

Effect of La_2O_3 Dopant on Microstructure and Electrical Nonlinearity of ZnO-CaMnO_3 Based Varistor Ceramics

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Abstract. In this research, zinc oxide based varistor are produce by using citrate-gel method compared to conventional solid-state method. The zinc oxide based varistor are fabricate using three different wt.% of $\text{ZnO-CaMnO}_3\text{-La}_2\text{O}_3$ and divided into three system which are 80 mol% $\text{ZnO} + 20 \text{ mol\% CaMnO}_3$, 79.5 mol% $\text{ZnO} + 20 \text{ mol\% CaMnO}_3 + 0.5 \text{ mol\% La}_2\text{O}_3$ and 78.5 mol% $\text{ZnO} + 20 \text{ mol\% CaMnO}_3 + 1.5 \text{ mol\% La}_2\text{O}_3$. $\text{ZnO-CaMnO}_3\text{-La}_2\text{O}_3$ compound experienced pre-sintering at 500 °C for 2 hours sintering time. In the sintering condition, sintering temperatures are manipulated, which are varied at 1100, 1200 and 1300 °C while, the sintering time is setting at 4.5 hours. X-ray diffraction patterns show this compound is high in crystallinity. The surface morphology with the average grains size between 2.0 ~ 10.0 μm was observed by Scanning Electron Microscopy. Energy Dispersive Spectroscopy confirmed that distribution of element are homogenous with high purity. Density of the sample product is range between 5.0 ~ 5.6 g cm^{-3} . J - E characteristic shows the value of non-linearity coefficient in the range of 1.10 to 4.35.

1. Introduction

Zinc oxide (ZnO) is used widely in cosmetics, paint, and textile industries as well as in semiconductor electronic industries [1-4]. In electrical and electronic industries, ZnO based varistor is most-likely used as an electronic component in automobile electronics and also in semiconductor electronic. They are fabricated with different types of dopants such as Bi_2O_3 , Co_3O_4 , MnO_2 , Sb_2O_3 , TiO_2 and CaMnO_3 [5-12]. Recent studies reported by Vijayanandhini and Kutty [13] CaMnO_3 exhibit high nonlinearity coefficient up to 380 and it is remarkably for low-voltage application. Its unique microstructure that can be tailored for application as low, moderate or high-voltage varistors by adding different dopants and liable for nonlinear current-voltage (I - V) characteristics of the device [2, 14] and thus, is suitable used



to protect electrical appliances over-voltage magnitude [15]. *I-V* studies have been colossally investigated by previous researchers in order to improve the sensitivity and nonlinear coefficient of ZnO varistor [7, 16].

In this study, rare earth element-lanthanum (La) used as dopant in ZnO based varistor together with calcium manganate. By doping La, it is expected to increase the nonlinear coefficient (α) of varistor.

2. Materials & Method

Samples were prepared by citrate gel processing based on nominal composition of (80-x) mol% ZnO + 20 mol% CaMnO_3 + x mol% La_2O_3 (x = 0, 0.5 & 1.5). Preparation nano powders of CaMnO_3 and La_2O_3 via citrate gel method [17] were start with raw material reagent grade of calcium acetate anhydrous, manganese acetate anhydrous, lanthanum (III) acetate and citric acid. The mixture was place in a beaker and then mixed with ZnO micro-powder and heat stirred for a couple of hours with deionized water to dissolve it. The solution was heated and dried. The complex compound was then granulated and pressed into discs of 10 mm in diameter and 1 mm in thickness at a pressure of 2 tons and sintered at 900, 950 and 1000 °C for 1 and 2 hours sintering time with slow heating and cooling rate of 2.66 °C min⁻¹ for sufficient oxygen supply. Silver paste was coated on both faces about 5 mm in diameter of the sample and was fired at 550 °C for 10 minutes soaking time to prepare the Ohmic contact on the both surfaces.

