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Thermal Diffusivity Studies Of ZnO-CuO At High Temperatures

Rabiatuladawiyah Md Akhir[a*] and Zaidan Abd Wahab[b]

[a]Faculty of Applied Sciences, Universiti Teknologi MARA, Shah Alam, Selangor, Malaysia
[b]Faculty of Science, Universiti Putra Malaysia, Serdang, Selangor, Malaysia

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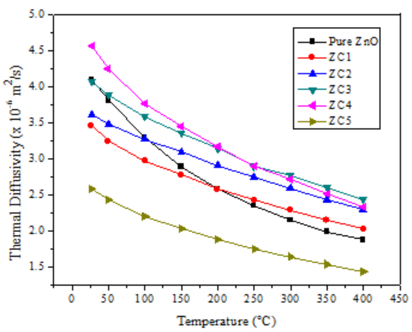
*Corresponding author
rabiatul9581@salam.uitm.edu.my

Graphical abstract



Abstract

An n-type semiconducting oxide such as Zinc Oxide (ZnO) has been exploited for their well-known gas sensing properties. Previous studies on these applications have mainly focused on electrical properties. Only limited reports were available on thermophysical properties of ZnO-based ceramics gas sensor. Therefore in this work, we report on the thermal diffusivity of Zinc Oxide-Copper Oxide (ZnO-CuO) ceramic composites by solid-state method using a laser flash technique. Thermal diffusivity of samples was measured at temperatures between 27 °C to 400 °C. The role of CuO was observed to enhance the thermal diffusivity of ZnO system with respect to the temperatures. ZnO-CuO samples played a significant role in improvement of thermal diffusivity value at temperature of 200 °C and above. Subsequently, sample of higher thermal diffusivity will exhibit lower initialization time for gas sensor to activate. Hence, the enhanced thermal diffusivity suggested that ZnO-CuO composite samples hold a promising possibility in gas sensor application.

Keywords: Zinc oxide, copper oxide, solid state, thermal diffusivity, Laser Flash Analysis

1.0 INTRODUCTION

There are several emerging applications of ZnO in the area of electronics and optoelectronics, driven by specific optical or electrical characteristics of this semiconductor. ZnO are of special interest due to their high conductivity and optical transparency, high thermal stability and relatively lower cost [1, 2]. The cost-effective and nontoxic CuO/ZnO composites are advantageous over other potential candidate systems [3]. The uses of ZnO have changed markedly over time. Most recently, ZnO is being investigated for applications such as semiconductor gas sensors. It can be an electrical conductor when suitably doped, and it is thermally stable to extremely high temperatures (at least ~1800°C). Among of all those additives, only CuO increases the density of the composites [4]. Electrical, optical and other properties of ZnO-CuO have been reported to date; however, reports on thermal properties are limited. Although thermal diffusivity is the least studied thermophysical properties in a material, it is much easier to determine than thermal conductivity due to the measurement of change of temperature rate only. Here, we report a study on the thermal diffusivity of ZnO-CuO. In this study, we applied Laser Flash Analysis (LFA) due to the practical, reliable and convenient method itself to study the effect of particle size, density, porosity and compositions of dopant on thermal diffusivity of ZnO-CuO. The great advantages of this technique is the use of small samples which makes the measuring process quite fast, since the time required to reach the desired measuring temperature is very short.

2.0 EXPERIMENTAL

The raw materials used were ZnO (99.9%, Alfa Aesar) as a based and CuO (99.9%, Alfa Aesar) as additive. CuO was incorporated into ZnO from 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt%. The pellets were then sintered at 1000°C for 3 hours at heating and cooling rate of 10°C/min. The dimensions of all sintered samples were calculated by Eq. 1:

$$\rho = m/[\pi (d/2)^2 l]. \quad (1)$$

where ρ, *m*, *d* and *l* are the density, mass, diameter and thickness of the pellet sample respectively. Meanwhile the theoretical density for each sample was calculated using Eq. 2:

