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PRELIMINARY CHARACTERISTIC OF ELECTRICAL NON-LINEARITY CO DOPED CMO-ZNO BASED VARISTOR CERAMIC

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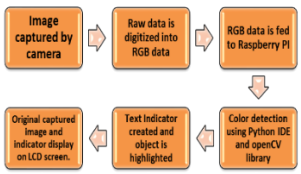
Graphical abstract



Abstract

Zinc oxide based varistor are widely used as circuit protective devices by literally absorbs these dangerous surge and spikes or grounding this unwanted magnitudes. In this research, zinc oxide is added with 20 mol% calcium manganite ($CaMnO_3$) as an additive and Cobalt oxide (CoO) as doping material. Citrate-gel method is used as fabrication method compared to conventional solid-state method. This compound (ZnO-$CaMnO_3$-CoO) undergoes pre-sintering at 500 °C for 2 hours. In the sintering process, sintering temperature at 1300 °C, while the sintering time are setting at 1.5 hours. X-ray diffraction (XRD) patterns shows the components and phases of the compounds. The change of functional group was observed by Furrier transform infra-red (FTIR). I-V characteristic shows the value of nonlinear coefficient in the range of 1.0-2.0.

Keywords: Zinc oxide, varistor; citrate-gel

Abstrak

Varistor berasaskan zink oksida digunakan secara meluas sebagai litar peranti perlindungan yang berperanan menyerap lonjakan berbahaya dan pancang atau pembumian magnitud yang tidak diingini. Dalam kajian ini, zink oksida ditambah dengan 20 % mol $CaMnO_3$ sebagai bahan tambahan dan oksida kobalt sebagai bahan dop. Kaedah Citrate -gel digunakan sebagai kaedah fabrikasi berbanding kaedah keadaan pepejal konvensional. Kompaun ini (ZnO - $CaMnO_3$ -CoO) mengalami pra- pensinteran pada 500 °C selama 2 jam. Dalam proses pensinteran, suhu pensinteran ditetapkan pada 1300 °C, manakala masa pensinteran ditetapkan selama 1.5 jam. Keputusan pembelauan sinar-X (XRD) menunjukkan komponen dan fasa yang terdapat dalam sebatian. Perubahan kumpulan berfungsi diperhatikan menggunakan *Furrier transform infra-red (FTIR)*. Pengujian IV menunjukkan nilai pekali linear di dalam julat 1.0-2.0.

Kata kunci: Zinc oksida, varistor; citrate-gel

1.0 INTRODUCTION

Wildly used of ZnO in multiple field research area make it become as promising semiconductor material especially in solar cells [1, 2], UV laser, chemical and biological sensor, photocatalyst [3] and so do varistor [4-6]. ZnO is an important and well as n-type semiconductor with a wide direct band gap (3.37 eV)

and large excitation binding energy (60 meV). Specialty possessing high nonlinear properties of current voltage characteristic make ZnO extensively use as surge protectors in power systems and electronic circuit. This ZnO based varistor literally absorb the transient voltage [7, 8].

Up to date, the varistor research are focusing in producing the low voltage varistor. Introduce calcium manganite (CaMnO) as additive material has been reported by [9]. Intensive study of additive CaMnO to produce low voltage varistor by [9, 10] shows a significant result. Beside the $CaMnO_3$, praseodymium oxide (PrO)also shows a potential doping material in order to produced low voltage varistor [11-13].

In the other hand, doping elements of rare-earth also shows a potential to be used as doping low voltage varistor [14]. Effect doping of Erbium (Er), lanthanum (La) and Cobalt (Co) also reported as suitable doping material in varistor ceramics application.

In this work, the combination of $CaMnO_3$ as additive and Co as doping material in ZnO based varistor ceramics is investigate. As a first step on revealed the potential of this combination, a preliminary study of electrical non-linearity are performed. This varistor ceramis are synthesis by sol-gel method and characterize by XRD, FTIR and IV source measure unit.

2.0 EXPERIMENTAL

2.1 Materials

Raw materials were prepared according to the composition of 78.5 mol % ZnO + 20.0 mol % $CaMnO_3$ + 1.5 mol % CoO. Reagent Calcium acetate monohydrate with the purity of 99.0% (Sigma Alderich), Manganese (II) acetate – 4 – hydrate (Hamburg Chemical) and Cobalt (II) acetate (Fisher Chemicals) was used as metal salt precursor and citric acid anhydrous ($C_2H_6O_8$) with the purity of 99.5% (Alfa Aesar) was selected as the complexing agent. ZnO powder with the particle size of less than 1 µm and 99.9% purity (Sigma Aldrich) was selected as the host material.

2.2 Samples Preparation

Fully coating of Ca-Mn-Co citrate gel with ZnO particles was produced by adding ZnO powder into bath solution that comprising Ca-Mn-Co acetate and citric acid in medium of deionized water. This gel moisture were continues stirr for 1 hour retention time at 60 to 80 °C. The molar ratio of calcium acetate/ manganese (II) acetate/ cobalt(II) acetate to citric acid anhydrous was fixed at 1:2 and vigorous stirring was applied to improve the contact.

Uniform coating of Ca-Mn-Co citrate gel with ZnO particles was produced by immersing ZnO powder in bath solution containing citric acid and Ca-Mn-Co acetate in deionized water medium for 1 hour retention time at 70–80 °C. Then, this mixtures dried at 120 °C for 19 h to produce powder with particle size of less than 100 µm. The dried powder was then calcined at 500 °C for 4 h at heating rate of 3 °C/min. The calcined powder comprising 1.75 wt.% polyvinyl alcohol binder was pressed into pellets with 13.0 mm diameter and 1.3 mm thickness using Specac Hydraulic Press machine. The pellet was finally sintered at 1300 °C for 1.5 h in a box furnace (CMTS Model HTS 1400).

