Low Electrical Resistivity of Nano WO_3-doped ZnO Thermoelectric Material

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Abstract

The ZnO thermoelectric material was reduced electrical resistivity by doping nano WO_3 powder in solid-state reaction process by using ZEM-3 at temperature range of 373 – 873 K in Ar atmosphere. The results found that the XRD patterns show the nebulous phase matches with of $ZnWO_4$ belonging to the monoclinic structure. In XRD patterns were appeared WO_3 peaks in crystalline structure of $ZnWO_4$ phases, and the SEM showed an intensive distribution of WO_3 into the grain boundaries. The average Seebeck coefficient of WO_3-doped ZnO sample was increased from −30 to −75 μV K^{-1} indicate n-type thermoelectric materials. Moreover, we can reduce the electrical resistivity ranged from 16 mΩ cm to 34 mΩ cm. The highest power factor of sample is 0.024 mW m^{-1} K^{-2} at 473 K. The results revealed that doping nano WO_3 with ZnO also could promote to using for the thermoelectric devices at high temperature application.

KEYWORDS: Nano materials; semi-conductors; thermoelectric materials
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Introduction

This attention of the researcher is attributed to their unique properties of thermoelectric materials which they could act to directly conversion of heat energy into electrical energy which numerous applications of thermoelectric materials have been found in different fields [1 − 3]. The significant knowledge of Seebeck and Peltier effects are essential fundamental phenomena for making a small amount of power at a very small voltage. The efficiency of thermoelectric materials could be quantified by the dimensionless figure of merit ZT, $ZT = \sigma S^2 T/\kappa$, where S is Seebeck coefficient, σ is electric conductivity, κ is thermal conductivity and T is temperature [4]. Therefore, the realization of high S and σ values and a low κ value is required for a high-performance material [5]. It is well known that the compositional or composite materials are used for the development and enhancement material's properties. In case of chemical doping in ZnO material, the structure parameters can be operated that affect to properties of material and even also into the semiconductor materials [6]. Among the thermoelectric materials, ZnO has become a promising thermoelectric material due to its high Seebeck coefficient, low-cost production, potential high-temperature chemical stability and non-toxicity [7]. Interesting of researchers ZnO-based materials showed that thermoelectric properties can be improved by substitution with transition element which showed to higher electrical conductivity, Seebeck coefficient and electrical resistivity. J. Liu and et al. [8] were demonstrated that Pb and Zn codoping in the SnSe single crystals in polycrystalline SnSe secondary phase contribute to remarkable enhancement of electrical conductivity and power factor and It can be concluded that the high thermoelectric performance ZT = 2.2 was achieved in polycrystalline SnSe through enhancing electrical transport properties while keeping ultralow thermal conductivity [9]. Interest in typical nanomaterials, whereas they are located in the bulk of conventional materials. Thus, the intrinsic properties of nanomaterials are different from conventional materials, since the majority of atoms are in different environment. Nanomaterials represent almost the ultimate in increasing surface area. Substances with high surface areas have enhanced chemical, mechanical, optical and magnetic properties, and this can be exploited for a variety of structural and non-structural application [10]. In fields of thermoelectric materials, ZnO nanoparticle have shown favorable TE properties, low cost, and earth abundance for large-scale application potentials. Additionally, Zinc can be obtained from waste materials. ZnO nanoparticles have shown remarkable performance in a wide variety of applications, including photocatalytic and photoluminescence, self-cleaning and pollution remediation for structures and environment [11]. In recent years, some other metal oxides have received considerable attention as thermoelectric materials, such as WO_3 which have optical bandgap of ~2.7 eV, which is attributed to a charge transfer transition from a filled valence band composed mainly of O_2 p orbitals to an empty conduction band (CB) composed mainly of W 5d orbitals, and is an electronic (n-type) conductor when the material has oxygen vacancies [12, 13]. Therefore, this work aims to improve thermoelectric properties of the nano ZnO thermoelectric material by doped with nano WO_3 were synthesized by solid state reaction method.

Materials and Methods

For sample, pure nano-WO_3 doped with nano-ZnO (ZnO: WO_3) were prepared by a solid-state reaction method. The powders each having a purity of 99% were used as starting materials. To obtain ideal sample, for each composition, the powders were mixed and ground in a ball mill at speed of 320 revolution per minute for 5 h. Then hot-pressed at 800 °C for 6 h in Ar (Argon) atmosphere. After the hot-pressed, Crystal structure of the sample was characterized by X-ray diffraction (XRD-6100, SHIMADZU Co., Ltd.) with Cu Kα (1.54056 A) radiation accelerated in a 2θ range of 25 – 80°. The nano-tructure of the sample were observed by a scanning electron microscope (SEM, JEOL, JSM5410LV Co., Ltd.). In order to measure the Seebeck coefficient, two surfaces of sample composite cubes (3 × 3 × 15 mm^3) were polished with sandpaper and kept at room temperature (25 ± 2 °C) shown in Fig. 1(a). The voltages were measured at temperatures at both sides of samples (Vroom) were recorded by a SANWA digital multi-meter Instrument (CD800a). The density was measured by Archimedes' method. Electrical conductivity and Seebeck coefficient were measured using a static DC thermoelectric property measurement system (ZEM-3, ADVANCE RIKO, Inc.) under at temperature range of 373 – 873 K in Ar atmosphere shown in Fig. 1(b).

