

EVOLUTION OF MICROSTRUCTURE AND ELECTRICAL NONLINEARITY OF ZnO-Pr₆O₁₁-Cr₂O₃ VARISTOR CERAMICS DERIVED THROUGH CITRATE GEL TECHNIQUE

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ABSTRACT

The evolution of microstructure and electrical nonlinear characteristics of ZnO doped with Pr₆O₁₁ and Cr₂O₃ varistor ceramics as a function of sintering temperature and time is discussed. The ceramics were prepared through combination of citrate gel process and solid phase sintering. Transformation in the grain microstructure and electrical behavior of the prepared ceramics was monitored by using field emission scanning electron microscope, X-ray diffractometer and *J-E* characteristic measurement. The findings showed that the elevation of solid phase sintering temperature between 1200 to 1275 °C has promoted the formation of secondary phase in the form of PrCrO₃ while minimally hindered the ZnO grain growth and densification rate of sintered ceramics. The nonlinear coefficient, α , that signifies the electrical nonlinearity of the ceramics decreased with increasing sintering temperature due to trade-off between effective number of Double Schottky Barrier at grain boundaries and grain size. Meanwhile, extending the sintering time from 1 to 7 hours caused the formation of the varistor ceramics with lower density and finer grains. Accumulation of intergrain pores and segregated phase at triple points led to deactivation of some grain boundaries. As a result, a decrement in both α and Φ_B values was observed implying to the loss of electrical nonlinear behavior.

Keywords: varistor ceramic; zinc oxide; microstructure; nonlinear;

INTRODUCTION

ZnO varistor is a small yet functional device to suppress damaging transient voltage in various consumer appliances. It is connected in parallel to load or circuit to be protected. In the event of overvoltages, the highly resistive varistor material would instantly change to highly conductive state. Current surge that carries excessive energy

is thus conducted through the varistor, bypassed from the load and safely grounded. The functionality of ZnO based varistor materials depends on its electrical nonlinearity. The current density, J -electrical field, E response of ZnO varistor ceramics in nonlinear region can be expressed by;

$$J = kE^{\alpha} \quad (1)$$

where k is a constant and α is the nonlinear coefficient. The higher the α value, the more prominent the electrical nonlinear characteristic of a material. The nonlinear property of ZnO varistor ceramic is associated to formation of a Double Schottky Barrier (DSB) in between two adjacent grains [1-3]. The electrostatic barrier develops when positively charged depletion region in ZnO bulk balances the negatively charged interface state at grain boundary. The degree of nonlinearity is closely related to the microstructure of varistor ceramic and thus can be controlled by selection of materials and the application of appropriate manufacturing processes particularly by applying optimum sintering conditions.

In these recent years, Pr_6O_{11} type ZnO ceramics have been aggressively developed as a new option to conventional Bi_2O_3 type ZnO varistor materials which suffer a partial loss of Bi_2O_3 due vaporization and formation of unintended secondary phases at the sintering temperature of over 1000 °C [4-7]. However, most of earlier works on Pr_6O_{11} type ZnO ceramics for varistor application have been focused on attainment of Co doped Pr_6O_{11} based ZnO varistor ceramics or ceramics with more complex formulation through conventional solid-state route for high voltage requirements [8-11]. The present study is therefore focused on comprehending the microstructure-electrical properties relationship in Cr doped Pr_6O_{11} based varistor ceramics synthesized through modified citrate gel technique. The progression of microstructure-electrical nonlinearity with sintering temperature and time is discussed.

EXPERIMENTAL

Raw materials which were required for obtaining the varistor ceramics include fine ZnO powder (Sigma Aldrich, 99.9 %), citric acid (Fluka, 99.5 %), praseodymium (III) acetate hydrate, $\text{Pr}(\text{CH}_2\text{COOH})_3 \cdot x\text{H}_2\text{O}$ (Sigma Aldrich, 99.9 %) and chromium (III) acetate hydroxide ($\text{Cr}_3(\text{OH})_2(\text{OOCCH}_3)_7$) containing 24% Cr (Alfa Aesar). Varistor ceramic pellets with nominal composition of 98.2 mol % ZnO + 0.8 mol % Pr_6O_{11} + 0.6 mol % Cr_2O_3 were prepared from its precursor powder. In this formulation, ZnO component serves as the host ceramic whereas Pr_6O_{11} and Cr_2O_3 additives respectively serves as the varistor forming oxide for electrically activating the grain boundary (GB) region and the varistor highlighter for inducing the formation of potential barrier at GB. The precursor powder was obtained through modified citrate gel method. Metal citrate gels were produced when citric acid in aqueous solution was reacted with Pr (III) acetate and Cr (III) acetate at 60 - 70 °C for 1 hour. The fine ZnO powder was gradually added to form a homogeneous suspension and the mixing temperature was increased to 80 - 90 °C until a semidried cake was obtained. Further drying in convective oven at

