

Synthesis of nano-sized ZnO powders prepared by precursor process

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Nano-sized ZnO powder was synthesized by a precursor process using zinc sulfate salt and aluminum sulfate salt as starting materials. Pulp and crystalline cellulose were used as precursor materials. The crystallization process, morphologies, and thermal decomposition were studied as a function of calcination temperatures and raw material compositions. The calcined powders were evaluated by SEM, XRD, TG-DTA, and volume resistivity. The volume resistivity of $1.5 \times 10^5 \Omega\text{-cm}$ was obtained by using 2.5 mol% Al_2O_3 doping. The particle size of 40 nm was obtained by selecting appropriate process conditions.

Key words: Zinc oxide, Nanoparticles, Organopolymeric precursor.

Introduction

The physical properties such as electric conductivity, magnetic, optical and mechanical characteristics of nano-sized metal oxide particles are known to be substantially different from those of bulk materials. For the precise control of the morphology at the nanometric scale, the preparation methods of metal oxide nanoparticles have been extensively studied. ZnO is one of the most important oxide materials for such wide ranging industrial applications, as varistors, transparent conductors, UV-protection films, and chemical sensors [1, 2]. ZnO nano-particles have also been extensively studied because of their size-dependent electronic and optical properties, which offer possibilities for micro-electronic devices [3]. Synthetic routes that have been employed to prepare ZnO nano-particles include a liquid phase method, vapor deposition and a precursor process [4-6]. Among them, the vapor deposition process is widely used. This process has already been commercialized on a large production scale. The powder is produced by vapor phase oxidation of zinc vapor at about 1000°C. The dispersion property of such powders, however, is low.

An organo-polymeric precursor method is reported here. This process allows different patterns of particles to be prepared, because the morphology of the particle is dependent on the microstructure of the precursors, which are micelle or microfibril. The particles have a nano-crystalline structure with a primary particle size

of smaller than 40 nm. Multi-component metal oxides powder can be obtained homogeneously by introducing impregnated salts to the precursor before firing. This process does not include a co-precipitation operation as in the sol-gel process, neither does it involve alkali solutions. However, some efforts are required to remove corrosive gases generated by the pyrolysis of the impregnated precursor.

Experimental procedures

Nano-sized ZnO Powder Synthesis

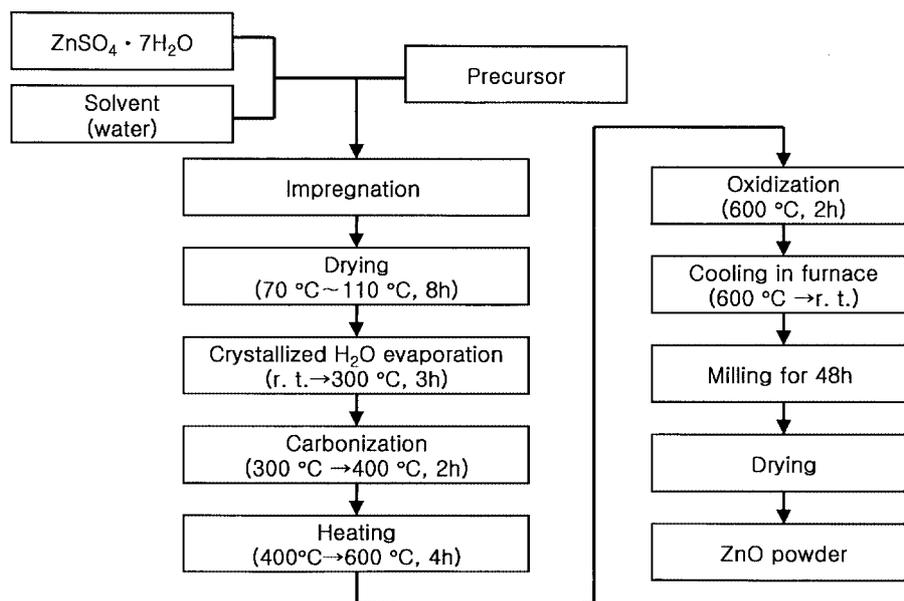
Pulp and crystalline cellulose (Asahi Kasei Chemical) were used as precursors. A mixed water solution having a predetermined Zn content was prepared with zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) of 99.9% purity and soaked in the precursor for 24h. The impregnated mixture was dried at 70 to 110°C. This mixture was passed through several stages of calcinations in the range of 300-600°C.