XRD measurement was performed by using Rigaku MiniFlex II in order to analyze and determines the crystalline phase and phase substitution of the sintered compound with different concentration of dopant. The samples scanned directly at 2θ angles between 50 and 80° with X-rays of 1.5406 Å wavelength generated by a CuK_α source. Density of the sintered samples was measure using Electronic Densimeter MDS-300. The surface of samples was ground and polished with SiC paper and 1 micron diamond suspension; respectively, until change into a mirror-like surface. The polished mirror-like samples were thermally etched in order to reveal fine microstructure morphology and observed then by SEM (JEOL JSM-6400).

The *J-E* characteristic of the varistor ceramics were evaluates by using a source measure unit (Keithley 2400). The important parameter like varistor voltage ($E_{1\text{mA}}$) was measured at a current density of 1.0 mA/cm² and the leakage current density (J_L) was measured at $0.80E_{1\text{mA}}$. Moreover, the nonlinear coefficient, α , was calculated from the following Eq. 1 [18]:

$$\alpha = \frac{\log J_2 - \log J_1}{\log E_2 - \log E} \quad (1)$$

where $J_1 = 1 \text{ mA/cm}^2$, $J_2 = 10 \text{ mA/cm}^2$, and E_1 and E_2 are the voltages corresponding to J_1 and J_2 ; respectively.

3. Results and Discussion

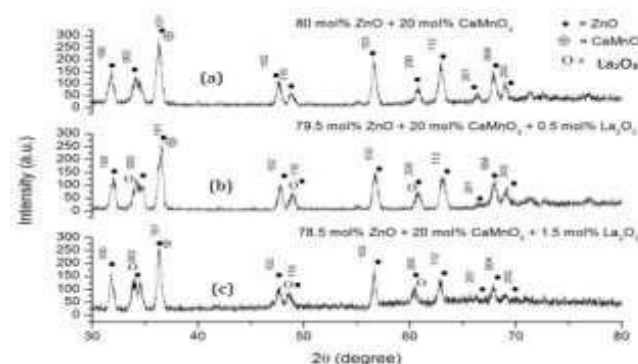


Figure 1. XRD patterns at 1300 °C sintering temperature at 4.5 hours sintering time of (a) without La doping, (b) 0.5 mol% La and (c) 1.5 mol% La

Figure 1 show the XRD patterns after sintering with temperature 1300 °C and soaking time 4.5 hours. Based on the Figure 1, it can be seen that ZnO characteristic which is hexagonal closed pack structure are remain based on ICSD code: 067454 [11] and all peaks was well observed. For Figure 1(a), 80 mol% ZnO + 20 mol% CaMnO_3 ceramics was fabricated which is high percentage of ZnO existed and the peaks revealed clearly and Figure 1(b), the sample with 79.5 mol% ZnO + 20 mol% CaMnO_3 + 0.5 mol% La_2O_3 was observed and the present of Lathanum was detected. Same trend has been seen in Figure 1(c), 78.5 mol% ZnO + 20 mol% CaMnO_3 + 1.5 mol% La_2O_3 , the present of lanthanum was observed.

