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Influence of supercritical drying on thermoelectric properties of Zinc Oxide

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Abstract: *Effect of supercritical drying on thermoelectric performance of aluminum doped zinc oxide is investigated. Oxide gels were obtained by sol-gel processing of alcoholic zinc nitrate solution, with addition of propylene oxide as a gelation agent. The gels then were processed and dried in supercritical ethanol conditions ("A-gel" powders) or left for slow evaporation in ambient conditions ("X-gel" powders). Powders were sintered using spark plasma sintering (SPS) method. On sintered samples, the electric conductivity, the Seebeck coefficient and the thermal conductivity were measured. Distinct difference in morphology of two types of the samples was studied with SEM. The samples prepared with supercritical method exhibited up to 45% lower thermal conductivity in low temperature region. Metallic-like behavior of the electrical conductivity as observed on A-gel samples. As a consequence of good electrical properties and lowered thermal conductivity, A-gels had better result of thermoelectric efficiency (ZT). The largest dimensionless figure-of-merit ZT = 0.10 was obtained for the A-gel sample.*

Keywords: Zinc Oxide; Supercritical Fluid; Thermoelectricity; Semiconductor; Nano-powder

1. INTRODUCTION

Zinc oxide is considered to be one of the most promising n-type thermoelectric oxide materials. Many factors including: abundance in earth crust, nontoxicity, resistance to high temperatures, high oxidation resistance and ease to process, are contributing to its scientific interests that is steadily rising during past years.

Oxides had been disregarded as possible thermoelectric materials due to two major factors limiting performance of this family of materials. They are composed of light elements, that makes propagation of phonons easier and thus increases lattice thermal conductivity. Second major factor is the ionicity of interatomic bonding in these compounds. Ionic bonds mean alternating positive (cations) and negative (anions) charges in the crystals, and thereby lower carrier mobility. However, this view changed in 1990s discovery of oxide thermoelectric materials with considerable ZT values. Since then many interesting papers has been published.

This work aims at reduction of the thermal conductivity of zinc oxide, the most promising n-type oxide in thermoelectrics. One of the best insulating materials known are aerogels. Aerogels are formed by sol-gel route. In this approach, reagents in solution form a colloidal solution (sol). The sol allowed to react further forms an integrated nanonetwork of particles or polymers – forming a gel. Utilizing some useful properties of supercritical fluids, the solvent can be evacuated from the gel pores without collapsing them and substituted with air – forming a final aerogel product.

2. EXPERIMENT

Experimental procedure is based on "alkoxide addition method" synthesis [1]. Synthesis is carried out under ambient conditions. Reagents were used as purchased without further purification. The thermoelectric properties of the samples were measured on an Ozawa Science RZ2001i. Samples for the measurement were cut from pellets to form rectangular bars (~2x4x10 mm), for four-wire method. Temperature step was 50K, maximum temperature was 800°C, and the measurements were carried out in air.

The thermal conductivity was studied using laser flash method. Thermal conductivity value was obtained from thermal diffusivity and specific heat capacity measured on a Kyoto Electronics Manufacturing LFA-502. Measurements were performed form room temperature to 800°C in vacuum, during heating. Sample was cut from the same pellet as bars for thermoelectric measurement. Sample geometry was rectangular (5x5x1 mm), and before measurement was coated with a graphite spray, together with reference.

2.1 Materials

As starting materials zinc nitrate hexahydrate (Chameleon reagent, Osaka, Japan), aluminum nitrate nonahydrate (Chameleon reagent, Osaka, Japan), Propylene Oxide (Wako Pure Chemical Inc.), and 99.5% ethanol were used.

