



Article Synergistic Effects of Pr₆O₁₁ and Co₃O₄ on Electrical and Microstructure Features of ZnO-BaTiO₃ Varistor Ceramics

Muhamad Syaizwadi Shaifudin ¹, Mohd Sabri Mohd Ghazali ^{1,2,*},

Wan Mohamad Ikhmal Wan Mohamad Kamaruzzaman ¹, Wan Rafizah Wan Abdullah ^{2,3}, Syara Kassim ¹, Nur Quratul Aini Ismail ⁴, Nor Kamilah Sa'at ⁴, Mohd Hafiz Mohd Zaid ^{2,4,*}, Maria Fazira Mohd Fekeri ¹ and Khamirul Amin Matori ^{2,4}

- ¹ Advanced Nano Materials (ANoMa) Research Group, Faculty of Science and Marine Environment, Universiti Malaysia Terengganu, Kuala Nerus 21030, Terengganu, Malaysia; syaizwadi@gmail.com (M.S.S.); ikhmal007@gmail.com (W.M.I.W.M.K.); syara.kassim@umt.edu.my (S.K.); mariafazirafekeri@gmail.com (M.F.M.F.)
- ² Materials Synthesis and Characterization Laboratory (MSCL), Institute of Advanced Technology, Universiti Putra Malaysia, Serdang 43400, Selangor, Malaysia; wanrafizah@umt.edu.my (W.R.W.A.); khamirul@upm.edu.my (K.A.M.)
- ³ Faculty of Ocean Engineering Technology and Informatics, Universiti Malaysia Terengganu, Kuala Nerus 21030, Terengganu, Malaysia
- ⁴ Department of Physics, Faculty of Science, Universiti Putra Malaysia, Serdang 43400, Selangor, Malaysia; nurquratulainiismail95@gmail.com (N.Q.A.I.); kamilah@upm.edu.my (N.K.S.)
- * Correspondence: mohdsabri@umt.edu.my (M.S.M.G.); mhmzaid@upm.edu.my (M.H.M.Z.); Tel.: +609-6683760 (M.S.M.G.)

Abstract: This paper investigated the effects of Pr_6O_{11} and Co_3O_4 on the electrical properties of ZnO-BaTiO₃ variator ceramics. The Pr_6O_{11} doping has a notable influence on the characteristics of the nonlinear coefficient, variator voltage, and leakage current where the values varied from 2.29 to 2.69, 12.36 to 68.36 V/mm and 599.33 to 548.16 μ A/cm², respectively. The nonlinear variator coefficient of 5.50 to 7.15 and the variator voltage of 7.38 to 8.10 V/mm was also influenced by the use of Co_3O_4 as a dopant. When the amount of Co_3O_4 was above 0.5 wt.%, the leakage current increased from 202.41 to 302.71 μ A/cm². The variator ceramics with 1.5 wt.% Pr_6O_{11} shows good nonlinear electrical performance at higher breakdown voltage and reduced the leakage current of the ceramic materials. Besides, the variator sample that was doped with 0.5 wt.% Co_3O_4 was able to enhance the nonlinear electrical properties at low breakdown voltage with a smaller value of leakage current.

Keywords: ZnO-BaTiO₃; varistor ceramics; electrical properties; Co₃O₄; Pr₆O₁₁

1. Introduction

A ZnO varistor is a semiconductor ceramic device possessing nonlinear electrical properties for surge protection applications. Due to these traits, a varistor is capable of sensing and absorbing surge energies quickly, protecting electronic circuits and electric power systems from being damaged. In general, a commercial varistor is mostly prepared by mixing and sintering ZnO powder with several types of varistor-forming oxides, such as Bi_2O_3 , transition metal oxide (V_2O_5), rare earth oxide (Pr_6O_{11}) and alkaline earth oxide (BaO) [1–3]. The varistor-former additives form a secondary phase and segregate at the grain boundary, thus imparting nonlinear electrical characteristics to the device [4,5]. The varistor properties originate from its microstructure, where within it contains conducting ZnO grains that are enclosed by a thin insulating oxide layer and some secondary phases which form during the sintering process. The nonlinear property of the ZnO varistor is also known to be dependent on the minor dopants, sintering condition, and final configuration of microstructure [6]. The resultant microstructures become the primary factors for the ZnO varistors to exhibit the nonlinear electrical properties with energy handling



Citation: Shaifudin, M.S.; Ghazali, M.S.M.; Kamaruzzaman, W.M.I.W.M.; Wan Abdullah, W.R.; Kassim, S.; Ismail, N.Q.A.; Sa'at, N.K.; Mohd Zaid, M.H.; Mohd Fekeri, M.F.; Matori, K.A. Synergistic Effects of Pr_6O_{11} and Co_3O_4 on Electrical and Microstructure Features of ZnO-BaTiO₃ Varistor Ceramics. *Materials* **2021**, *14*, 702. https:// doi.org/10.3390/ma14040702

Received: 30 November 2020 Accepted: 4 January 2021 Published: 3 February 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/). capabilities [7]. The other resultant microstructure includes grain boundaries and triple junctions of ZnO grains.

In order to manufacture varistors with good performance, it is essential to study the influence of different additives on the performance of these ceramics. The electrical characteristics of ZnO varistors are directly related to the grain boundary mechanism since both nonlinearity and breakdown voltage is affected by the ZnO grain and grain boundary [8,9]. In the grain boundary, a large number of electronic defects are segregated at the interface layer, forming a potential barrier and enhanced nonlinearity [10]. It is known that dopant additives can control the varistor behavior, particularly when it has a large ionic radius. The dopant ions create a thin intergranular layer and separate the ZnO grains [11,12]. The circumstance then gives rise to the potential barriers which are located at the interface state, where it acts as a trap for the conduction of electrons in the grain boundaries [13]. In varistor applications, the dopant involves adjusting the defect concentration on the ZnO microstructure. The employment of dopant is significant since the varistor performance is sensitive to the presence of dopant additives, even though in a small proportion of their composition [14,15]. Some dopants have their properties in modifying varistor microstructures by either inhibiting the grain growth in the application of high voltage causing it to have a smaller average grain size, or exhibit grain growth and induced a larger average grain size suitable for low voltage application [16].

The present ZnO based varistors are usually doped with several metal oxides that are inserted into their microstructure. Nevertheless, to date, only a few studies have focused on using the perovskite material as an additive. The use of barium titanate ($BaTiO_3$) as the varistor forming oxide has attracted much attention due to its unique properties and broad applications in the electronics industry [17]. In a previous study, the ZnO varistor doped with $BaTiO_3$ was found to greatly enhance the nonlinear electrical characteristics [18]. The presence of TiO_2 within the BaTiO₃ can considerably improve the grain growth of ZnO, making it suitable for the application of low-voltage varistors [19]. In our previous study, the electrical performance of ZnO varistors was investigated using different $BaTiO_3$ contents as an additive and found that the optimum nonlinear coefficient (α) value was obtained from the sample made with 12 wt.% content of BaTiO₃ [20]. The most desirable properties of a varistor are a high value of nonlinear coefficients (α) and a low value of leakage current density (J_L) [21]. Therefore, it is essential to elucidate the effect of Co_3O_4 and Pr_6O_{11} doping into ZnO-BaTiO₃ based varistor to improve their performance. It is also recognized that transitional metal oxide such as Co and Mn generally improves the nonlinearity coefficient at lower current density region due to an increase in barrier height by electron trapping [22,23]. Moreover, the use of Pr_6O_{11} dopant can inhibit grain growth that can manage the generation of ZnO grain during the sintering process by promoting more uniform and compact microstructures [24].