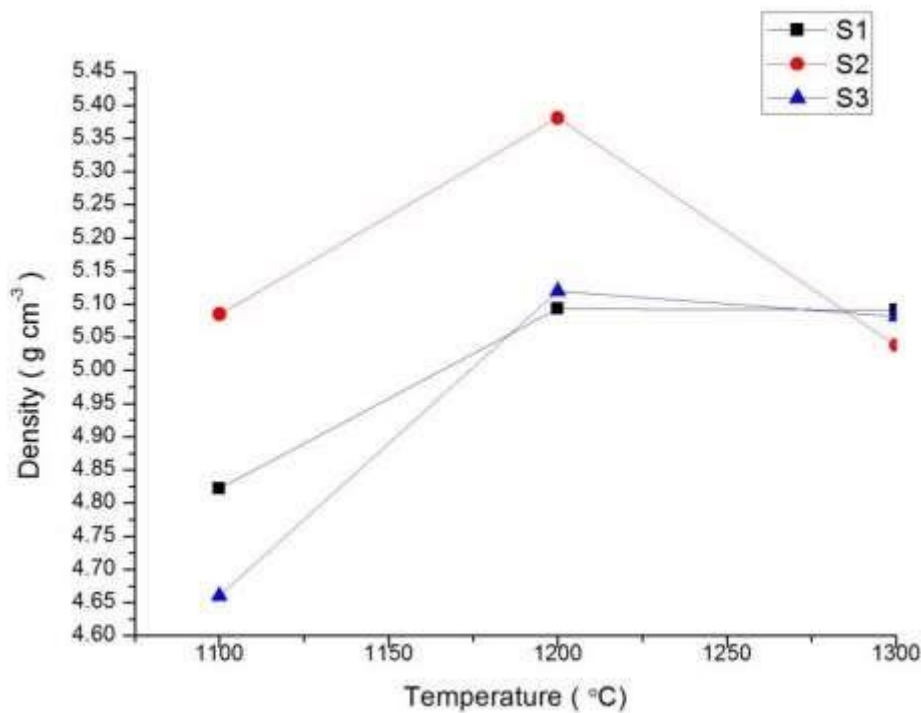


Figure 2. Density of the pellets for S1 (without La doping), S2 (0.5 mol% La) and S3 (1.5 mol% La)

Figure 2 shows the graph density of the sample produced. The higher density were obtain from pellet of S2 with 79.5 mol% ZnO + 20 mol% CaMnO_3 + 0.5 mol% La_2O_3 , however, at higher temperature, the density dropped dramatically probably due to the trapping of pores and the limited of pores elimination [19]. As the temperature increases up to 1300 °C, the density increases as a result in the elimination of pores [20], whereas the further increase of temperature did not affect the density, which saturated at 5.10 g cm^{-3} . At 1200 °C with 4.5 hours soaking time, the density projected the highest value. It can be seen that the density of produced varistor are very similar with the ZnO varistor in commercial which is in range between 5.0 to 5.3 g cm^{-3} [21].