Results and Discussion

In this work, the WO_3:BaO:ZnO:B_2O_3 glasses in composition xWO_3:20BaO:20ZnO:(60 − x)B_2O_3 (where x = 0, 5, 10, 15, 20 and 25 mol%) have been studied the photon interaction in the energy range 1 − 10^5 keV by using WinXCom program. Fig. 1. shown that the photoelectric absorption were the main interaction at low photon energy (1 − 10^3 keV), the values were decreased with increasing of photon energy.

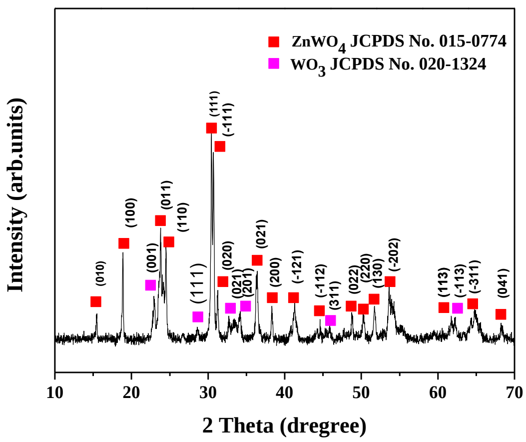

Fig. 2 XRD patterns of samples hot-pressing.

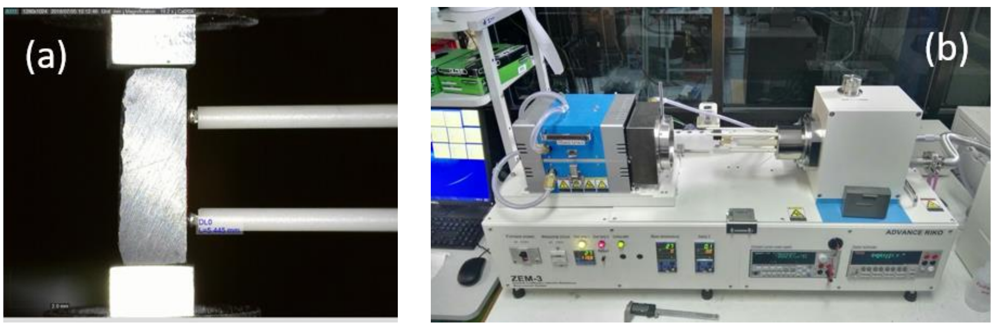

Fig. 1 Measurement system of thermoelectric properties (ZEM-3, ADVANCE RIKO, Inc.).

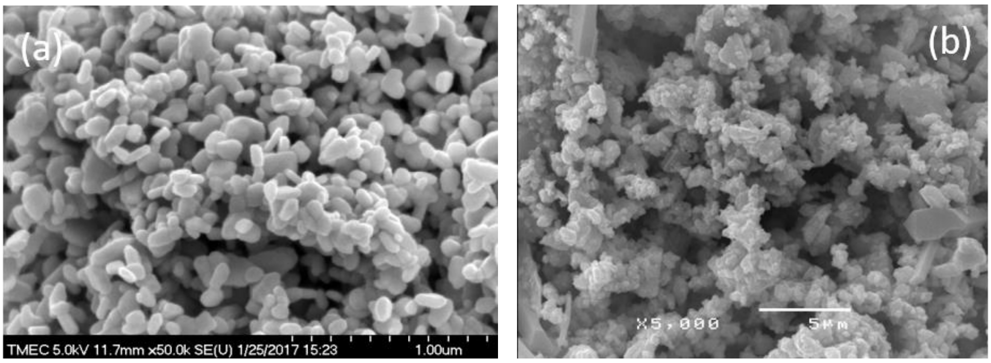

Fig. 3 SEM images of the fraction to the hot-pressing direction for WO_3 (a) and $ZnWO_4$ (b).