110 °C for 19 hours was required to remove excess moisture from the cake. The dried mixture was pulverized and calcination was then performed at 500 °C for 4 hours to remove organic matters. The calcined powder was granulated using 1.75 wt% of polyvinyl alcohol binder and it was pressed into disc shaped pellets having 5.0 mm radius and 1.3 mm thickness under the compression force of 3.5 tonnes. Sintering process was conducted in a box furnace (CMTS HTS 1400) at 1200 - 1275 °C for 1-7 hours to produce dense ceramic pellets.

The microstructure of ceramics was analyzed under field emission scanning electron microscopy, FESEM (FEI NovaTM NanoSEM 630 Series) and the distribution of element on the sintered ceramic was observed using energy dispersive X-ray spectroscopy (EDX). Prior to analysis, the sample was polished and thermal etched at 1100 °C for 10 min.

Based on the FESEM micrograph, the average grain size, d was determined based on lineal intercept method [12];

$$d = \frac{1.56L}{MN} \quad (2)$$

where M is the magnification of the micrograph, L is the length of a random line drawn on a micrograph of polished sample surface, and N is the number of grain boundaries intercepted by the line. The density of ceramic was expressed in term of average relative density, ρ_{rel} . The average density ρ_{avg} in g/cm³ was initially determined using an electronic densimeter (Alfa Mirage, Model MD-300S) and the ρ_{rel} was derived based on Eq. 3. The theoretical density, $\rho_{theoretical}$ of ceramic was 5.70 g/cm³.

$$\rho_{rel} = \frac{\rho_{avg}}{\rho_{theoretical}} \times 100\% \quad (3)$$

J-E characteristics measurement was performed using source measure unit (Keithley 236). The applied voltage was varied between 0 to 100 V (step size of 2.5 V). The nonlinear parameters were derived from the plot of current density, J versus applied electrical field, E , where J is the current per unit area of electrode (mA/cm²) and E is the voltage per unit thickness (V/mm). The nonlinear coefficient, α is calculated as $d(\log J)/d(\log E)$ within the J range of 1 to 10 mA/cm².

In addition, it is well accepted that thermionic emission is the predominant conduction mechanism in pre-breakdown region. For this reason, the potential barrier height, Φ_B could be estimated according to,

$$J = AT^2 \exp \left[\frac{\beta E^{1/2} - \Phi_B}{k_B T} \right] \quad (5)$$

where k_B is the Boltzmann constant (8.167×10^{-5} eV/K), A is the Richardson's constant ($30 \text{ A/cm}^2 \text{K}^2$) for ZnO, T is the absolute temperature, β is a constant and is related to the relation as $\beta \sim (r\omega)^{-1}$, where r is grains per unit length and ω is the barrier width. This estimation approach has been adopted by a number of studies including [13, 14].

RESULTS AND DISCUSSION

Varistor ceramics pellets with nominal formulation of 98.4 mol% ZnO, 0.8 mol% Pr_6O_{11} and 0.6 mol% Cr_2O_3 coded as ZPC were successfully obtained after sintering for 1 h at various temperatures. The progression of ZPC varistor ceramics' microstructures and development of its electrical nonlinear characteristics with increasing sintering temperature are summarized in Table 1. The results are based on the measurements from J-E characteristic measurement and observations from XRD, FESEM and EDX analyses.

The microstructure of ZPC varistor ceramics evolved slowly from ceramics with two-phase microstructure to three-phase microstructure due to elevation of sintering temperature. The "two-phase" term refers to the presence of two single phases in the sintered ceramic which are the polycrystalline ZnO major phase in grains and the intergranular layer containing segregated phase due to addition of dopant and additives. The third phase in a three-phase microstructure otherwise is assigned to the formation of any secondary phase either in the form of spinels or pyrochlores. The secondary phase is made of a solid solution between the ZnO and other oxide additives during liquid phase sintering. In this work, ZPC ceramics sintered at 1200 to 1250 °C contained only the hexagonal wurtzite structure ZnO phase (in grains) and the Pr-Cr rich intergranular phase (mixture of Cr and Pr oxides) as confirmed in both XRD and EDX. The ZPC ceramics sintered at 1275 °C contained additional secondary phase in the form of PrCrO_3 spinel. This observation implies that the formation of spinel phase was promoted by high temperature sintering approaching to the eutectic temperature of ZnO-PrOx system (1382 °C as reported in [15]). The formation of spinels around the grain boundary is unintended as these additional insulating phases not only have passive electrical functionality but also give rise to inactive grain boundaries in varistor ceramics.