The present study further addresses the effect of Pr_6O_{11} and Co_3O_4 doping on ZnO-BaTiO₃ based variator ceramics by varying the dopant content in the formulation. The influence of dopants on the microstructure development and electrical properties of ZnO-BaTiO₃ binary variators have been analyzed.

2. Materials and Methods

2.1. Preparation of Powder and Ceramics

The composition of ZnO ceramics (88 – *x*) wt.% with 12 wt.% BaTiO₃, and *x* wt.% Pr_6O_{11}/Co_3O_4 (*x* = 0.5, 1.0, and 1.5 wt.%) were fabricated via the solid-state reaction method. The step began by mixing all ceramic powders using a planetary ball milling for 3 h. Then, the compositions were combined with 1.75 wt.% polyvinyl alcohol (PVA) binder, and the slurry was dried at 80 °C for 2 h. The dried powders were pulverized using an agate mortar and granulated by sieving to produce a starting powder. The resulting powders were next pressed onto ceramic discs or pellets with a diameter of 10.0 mm and about 1.0 mm of thickness at a pressure of 2.6 ton/5 min. The pellets were sintered in a box furnace at 1300 °C for 90 min with a heating and cooling rate of 3 °C/min. Finally,

the pellets were polished with sandpapers (P2400 and P4000), and then a silver paste was coated on both sides as an electrode.

2.2. Characterizations

The phase content of sample pellets was characterized by X-ray Diffraction (XRD, MiniFlex II, Rigaku, Shibuya, Japan). The surface morphology of the pellets was examined by using a Scanning Electron Microscope (SEM) JEOL JSM-6360LA model (JEOL USA, Peabody, MA, USA), and the elements present on samples were identified using the Energy Dispersive Spectroscopy (EDS). The average density of the sintered samples, ρ_{avg} was measured using the Archimedes method, and it was determined based on the following equation:

$$o_{avg} = \frac{m_{air}}{(m_{air} - m_{water})} \times \rho_{water} \tag{1}$$

where m_{air} is the mass of the sintered sample pellet in air, m_{water} is the mass of sample pellet when immersed in water, and ρ_{water} is the density of water used (1.00 g/cm³). The average relative density, ρ_{rel} is the ratio of ρ_{avg} to theoretical density, $\rho_{theoretical}$ of sample is evaluated from the expression:

$$o_{rel} = \frac{\rho_{avg}}{\rho_{theoretical}} \times 100\%$$
(2)

Electrical characteristics analysis was performed to measure the current densityelectrical field (*J*–*E*) property of varistor samples using a source meter (Keithley 2400, Beaverton, OR, USA). The breakdown voltage (E_b) was determined at a current density of 1.0 mA/cm², while the leakage current density (J_L) was determined at 0.80 E_{1mA} . The coefficient of nonlinearity (α) can be estimated by the following equation:

$$\alpha = \frac{\log J_2 - \log J_1}{\log E_2 - \log E_1}$$
(3)

where J_1 and J_2 are the current density at the electrical field E_1 and E_2 in the range of 1.0 mA/cm² to 10 mA/cm², respectively [25]. Besides, the nonlinearity can be defined from the relation of $J = KE^{\alpha}$, where K is related to the electrical resistivity, and α is a nonlinear coefficient [26]. The potential barrier height, \emptyset_B is an electrical parameter for grain boundaries, which induced the nonlinear properties of varistor ceramics and can be estimated according to,

$$I = AT^2 \exp\left[\frac{\beta E^{\frac{1}{2}} - \varnothing_B}{k_B T}\right]$$
(4)

where *J* is the current density, *E* is the applied electrical field, *A* is the Richardson's constant (30 A/cm²K²), *T* is the absolute temperature, β is a constant governed by the relationship $\beta \propto 1/(r\omega)$, where *r* is grains per unit length and ω is the potential barrier width and k^B is the Boltzmann constant (8.167 × 10⁻⁵ eV/K). The value of potential barrier height, \emptyset_B can be estimated by plotting a graph of ln *J* versus $E^{1/2}$ which was deduced from the intercept of the linear fit of ln *J* vs. \sqrt{E} . The lineal intercept method was utilized to obtain the average grain size (*d*) of the microstructure [27].

3. Results and Discussions

3.1. Scanning Electron Microscopy (SEM)

Figure 1 illustrates the morphology of ZnO-BaTiO₃ based varistor doped with different contents of Pr_6O_{11} and Co_3O_4 . These SEM images show that the surface morphology for varistors with a different dispersion of dopant content induced varied average ZnO grain sizes. For comparison, the microstructure of ZnO-BaTiO₃ is depicted in Figure 1a. Figure 1a shows that the ceramics have a two-phase microstructure with ZnO grain as the primary phase and BaTiO₃ phase as the intergranular phase. These phases in the microstructure

