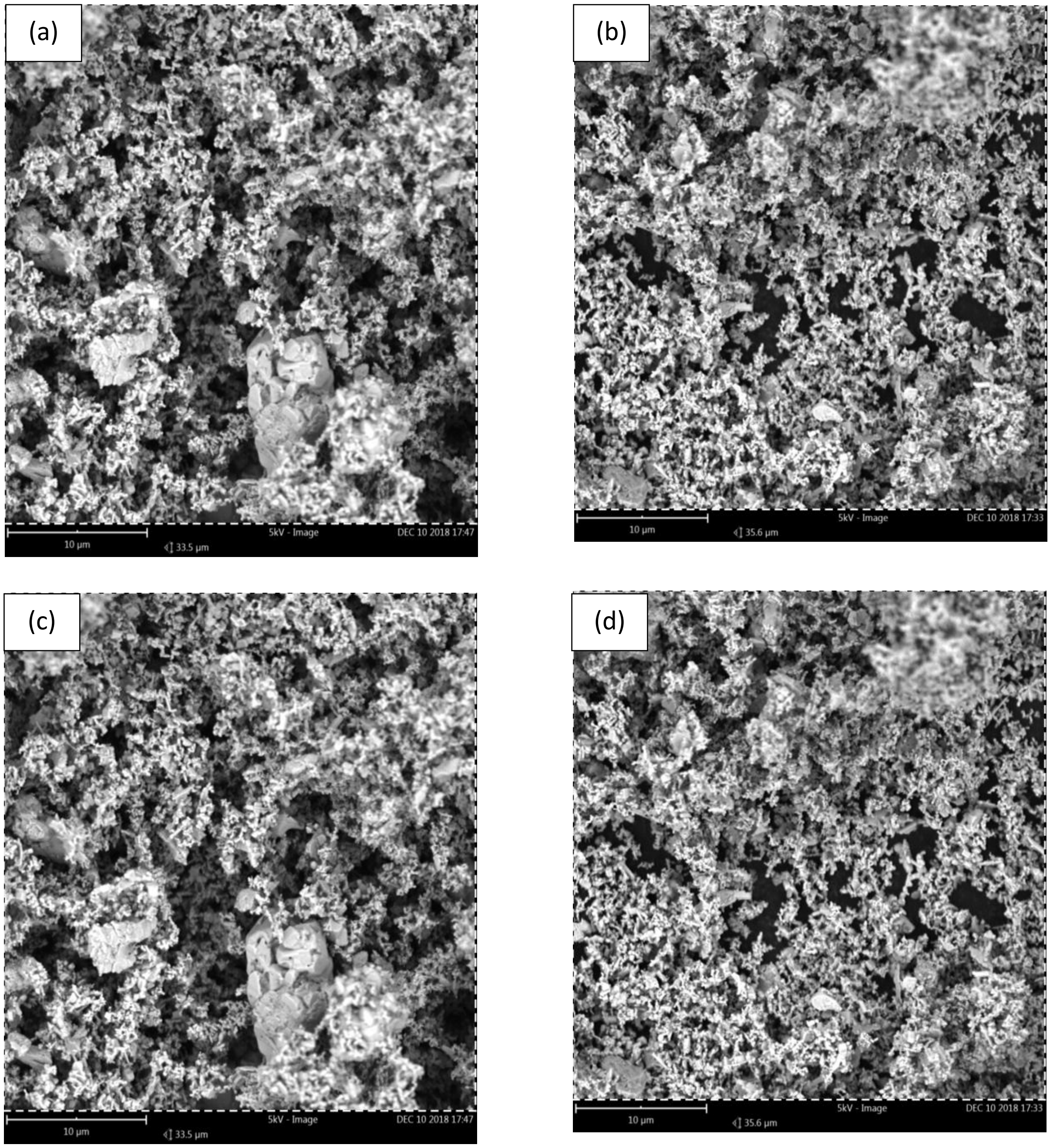

Figure 3 SEM image of CMZO composite (a) at 200ºC/1h (b) at 300ºC/1h (c) at 400ºC/1h (d) at 500ºC/1h

Table 2 Elemental composition CuO-MnO_2-ZnO (CMZO) mixed oxide composite determined by EDX at various point

(a) at 200ºC/1h

Elements	Position 1 (%)	Position 2 (%)
O	46.83	75.26
Cu	2.59	0
Mn	0	18.06
Zn	50.40	6.61

(b) at 300ºC/1h

Elements	Position 1 (%)	Position 2 (%)	Position 3 (%)	Position 4 (%)
O	41.81	27.95	32.64	17.00
Cu	2.30	34.56	0	0
Mn	0	0	0	0
Zn	55.70	37.50	47.55	79.33