$$\rho_{theo} = [m_s/(V_{ZnO} + V_{CuO})]. \quad (2)$$

where ρ_{theo}, m_s, V_{ZnO} and V_{CuO} are theoretical density, the mass of mixture of sample, volume of ZnO and volume of CuO, respectively. Relative density, ρ/ρ_{th} is the ratio of the density of a substance to the known density of a given reference material. Hence porosity, Φ can be calculated using Eq. 3:

$$\Phi = 1 - \rho/\rho_{th}. \quad (3)$$

XRD analysis was carried out on pure sample of ZnO, and ceramic composite of both ZnO and CuO to recognize and determine the degree of crystallinity of polycrystalline samples. Microstructure observations of samples were investigated by SEM at 20 kV of accelerating voltage. Thermal diffusivity measurements of ZnO-based samples were done from 27°C to 400°C by using NETZSCH LFA 457 Microflash. The thermal diffusivity measurement is carried out by determination of the relative temperature change as a function of time only. In this technique, a short laser pulse is used to heat the front side of specimen and the temperature rise at its rear surface was measured by IR detector.

3.0 RESULTS AND DISCUSSION

Fig. 1 shows the relative density and porosity as a function of CuO compositions. The relative density of sample was getting higher as more CuO was introduced but decrease when reach 50 wt% of CuO. The increasing of density of sample corresponds to the decrement of porosity. The decreasing in porosity could be understood since the densification occurred with the increasing of sintering temperature [5,6]. In this study, sintering aids such as CuO are added to improve the densification of sample.

Sample of pure ZnO produced after sintering are very porous with about 37% porosity compared to other composite samples. However, when ZnO was doped with CuO, the densification can be significantly improved up to 53%. This was in agreement with the SEM micrographs which showed that the porosity was getting smaller as higher amount were incorporated into ZnO system.