concurred with the observation by XRD analysis in Figures 2a and 3a at 0.0 wt.% of Pr_6O_{11} and Co_3O_4 . The highest peaks match well with the ZnO phase, and the lowest peaks have been matched to the BaTiO₃-rich phase. A high proportion of BaTiO₃ rich phase shows that many $BaTiO_3$ particles were diffused into some ZnO grains to form an intergranular layer. Another amount segregates near the grain boundaries forms solid solutions. During the sintering process, a liquid phase occurred in the grain boundaries and formed a thick layer along the grain boundary and triple junctions of matrix grains. The remaining amount of solid solutions shows that many BaTiO₃ particles formed into melt and filled the grain boundaries with a liquid phase during sintering. When the grain boundaries are completely formed at the interface state, no more liquid phase can occur in the grain boundaries. It can be attributed to the precipitation of BaTiO₃-rich phase near the grain boundaries and nodal points. It is believed that an amount of $BaTiO_3$ phase remains at the grain boundaries of two differently matrix which can affect the grain boundaries resistivity. In general, the varistor microstructure is composed of ZnO grains and secondary phase, which usually located at the grain boundaries and junctions of multiple grains [28]. Figure 1b-d show the microstructure of ZnO-BaTiO₃ varistor ceramics doped with 0.5 to 1.5 wt.% of Pr₆O₁₁. It can be seen that the addition of Pr_6O_{11} increases the size and number of BaTiO₃ phase with a slight difference in the shape of the particles in comparison with the sample at 0.0 wt.% Pr_6O_{11} . The difference indicates that the precipitation of Pr_6O_{11} phase located in the grain boundaries leading to the increase of BaTiO₃-Pr-rich phase in the form of solid solutions. The presence of BaTiO₃-Pr-rich phase can enhance the nonlinear electrical properties due to the increase in barrier height at the grain boundaries. This tendency can be observed in Figure 1b-d, where the Pr species have been distributed in the grain boundary and at triple points along with the BaTiO₃-rich phase. Meanwhile, segregated Pr at the grain boundaries can increase the number of grain boundary that is required for improving the varistor breakdown voltage. By increasing Pr-doping amounts to 1.5, the varistor breakdown voltage of the ceramics gradually increased. This finding are in accordance with the current density-electric field (J-E) curves where the variator breakdown voltage (E_b) of the sample evidently increased when the doping amount is increased up to 1.5. Since Pr^{3+} (1.113 Å) are relatively larger ions than Zn²⁺ (0.74 Å), the chance for Pr ions to dissolve in ZnO matrix grains is extremely small and induced the formation of Pr-rich phase by contributing more solid solutions near the grain boundaries and triple point junctions. The microstructures of the Pr₆O₁₁ doping system did not differ so much, but the grain size increases when doped with 0.5 wt.% of Pr_6O_{11} . The average grain size decreased from 2.0 to 1.6 µm by increasing the Pr₆O₁₁ doping amount up to 1.5 wt.%. It has been well accepted that the ZnO grain growth can be suppressed by excessively doping with Pr₆O₁₁ [29].

The addition of Co_3O_4 dopant content enhanced the grain size of ZnO compared to Pr_6O_{11} -doped samples, whereas the average grain size increased from 1.5 to 2.5 μ m with increasing cobalt dopant. As shown in Figure 1e-g, the addition of Co_3O_4 encourages the growth of ZnO grains and promoted densification of varistors. It was observed that ceramics doped with Co₃O₄ contained low of solid solutions with more uniform grains. This effect is due to the solubility of Co ions in ZnO grain. The ionic radii of Co^{3+} (0.65 Å) which is approximately the same as Zn ion and could be induced the solubility of Co ions in ZnO lattice. The incorporation of Co_3O_4 decreased the size and number of BaTiO₃ phase with more resolve BaTiO₃ particles and diffused into grain boundaries in comparison with that of 0.0 wt.% Co_3O_4 -doped samples. The Co_3O_4 dopant has induced Co ions in the interior of ZnO grains and creates interface states and deep bulk traps that are required for the formation of the potential barrier at the grain boundary and enhance the nonlinearity coefficient of ZnO varistor ceramics [30]. Figure 1e-g indicates that Co species have been diffused into grain boundaries and formed BaTiO₃-Co-rich phase. By increasing Co-doping amounts up to 1.5, reduced the BaTiO₃-rich phase due to the segregated of Co ions in the grain boundary and generated the interface traps. A part of Co₃O₄ dopant diffused into matrix grains by increasing densification and grain growth of ZnO ceramics during the



sintering process. From these findings, the Co_3O_4 dopant has increased the barrier height while promoted grain growth and densification of ZnO varistor ceramics.

Figure 1. SEM images of ZnO-BaTiO₃ and doped ZnO-BaTiO₃ variator with different concentration of Pr_6O_{11} and Co_3O_4 : (a) ZnO-BaTiO₃ without dopant, (b) 0.5 wt.% (Pr_6O_{11}), (c) 1.0 wt.% (Pr_6O_{11}), (d) 1.5 wt.% (Pr_6O_{11}), (e) 0.5 wt.% (Co_3O_4), (f) 1.0 wt.% (Co_3O_4) and (g) 1.5 wt.% (Co_3O_4).



Figure 2. The XRD spectra of ZnO-BaTiO₃ based variator doped with different amounts of Pr_6O_{11} (**a**) XRD patterns of Pr_6O_{11} -doped ZnO-BaTiO₃ variator ceramics and (**b**) XRD patterns of (220) diffraction.



Figure 3. The XRD spectra of ZnO-BaTiO₃ based varistor doped with different amounts of Co_3O_4 (a) XRD patterns of Co_3O_4 -doped ZnO-BaTiO₃ varistor ceramics and (b) XRD patterns of (331) diffraction.

3.2. Energy Dispersive Spectroscopy (EDS)

Additionally, the presence of doping elements was indicated by EDS analysis. Tables 1 and 2 are the confirmed existing elements in the sample surfaces with different Pr_6O_{11} and Co_3O_4 doping contents. It was observed that the element ratio of Pr increased

with the increase of dopant content. However, the element ratio of Ba and Ti was discerned to decrease, which indicates that Pr ions can disturb the BaTiO₃ phase by segregated near the grain boundaries and triple point junctions. Since the Pr ions are larger than Zn ions, the solubility of Pr ions in ZnO grains is low, and it can attribute to the formation of more intergranular layer by segregating into the grain boundaries. Therefore, the presence of Pr element can reduce the Ba and Ti content at the grain boundaries. Incorporation of Pr ions in the grain boundaries, in this case, caused the formation of more solid solutions near the grain boundaries, which can influence the effective grain boundaries of ZnO varistors.

Table 1. The element contents of ZnO-BaTiO₃ variator ceramics with different amounts of Pr_6O_{11} compositions.

Pr ₆ O ₁₁ Content (wt.%)	Element	Mass (%)
	ОК	19.82
	Ti K	6.49
0 5	Zn K	54.65
0.5	Ba L	17.90
	Pr L	1.13
	Total	100.00
	ОК	19.82
	Ti K	4.85
1.0	Zn K	61.84
1.0	Ba L	12.20
	Pr L	1.30
	Total	100.00
	ОК	19.66
1.5	Ti K	4.28
	Zn K	63.12
	Ba L	11.33
	Pr L	1.62
	Total	100.00

Table 2. The element contents of ZnO-BaTiO₃ variator ceramics with different amounts of Co_3O_4 compositions.

Co ₃ O ₄ Content (wt.%)	Element	Mass (%)
	ОК	20.23
	Ti K	7.52
0 5	Co K	0.37
0.5	Zn K	52.48
	Ba L	19.40
	Total	100.00
	O K	20.42
	Ti K	10.47
1.0	Co K	0.87
1.0	Zn K	40.84
	Ba L	27.41
	Total	100.00
	O K	20.24
	Ti K	8.09
1 5	Co K	0.91
1.5	Zn K	49.51
	Ba L	21.25
	Total	100.00

Nevertheless, the increase of element ratio of Co can increase the electrical charge carriers for better conductivity in ZnO grains. The high solubility of Co ions in ZnO grains

makes it easier to segregate in the grain boundary layer by generating the interface state traps, which is essential to enhance the nonlinear properties of ZnO varistor ceramics. As shown in Table 2, better distribution of Ba and Ti elements near the grain boundary led to the increment of Ba and Ti contents. It was indicated that segregation of Co species in the grain boundary promotes the formation of a potential barrier for greater nonlinearity in ZnO varistors.

