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SYNTHESIS OF ZnO NANOPARTICLES FOR VARISTOR APPLICATION USING Zn-SUBSTITUTED AEROSOL OT MICROEMULSION

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ABSTRACT

This paper describes a new method for the synthesis of zinc oxide nanoparticles using ethanol-in-oil microemulsions with Zn–DEHSS (diethylhexyl sulfosuccinate) as surfactant. The zinc oxide nanoparticles find application in varistors and other functional devices. These particles have been characterized by X-ray diffraction, TEM, and BET surface area. Microemulsion droplets were characterized by quasi elastic light scattering (QELS). Varistors formed from doped zinc oxide nanoparticles finds application as low voltage surge devices with low leakage current and high coefficient of nonlinearity (α). In this paper, we have shown that the critical voltage of the varistor is related to the grain size which is related to size of ZnO particles. The smaller ZnO particles lead to larger grain size, thereby lowering the critical voltage.

KEYWORDS: A. nanostructures, A. oxides, C. electron microscopy, C. X-ray diffraction, D. electrical properties

INTRODUCTION

Nanophase ceramics have found many applications in science and technology because of the improvements in a variety of properties that are expected to result from the reduction in particle size to nanometer scale [1]. Zinc oxide varistors are electronic ceramic devices, the primary function of which is to sense and limit transient voltage surges and to do so

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repeatedly without being destroyed. Their current–voltage (I–V) characteristic is nonlinear, similar to that of a Zener diode. But unlike a diode, varistors can limit overvoltage equally in both polarities, thus giving rise to a I–V characteristic which is analogous to two back-to-back diodes [2]. The electrical characteristics of a varistor depends on the chemical composition as well as the processing techniques used to synthesize the varistor. In the past, various techniques have been used for preparation of zinc oxide particles, such as conventional ceramic fabrication [3], sol–gel method [4], reaction spray pyrolysis [5,6], use of powders produced during urea production [7], hydrolysis of bis(acetyl acetonato)-zinc (II) [8], and wet chemical synthesis [9]. Porosity and inhomogeneous distribution of particles in a varistor result in the formation of hot spots, as the current follows the path of least resistance. This causes failure of the varistor at a lower current density than the expected value. For this reason, the present research focused on synthesizing zinc oxide varistor by a method which ensures homogeneity. This can effectively be done by using the aqueous core of water or alcohol in microemulsions as nanoreactors for the synthesis of precursor particles. It uniquely controls the particle formation environment by compartmentalizing the solution into droplets which are isolated from one another by the interfacial film of surfactant [10], providing a large number of nucleation sites. Synthesis in microemulsion offers many opportunities to prepare powders with tailored physical and chemical characteristics [11].

A microemulsion is generally defined as a thermodynamically stable, optically isotropic dispersion of two immiscible liquids (usually water and hydrocarbon), one or both of which are dispersed as microdomains which are 10–50 nm in dimension. These type of fluid droplets are stabilized by the presence of one or more species of surfactant molecules, as a monomolecular layer at the liquid-liquid interface and drastically reduce the interfacial tension. The aqueous cores of microemulsion, containing soluble metal salt are used for the synthesis of nanoparticles [12,13]. The growth of these particles in microemulsions is suggested to involve interdroplet exchange and nuclei aggregation [14,15]. Microemulsions have previously been used to prepare nanoparticles of metal particles [16], metal boride [17], silver halides[18,19], barium carbonate [20], oxalate precursor for $YBa_2Cu_3O_{7-x}$ superconductor [21], barium ferrite [22], TiO_2 [23] and γ-ferric oxide [24].

In the past, the method described for the preparation of ZnO particles through microemulsion [27], salt of zinc (normally $Zn(NO)_3$) had been incorporated in aqueous core of microemulsion was precipitated to get precursor particles. In this work, we report the formation of zinc oxide particles using zinc-substituted surfactant, which is used to prepare the microemulsion, and subsequently adding ethanol and oxalic acid powder to get the precursor nanoparticles. The surfactant used in this microemulsion system was derived from the commercially available Aerosol–OT or sodium-di-2-ethylhexyl sulfosuccinate (Na–DEHSS). This is an anionic surfactant with a double hydrocarbon tail which is lypophilic and a SO^{3-} head group which has affinity for water (or alcohol, in the present case). In such a water or alcohol-in-oil microemulsion, the Na^+ (counter-ion) is "dissolved" in the dispersed phase. The Zn^{2+} ions were incorporated in the dispersed phase by replacing the counter-ion of Na by Zn in Na–DEHSS. Such counter-ions substitution in anionic surfactants has attracted interest of late, in the synthesis of copper [24] and barium ferrite [25].