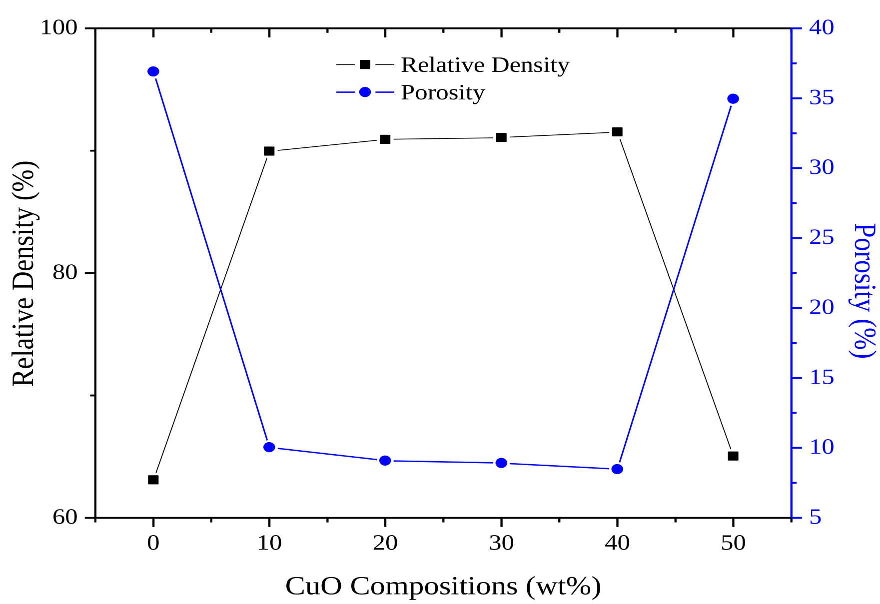


Figure 1 The relative density and porosity as a function of CuO compositions

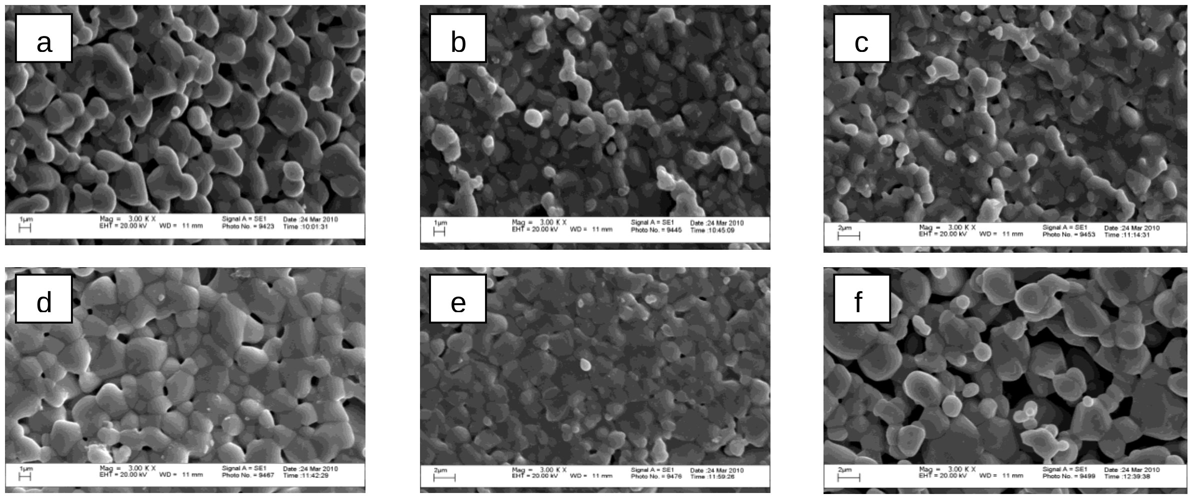


Figure 2 SEM micrograph of ZnO-CuO at different composition (a) pure ZnO (b) 10 wt% CuO (c) 20 wt% CuO (d) 30 wt% CuO (e) 40 wt% CuO (f) 50 wt% CuO at 3000 magnification.

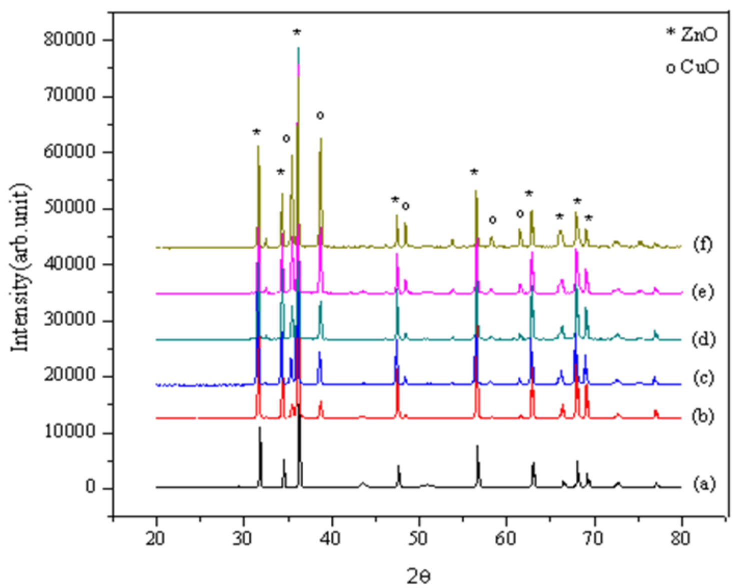


Figure 3 XRD patterns of (a) pure ZnO, (b) 10 wt% CuO, (c) 20 wt% CuO, (d) 30 wt% CuO, (e) 40 wt% CuO and (f) 50 wt% CuO

XRD patterns for pure ZnO and ZnO-CuO ceramic composite sintered at 1000 °C are shown in Fig. 3. The intensity of peaks corresponding to the CuO phase increased slightly from 10 wt% CuO to 50 wt% CuO. The increment of intensity of peaks may correspond to the relative increment of crystallintiy of ZnO-CuO ceramics composite. This observation was found to be related with thermal diffusivity behavior. Polycrystalline material consists of highly ordered arrangement of atom would give faster speed of heat propagation through sample as heat transfer between one atom to adjacent atom becomes easy due to less in phonons scattering. Hence leads to the increment of the thermal diffusivity value of ZnO-CuO samples.