3.3. X-ray Diffraction (XRD)

The XRD study was used to examine the different phases present in the prepared and sintered samples. Figures 2 and 3 show the X-ray diffraction patterns of the as-prepared ZnO-BaTiO₃ based variator doped with different contents of Pr_6O_{11} and Co_3O_4 dopants. The XRD patterns revealed the presence of the ZnO main phase, according to the inorganic crystal structure database (ICSD) No. 067849, with a hexagonal wurtzite structure. The additives were observed due to the presence of the BaTiO₃ phase within the ZnO ceramics, as indicated by the ICSD No. 028851. XRD spectrum demonstrates that the presence of two major phases which were ZnO phase and BaTiO₃-rich phase that co-existed with Pr-rich phase. The addition of Pr_6O_{11} dopant increases the number of intergranular phases and induced solid solutions near the grain boundaries. The diffraction peaks belong to the Prrich phase are located at (220) peak, and no secondary phase was observed, suggesting that the Pr ions may be doped into ZnO. Figure 2b shows the magnified region of (220) peak, in which the diffraction angle of Pr-doped ZnO-BaTiO₃ ceramics with different content shifted to smaller angle side in comparison with that of BaTiO₃-doped ZnO ceramics. This shifting was due to the difference in ionic radii of Pr^{3+} (1.113 Å) and Zn^{2+} (0.74 Å) which cause to the change of ZnO lattice and the observation are also similar with Pr-doped ZnO ceramic systems reported in [31]. Therefore, the peak shift in different Pr-doped ZnO-BaTiO₃, in this case, indicates that the doping element with a larger ionic radius than Zn^{2+} is replaced at the substitution sites of the ZnO crystal lattice. Further increase of Pr-doping content up to 1.5, the peak position is shifted towards the larger 2θ side, which suggests that the Pr ion has occupied the interstitial sites of ZnO. In addition, the full width at half maximum (FWHM) of diffraction peaks increase with an increase of Pr doping level, which means that the crystallite size decreases with the increase of Pr content. The mean crystallite size can be calculated using Scherrer's formula

$$D = 0.9\lambda/\beta\cos\theta \tag{5}$$

where λ is the wavelength of X-ray radiation (0.15406 nm), β is the full width at half maximum of a distinctive peak, and θ is Bragg's diffraction angle. The micro-strain (ε) can be calculated using formula

Micro-strain (
$$\varepsilon$$
) = $\beta \cos\theta/4$ (6)

The calculated full width at half maximum (FWHM) value, the crystallite size (*D*) and micro-strain (ε) of all samples was indicated in Table 3. It can be seen that the crystallite size of ZnO decreased from 57.95 nm to 36.94 nm when Pr concentration increased from 0.5 wt.% to 1.5 wt.%. The data indicate that the presence of Pr³⁺ ions in ZnO reduced the growth of crystal grains. The decrease in crystallite size is due to the compressive strain of crystal lattice. It is clear from Table 3 that the micro-strain is increased from 20.90 × 10⁻⁴ to 21.20 × 10⁻⁴. The presence of Pr content in ZnO is able to change the reaction rate as well as the growth mechanism of crystal grains. The decrease in crystal size is well understood by the grain growth suppressing effect of ZnO by Pr-doping [24]. The decrease in the XRD peak position is generally observed when the crystallite size increased and then increased due to the decrease in lattice size. With the addition of Pr₆O₁₁, the Pr³⁺ ions may concentrate at the grain boundaries or on the surface of ZnO in the first segregation. Afterwards, an increase of Pr₆O₁₁ content leads to the formation of BaTiO₃-Pr-rich phase

segregation locating on the surface of the sample and in the grain boundary near the junctions between ZnO grains, which will inhibit ZnO grains.

Table 3. Variation of FWHM value, crystallite size and micro-strain (ϵ) of Pr-doped ZnO-BaTiO₃ varistor ceramics with different content.

Pr ₆ O ₁₁ Content (wt.%)	FWHM, β (Degree)	2θ (Degree)	Crystallite Size (nm)	Micro-Strain, ε (10 ⁻⁴)
0.0	0.154	47.43	56.28	21.90
0.5	0.149	47.10	57.95	20.90
1.0	0.168	47.12	51.57	21.20
1.5	0.234	47.18	36.94	9.15

It was observed that the ceramics doped with Co_3O_4 contained two-phase microstructure with ZnO as the major phase and $BaTiO_3$ phase as the minor phase. Traces of Co-rich phases were also detected where some minor peaks had been matched to Co₃O₄. The formation of intergranular phase was also induced by Co-rich phase at the grain boundaries. However, the addition of Co_3O_4 decreased the number of observable intergranular phase and enhanced the grain growth compared to the sample doped with Pr_6O_{11} . In the enlarged view of the (331) peak in Figure 3b, the peak gradually moves to a lower angle with the addition of Co_3O_4 dopant, indicating increased in crystallite size as a result of Zn^{2+} (0.74 Å) with the smaller radius being substituted by Co^{2+} (0.75 Å). Table 4 shows the value of full width at half maximum (FWHM), the crystallite size (D) and micro-strain (ε) with Co-doping content. With increasing Co content from 0.5 to 1.5 wt.%, the crystallite size is decreased from 36.89 to 35.11 nm. The decrease in peak position value in this case is also due to the increased in crystal size and the effect of tensile strain. Based on this evidence, the micro-strain is increased from 21.90×10^{-4} to 24.10×10^{-4} and exhibited a larger crystallite size in comparison with that of 0.0 wt.% Co₃O₄ addition. Moreover, the value of FWHM decreases with the addition of Co₃O₄, which indicates that the crystallite size increases with the addition of Co_3O_4 dopant. Then the 2θ shifted to larger angle side for 1.5 wt.% Co-doped ZnO-BaTiO₃ ceramic materials are attributed to the existence of Co₃O₄ in ZnO. Therefore, the crystal grains decreased with a further increase of Co-doping content up to 1.5 wt.%.

Table 4. Variation of FWHM value, crystallite size and micro-strain (ε) of Co-doped ZnO-BaTiO₃ variator ceramics with different content.

Co ₃ O ₄ Content (wt.%)	FWHM, β (Degree)	2θ (Degree)	Crystallite Size (nm)	Micro-Strain, ε (10 ⁻⁴)
0.0	0.264	56.48	34.17	21.90
0.5	0.244	56.28	36.89	15.90
1.0	0.245	56.16	36.67	24.10
1.5	0.256	56.20	35.11	20.10

Moreover, some minor peaks could be observed where their peaks are located in the closed angles of the ZnO and BaTiO₃ phases. The presence of a new phase might be due to the addition of Pr_6O_{11} and Co_3O_4 dopants, but some phases could not be detected in all samples, which indicates that Co and Pr ions were completely diffused into ZnO and BaTiO₃ phases. The existence of these phases promotes the formation of intergranular layer and solid solutions at the ZnO grain and grain boundary, which also acts as a donor that forms the depletion layer or as an acceptor by dominating the grain boundary layer [32,33]. Furthermore, the presence of these solid solutions has significant effects on the nonlinear electrical properties of the varistor ceramics.