2.2 Aerogel powder

13.03 g of zinc nitrate hexahydrate and 0.33 g of aluminum nitrate nonahydrate where mixed with 53.98 g of 99.5% EtOH. The mixture is then stirred on a hotplate until a clear solution is obtained. The solution is gently warmed to 30°C, and 26.21 g of propylene oxide was rapidly added. The mixture was stirred vigorously for 2 minutes, and a visible change in transparency occurred. The sol was transferred to vials, sealed, and allowed for gelation. Formation of white opaque gel completed after 7 hours. The gels were allowed to age in the sealed vials for 4 days under ambient conditions. The gel was then transferred to a beaker and washed with ethanol 3-4 times. A half of gel was allowed to dry slowly under ambient conditions. Another half was transferred back to the vials and dried under supercritical conditions of ethanol. For supercritical drying, a Taiatsu SUS316 500 ml autoclave was used. Temperature was increased over a period of two hours to 260°C and a pressure of 70 kgf/cm^2. Then the pressure was released over the course of one hour.

This procedure resulted in ~12g of a white aerogel powder of aluminum doped zinc oxide. The powders were annealed in 600℃ for 6h to improve the crystallinity, as well as to purge any organic residues.
The powders were loaded in a graphite die and sintered with spark plasma sintering (SPS) method at a high heating rate of 100℃/min, and natural cooling rate.
Resulting sintered pellets were cut, polished and their properties were measured. Sample treatment are shown in Table. 1

Table 1. Sample treatment conditions

Sample name	Drying condition	Sintering temperature	Sintering pressure
A-gel 950	Supercritical	950 °C	50 MPa
A-gel 1050	Supercritical	1050 °C	50 MPa
X-gel 950	Ambient	950 °C	50 MPa
X-gel 1050	Ambient	1050 °C	50 MPa

3. RESULTS

As evidenced by XRD results in Figure 1, zinc oxide with a high crystallinity was obtained. No signal from aluminum oxide was observed.

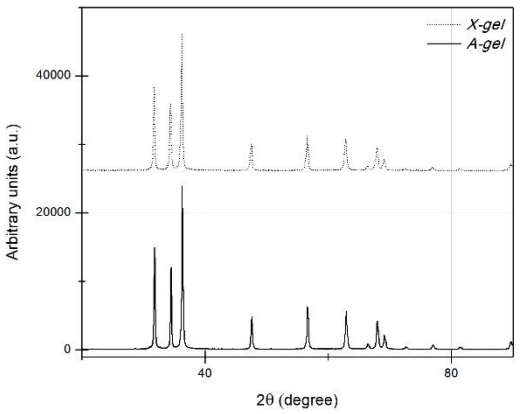
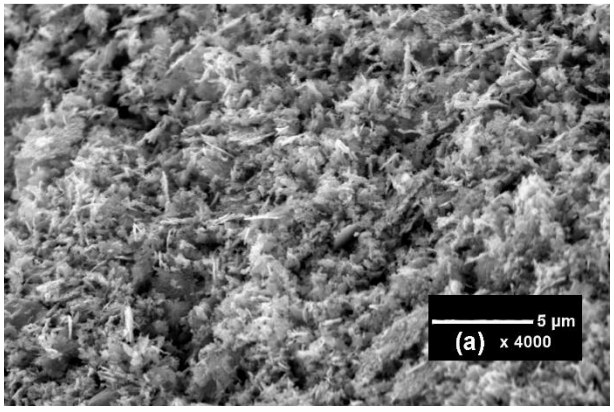


Fig. 1. XRD patterns of the annealed powders

An SEM observation revealed distinct differences in a morphology of the particles (figure 2).



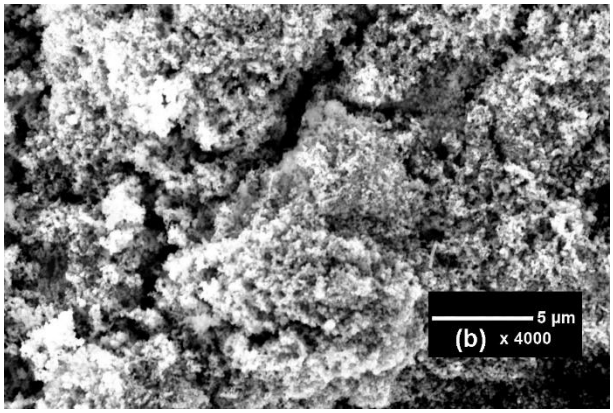


Fig. 2. SEM images of (a) *X-gel* powder and (b) *A-gel*.