The elevation of sintering temperature at the same time encouraged the densification and grain coarsening mechanism in ZPC varistor ceramics. A dense and pore free structure will increase the electrically effective cross-section area of the varistor and minimize Watt loss due to leakage current. As supported by Figure 1, the ZPC ceramics became denser with increasing sintering temperature. The observable porosity has greatly suppressed between sintering temperature of 1225 to 1275 °C. The improvement in ceramic densification is reflected by the gradual increment in average relative density, ρ_{rel} value. The value increases from $92.62 \pm 0.22\%$ to the highest point of $97.76 \pm 0.37\%$ as the temperature increased from 1200 to 1275 °C. The noticeable progression of grains with increasing sintering temperature can be observed from Figure

1 as well. The average grain size, d of ZPC ceramics drastically increased from $4.10 \mu\text{m}$ to $11.58 \mu\text{m}$. However, it was also noticed that the grain size distribution was broadened as the sintering temperature increased up to 1275°C . The precipitation of spinel phase in the grain boundary could act as the pinning particle and led to discontinuous grain growth. The ZPC ceramics with the highest d value ($11.58 \pm 3.54 \mu\text{m}$) and the highest ρ_{rel} value ($97.76 \pm 0.37\%$) were obtained after sintering at 1275°C .

Table 1: Microstructure-electrical nonlinear characteristics of ZPC varistor ceramics sintered at different temperature, T_s

T_s ($^\circ\text{C}$)	Phase Segregation		Densification and Grain growth		Nonlinear Characteristics
			Average relative density, ρ_{rel} (%)	Average grain size, d (μm)	
1200	Two-phase	• ZnO in grains • Pr-Cr-rich intergranular phase	92.62 ± 0.22 (7.3% porosity) (The most porous)	4.10 ± 0.43 (Fine and uniform grains)	$\alpha = 6.04 \pm 0.02$ $\Phi_B = 0.83 \pm 0.01\text{eV}$ (Most pronounce nonlinearity)
1225	Two-phase	• ZnO in grains • Pr-Cr-rich intergranular phase	93.69 ± 0.59 (6.31 % Porosity)	4.07 ± 0.37 (Fine and uniform grains)	$\alpha = 4.55 \pm 0.02$ $\Phi_B = 0.78 \pm 0.01\text{eV}$ (Nonlinear)
1250	Two-phase	• ZnO in grains • Pr-Cr-rich intergranular phase	97.55 ± 0.23 (2.41 % Porosity)	7.36 ± 0.85 (Large and irregular grains)	$\alpha = 5.39 \pm 0.02$ $\Phi_B = 0.81 \pm 0.01\text{eV}$ (Nonlinear)
1275	Three-phase	• ZnO in grains • Pr-Cr-rich intergranular phase • PrCrO_3 spinel phase	97.76 ± 0.37 (2.24 % Porosity) (The most dense)	11.58 ± 3.54 (Large and irregular grains (broad distribution of grain size))	$\alpha = 3.45 \pm 0.20$ $\Phi_B = 0.80 \pm 0.01\text{eV}$ (Nonlinear)

Microstructure evolution in ZPC ceramics eventually lead to variation in electrical nonlinearity. The electrical conduction in ZPC ceramics slowly shifted from nonlinear to more Ohmic behaviour. According to the nonlinear coefficient, α in Table 1, the nonlinear characteristics of ZPC ceramics declined from 6.04 to 3.45 with increasing sintering temperature. However, the potential barrier height, Φ_B value marginally changed. The ZPC ceramics with higher α were obtained by sintering at lower temperature. This is attributed to the trade-off between effective number of Double Schottky Barrier at grain boundaries and grain size. The bigger the grain size, the less number of grain boundaries are formed and thus the nonlinear behaviour became less prominent.