3.4. Current Density-Electric Field (J-E) Characteristics

A preliminary test of electrical properties on finalizing the composition of the ZnO-BaTiO₃ based varistor was characterized by nonlinearity measurement [20]. The samples added with 12 wt.% BaTiO₃ showed a relatively higher barrier height than other samples with dissimilar BaTiO₃ contents; the result is consistent with the standard nonlinear coefficient characteristics. The presence of a potential barrier at the grain boundary caused the nonlinearity characteristics of the varistor [34]. Therefore, the presence of grain boundary contributed to the nonlinearity of the varistor ceramics. Figure 4 shows a significant difference in the *J*-*E* characteristics of the varistor samples doping with various of Pr_6O_{11} . The conduction mechanism is divided into three regions: pre-breakdown region, breakdown region and upturn region.



Figure 4. J-E characteristics of the varistor ceramics doping with various Pr₆O₁₁.

In the pre-breakdown region, the linear curves of J-E response for all samples indicate that the resistivity of the varistor ceramic samples before breakdown voltage is slightly higher than the nonlinear curves of J-E response. The J-E curves at different concentrations of Pr_6O_{11} resemble a nonlinear response with a high resistivity region at the left of the breakdown voltage and a low resistivity region at the right of the breakdown voltage. The values of the nonlinear coefficient are decreased for Pr-doped samples, whereas the *J*-E curves are shifted to the right of breakdown voltage by Pr. However, the most important parameter here is the breakdown voltage. By increasing the Pr-doping amounts to 1.5, the varistor breakdown field of the ceramic evidently increased. The breakdown field of the varistor ceramics is related to the ZnO grain size and the applied electric field at each grain boundary [35,36]. The decrease in the average grain size with further increase in the Prdoping amount can be clarified by the increase in the numbers of grain boundaries between the electrodes, thereby increasing the breakdown voltage and enhanced the nonlinearity of the varistor ceramics. A high nonlinear coefficient leads to the increased breakdown field of the ceramic samples [37]. The increase in the breakdown voltage with further increase in the Pr-doping content also reduced the leakage current, indicating that it occurs at lower current density due to the increase in barrier height at the grain boundaries. The nonlinear electrical properties of the Pr-added samples is lower than that of the BaTiO₃doped ceramic for electric fields with strengths lower than 10 V/mm. It has been reported that most of the Pr₆O₁₁-doped ZnO varistor system exhibited low nonlinear coefficient value at a low-voltage range [38].

It can be observed from Figure 5 that the *J*-*E* curves at two regions with the prebreakdown region at the low electric field and breakdown area at the high electric field. The sharper the knee of *J*-*E* curves between the two regions, the higher the nonlinearity coefficient. However, the varistor samples doping with Co₃O₄ exhibited higher breakdown voltage in the breakdown region or nonlinear region and showed higher nonlinearity coefficients in comparison with that of BaTiO₃-doped samples. The varistor's breakdown field is directly proportional to the grain boundaries number per unit of thickness where the improvement in the nonlinear behavior of the samples is attributed to the formation of the potential barrier at the ZnO grain boundaries. By increasing Co-doping amounts to 1.0, the varistor breakdown voltage of the ceramic apparently decreased first and then gradually increased when the doping amount is increased up to 1.5. The *J*-*E* curves with different concentrations of Co₃O₄ exhibited similar shapes at electric fields below 10 V/mm, however under the varistor voltage at 1 mA (V_{1mA}) the varistor samples doping with 0.5 wt.% showed higher breakdown voltage compared to the ceramics doping with 1.0 and 1.5 wt.%. At V1mA, the varistor breakdown voltage obviously decreased when the Co-doping amount is increased up to 1.5, thereby decreasing the values of the nonlinear coefficient of the samples. The reduction in nonlinearity coefficient and breakdown voltage with further increase in the Co-doping content could be attributed to the formation of oxygen vacancies at the grain boundary [39]. It was reported that the oxygen species could increase the density of interface states at the grain boundary and enhanced Schottky barrier height [29].



Figure 5. J-E characteristics of the varistor ceramics doping with various Co₃O₄.

With an increased amount of doped Co_3O_4 , more Co ions diffused into the ZnO grain and grain boundary which can improve the characteristic of the varistor samples, including the increment of the breakdown voltage (V_{1mA}) to a small extent. However, the excessive Co ions enter into ZnO grains and grain boundaries with the BaTiO₃-rich phase could destroy the original microstructure due to the accumulation of excessive Co ions which depleted the O ions and promoted the formation of O vacancies in the grain boundary. As a result, the density of interface states decreased and reduced the interface barrier height, thus increase the leakage current density within the varistor samples. The electrical parameters for the current density-electric field (*J-E*) of varistor with different amounts of Pr_6O_{11} and Co₃O₄ are summarized in Tables 5 and 6. The knee of the *J*-*E* curve at 0.0 wt.% of Pr_6O_{11} and Co₃O₄ only appeared when a lower electric field was applied as shown in Figure 5, which indicates that the ceramic materials exhibited low breakdown voltage. This suggests that ZnO-BaTiO₃ varistor ceramics can provide excellent protection performance at low-varistor voltage. Figure 4 shows that the *J*-*E* curve at 0.0 wt.% is disappeared when a stronger electric field was applied. However, with the addition of Pr_6O_{11} the knee of the curve is appeared when the electric field was increased, indicating an improvement in breakdown voltage of the materials. The enhancement in the nonlinear electrical performance of Pr-doped ZnO-BaTiO₃ varistor ceramics is suitable for the application in high-voltage varistor systems. Enhancing protection performance for multilayer ceramic varistors (MLCVs) is required since it shows excellent protection performance with low-voltage and small size [8]. Therefore, they are mostly employed in mobile devices. The improvement in nonlinear electrical properties of Co-doped ZnO-BaTiO₃ varistor systems at low breakdown voltage can provide excellent protection performance for the application in chip varistors.

Table 5. Average grain size (*d*), Relative density, nonlinear coefficient (α), breakdown voltage (E_b), leakage current density (J_L), and Schottky barrier height (Φ_B) of Pr₆O₁₁ at different content.

Pr ₆ O ₁₁ Content (wt.%)	d (µm)	Relative Density (%)	$\alpha \pm SE$	<i>E_b</i> (V/mm)	J _L (µA/cm ²)	Φ_B (eV)
0.0	1.5	89.3	4.83 ± 0.16	6.09	348.00	0.88
0.5	2.0	96.8	2.29 ± 0.01	12.36	599.33	0.81
1.0	1.8	97.5	2.66 ± 0.01	33.67	553.33	0.84
1.5	1.6	97.8	2.69 ± 0.02	68.36	548.16	0.86

Table 6. Average grain size (*d*), Relative density, nonlinear coefficient (α), breakdown voltage (E_b), leakage current density (J_L), and Schottky barrier height (Φ_B) of Co₃O₄ at different content.