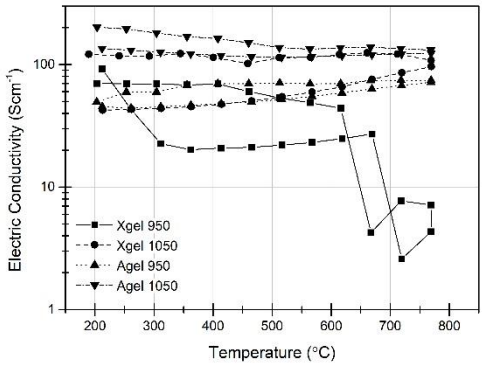


Fig. 3. Electrical Conductivity

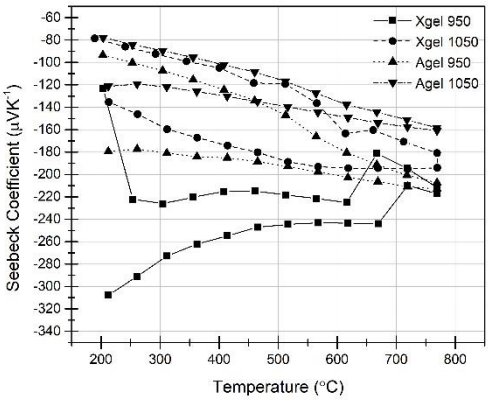


Fig. 4. Seebeck coefficient

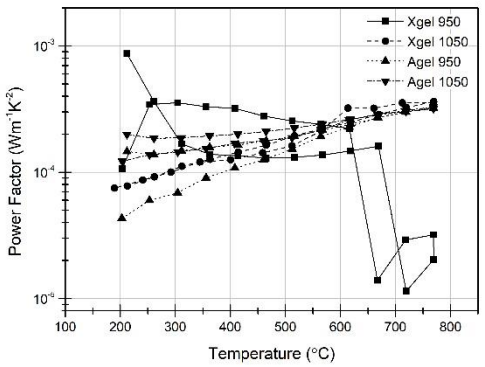


Fig. 5. Power factor

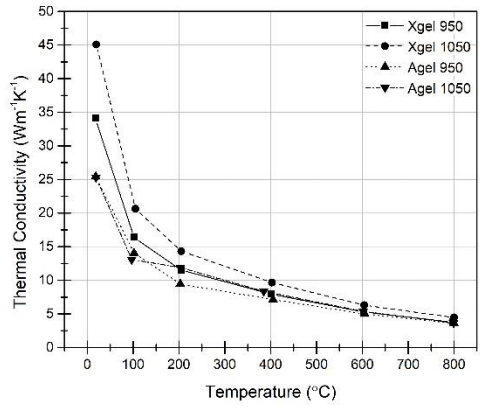


Fig. 6. Thermal Conductivity

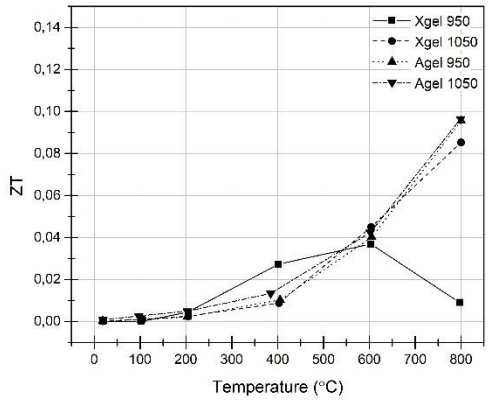


Fig. 7. Thermoelectric figure of merit

4. DISCUSSION

Samples consist of single crystalline phase. In XRD there were no signals from aluminum oxide, showing that Al was dissolved into the zinc oxide crystal lattice. Aluminum-doped zinc oxide powders with different particle morphology were thus obtained.

The SEM imagining was employed to study the size and distribution of the particles in the samples. The *X-gel* particles were elongated and irregularly shaped. Flakes and needles were evenly distributed in the sample. The particles formed large aggregates, consisting of 1 to 5.2 μm long particles (Fig. 2(a)). Contrastingly the *A-gel* particles were spheroidal, with width and length ranging from 23 to 250 nm. The *A-gel* agglomerates were much smaller as seen in Fig. 2(b).