Refer to Fig. 4, pure ZnO and ZnO-CuO composite samples show a steady reduction with temperature. The decreased of thermal diffusivity of sample with temperature suggests that the dominant contribution to the thermal diffusivity is due to thermally enhanced phonon-phonon scattering [10]. The increased density have improves the value of thermal diffusivity up to 33% due to the inter-particle bonding becomes stronger and molecules transferring heat better. However, due to the increased size of pores within the grain as can be observed in Fig. 2 (f), the percentage of porosity shows a progressive increment up to approximately 35% and resulted to the decreased of thermal diffusivity from 4.58 x 10^{-6} m^2s^{-1} to 2.59 x 10^{-6} m^2s^{-1}. This behavior is in line with previous study [7]. The decreased in the thermal diffusivity with increased porosity is a consequence of the decrease in the mean free path, due to the phonon confinement in the crystallite [8,9]. It was observed that the thermal diffusivity of pure ZnO exhibited within high range at only room temperature, 27 °C. The increment of thermal diffusivity with higher composition of CuO was attributed to the increasing of sintered density. 40 wt % of CuO gave the highest sintered density (5400 kg/m^3). When exposed to heat, the lattice vibration of atom will be easily pass to another atom and will be less in phonon scattering. Hence, lead to the increasing of heat transfer through the sample and so does its thermal diffusivity. This theory coincided well with the results which addition of 40 wt % of CuO had contributed to the greatest thermal diffusivity (4.58 x 10^{-6} m^{2}s^{-1}). However, it is unreliable to choose pure ZnO as a potential candidate in gas sensor application. High operating temperature is required for gas sensor application. ZnO-CuO composite sample play a significant role in improvement of thermal diffusivity value at temperature between 200°C and above. Sample of higher thermal diffusivity is therefore believed will exhibit lower initialization time for gas sensor to activate.

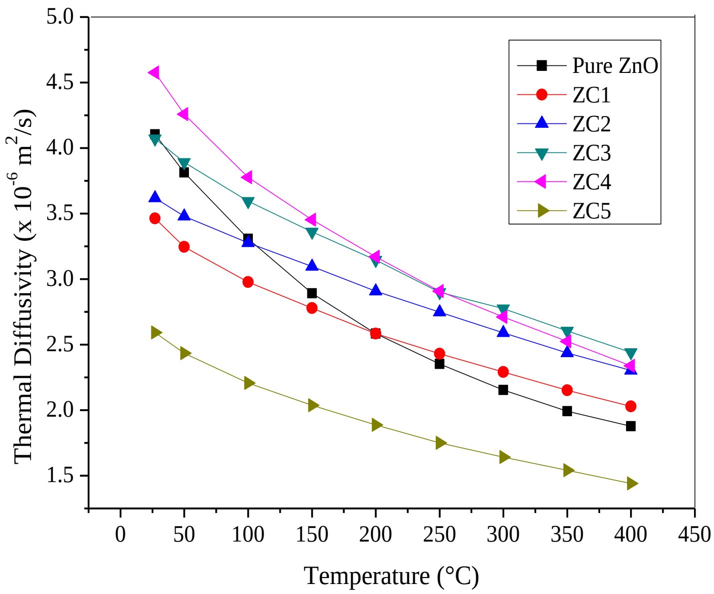


Figure 4 Thermal diffusivity of pure ZnO and ZnO-CuO system at different temperatures

4.0 CONCLUSION

To conclude, the LFA technique has been used to study the thermal diffusivity of the samples. Easy sample preparation, fast measurement times and high accuracy are some of the advantages of this technique. The way that the thermal diffusivity behaves towards the change of dopant concentration and different temperatures were investigated. Doping of p-type (CuO) into n-type (ZnO) based system had improved thermal diffusivity of samples as compared to the n-type/n-type based system. The thermal diffusivity increased progressively as the CuO content increased. The variations of the thermal diffusivity depend not only on the temperature but also can be controlled by the effects of dopant compositional, density-porosity, crystallinity, morphology and the synthesis conditions and then holds a possibility as a tuneable semiconductor in ZnO based devices with respects to thermal diffusivity. SEM micrographs confirmed that grain size distribution leads to the enhanced thermal diffusivity. XRD also confirmed the crystallinity of the sample had a great effect towards the improvement of thermal diffusivity. Thermal diffusivity is a significant characteristic and could be considered for the purpose of lowering the initializing time for the activation of gas sensor.

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