The calcination conditions were as follows: heating from room temperature to 300°C for 3h, maintained at 300°C for 2h, heating from 300 to 600°C at the rate of 50K h^{-1} , maintained at 500 to 600°C for 2h, and cooling in the furnace (Scheme 1). The color of the resulting powder was light yellow to white. Distilled water was added to the calcined powder and the powder was wet milled in a pot mill for 48h, and then dried.

Al_2O_3 doping

Aluminum sulfate octahydrate [$\text{Al}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$] was added to the zinc sulfate heptahydrate aqueous solution. The calcination procedure was the same as the one for undoped ZnO powder. Heat treatment under an argon

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Scheme 1. Flow diagram for the synthesis of nanosized ZnO powders.

gas atmosphere containing 0.5% hydrogen was conducted in an electric furnace at 900 or 1000°C for 2h. The flow rate of the gas was 10 ml minute^{-1} .

Characterization

The morphology of the powder was examined by Scanning Electron Microscopy (SEM; HITACHI S-4700). The powders were analyzed by an X-ray diffractometer (BROKERS axs D5005) using $\text{CuK}\alpha$ radiation (40 kV, 150 mA) with a scanning speed of 4°/minute and a sampling interval of 0.02°. The particle size was calculated from BET data and also confirmed by direct observation by SEM. The pyrolysis and decomposition behaviors of the impregnated precursor were monitored by simultaneous Differential Thermal Analysis and Thermogravimetric analysis (TG-DTA; V2.2A DuPont 9900) up to 1200°C, at a heating rate of 20 K minute^{-1} in air.

Result and Discussions

Pure ZnO powder is obtained after thermal decomposition and calcination in air. The calcination temperatures are relatively low, in the range of 400 to 600°C and the

reaction time is usually set for 2h. Table 1 shows the characteristics of the raw materials and the ZnO powder obtained. The mixing ratio (aqueous zinc salt divided by pulp) is changed from 0.2 to 1.0. The ratio of ZnO after calcinations against pulp weight (ZnO/Pulp) obtained was from 0.04 to 0.2.

A systematic study of the effect of the dilute ratio of the raw materials, calcination temperature, precursor, and Al_2O_3 doping was conducted. The morphology of the particles is granular and the particles are loosely agglomerated because of the shape of the micelle or microfibril in the precursor. The sizes of ZnO nanoparticles are in the range of 40-290 nm, with a surface area of 3-22 m^2/g . The particle size of 40 nm was obtained by selecting the following process conditions: pulp, dilute ratio of 0.2, Al_2O_3 doping of 2.5 mol%, and calcination temperature of 500°C.

Figure 1 shows SEM micrographs of powders. Figure 1(a) is a powder calcined at 400°C before milling. The distribution of particles reflects the structure of the microfibril. In Fig. 1(b), we show that the agglomerate size is growing with the rise in calcination temperature.

Figure 2 shows the XRD results of the calcined ZnO powders at different calcination temperatures. All these

Table 1. Powder Characteristics and their Calcining Conditions.

Sample	Reaction temp. (°C), time (h)	ZnO mol%	Al_2O_3 mol%	Dilute ratio	Precursor	Specific surface (m^2/g)	Particle size (nm)
Zn Ab1	500, 2	100		1	Crystalline cellulose	4	190
Zn Ab2	600, 2	100		1	Crystalline cellulose	3	290
Zn P1	500, 2	100		1	Pulp	9	90
Zn P2	600, 2	100		1	Pulp	5	180
Zn 1/2 P	500, 2	97.5	2.5	0.5	Pulp	17	50
Zn 1/5 P	550, 2	97.5	2.5	0.2	Pulp	22	40

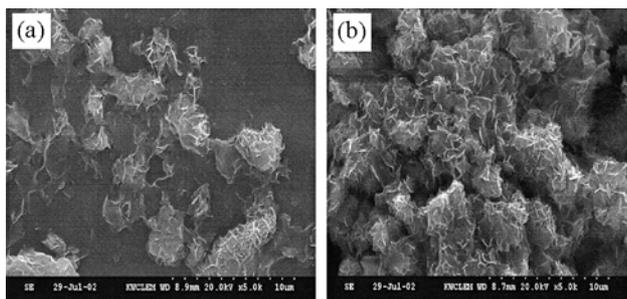


Fig. 1. SEM micrograph of the calcined ZnO powders (a) calcined at 400°C and (b) calcined at 600°C.