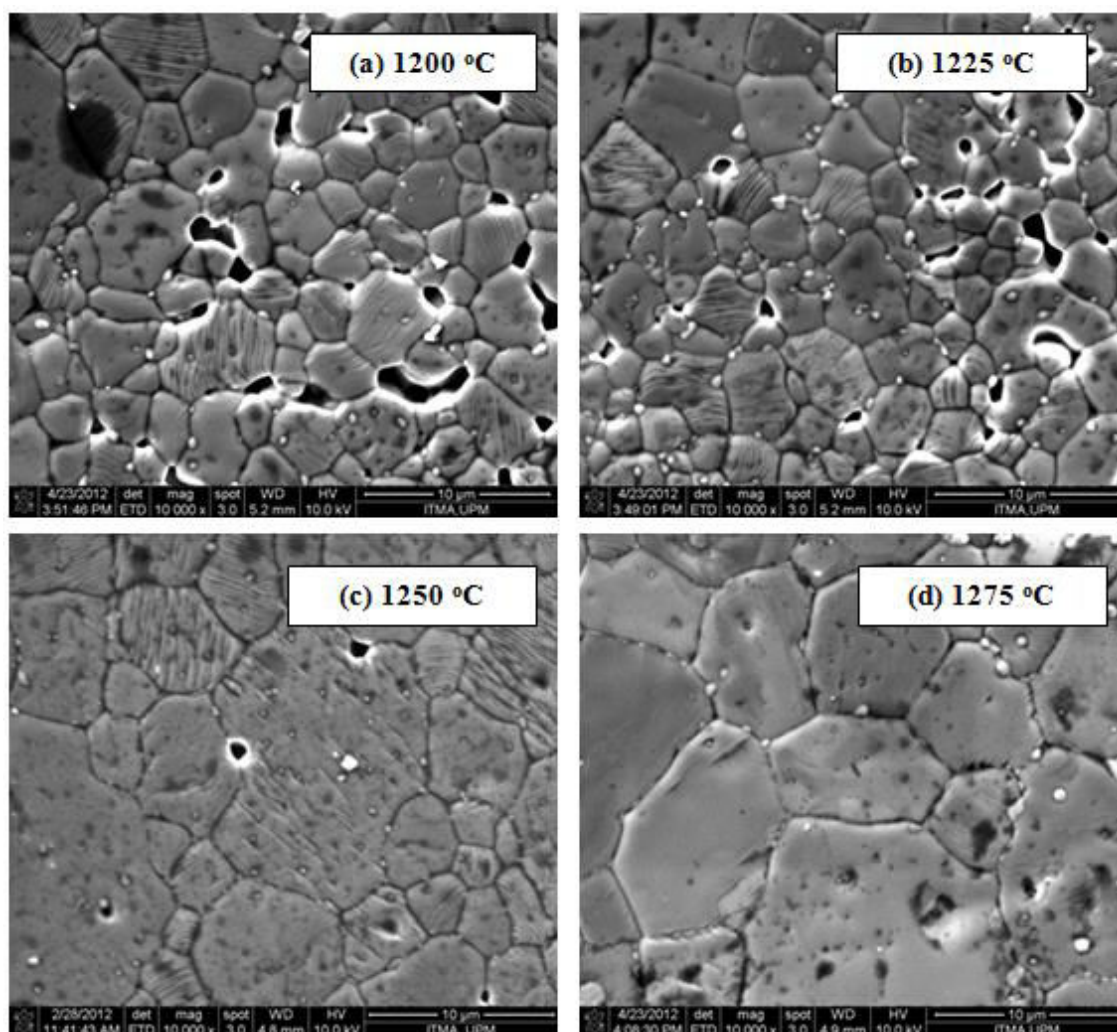


Figure 1: FESEM images for the grain structure of ZPC varistor ceramics sintered at different sintering temperatures for 1 h

In order to observe the influence of sintering time on evolution of microstructure and electrical nonlinearity of ZPC ceramics, the pellets were sintered at 1250 °C for various sintering time. Table 2 summarises the microstructure and electrical nonlinear properties of the resultant ZPC ceramics with respect to the applied sintering time. It was found that the microstructure of ZPC varistor ceramics sintered at the applied conditions sustained in two-phase microstructure. The two phases identified in the sintered ceramic using XRD and EDX were the hexagonal wurtzite structured ZnO in grains and the Pr-Cr-rich intergranular phase that was segregated during sintering process. No formation of any secondary phase was detected.