Co ₃ O ₄ Content (wt.%)	d (µm)	Relative Density (%)	$\alpha \pm SE$	E _b (V/mm)	J_L (µA/cm ²)	Φ_B (eV)
0.0	1.5	89.3	4.83 ± 0.16	6.09	348.00	0.88
0.5	1.7	99.2	7.15 ± 0.42	7.58	202.41	0.94
1.0	2.2	99.1	5.62 ± 0.18	7.38	294.76	0.92
1.5	2.5	97.9	5.50 ± 0.33	8.10	302.71	0.91

The relative density of Pr_6O_{11} dopants was above 96% of the theoretical density of bulk ZnO (5.61 g/cm³), and the average grain size was in the range of 1.6 to 2.0 µm. A significant change in the grain size can produce a dense ceramic body with better varistor properties. The varistor breakdown voltage (E_b) of Pr_6O_{11} dopants increased from 12.36 to 68.36 V/mm, which indicates that doping with Pr_6O_{11} decreased grain growth. The increase of varistor voltage is due to the ionic radius of rare earth oxides (Pr_6O_{11}) is larger than that of Zn ions. During the sintering process, the interface layer is formed by the segregation of rare earth oxides into the ZnO grain boundary, resulting in the pinning effect and therefore inhibit the grain growth of ZnO varistors [40].

Meanwhile, the leakage current density decreased with the increase of Pr_6O_{11} doping amounts. This is due to the increase in the density of varistors, where the use of Pr_6O_{11} doping had restrained the formation of secondary phases and enhanced the densification of the ceramic structure [38]. However, the increases in the leakage current densities in the Pr_6O_{11} doping samples compared with the undoped sample may be due to the accumulation of excessive dopants has increased the O vacancies and promote the formation of the depletion layer. It is well known that the O species can increase the density of interface states at the grain boundary, thus enhancing the potential barrier height [39,41]. The addition of Pr_6O_{11} dopant leads to the inhibition of the potential barrier formation in

14 of 17

the grain boundary of the varistor. In contrast, the excessive amount of dopant can cause a variation of the electronic state at the ZnO grain boundary and deteriorate the performance of varistor ceramics. Conclusively, the electrical characteristics of ZnO varistors are greatly enhanced with small amounts of rare earth dopants but critically deteriorated when excessive quantities of rare-earth dopants are used [42]. These varistor formers change the property of ZnO varistors by varying the inter-composition ratio of dopants. Through such changes, it will result in a complication for the multi-layer structure of chip varistors by generating a large quantity of the secondary phases with an insulating spinel phase that played no significant electrical role. This phenomenon will then result in the degradation of varistor properties [43].

For the varistors with Co_3O_4 dopants, the α value initially increased when Co_3O_4 doping amounts were increased up to 0.5 wt.%. Later, the α decreased when Co₃O₄ doping amount was increased up to 1.5 wt.%. The performance of varistors depends on the amount of secondary phase at the grain boundaries since the presence of the BaTiO₃-rich phase can increase the effective grain boundary region and improve its performance. The increase of dopant content has changed these varistor formers, which resulted in a complication for the grain boundary layer structure by generating a large number of secondary phases. It is known that the addition of transition metal oxides such as Co_3O_4 can generally improve the nonlinear coefficient at lower current density region by trapping the electrons and increasing the barrier height [44]. The average relative densities of Co₃O₄ dopants exceeded 97% of theoretical density, and the average grain size increased from 1.7 to 2.5 μ m as the Co₃O₄ content was increased from 0.5 to 1.5 wt.%, respectively. Due to the similar ionic radius of Co and Zn, a solid solution of Zn and Co is formed because of the complete substitution of Co in the Zn structure, which neglects the presence of pores. Moreover, when a sample was strongly doped with Co_3O_4 , it can increase the defect concentration and the density, which leads to a decrease in the porosity [45].

The varistor breakdown voltage initially increased when Co_3O_4 doping content was increased up to 0.5 wt.%. Then, when the doping level was increased up to 1.0 wt.%, it decreased. Also, the E_b value decreased after the Co_3O_4 doping amount was increased up to 1.5 wt.%. The decrease of these E_b can be clarified by the increase of the average grain size since both are correlated [46]. The decrease of leakage current density (J_L) at 0.5 wt.% Co_3O_4 is due to the electrons which come from the grain are trapped by the defects or dopants at the grain boundary. Therefore, the high density of samples doped with Co_3O_4 enhanced the varistor performance by restricting the current flow using high resistance and reduced the leakage current density. By increasing the Co_3O_4 doping amount up to 1.5 wt.%, the J_L value was increased due to the presence of multiple defects at the grain boundary. The state also deteriorates the surge absorption capabilities by decreasing the number of active grain boundary region [47]. The nonlinear electrical properties are related to the Schottky barrier height at the grain boundary. Therefore, the increase of α value signifies a higher barrier height and consequently reduced the leakage current density of the varistor.

4. Conclusions

In conclusion, Pr-doped ZnO-BaTiO₃ and Co-doped ZnO-BaTiO₃ varistor ceramics were fabricated via a solid-state reaction method. The effects of different Pr_6O_{11} and Co_3O_4 dopants compositions on the characteristics of ZnO-BaTiO₃ based varistor ceramics were investigated. SEM images of Pr-doped ZnO-BaTiO₃ and Co-doped ZnO-BaTiO₃ with different contents shows that the microstructure was mostly contained a particle in the form of BaTiO₃-Pr rich and BaTiO₃-Co rich phase. The results indicate that the additive was well incorporated into ZnO grain and its interface state by segregating the Pr and Co ions near the grain boundaries and triple point junctions. The EDS analysis confirmed the existence of Ba, Ti, Pr, and Co in the ZnO structure. The formation of ZnO, BaTiO₃, Pr_6O_{11} and Co_3O_4 phases in the prepared samples were shown by XRD analysis. The diffraction peak position of Pr-doped ZnO-BaTiO₃ and Co-doped ZnO-BaTiO₃ shifts towards a smaller-

angle side due to the substitution of Pr^{3+} and Co^{2+} into the ZnO lattice. The addition of Pr_6O_{11} and Co_3O_4 significantly influences the nonlinear coefficient. However, for both dopants, the effects were diverse. With the addition of Pr_6O_{11} , the nonlinear coefficient value decreased and caused a reduction of the barrier height due to the variety of defects. The excessive amount has lowered the potential barriers, thereby causing the degradation of the active grain boundary. In contrast, the addition of Co_3O_4 enhanced the barrier height by providing charge carriers to the grain boundary. The excessive amount of Co_3O_4 dopant could be contributed to the oxygen vacancies at the grain boundary and lowered the potential barriers, thereby causing the degradation of the active grain boundary. The leakage current density and varistor breakdown voltage were lower for Co_3O_4 than Pr_6O_{11} . Therefore, for the application of low-voltage varistors, the Co_3O_4 dopant is proven to improve the nonlinear electrical properties better than the Pr_6O_{11} . The use of Pr_6O_{11} and Co_3O_4 as additives in ZnO-BaTiO_3 based varistor ceramics has synergistic effects in improving the microstructure homogeneity and enhances their electrical properties for the application in surge arresters.