The results shown in Fig. 3 suggest that the samples derived from *A-gel* exhibited higher electrical conductivity in comparison to their *X-gel* counterparts, with the largest difference of almost and order of magnitude between *X-gel 950* and *A-gel 950*. This can be explained by more efficient doping of Al into the crystal lattice of ZnO. Smaller particle size of *A-gel* implies higher surface areas. Since doping during sintering is a diffusion-driven process, it depends on surface area according to Fick's first law. Equation describing most accurately process occurring in sample can be written as follows:

$$\frac{\partial \varphi(x,t)}{\partial t} = \nabla \cdot \left(\mathrm{AD(x)}\nabla\varphi(\mathrm{x,t})\right) = \sum_{i,j=1}^{3}\left(A_{ij}D_{ij}\frac{\partial^2\varphi(x,t)}{\partial x_i \partial x_j} + \frac{\partial D_{ij}(x)}{\partial x_i}\frac{\partial \varphi(x,t)}{\partial x_j}\right)$$

In this equation, the diffusion coefficient (D) is direction dependent and proportional to the surface area. Assuming that there was inhomogeneity during gel formation, that might arise from inhomogeneous concentration of reagents in mixture with increasing viscosity over time. Powders with higher surface area shall exhibit faster diffusion, given that time and temperature of sintering are the same. This observation requires further confirmation and study to eliminate any possible sources of error.

The electrical conductivity observed on A-gels was metallic like. As shown in Fig. 6, the thermal conductivity of *A-gel* was lower than those of X-gels, and the difference was most pronounced at lower temperature, the where difference was 45%. This difference slowly diminished at highest temperature, where *A-gel* samples were exhibiting 20% lower in the thermal conductivity. This would be attributed to a much smaller average size of crystallites in *A-gels* since the density of the samples was similar (~90% dense).

Existence of nano-crystallites in sintered *A-gel* samples was confirmed by external standard method (The pure phase served as an external standard, and its diffraction pattern was performed in a separate measurement). Apparatus used was MiniFlex600 manufactured by Rigaku. As an external standard, spectrum of Lanthanum Hexaboride was used, and result compared to commercial nanosized ZnO (Sakai Chemical, FINEX-25, particle size 60 nm). Part of the pellet that other samples were cut from, was pulverized with mortar and pestle. Resulting powder was measured. Angles from 10 to 90° 2θ, with step of 0.01°, at room temperature were scanned. Two analysis method were used - Sherrer; Halder and Wagner. For commercial powder crystallite size was 58 nm. For *A-gels* this value was between 57 and 103 nm. Due to large number of grain boundaries, phonon scattering lowered bulk thermal conductivity.

All samples exhibited Seebeck coefficient below -150 μVK^{-1} as seen in Fig.4. Best result (-260 μVK^{-1}) that combined with moderate conductivity of this sample (~100 Scm^{-1}) gave a rise to considerable (~0.09) figure of merit, similar to results of the *A-gels*. In case of the *A-gels* best obtained thermoelectric figure of merit was ~0.10 (Fig.7.). The seebeck coefficient behaved similar to other examples presented in papers on aluminum doped zinc oxide, and gradually decreased with temperature. Power factor (Fig. 5.) that describes electrical contribution to the ZT shows that *X-gel 1050* was electrically superior to *A-gel 950 and A-gel 1050*. This gives basis to conclude that higher ZT of the *A-gels* was a result of lowered thermal conductivity.

5. CONCLUSION

Super critically dried powders derived from gels were obtained and sintered in range of temperatures. For comparison the powders derived from gels dried in an ambient temperature were obtained and sintered. Performed measurements found that the samples obtained from super critically dried powders exhibited lower thermal conductivity, and similar thermoelectric efficiency. SEM observations revealed different morphology of the powders that were deemed to be reason of different properties exhibited by samples. Supercritical approach to lower lattice thermal conductivity shows promise in achieving that goal.

6. REFERENCES

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