(c) at 400ºC/1h

Elements	Position 1 (%)	Position 2 (%)
O	14.00	13.32
Cu	8.30	11.14
Mn	0	0
Zn	73.33	59.64

(d) at 500ºC/1h

Elements	Position 1 (%)	Position 2 (%)	Position 3 (%)
O	46.02	43.70	41.74
Cu	11.25	32.41	8.05
Mn	0	0	0
Zn	42.66	23.81	44.55

UV-vis absorption spectroscopy is widely used tool for checking the optical properties of nanosized particles. Figure 4(a-d) showed the absorption spectrum of CMZO composite at different annealing temperature (200˚C, 300˚C, 400˚C and 500˚C). The absorption coefficient can be calculated by using this equation,

$$\alpha = \frac{2.303\,A}{t}$$

Where, α is the absorption coefficient, A is absorbance and t is sample holder thickness. From the spectrums, the absorbance and relation wavelengths of CMZO composite at different temperatures were described in table 3(a-d). Figure 5(a-d) showed the values of $(\alpha h\upsilon)^2$ plotted against hυ. The energy band gap of the composite E_g was determined by extrapolating the linear of the plot to the hυ axis. The resultant value of E_g for CMZO composite were found to be about 3.27eV, 3.7eV, 3.1eV and 3.25eV at different temperature.

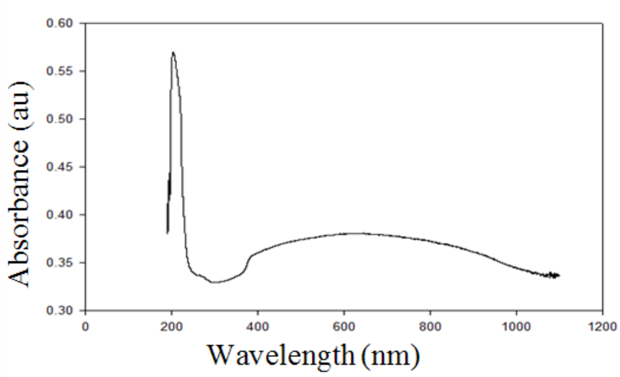

Figure 4(a) Absorbance spectrum of CMZO composite at 200˚C

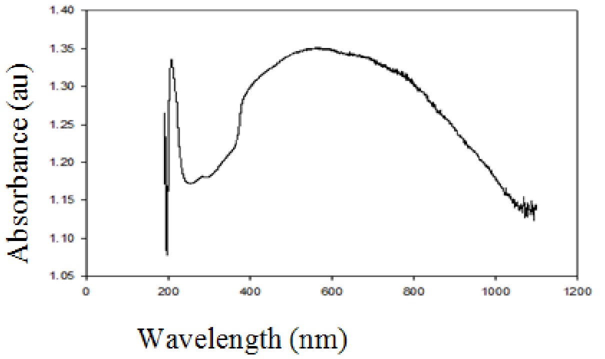

Figure 4(b) Absorbance spectrum of CMZO composite at 300˚C

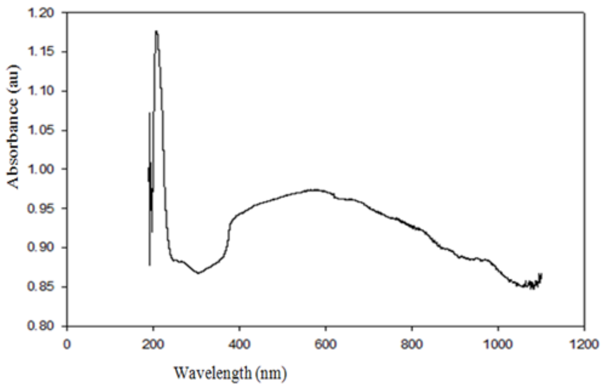

Figure 4(c) Absorbance spectrum of CMZO composite at 400˚C

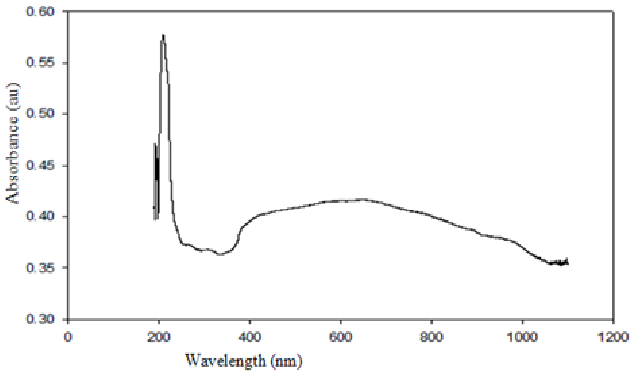

Figure 4(d) Absorbance spectrum of CMZO composite at 500˚C

Table 3 (a) Absorbance and wavelength of CMZO composite from absorption spectrum at 200˚C