In the work reported in this paper, we attempted to synthesize ZnO particles using the new micellar system and observed that the size of the precursor particles affects the properties of varistors. This technique leads to certain advantages, such as (a) prevention of the aqueous core of the microemulsion from being contaminated by additional and

undesirable cations which may normally be present in the surfactant; (b) precise control over stoichiometry within the aqueous core, particularly when more than one cation is involved, e.g., in the preparation of stoichiometric $BaFe_{12}O_{19}$ [26]; (c) the surfactant not only stabilizing the microemulsion but also acting as a source for the metal ion(s) of the desired oxide; and (d) control of the size of droplets and, hence, the number of surfactant molecules per droplet, one can synthesize nanoparticles of predetermined size or number of atoms in the nanoparticle.

METHODS

Zinc nitrate (99.9% pure) was bought from Aldrich. Oxalic acid, isooctane, anhydrous benzene, ethanol, diethyl ether, chloroform, acetone, and methanol (all high purity HPLC

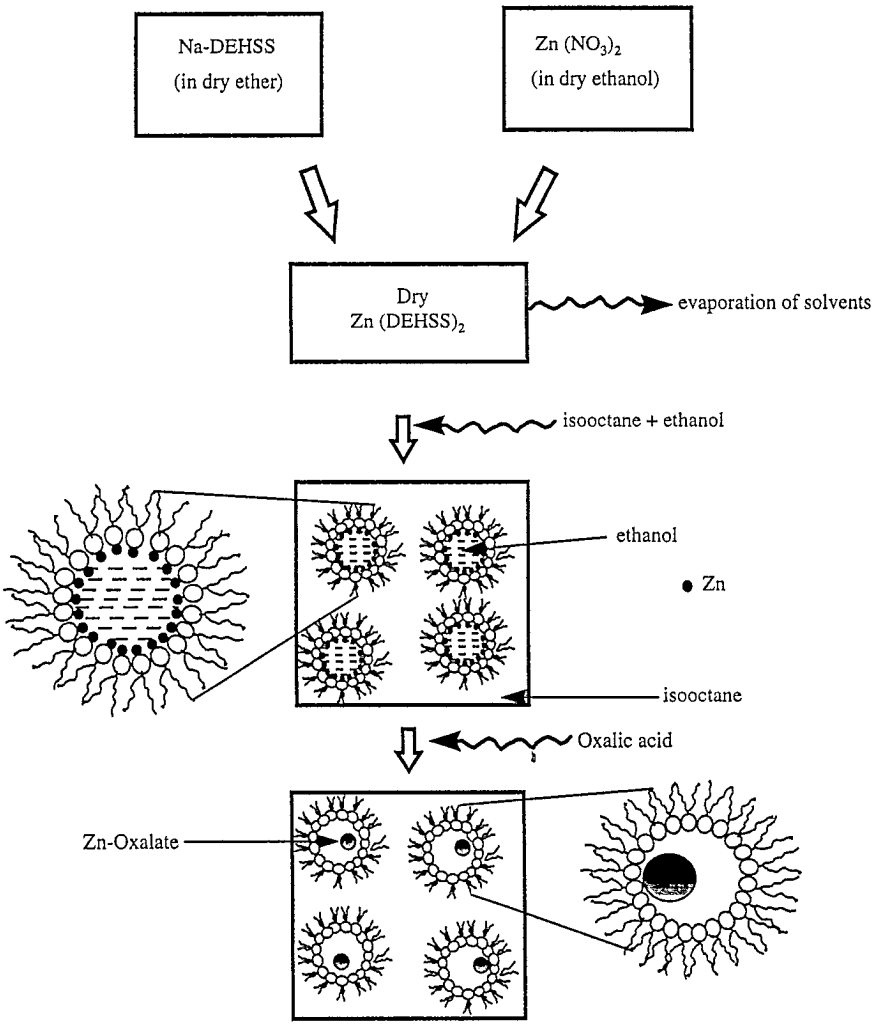

FIG. 1
Schematic diagram for precipitation of precursor (zinc oxalate) nanoparticles using Zn-AOT/ethanol/isooctane microemulsion system.