Author Contributions: Conceptualization, methodology, software, formal analysis, visualization and investigation, M.S.S., W.M.I.W.M.K., N.Q.A.I., W.R.W.A., S.K. and M.F.M.F.; validation, W.R.W.A. and K.A.M.; resources, M.S.M.G., N.K.S., W.R.W.A., K.A.M. and S.K.; data curation, M.S.S., N.K.S. and N.Q.A.I.; writing—original draft preparation, review and editing, M.S.S. and M.S.M.G.; supervision, project administration and funding acquisition, M.S.M.G., S.K., K.A.M. and M.H.M.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Ministry of Higher Education Malaysia and Universiti Malaysia Terengganu under the research project through Talent and Publication Enhancement-Research Grant (TAPE-RG/2018/Vot. No. 55139).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sharing is not applicable to this article.

Acknowledgments: The authors extend an appreciation for the support of analytical analysis and testing centre of Universiti Malaysia Terengganu and Universiti Putra Malaysia.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Cao, W.; Xie, X.; Wang, Y.; Chen, M.; Qiao, Y.; Wang, P.; Zhang, Y.; Liu, J. Effect of Pr₆O₁₁ doping on the microstructure and electrical properties of ZnO varistors. *Ceram. Int.* **2019**, *45*, 24777–24783. [CrossRef]
- 2. Shreevats, P.; Devendra, K.; Om, P. Electrical impedance spectroscopy and structural characterization of liquid-phase sintered ZnO–V₂O₅–Nb₂O₅ varistor ceramics doped with MnO. *Ceram. Int.* **2016**, *42*, 9686–9696.
- 3. Zhao, M.; Wang, Y.-H.; Sun, T.-T.; Song, H.-H. Effect of bismuth and vanadium as the varistor forming element in ZnO-based ceramics. *J. Mater. Sci. Mater. Electron.* 2020, *31*, 8206–8211. [CrossRef]
- Ortíz-Trejo, F.; Trejo-Valdez, M.; Campos-López, J.P.; Castro-Chacón, J.H.; Torres-Torres, C. Multipath Data Storage by Third-Order Nonlinear Optical Properties in Zinc Oxide Nanostructures. *Appl. Sci.* 2020, 10, 5688. [CrossRef]
- Tonkoshkur, A.S.; Glot, A.B.; Ivanchenko, A.V. Percolation effects in dc degradation of ZnO varistors. J. Adv. Dielectr. 2015, 5, 1–8. [CrossRef]
- 6. Fan, J.; Poosimma, P.; Freer, R. Phase development in ZnO varistors. Adv. Appl. Ceram. 2015, 114, 14–17. [CrossRef]
- Anas, S.; Mangalaraja, R.; Poothayal, M.; Shukla, S.K.; Ananthakumar, S. Direct synthesis of varistor-grade doped nanocrystalline ZnO and its densification through a step-sintering technique. *Acta Mater.* 2007, 55, 5792–5801. [CrossRef]
- 8. Higashi, Y.; Koga, E. Barrier formation of single junctions with oxidation in SrCoO₃-doped ZnO varistors sintered in a reducing atmosphere. *J. Ceram. Soc. Jpn.* **2019**, *127*, 912–917. [CrossRef]
- Viswanath, N.; Pandey, S.; Kumar, D. Effect of sintering temperature on electrical characteristics of ZnO-0.5 mol% V₂O₅-2 mol% MnO varistors. *Adv. Mater. Sci. Res.* 2016, 1, 14–19.
- Li, Z.; Yang, Z.; Du, B. Surface Charge Transport Characteristics of ZnO/Silicone Rubber Composites Under Impulse Superimposed on DC Voltage. *IEEE Access* 2018, 7, 3008–3017. [CrossRef]
- 11. Clarke, D.R. Varistor ceramics. J. Am. Ceram. Soc. 1999, 82, 485–502. [CrossRef]

