Effect of Sintering Temperature to The Thermal Conductivity of Cu doped ZnO

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***Abstract*—Zinc Oxide (ZnO) is a one of interesting materials to be developed as semiconductor materials because of its advantages for many applications, while research about Cu doped ZnO in the pellet form is seldom. This research aims to synthesize the material for p-type thermoelectric semiconductor of ZnxCu1-xO and to obtain the thermal conductivity as a one of important material characteristic of thermoelectric semiconductor. Zinc nitrate tetra hydrate as a raw material was mixed with copper nitrate trihidrate, dried, calcined, and compacted to be a pellet form finally. Furthermore, the sintering process was conducted at temperature from 1,100°C to 1,500°C. The thermal conductivity was measured using steady state method. The highest thermal conductivity of 3.14 W/mK was obtained by which sintering temperature of 1,300°C and operational temperature of 450°C.**

Key words - Semiconductor material p-type, thermal conductivity, thermoelectric, Cu doped ZnO.

I. INTRODUCTION

One of interesting materials to be developed as semiconductor materials is Zinc Oxide (ZnO)[1, 2]. Base on several advantages of ZnO such as the wide direct band gap of 3.37 eV, exiton binding energy of 60 meV[3-5], physically and chemically stable properties [5, 6], cheap and kindly environmental [5], semiconductor materials of ZnO is used in a lot of applications of piezoelectric tranducers[1], gas sensor, solar cells, varistors, light emitting devices, photochatalyst, antibacterial activity, cancer treatment [5], laser ultra violet, piezonanogenerators, diluted magnetic semiconductor for spintronics[7], laser diode, UV photodetectors[8] and termoelectric[9-15]. Doping process of the ZnO by atomic molecule such as Cu [1, 2, 4, 5, 7, 8, 16-37], Ag, Au, Pt [8], Al [11, 14, 15] and Mn, Fe, Co, Ni [16, 17] based on specification and application is a one of the effort to increase ZnO performance [5, 16].

As a prominent luminescence activator in compounds in groups II–VI of the periodic table, Cu or copper is a reasonable matter as a doping material for ZnO. Copper has a capability to replace the atom of Zn easily because the ionic radii of Cu closes to the ionic radii of Zn. It means Cu able to infiltrate into the polycrystalstructureofZnO [4, 38]. Other facts, Cu have similar physical and chemical properties of Zn [2, 33]. Study in the electric, optic and ferromagnetic characteristic of Cu doped ZnO has already done [2, 16]. Researches of optical capability in thin film of ZnO [2], magnetic capability in the form of diluted magnetic semiconductor (DMS) in thin film [28, 34, 36, 37], and gas sensor [27, 29] have already done while research in the pellet form is seldom until now. Several synthesis methods to doping Cu in ZnO are solvothermal [4, 31], co-precipitation [5, 33], sonication [16], sol-gel [18, 38], inexpensive advanced spray pyrolysis method [19, 29], economical hydrothermal [23], rapid hydrothermal [27], radio frequency magnetron sputtering (RF-MS) [28, 30], and inductively coupled plasma enhanced physical vapor deposition (ICP-PVD) [37].

Thermal conductivity is an important aspect to studying thermoelectric, as shown in figure of merit, *ZT*, for isolator, semiconductor and metal material in Fig 1. All properties of the semiconductor material, electric (σ) and thermal (κ) conductivity, were related to each other. Materials which have high electric and thermal conductivity usually have low Seebeckcoefficient. In the contrary, materials which have low electric and thermal conductivity become material with high Seebeck coefficient. This is a reason why pure metal or non-metal materials are bad to be thermoelectric materials.