TABLE 1
A Comparative Study for Properties of ZnO Particles and Microemulsions Droplet Size

Method of Synthesis	Properties of ZnO Particles		Size of Microemulsion Droplet (nm)
	BET surface area (m^2/gm)	ESD* (nm)	
Zn–AOT/ethanol/isooctane Microemulsion B	91.8	11.7	8.5
Zn–AOT/ethanol/isooctane Microemulsion A	82.87	12.9	11.2

* Equivalent Spherical Diameter

grade) were bought from Fisher Scientific Company. Sodium-di-2-ethylhexyl sulfosuccinate (Aerosol OT) was bought from American Cyanamid Inc.

Figure 1 shows the schematic diagram for precipitation of precursor (zinc oxalate) nanoparticles using Zn–AOT/ethanol/isooctane microemulsion system. In order to convert Na(DEHSS) to M(DEHSS)x (M = Zn in this case), one requires a solvent which dissolves the M(DEHSS) but not the precipitate ($NaNO_3$ in this case). To prepare $Zn(DEHSS)_2$, the required quantities of Na(DEHSS) (dissolved in dry ether) and $Zn(NO_3)_2$ (in dry ethanol) were mixed and stirred thoroughly for 4 h at room temperature.

It is necessary that all the solvents used in the reaction (dry ethanol and dry ether) be completely dry, because $NaNO_3$, which forms during the reaction, is soluble in water. If a solvent contains water, some of the sodium nitrate which forms during the reaction will dissolves in it and cause impurities in the precursor particles for ZnO. $NaNO_3$ precipitates out according to the reaction

$$2\ Na(DEHSS) + Zn(NO_3)_2 \rightarrow Zn(DEHSS)_2 + 2\ NaNO_3 \downarrow$$

The solution was filtered and the filtrate dried on a Buchi rotavaccum pump. Last traces of water were removed from the $Zn(DEHSS)_2$ by repeatedly washing with dry benzene. We ensured the absence of sodium in Zn–DEHSS by adding extra $Zn(NO_3)_2$ in the solution. There was no precipitation of $NaNO_3$. There was no measurable sodium content after preparing the $Zn(DEHSS)_2$.

$Zn(DEHSS)_2$ was dissolved in isooctane to get a 0.236 M solution. Dry ethanol (8.7 wt% for Zn–AOT/ethanol/isooctane microemulsion A and 4.5 wt% for Zn–AOT/ethanol/isooctane microemulsion B, based on total volume) was added to form a non-aqueous alcohol-in-oil microemulsion. Oxalic acid in the form of fine powder was added in excess to the microemulsion to precipitate Zn^{2+} in oxalate form. This solution was stirred thoroughly for 1 h to ensure complete precipitation. The precipitate was separated by centrifuging at 7000 rpm for 10 min. It was washed with 1:1 mixture of methanol and chloroform to remove the contaminated surfactant and oil. Second wash with 1:1 acetone and methanol was done to remove surfactant and excess of oxalic acid. The dried precipitate was calcined at 300 °C for 3 h to get ZnO nanoparticles.

For making the varistor, the dopants were added by wet grinding with the ZnO particles, to obtain an overall base composition of 96.5 mol% ZnO, 1.0 mol% Bi_2O_3, 1.0 mol% Sb_2O_3, 0.5 mol% MnO, 1.0 mol% CoO, and 0.5 mol% Cr_2O_3. The resulting powder was calcined at 300 °C for 2 h. We have shown elsewhere [28] that the electrical properties of varistors