- 12. Godavarti, U.; Mote, V.D.; Dasari, M. Role of cobalt doping on the electrical conductivity of ZnO nanoparticles. *J. Asian Ceram. Soc.* 2017, *5*, 391–396. [CrossRef]
- 13. Akinnifesi, J.; Akinwunmi, O. Fabrication and Electrical Characterization of Pb²⁺-Mn²⁺-Zinc oxide based varistor ceramics. *Int. J. Innov. Res. Technol. Sci.* **2017**, *5*, 1–5.
- 14. Huang, Y.; Guo, M.; Li, J. Multiscale defect responses in understanding degradation in zinc oxide varistor ceramics. *Ceram. Int.* **2020**, *42*, 22134–22139. [CrossRef]
- 15. Lao, Y.; Kuo, S.; Tuan, W. Influence of ball milling on the sintering behaviour of ZnO powder. *Ceram. Int.* 2009, 35, 1317–1320. [CrossRef]
- Daneu, N.; Bernik, S.; Rečnik, A. Inversion boundary induced grain growth in ZnO ceramics: From atomic-scale investigations to microstructural engineering. J. Phys. Conf. Ser. 2011, 326, 012003. [CrossRef]
- 17. Muhammad, Q.K.; Waqar, M.; Rafiq, M.A.; Rafiq, M.N.; Usman, M.; Anwar, M.S. Structural, dielectric, and impedance study of ZnO-doped barium zirconium titanate (BZT) ceramics. *J. Mater. Sci.* **2016**, *51*, 10048–10058. [CrossRef]
- Kharchouche, F.; Belkhiat, S.; Belkhiat, D.E.C. Non-linear coefficient of BaTiO₃-doped ZnO varistor. *IET Sci. Meas. Technol.* 2013, 7, 326–333. [CrossRef]
- 19. Wang, M.-h.; Yao, C.; Zhang, N.-F. Degradation characteristics of low-voltage ZnO varistor manufactured by chemical coprecipitation processing. *J. Mater. Process.* **2008**, 202, 406–411. [CrossRef]
- Shaifudin, M.S.; Ghazali, M.S.M.; Abdullah, W.R.W.; Kassim, S.; Kamaruzzaman, W.M.I.W.M. Microstructure and Electrical Properties of Low-Voltage Barium Titanate Doped Zinc Oxide Varistor Ceramics. J. Recent Technol. 2019, 8, 2713–2718.
- 21. Pillai, S.C.; Kelly, J.M.; Ramesh, R.; McCormack, D.E. Advances in the synthesis of ZnO nanomaterials for varistor devices. *J. Mater. Chem.* **2013**, *1*, 3268–3281. [CrossRef]
- 22. Hembram, K.; Rao, T.; Ramakrishna, M.; Srinivasa, R.; Kulkarni, A. A novel economical grain boundary engineered ultra-high performance ZnO varistor with lesser dopants. *J. Eur. Ceram. Soc.* **2018**, *38*, 5021–5029. [CrossRef]
- 23. Hembram, K.; Sivaprahasam, D.; Rao, T. Combustion synthesis of doped nanocrystalline ZnO powders for varistors applications. *J. Eur. Ceram.* **2011**, *31*, 1905–1913. [CrossRef]
- 24. Zhu, J.F.; Gao, J.Q.; Wang, F.; Chen, P. Influence of Pr₆O₁₁ on the characteristics and microstructure of zinc varistors. *Key Eng. Mater.* **2008**, *368–372*, 500–502. [CrossRef]
- 25. Lakin, I.; Zakaria, A.; Abdollah, Y.; Umaru, D. Effect of sintering temperature on microstructure and electrical properties of ZnO+ CaMnO₃ ceramics used in low voltage varistors. *Dig. J. Nanomater. Bios.* **2015**, *10*, 189–197.
- 26. Rečnik, A.; Bernik, S.; Daneu, N. Microstructural engineering of ZnO-based varistor ceramics. J. Mater. Sci. 2012, 47, 1655–1668. [CrossRef]
- 27. Wurst, J.; Nelson, J. Lineal intercept technique for measuring grain size in two-phase polycrystalline ceramics. *J. Am. Ceram. Soc.* **1972**, 55, 109. [CrossRef]
- Xu, D.; Shi, L.; Wu, Z.; Zhong, Q.; Wu, X. Microstructure and electrical properties of ZnO-Bi₂O₃-based varistor ceramics by different sintering processes. J. Eur. Ceram. 2009, 29, 1789–1794. [CrossRef]
- Abdullah, W.; Rafizah, W.; Zakaria, A.; Ghazali, M.S.M. Synthesis Mechanism of Low-Voltage Praseodymium Oxide doped Zinc Oxide Varistor Ceramics Prepared Through Modified Citrate Gel Coating. *Int. J. Mol. Sci.* 2012, 13, 5278–5289. [CrossRef]
- Ma, S.; Xu, Z.; Chu, R.; Hao, J.; Cheng, L.; Li, G. Low-temperature sintering and electrical properties of Co-doped ZnO varistors. J. Mater. Sci. Mater. Electron. 2014, 25, 3878–3884. [CrossRef]
- 31. Wang, M.-H.; Zhao, Z.-Y.; Liu, T.-T. Synthesis of Pr-doped ZnO nanoparticles by sol–gel method and varistor properties study. *J. Alloys Compd.* **2015**, *621*, 220–224. [CrossRef]
- 32. Liu, L.; Ge, M.; Liu, H.; Guo, C.; Wang, Y.; Zhou, Z. Controlled synthesis of ZnO with adjustable morphologies from nanosheets to microspheres. *Colloid Surf. A* 2009, 348, 124–129. [CrossRef]
- 33. Selim, F.; Gupta, T.; Hower, P.; Carlson, W.G. Low voltage ZnO varistor: Device process and defect model. *J. Appl. Phys.* **1980**, *51*, 765–768. [CrossRef]
- 34. Alim, M.A.; Li, S.; Liu, F.; Cheng, P. Electrical barriers in the ZnO varistor grain boundaries. *Phys. Status Solidi A* **2006**, 203, 410–427. [CrossRef]
- 35. Nahm, C.-W. Al doping effect on electrical and dielectric aging behavior against impulse surge in ZPCCYA-based varistors. *Mater. Sci. Eng. B* 2010, *170*, 123–128. [CrossRef]
- 36. Nahm, C.-W. Electrical behavior against current impulse in ZnO–Pr6O11-based varistor ceramics with terbium addition. *Ceram. Int.* **2010**, *36*, 1495–1501. [CrossRef]
- 37. Sendi, R.K. Effects of Different Compositions from Magnetic and Nonmagnetic Dopants on Structural and Electrical Properties of ZnO Nanoparticles-based Varistor Ceramics. *Solid State Sci.* **2018**, *77*, 54–61. [CrossRef]
- Furtado, J.G.D.M.; Saléh, L.A.; Serra, E.T.; Oliveira, G.S.G.D.; Nóbrega, M.C.D.S. Microstructural evaluation of rare-earth-zinc oxide-based varistor ceramics. *Mater. Res.* 2005, *8*, 425–429. [CrossRef]
- 39. Leite, E.; Varela, J.A.; Longo, E. A new interpretation for the degradation phenomenon of ZnO varistors. *J. Mater. Sci.* **1992**, 27, 5325–5329. [CrossRef]
- 40. Lei, M.; Li, S.; Jiao, X.; Li, J.; Alim, M.A. The influence of CeO₂ on the microstructure and electrical behaviour of ZnO–Bi₂O₃ based varistors. *J. Phys. D Appl. Phys.* **2004**, *37*, 804. [CrossRef]
- 41. Kutty, T.; Philip, S. Low voltage varistors based on SrTiO₃ ceramics. Mat. Sci. Eng. B 1995, 33, 58–66. [CrossRef]

- 42. Ke, L.; Hu, M.; Ma, X. Preparation of Ultrahigh Potential Gradient of ZnO Varistors by Rare-Earth Doping and Low-Temperature Sintering. *J. Mater.* **2013**, 2013, 726314. [CrossRef]
- 43. Dong, X.; Cheng, X.-N.; Yan, X.-H.; Xu, H.-X.; Shi, L.-Y. Sintering process as relevant parameter for Bi₂O₃ vaporization from ZnO-Bi₂O₃-based varistor ceramics. *Trans. Nonferr. Met. Soc.* **2009**, *19*, 1526–1532.
- 44. Norailiana, A.; Azmi, B.; Ismayadi, I.; Hashim, M.; Ibrahim, I.; Nazlan, R.; Mohd Idris, F. Parallel development of microstructure and electrical properties in doped-zinc oxide. *J. Mater. Sci. Surf. Eng.* **2017**, *5*, 528–532.
- 45. Hamdelou, S.; Guergouri, K.; Arab, L. The effect of the starting powders particle size on the electrical properties of sintered Co doped ZnO varistors. *Appl. Nanosci.* 2015, *5*, 817–825. [CrossRef]
- 46. Onreabroy, W.; Sirikulrat, N. Effects of cobalt doping on nonlinearity of zinc oxide. Mat. Sci. Eng. B 2006, 130, 108–113. [CrossRef]
- 47. Wong, J. Microstructure and phase transformation in a highly non–ohmic metal oxide varistor ceramic. *J. Appl. Phys.* **1975**, *46*, 1653–1659. [CrossRef]