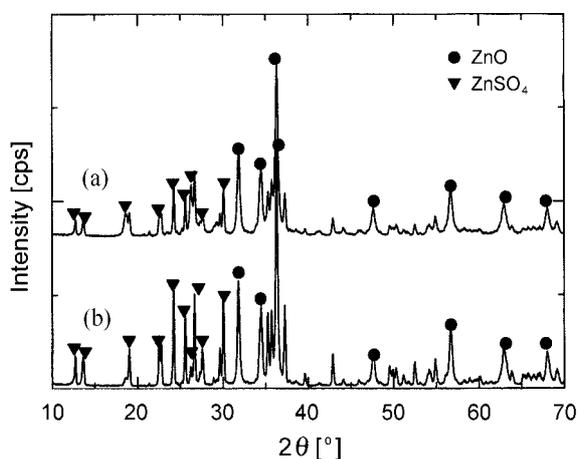


Fig. 2. XRD patterns of the ZnO powders (a) calcined at 500°C and (b) calcined at 600°C.

XRD diffraction patterns show that the materials are crystallized and they match that of ZnO (JCPDS card no. 36:1451). Other peaks corresponding to zinc sulfate, however, still remain after calcination. The peak intensity after calcination at 600°C is larger compared with those at 400 and 500°C.

Figure 3 shows the TG-DTA curve of the ZnO powder calcined at 400°C. The DTA curve shows an endothermic reaction at below 200°C, which is attributed to the loss of the remaining adsorbed water. A peak that appears at 292°C is due to the endothermic reaction by the decomposition of organic materials as shown in Fig. 3(b). This agrees with the weight loss given by TG data as shown in Fig. 3(a). In Figure 3(b), an endothermic peak at about 380°C is assumed to be due to the generation of a ZnO particle. A broad exothermic peak due to the crystallization of ZnO is observed in the range of 400 to 800°C, which agrees well with the XRD results as shown in Fig. 2. Therefore, ZnO crystals begin to nucleate at about 380°C, and then ZnO crystal growth is completed by 800°C. In Figure 3(a), a rapid weight loss from 750 to 900°C is caused by the decomposition and combustion of the ZnSO₄ compound. It is suggested that the peak at 947°C is the result of an endothermic reaction caused by the decomposition of ZnS as shown in Fig. 3(b).

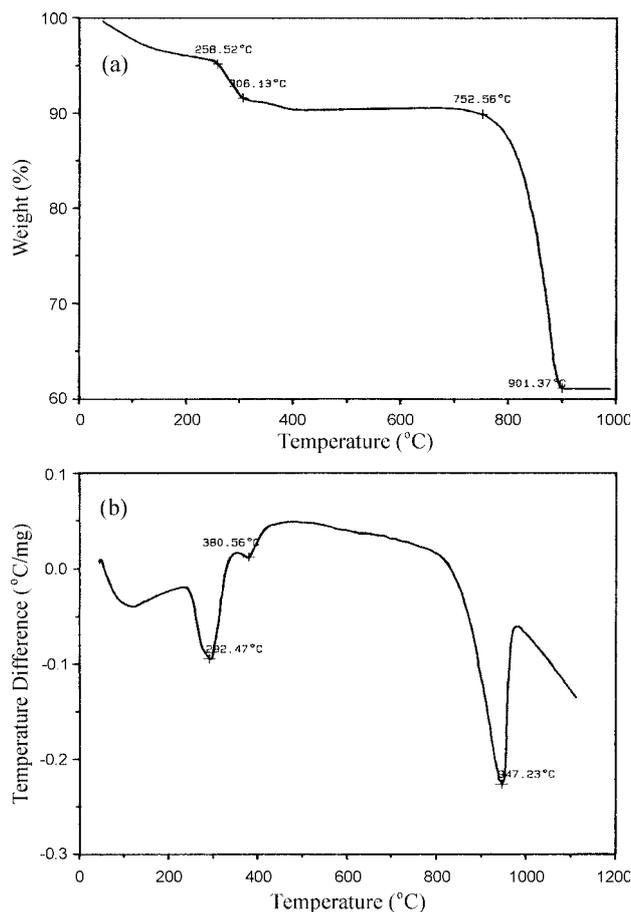


Fig. 3. TG-DTA analysis of calcined ZnO powder calcined at 400°C.