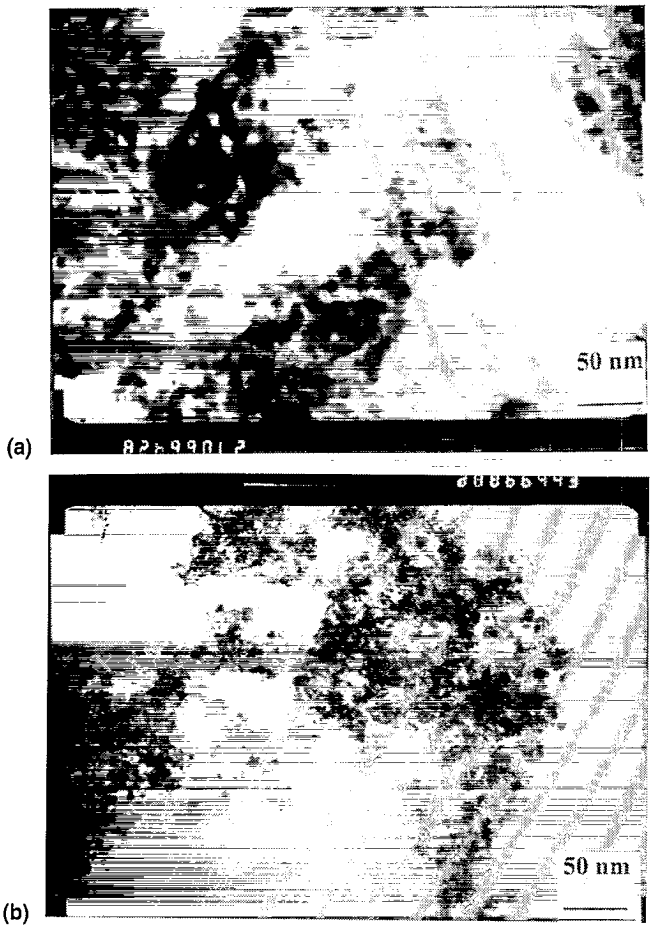

FIG. 2
TEM of the ZnO nanoparticles prepared from Zn-AOT/ethanol/isooctane: (a) microemulsion A and (b) microemulsion B.

prepared in this manner are reproducible and, hence, the wet grinding method is a suitable method for the addition of dopants.

Powder X-ray diffraction of the nanoparticles was carried out on a Phillips APD 3720 X-ray powder diffractometer using Cu–Kα radiation at room temperature. Surface area measurements were obtained by nitrogen gas adsorption (BET) on a Quantasorb Surface Area Analyzer, model QS-17. The powder sample was outgassed in nitrogen for 24 hr at 1 20°C prior to analysis. Transmission electron microscopy (TEM) was done by ultrasonically dispersing the precursor powder in methanol prior to depositing it onto a carbon-coated TEM grid. A JEOL 200CX transmission electron microscope was used for these studies. ZnO disks of 1 cm diameter were prepared by pressing the doped ZnO nanoparticles under a pressure of 70 Mpa. The disk was sintered at 1200°C for 2 h to get ZnO varistor. The microstructure of the sintered samples was studied by close examination of their photomicrographs taken on a JEOL 6400 scanning electron microscope. For electrical measurements, ohmic contacts were applied to both surfaces of the disk by coating with

colloidal silver paint. Standard I–V measurements were carried out using a Keithley 610C electrometer and a Bio-rad Laboratories 500 Model dc-power supply.

Dynamic (quasi-elastic) laser light scattering measurements for determining the droplet size in microemulsions was performed at 25°C using Brookhaven Instrument, model BI 2030 AT. Water cooled Ar^+ laser was operated at 514 nm as a light source. Stokes–Einstein relationship was used to calculate the hydrodynamic radius of ethanol droplets dispersed in continuous oil medium (isooctane).

RESULTS AND DISCUSSION

Table 1 shows the comparison of selected physical properties of ZnO particles and the size of microemulsion droplets used to prepare these particles. The highest surface area of ZnO nanoparticles prepared using Zn–AOT/ethanol/isooctane microemulsion B corresponds to the smaller particle size (11.7 nm). The particles formed in the constrained nanoreactors of Zn–AOT/ethanol/isooctane microemulsion droplets are fairly uniform and homogeneous and have high surface area with very small particle size (Fig. 2).

In the Zn–AOT microemulsion, the volume of the dispersed phase (in this case dry ethanol) controls the droplet size which in turn controls the particle size, so we can fine tune the particle size by adjusting the volume fraction of ethanol. QELS results give a droplet size of 11.2 nm for Zn–AOT/ethanol/isooctane microemulsion A and 8.5 nm for Zn–AOT/ethanol/isooctane microemulsion B (Table 1). The use of these microemulsions (A and B) result in zinc oxide precursor particles size of about 10–13 and 5–8 nm, respectively. They follow the same trend as seen in the droplet size of the respective microemulsions measured using light scattering. Figure 2 shows the transmission electron micrographs of the ZnO particles prepared through Zn–AOT/ethanol/isooctane microemulsion A and B, respectively. These particles are agglomerated, but individual particles have the size of about 10–13 nm for Zn–AOT/ethanol/isooctane microemulsion A and about 5–8 nm for microemulsion B.