Fig. 2 shows the XRD pattern at the hot pressing at 800 °C for 6 h in Ar atmosphere on 60 MPa of the sample almost all diffraction peaks can be indexed to the nebulous phase matches with of $ZnWO_4$ (JCPDS No. 015-0774), belonging to the monoclinic structure. In XRD patterns were appeared WO_3 peaks (JCPDS No. 020-1324) in crystalline structure of $ZnWO_4$ phases due to the powder's preparation to $ZnWO_4$ are not completely oxidation. In Fig. 3 the scanning electron microscopy micrographs of the nano WO_3 (a) and with distribution amount of nano WO_3 in nano ZnO based (b) are shown that the distribution of nano WO_3 packing with the nano ZnO based and show that the grain size of samples increases with the addition of nanoWO_3 in nano ZnO based.

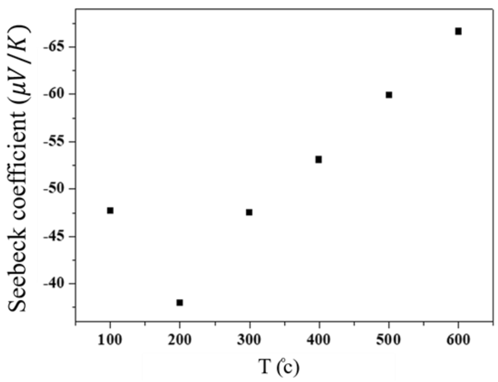

Fig. 4 Temperature dependence of Seebeck coefficient of hot-pressing sample.

Fig. 4 presents the Seebeck coefficients (s) for the samples at different temperatures. The absolute value of the s increases with the increment of the temperature, and the Seebeck coefficient values are all negative over the whole temperature range, indicating an n-type conduction. The electrical resistivity of hot-pressing sample shows highest electrical resistivity 34 mΩ cm at 200 °C and electrical resistivity decreases with increasing temperature show lowed electrical resistivity at 16 mΩ cm at 400 °C.

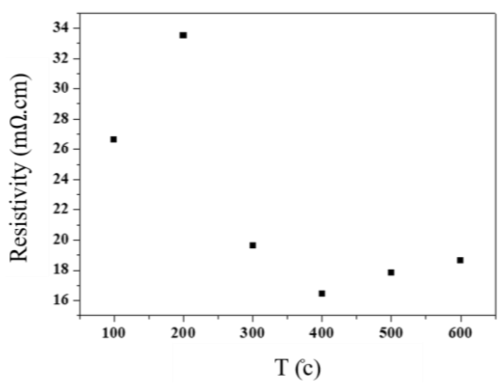

Fig. 5 Temperature dependence of the electrical resistivity of hot-pressing sample.

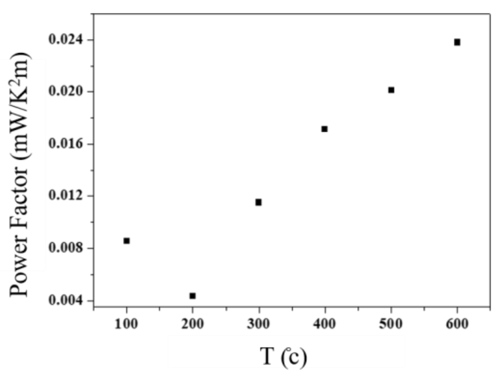

Fig. 6 Temperature dependence of the Power factor of hot-pressing sample.

The power fartor is another path of the values which can be predict reliably and accurately the efficiency of materials at a large temperature difference between the hot and cold sides of the materials. In this case the power factor of hot-pressing sample has the same trend of the Seebeck coefficient which have increased with the increasing of the temperature. The hot-pressing sample have good the power factor when compared with the hot-pressing sample and showed highest power factor value of $ZnWO_4$ at 0.024 mW m^{-1} K^{-2} and lowed power factor value is 0.004 mW m^{-1} K^{-2} approximately.

Conclusion

For sample, pure nano-WO_3 doped with nano-ZnO (ZnO: WO_3) were prepared by a solid-state reaction method by hot-pressing process. The powders were mixed and ground in a ball mill at speed of 320 revolution per minute for 5 h. Then hot-pressed at 800 °C for 6 h in Ar atmosphere. It can be concluded that XRD patterns did not show evidence for $ZnWO_4$ inclusion into the ZnO lattice, but the SEM showed an intensive distribution of WO_3 into the grain boundaries. The average Seebeck coefficient of WO_3-doped ZnO sample was increased from −30 to −75 μV K^{-1}indicate n-type thermoelectric materials. Found that we can reduce the electrical resistivity ranged from 16 mΩ cm to 34 mΩ cm. The power factor showed highest power factor value of $ZnWO_4$ at 0.024 mW m^{-1} K^{-2} and lowed power factor value is 0.004 mW m^{-1} K^{-2}.

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