Figure 4 shows the XRD patterns of specimens treated at 900 and 1000°C for 2h under the hydrogen-containing atmosphere. In Figure 4(a), three diffraction peaks due to ZnS are observed. These diffractions peaks, however, are not observed at 1000°C. On the other hand, ZnO and ZnAl₂SO₄ peaks are observed. This is the result of an endothermic reaction caused by the decomposition of ZnS at around 957°C and agrees with the result of the DTA analysis as shown in Fig. 3.

Figure 5(a) and (b) show SEM photographs of ZnO powders with no doping and with doping of 2.5 mol% Al₂O₃, respectively. A particle size of D50=90 nm is obtained without doping, while a particle size of 37 nm is obtained with Al₂O₃ doping. It seems that Al₂O₃ doping has prevented the ZnO particles from rapid grain growth.

Figure 6 shows the XRD results of the ZnO powders at different mixing ratios (aqueous zinc salt divided by pulp). The mixing ratio is changed from 0.2 to 1.0 and calcined at 500°C. Figure 6(a) shows the XRD data of the ZnO powder produced by the mixing ratio (=zinc/pulp) of 1.0. The diffraction pattern of zinc sulfate is observed between the 2θ values of 10 and 30°. A peak intensity of ZnSO₄ becomes smaller when the ratio of pulp changes from 1 to 0.2. Therefore, ZnO powder of

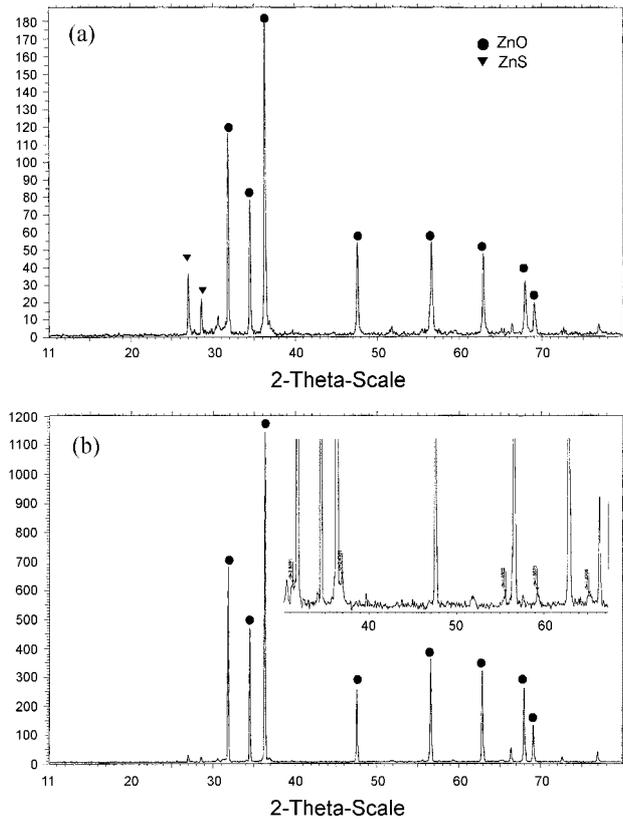


Fig. 4. XRD patterns of ZnO powders measured after reduction treatment (a) at 900°C and (b) at 1000°C.

high purity can be obtained when the ratio of zinc to pulp is 5.

It was reported that the volume resistivity increased when M_2O_3 (M:Cr,Al) was added to ZnO [7]. $[Al_2(SO_4)_3 \cdot 8H_2O]$ was selected as a doping agent in this experiment. The elements of Al, S, Zn, O, C were analyzed by an energy dispersive X-ray spectrometer (EDX) method as shown in Fig. 7. 2.45 mol% Al_2O_3 in ZnO powder was analyzed by ICP (Induction Coupled Plasma) method after firing at 1000°C. Figure 8 shows SEM micrographs of reduction-treated ZnO powders. It is observed that the particle size of Al_2O_3 -doped ZnO powder increases with an increase of calcination temperature. As shown in Fig. 8(b), some particles treated at 900°C have grown to 500 nm in size. On the other hand, other particles remain at a size of around 40 nm.