The SEM of the varistors made using alcohol-in-oil microemulsions (Zn–AOT/ethanol/isooctane microemulsions A and B) are shown in Figure 3. The grain sizes were measured directly from photomicrographs. The sintered pellets of the zinc oxide varistor show a change in grain size depending on the particle size of the starting ZnO nanoparticles. Smaller particles have a higher diffusivity, thus their presence results in higher sintering rates for a given sintering time and temperature. The microemulsion-B-

TABLE 2
Comparative Study of Electrical Properties for ZnO Varistor Synthesized Using Microemulsion A and Microemulsion B

Method of Synthesis	Properties of ZnO Particles		Leakage Current	α_{max}
	Grain size (μm)	Critical voltage KV/Cm		
Zn–AOT/ethanol/isooctane Microemulsion B	13.90	1.05	8.0×10^{-4}	76.05
Zn–AOT/ethanol/isooctane Microemulsion A	11.45	1.5	2.5×10^{-5}	121.8

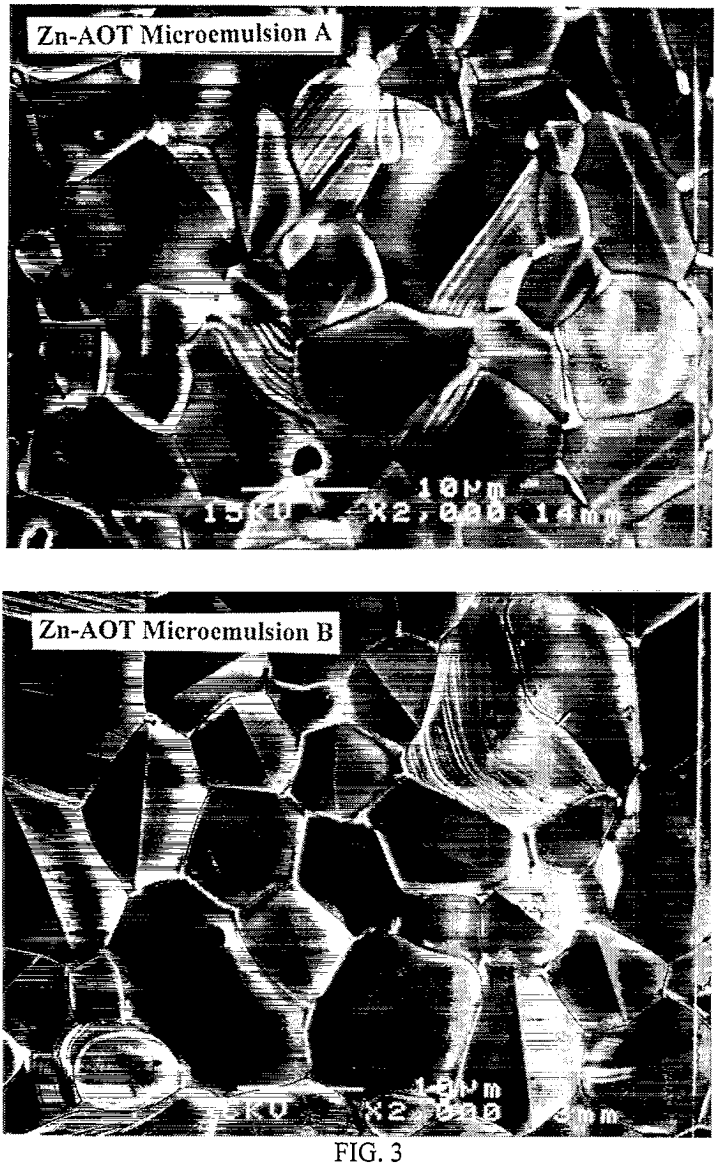

FIG. 3
Scanning electron micrograph of varistor derived from Zn-AOT/ethanol/isooctane: (a) microemulsion A and (b) microemulsion B.

derived nanoparticles are the smaller and result in the larger grain size in the sintered disk (Table 2).