Table 2: Microstructure-electrical nonlinear characteristics of ZPC varistor ceramics sintered for different sintering time, t_s

t_s (h)	Phase Segregation		Densification and Grain growth		Nonlinear Characteristics
			Average relative density, ρ_{rel} (%)	Average grain size, d (μm)	
1	Two-phase	• ZnO in grains • Pr-Cr-rich intergranular phase	97.55 ± 0.23 (2.45% porosity) (The most dense)	7.36 ± 0.85 (Irregular large grains in between smaller grains)	$\alpha = 5.39 \pm 0.02$ $\Phi_B = 0.81 \pm 0.01\text{eV}$ (Nonlinear)
3	Two-phase	• ZnO in grains • Pr-Cr-rich intergranular phase	96.85 ± 1.01 (3.15% porosity)	8.00 ± 1.38 (Irregular large grains in between smaller grains)	$\alpha = 5.47 \pm 0.08$ $\Phi_B = 0.80 \pm 0.01\text{eV}$ (Most pronounce nonlinearity)
5	Two-phase	• ZnO in grains • Pr-Cr-rich intergranular phase	93.89 ± 0.77 (6.11% porosity)	7.42 ± 0.86 (Irregular large grains in between smaller grains)	$\alpha = 4.98 \pm 0.02$ $\Phi_B = 0.77 \pm 0.01\text{eV}$ (Nonlinear)
7	Two-phase	• ZnO in grains • Pr-Cr-rich intergranular phase	92.30 ± 0.28 (7.70% porosity) (The most porous)	7.49 ± 0.93 (Irregular grains in between smaller grains)	$\alpha = 3.94 \pm 0.21$ $\Phi_B = 0.70 \pm 0.01\text{eV}$ (Nonlinear)

Development of grain structures with respect to sintering time is shown in Figure 2. It was noticed that small grains appear more frequently as the sintering time increased. In addition, the number as well as the diameter of intergrain and isolated pores (pore on grain) multiplied with prolonged sintering. It is proposed that prolonged sintering time increased the evaporation rate of ZnO and additives. In agreement with Bernik et al., [16], the tendency of Cr_2O_3 to accumulate at triple points was more obvious when ceramics were sintered for more than 3 h. The presence of pores and heavy agglomerates at triple point regions retarded the grain growth during sintering.

The observation in FESEM analysis is supported with the average grain size and average relative density data provided in Table 2. The d value was not strongly affected by the variation in the sintering time. The value marginally increases from 7.36 to 8.00 μm when the time increases from 1 to 3 h and it eventually reduces to 7.49 μm as the time extended to 7 h. The ρ_{rel} value on the other hand deteriorates gradually from 97.55% to as low as 92.30% after sintering for 7 h. The grain growth inhibiting effects were strongly attributed to the presence of Cr_2O_3 and the intergrain pores. The decreasing trend of ρ_{rel} value especially after the sintering time of 3 h has suppressed the grain coarsening process and limited the d value in 7 – 8 μm range. Ceramics with the largest d value were obtained after 3 h of sintering whereas ceramics with the highest ρ_{rel} value were obtained after 1 h of sintering.