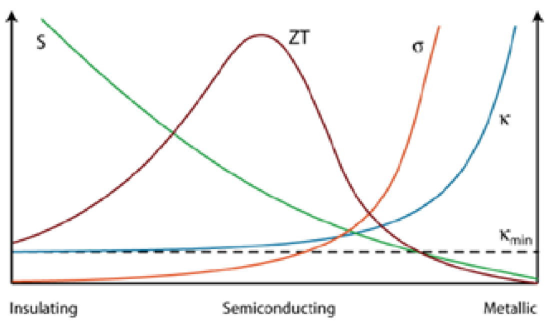

Fig 1. Figure of Merit of Thermoelectric Materials [38]

Thermal conductivity is a capability of the material to transfer heat through the materials. Materials consist of free electron and atom which bound in the *lattice*. Therefore heat transfer could be as a phenomenon of moving the free electron and oscillation of the lattice wave. [39, 40]. Materials which have high electric and Seebeck coefficient along with the low thermal conductivity are propose good performance for the thermoelectric. Materials of semiconductor have those capabilities cause of its high charge carriers of $10^{18} - 10^{19}$ cm^{-3} [38].

In this research, thermal conductivity of Cu doped ZnO in the pellet form after sintering process at temperature of 1,100°C, 1,200°C, 1,300°C, 1,400°C and 1,500°C using sol gel synthesis method is obtained. To support the hypothesis, morphology structure of the material was also be tested by X-Ray Diffraction (XRD) and Energy Dispersive X-ray analysis (EDAX).

II. RESEARCH METHOD

The $Zn(NO_3)_2.4H_2O$ (99.9%), powder of $Cu(NO_3)_2.3H_2O$ (99.9%) and citric acid [$C_6H_8O_7$] (99.5%) were used in this research. Solvent of $Zn_xCu_{1-x}O$ contains Cu of 2 wt%. $Zn(NO_3)_2.4H_2O$ (99.9%) and $Cu(NO_3)_2$.3H2O (99.9%) were blended in composition of 99%:1%. Then the mixture was mixed with Aquades in composition of 1:5 wt%. The solvent constantly was stirred during 4 hours at temperature 60 - 70°C using magnetic stirrer Nesco MS-H280-Pro. Then solvent was mixed again with citric acid [$C_6H_8O_7$] (99.5%) in composition 4:1 through 4 hours at temperature of within 60°C – 70°C. After 24 hours in the settle condition, the void and bubbles were disappeared.

Furthermore, the fluid was heated at temperature of 130°C in the course of 2 hours in order to obtain dried xerogel. Using agate mortar, dried materials were proceed to be a powder manually, furthermore obtained powder was calcined at temperature of 400°C during 1 hour and sintered at temperature of 840°C for 2 hours. After the powder was mixed by ethanol 4%, the powder then was pressed to be a pellet form of ∅13 x 3 mm using hydraulic press machine at pressure of 30 bar. Finally materials were sintered at temperature of 1,100°C, 1,200°C, 1,300°C, 1,400°C, dan 1,500°C in 2 hours.

The thermal conductivity of material was measured using steady state method (Thermal Interface Material (TIM) based on ASTM Standard D5470-06). The sample was sandwiched between two identic substrates which 3 thermocouples were attached in each substrate. Base on the measured temperature at all thermocouples, temperatures at each surface of sample were obtained. Crystal structure of Cu doped ZnO was tested by X-ray Diffraction (XRD) with CuK_{alpha2} (λ=0.15406nm) radiation at 60kV and 60mA, scanning rate at 0.020/s in 2θ method with range distance from 100 to 800. Contain of the materials was looked by Energy Dispersive X-ray analysis (EDAX) test with FEI Inspect-S50 machine.

III. RESULTS AND DISCUSSION.

This research shows that the thermal conductivity sharply alter when the sintering temperature rise from 1,100 to 1,300°C and then decrease, Fig. 2. These thermal conductivity results were obtained at operational temperature 400°C and 450°C which the value for 450°C little bigger than 400°C. It might be influenced by size of the granules [10]. Thermal conductivity (k) consists electronic conductivity (k_e) and lattice conductivity (k_L). Smaller value of k_L was happened if the value of grain diameter drop below 10 μm[41]. This drastically drop of k_L value is effect from *boundary scattering*. For example, value of k_L for materials of $Si_{70}Ge_{30}$ drops from 8.2 to 4.3 W/mK when the value of grain drop to 2 μm[41].