The varistor response is described by the nonlinear equation $I = CV^{\alpha}$, where C is a material parameter and α is a nonlinear exponent. The electrical properties are manifested by the microstructure of the material. For a given chemical composition and thickness of pellets, the critical voltage of the varistor depends on the grain size. As the number of grain boundaries across a pellet of given thickness increase (i.e., the grain size decreases), the resistance associated with the varistor increases, resulting in an increase in the critical

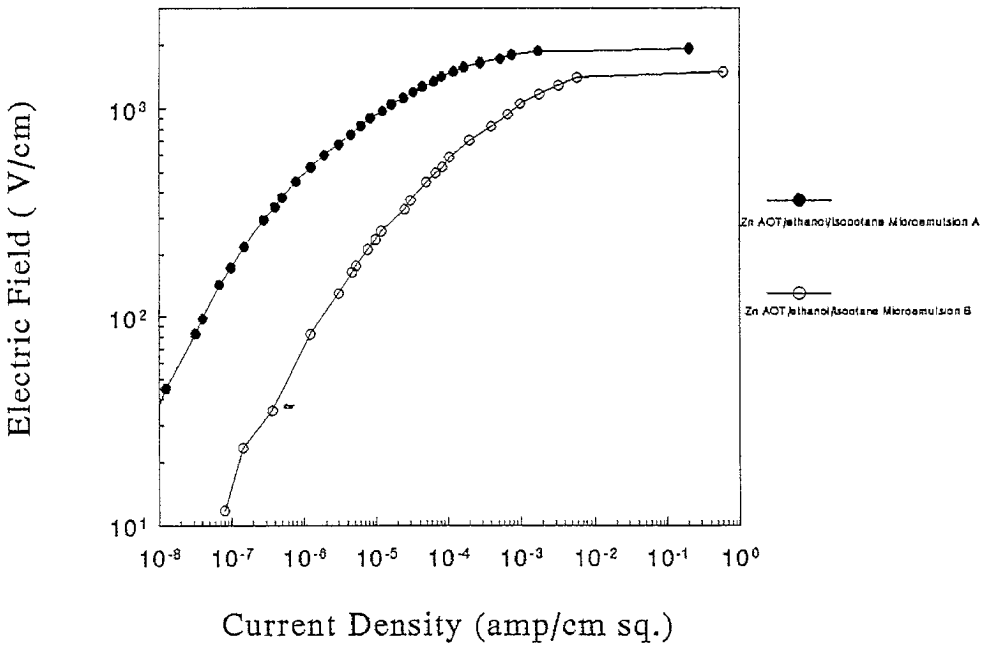

FIG. 4
Current–voltage response of varistor derived from different microemulsion systems.

voltage for the varistor. The current–voltage response of the varistor disks are plotted in Figure 4.

The varistor showed a sharp change from linear to nonlinear electrical characteristics. The varistor follows the Ohm's law ($\alpha = 1$) for voltage less than the critical voltage of the varistor. Above the critical voltage, in the nonlinear region, the varistors show a nonlinear exponent (α) value 76.05 and 121.8 for microemulsions A and B, respectively. Higher value of α indicates a narrow clamping or critical voltage band. The critical voltage, coefficient of nonlinearity (α) increases and leakage current decreases with increase in precursor particle size. These results show that electrical properties in varistor depend upon the size of precursor particles.

CONCLUSIONS

A new microemulsion system for the synthesis of ZnO nanoparticles has been developed. The microemulsion consisted of modified surfactant $Zn(DEHSS)_2$, isooctane as the continuous phase and dry ethanol as the dispersed phase. The precipitation of Zn atom is induced by adding oxalic acid. The microdroplets act as constrained microreactors for the precipitation reaction. The droplet size as well as the precursor particle size is controlled by the volume of the dispersed phase and the concentration of surfactant in the system. A study of the precursor particle size/grain size and electrical properties of varistor has been carried out. This new method gives us an approach to vary the critical voltage of the varistor by changing the size of precursor particles. We have found that decrease in the precursor size leads to the formation of varistors with large grain size, lower critical voltage and lower

value of nonlinear coefficient (α). These results are important in the preparation of low voltage zinc oxide varistors.

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