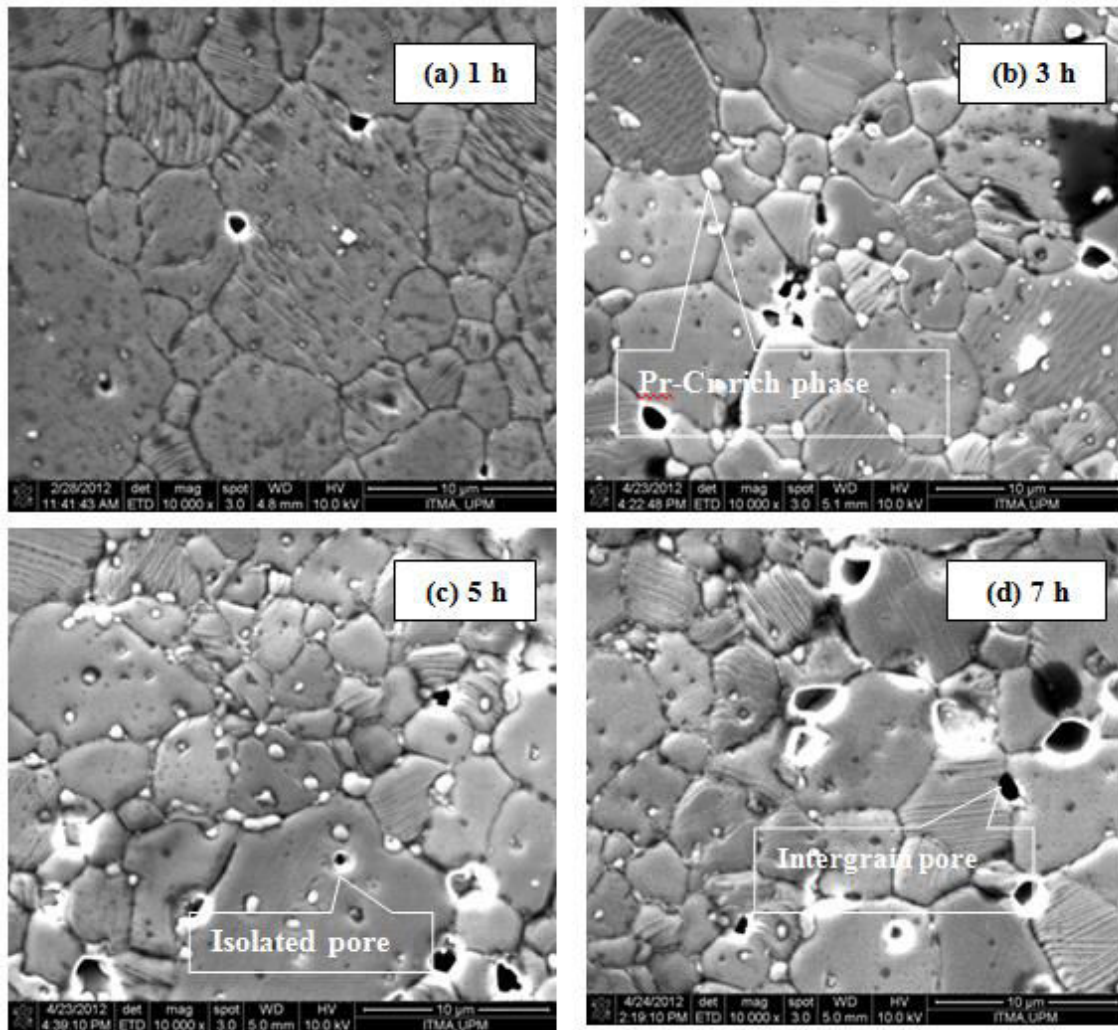


Figure 2: FESEM images for the grain structure of ZPC varistor ceramics sintered at 1250 °C for different sintering time

Extension of sintering time caused apparent changes on J-E curves. The ZPC ceramics sintered below than 7 h exhibited nonlinear characteristics whereas the ceramics sintered for 7 h exhibited nearly Ohmic J-E response. The disappearance of nonlinearity in ZPC with extended sintering time was evidenced by a reduction in the α and Φ_B values. The value of α drops from 5.39 to 3.94 as the time prolonged from 1 to 7 h whereas the Φ_B collapsed from 0.81 to 0.70 eV to implies that the formation of DSB at grain boundary has been discouraged by application of longer sintering time. Since the grain size was not significantly affected, the vanishing of nonlinear characteristics over sintering time could be associated to a decrease in number of electrically active grain boundary. As supported in FESEM analysis, intergrain pore formation and accumulation of segregated phase at triple points that preferentially occurred during longer sintering time leading to deactivation of some grain boundaries.

CONCLUSIONS

ZPC ceramics pellets with the nominal composition of 98.4 mol% ZnO, 0.8 mol% Pr₆O₁₁ and 0.6 mol% Cr₂O₃ were successfully obtained through modified citrate gel method and solid-state sintering. The evolution of microstructure and electrical nonlinear characteristics of the resultant varistor ceramics due to different application of sintering temperature and time was studied. Elevation of sintering temperature produced ZPC ceramics with more complex microstructure as the condition promoted the formation of secondary phase in the form of PrCrO₃. Meanwhile, ZnO grain growth and densification rate of sintered ceramics increased with higher sintering temperature. The development of nonlinear characteristics in ZPC ceramics adversely deteriorates with temperature due to trade-off between effective number of Double Schottky Barrier at grain boundaries and grain size. Meanwhile, extending the sintering time from 1 to 7 h resulted in the ZPC varistor ceramics with lower density and finer grains. Accumulation of intergrain pores and segregated phase at triple points led to deactivation of some grain boundaries. As a result, a decrement in both α and Φ_B values was observed due to the loss of electrical nonlinear behavior.

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