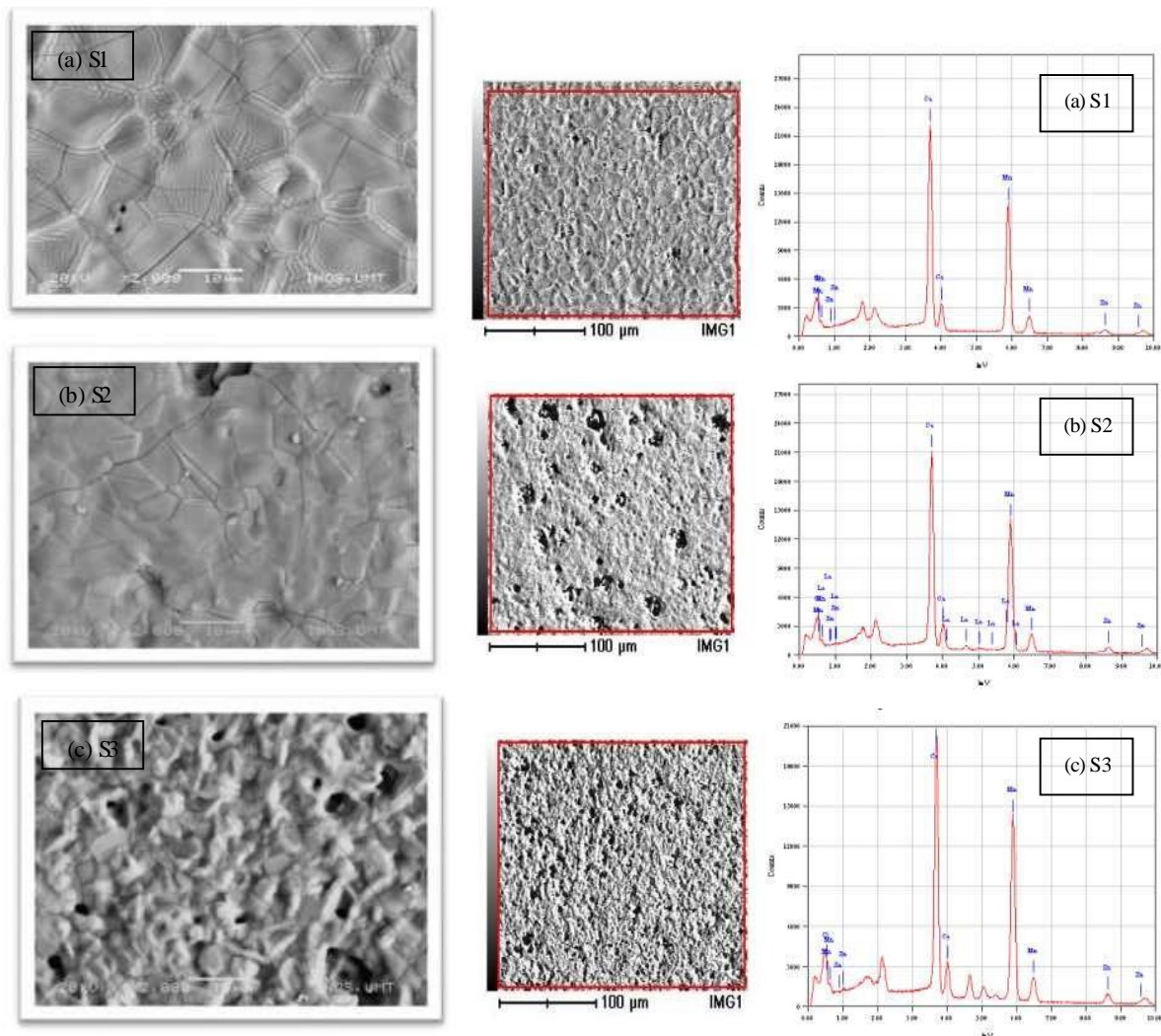


Figure 3. SEM micrographs of sintered varistor ceramics at 1300 °C for 4.5 hours of (a) without La doping, (b) 0.5 mol% La and (c) 1.5 mol% La

Figure 4. EDX spectra of (a) without La doping, (b) 0.5 mol% La and (c) 1.5 mol% La

Based on SEM micrographs in Figure 3, it is clearly observed that the average grain size decreases from 16, 8 and 3 μm as the concentration of La_2O_3 increases, respectively, which is in agreement with the reported by Nahm (2014) [22]. Other than that, as the La_2O_3 concentration increases, the intergranular phase gradually becomes more concentrated at the nodal points. It is believed that, La ion segregated at grain boundaries due to the difference of ionic radii which is La radii (1.3 Å) is larger as compared to Zn radii (0.74 Å) [23]. It is proved by EDX, there are no evidence of La coexisted in Figure 4(a), meanwhile, La element are traced in the sample S2 and S3 as shows in Figure 4(b) and Figure 4(c).

Table 1. The electrical nonlinearity coefficient (α) of the varistor

System	Sintering Tmax (°C) / Soaking time (hours)	Electrical non-linearity (α)
1	1100/4.5	1.10
2	1100/4.5	-
3	1100/4.5	-
1	1200/4.5	1.44
2	1200/4.5	-
3	1200/4.5	3.68
1	1300/4.5	4.35
2	1300/4.5	1.47
3	1300/4.5	2.19

*The non-linear coefficient (α) was calculated from equation, $\alpha = \log J_2 - \log J_1 / \log E_2 - \log E_1$

Table 1 represents the electrical nonlinearity coefficient (α) of ZnO varistor doped with $\text{CaMnO}_3\text{La}_2\text{O}_3$ at temperature 1100, 1200 and 1300 °C for S1 (without La doping), S2 (0.5 mol% La doping) and S3 (1.5 mol% La doping). It can be seen that α initially increases and then decreases with the increases of La_2O_3 concentration. The decrement of α is due to the existence of porosity at higher dopant concentration as observed in Figure 3. The high value of α was obtained from the sample S1 and S3 are 4.35 and 3.68 at 1300 and 1200 °C; respectively. This indicates the possible sintering temperature for doped sample is 1200 °C and it is enough to achieve high α as compared to other sintering temperatures. Other than that, at 1200 °C sintering temperatures gave positive effect for La doping towards density and hence, enhance the α value.

4. Conclusion

The sample with La doping exhibit low porosity (high density) at 1200 °C result in the elimination of pores. The highest α value (3.68) with high density was achieved with La doping at 1200 °C sintering temperature.

5. References

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