Figure 9 shows the volume resistivities of Al_2O_3 -doped ZnO powders. The volume resistivity of non-doped ZnO powders gives the same order of value of $10^7 \Omega \cdot cm$ regardless of the calcination temperature. The resistivity can drop down to $10^5 \Omega \cdot m$ after heat treatment at 1000°C. This low resistivity is probably due to the formation of lattice vacancies in the zinc oxide crystal structure.

It is found that the formation of the ZnO crystal phase is initiated at 370°C, and the crystallization of ZnO is completed at about 1000°C through the XRD,

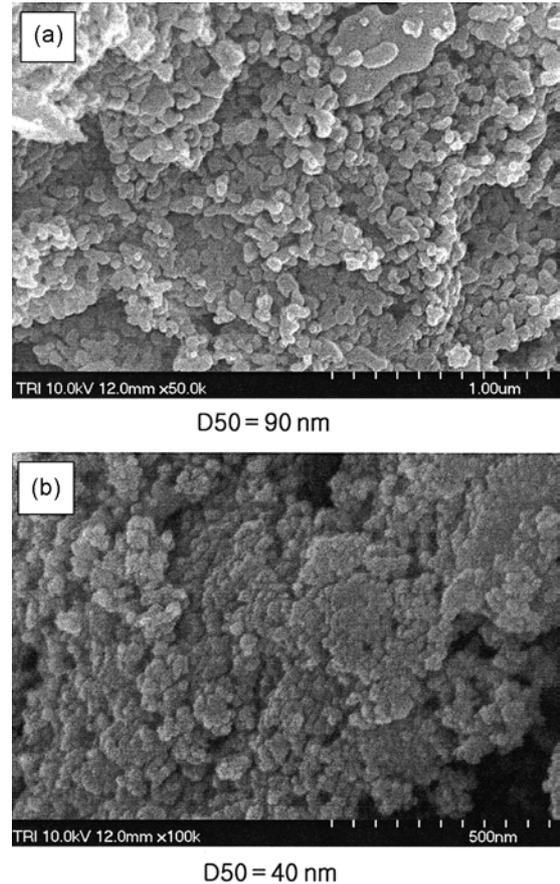


Fig. 5. SEM micrographs ZnO powders (a) with no doping and (b) with doping of 2.5 mol% Al_2O_3 , calcined at 500°C for 2 h, respectively.

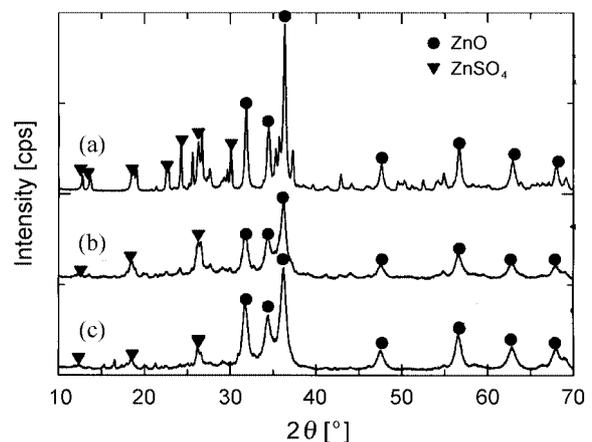


Fig. 6. XRD patterns of the ZnO powders at measured different mixing ratios (a) ZnO/pulp: 1, (b) ZnO/pulp: 0.2 and (c) ZnO/pulp: 0.5.

SEM and TG-DTA analyses. The crystal sizes of nano-sized ZnO powders show an increasing tendency with an increase of calcination temperatures from 600 to 1000°C. Small amounts of sulfur compounds such as $ZnSO_4$ and ZnS were decomposed to ZnO in the range of 750 to 1000°C.