No	Absorbance (au)	Wavelength (nm)
1	0.570	203.368
2	0.443	194.200
3	0.381	644.000

Table 3 (b) Absorbance and wavelength of CMZO composite from absorption spectrum at 300˚C

No	Absorbance (au)	Wavelength (nm)
1	1.351	570.011
2	1.336	207.655
3	1.324	750.955
4	1.320	772.977
5	1.316	782.377
6	1.280	845.912

Table 3 (c) Absorbance and wavelength of CMZO composite from absorption spectrum at 400˚C

No	Absorbance (au)	Wavelength (nm)
1	0.577	208.902
2	0.472	192.175
3	0.468	194.917
4	0.417	648.752

Table 3 (d) Absorbance and wavelength of CMZO composite from absorption spectrum at 500˚C

No	Absorbance (au)	Wavelength (nm)
1	1.177	207.426
2	1.074	192.198
3	1.011	193.764
4	0.976	195.855
5	0.974	578.983

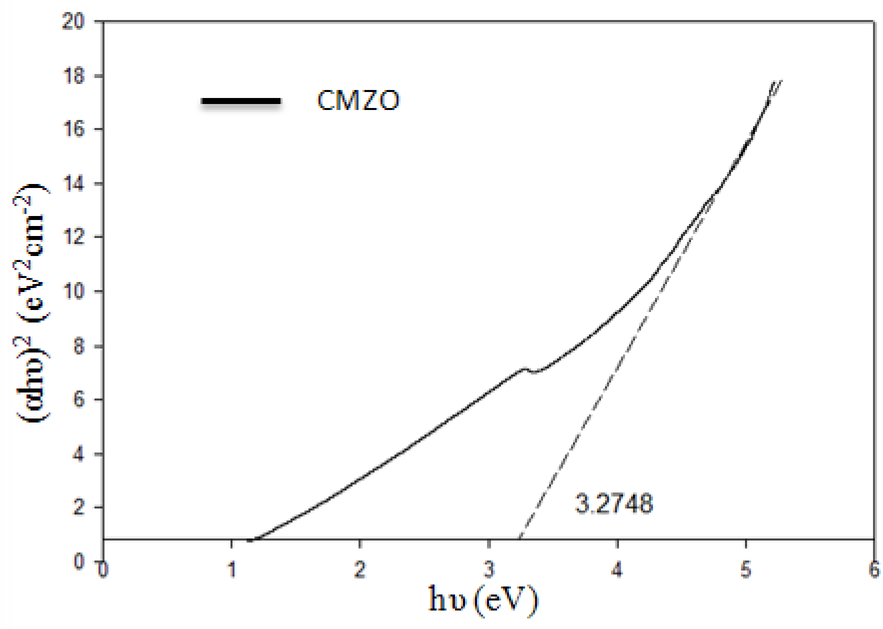

Figure 5(a) Plot of $(\alpha h\upsilon)^2$ versus photon energy (hυ) of CMZO composite at 200˚C

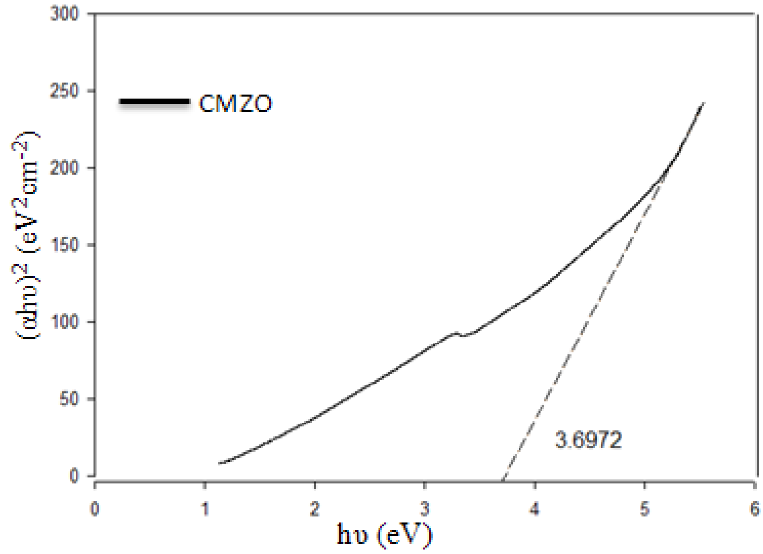

Figure 5(b) Plot of $(\alpha h\upsilon)^2$ verus photon energy (hυ) of CMZO composite at 400˚C