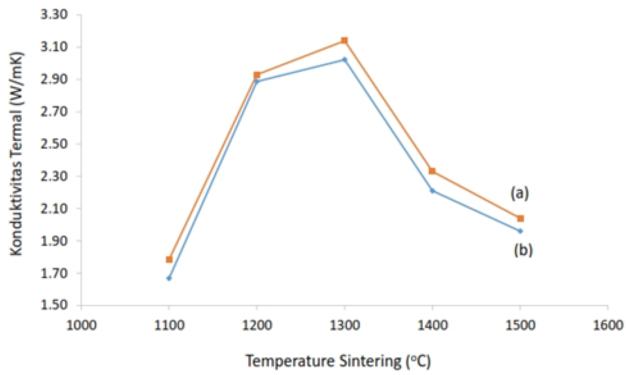

Fig 2. Thermal conductivity of Cu doped ZnO semiconductor at operations temperature (a) 450°C and (b) 400°C.

This phenomenon have already showed by other research [42]. Based on Wiedemann-Frans law, k_e can be estimate by equation of [42]:

$$k_e = L\sigma T$$

which L is Lorentz number (2.45 x 10^{-8} V^2/K^2 for free electron), T is temperature, and σ is electric conductivity.

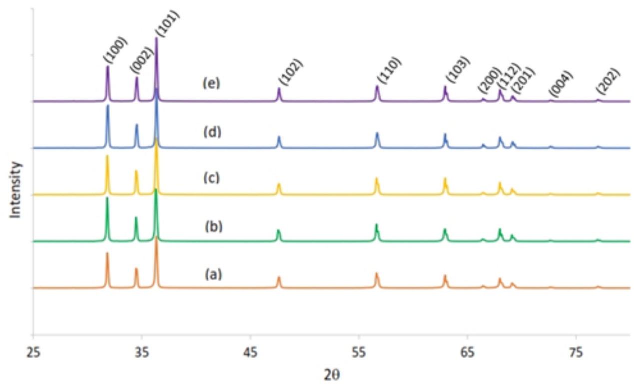

Fig 3. The resultof XRD test (a) 1,100°C (b) 1,200°C (c) 1,300°C (d) 1,400°C (e) 1,500°C

Capability to transfer of heat is influenced by electron and wave in the lattice movement or phonon. For semiconductor, capability to transfer of heat by phonon is better than by electron. The well-ordered formation of crystalite lattice has higher conductivity than disorder formation of crystalite lattice (amorf) because of easily capability of phonon to move [39].

TABLE I.
XRD results at (1 0 1)

No	Temperature of Sintering (°C)	2θ	FWHM	d()
1	1,100	36.33	0.214	2.471
2	1,200	36.30	0.216	2.473
3	1,300	36.34	0.189	2.470
4	1,400	36.32	0.223	2.471
5	1,500	36.35	0.174	2.469

TABLEII.
The results of EDAX test for Cu doped ZnO

No	Sintering Temperature (°C)	wt (%)		
		Zn	Cu	O
1	1,100	62.94	1.58	35.48
2	1,200	70.45	1.72	27.83
3	1,300	73.92	1.87	24.21
4	1,400	74.66	1.67	23.67
5	1,500	70.95	1.57	27.48

The results of XRD at sintering temperature of 1,100 to 1,500^{0}C shows that semiconductor ZnO is suitable with the standard of ZnO of PDF 36-1451 with *space group* P63mc (186) and crystaline structure of hexagonal wurtzwite. There is no new peak point exist at Fig. 3 for all samples which means there is no new phase which enter at lattice crystal like at EDAX analysis for Cu in the ZnO[43, 44]. Top of the peak from XRD test occurred at (1 0 1) for every materials, Table I.

Table II shows the split of the 2θ value frommaterial of pure ZnO 36.253^o bigger (move to rigth) than Cu doped ZnO. Furthermore, there is no difference of crystal diameter of ZnO as effect of sintering temperature for Cu doped ZnO semiconductor, see Table II.

IV. CONCLUSIONS

Material of Cu doped ZnO p-type has already manufactured using process of mixing with the solvent, pre-heating (130°C), initial grinding, initial sintering (temperature < 800°C), second grinding, compaction (30 bar), and second sintering (1,100 - 1,300°C). The value of thermal conductivity at sintering temperature of 1300°C is 3,14 W/mK. These values were influenced by sintering and operational temperature.

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