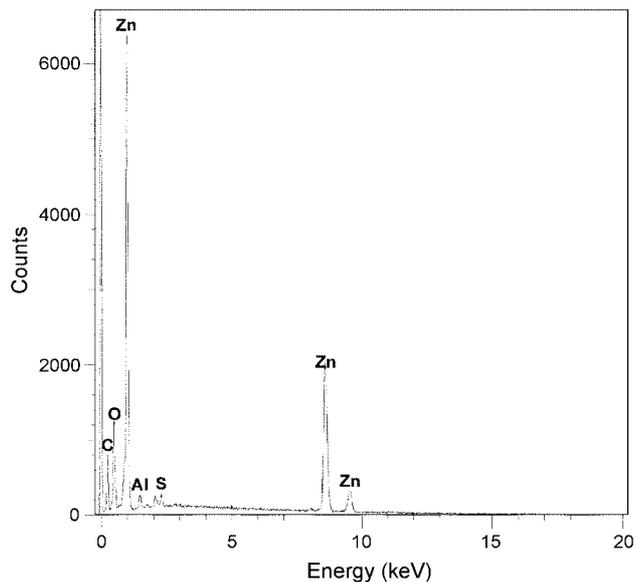


Fig. 7. EDX mapping analysis of 2.5 mol% Al_2O_3 doped ZnO powder heat treated at 1000°C .

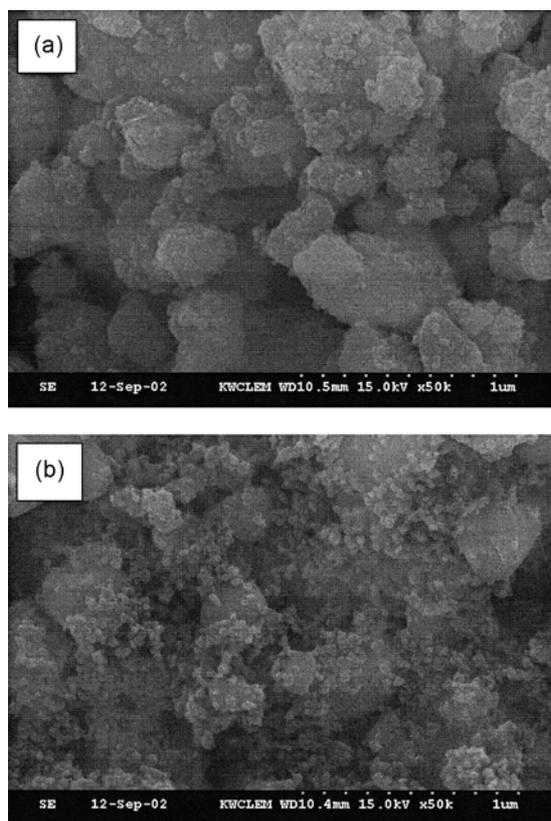


Fig. 8. SEM micrographs 2.5 mol% Al_2O_3 doped ZnO powders (a) heat treated at 900°C and (b) heat treated at 1000°C .

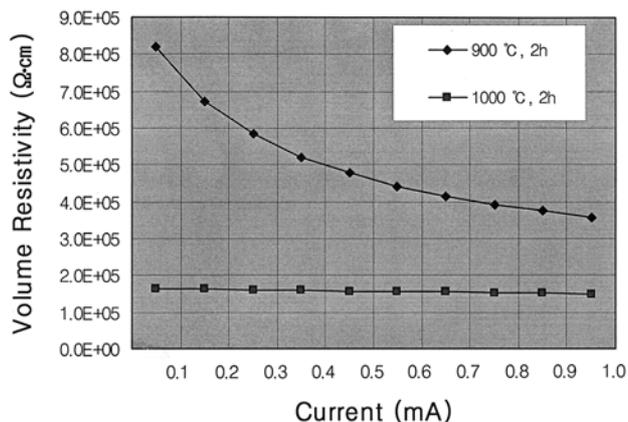


Fig. 9. Volume resistivity of Al_2O_3 doped ZnO powders.

Conclusions

Our organo-polymeric precursor process enables the size-selective preparation of ZnO nano-particles over the range of 40 to 200 nm. In the present study, we find that a precursor process is a suitable method for synthesizing a small quantity of ZnO nano-particles. The morphology of the particle can be controlled by selecting the precursor, calcination temperature, the starting composition, and the microstructure of the precursors. Using Al_2O_3 doping, ZnO powders give good electric resistivity of the order of $10^5 \Omega\text{-cm}$.

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