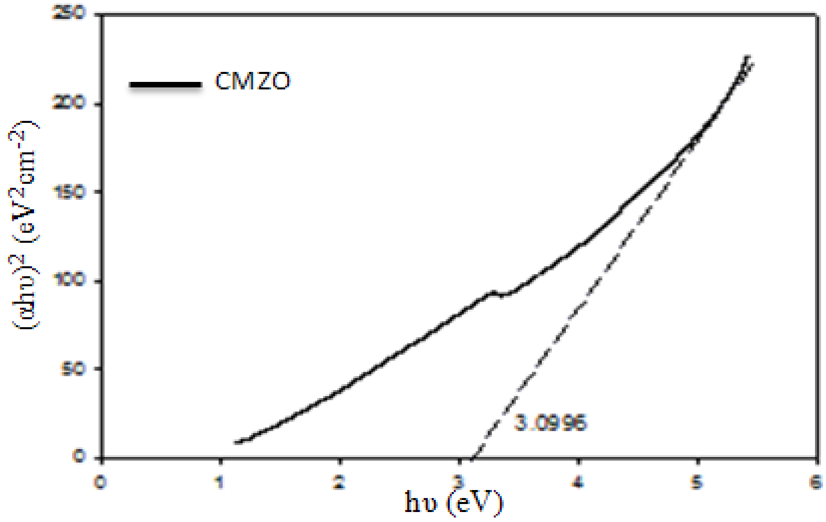

Figure 5(c) Plot of $(\alpha h\upsilon)^2$ versus photon energy (hυ) of CMZO composite at 400˚C

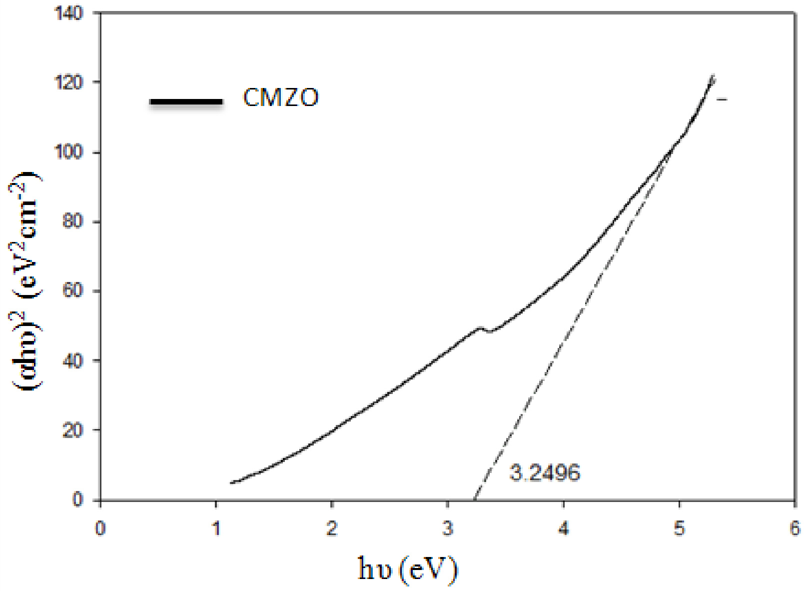

Figure 5(d) Plot of $(\alpha h\upsilon)^2$ versus photon energy (hυ) of CMZO composite at 500˚C

Conclusion

CuO-MnO_2-ZnO (CMZO) mixed oxide was prepared by solid state reaction method and annealed at 200˚C, 300˚C, 400˚C and 500˚C. CuO-MnO_2-ZnO (CMZO) phases were observed from the XRD measurements after annealing the sample at given temperatures. XRD studies showed distinct monoclinic for CuO, tetragonal for MnO_2 and hexagonal for ZnO. The crystallite sizes was found to be between 29 nm and 42 nm for CuO, 43-79 nm and for ZnO and 35-53 nm for MnO_2. The average crystallite sizes for the three oxide phases in the composite were found to be between 30 nm and 79 nm. These results introduce multiphase mixed oxide composite. SEM data showed that the distribution of Cu, Mn and Zn was not uniform across the selected area of the sample, which suggested that the oxides were not uniformly intermixed in the composite. The observed band gap of 3.27eV, 3.7eV, 3.1eV and 3.25eV lie between that of CuO, MnO_2 and ZnO. It is possible to use in anode or cathode of solid oxide fuel cell.

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