2.3 Characterizations

2.3.1 XRD

The phase structure of ZnO-$CaMnO_3$–CoO compounds before and after sintering were measured using Rigaku Mini Flex II Diffractometer with Cu K_α radiation. A small amount sample (compound sample) was spread uniformly on the sample holder, 2θ scan were carried out over the diffraction angles from 5° to 80° at the speed of 2.00°/min.

2.3.2 FTIR

Functional group of compound elements in stage after calcined and after sintering were identified using IRTracer-100 Fourier Transform Infrared Spectrophotometer (SHIMADZU). 1:7 ratio were mixed and prepared between samples compound to KBr. The compressed transparence film (sample compound) exposed to infrared penetration starting wavelength of 400 cm^{-1} until the stop wavelength at 4000 cm^{-1}.

2.3.3 I-V Source Measure Unit

Electrical behavior of pelleted sintered sample were measured using a KEITHLEY 4200-SCS Semiconductor Characterization System. 15Wt% and pure silver conductive paint were place on the both side of samples as an electrodes. The nonlinear coefficient (α) was determined from the equation (1),

$$\alpha = \frac{dI/I}{dV/V} = \frac{d(\log I)}{d(\log V)} \approx \frac{\log_{10} I_2 - \log_{10} I_1}{\log_{10} V_2 - \log_{10} V_1} \quad (1)$$

3.0 RESULTS AND DISCUSSION

3.1 XRD

XRD petterns of pure ZnO before and after sintering are shown in Figure 1.

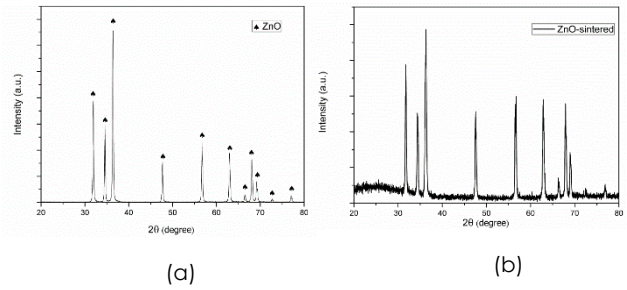


Figure 1 (a) Starting powder ZnO. (b) ZnO after sintered

Figure 1 (a) and (b) shows all diffraction peaks in a good agreement with single phase polycrystalline hexagonal ZnO of wurzite structure according to ICSD code: 067454 [15]. The scattered plot of Figure 1(b) indicated the change of crystallite size or grain size of ZnO after undergoes sintering process at 1300 °C.
The formation of $CaMnO_3$ in the sintered compound ZnO-$CaMnO_3$ observed by the presence of minor peaks as shown in Figure 2.

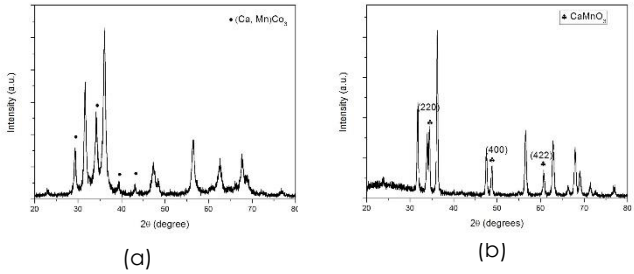


Figure 2 (a) ZnO-$CaMnO_3$–CoO after calcined. (b) ZnO-$CaMnO_3$–CoO after sintered

Figure 2 (a) shows the appeared of manganocalcite ((Ca, Mn)CO_3) peaks. Appeared peeks identified using Crystallographica Search-match and its shows the good match with reference Pdf No: 2-604 and Pdf N0: 2-630. However, after sintered process disappeared of (Ca, Mn)CO_3 peaks suggest carbonate (CO_3) compound released during the sintering process. Throughout the sintering process, (Ca, Mn)CO_3 expected transform to $CaMnO_3$. Transformation result indicated by the appearing minor peaks of $CaMnO_3$ in Figure 2 (b). Figure 2 (b) shows the reveals of hkl plane in perovskite structures $CaMnO_3$ at 34° (2,2,0), 49° (4,0,0) and 61°(4,2,2) shows the good agreements with [16] and [17].

Beside the transformation process, Figure 2 (b) also shows the ZnO-$CaMnO_3$ become highly crystalline. Its obviously can see by decreasing of peaks broadening. The differ peaks broadening illustrated the change of inhomogeneous crystallize size and also microstrain in the compound.

Same phenomena occur in ZnO-$CaMnO_3$–CoO compound between before and after sintered process. Figure 3 shows the XRD result in stages of before and after sintering at 1300°C.

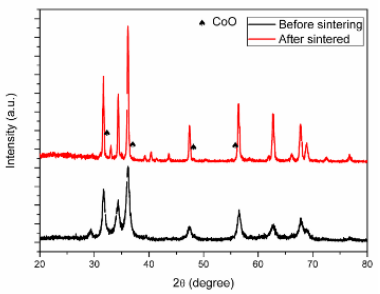


Figure 3 ZnO-$CaMnO_3$–CoO before and after sintered

Identification of CoO peaks are referring to Pdf No: 89.2803 and Pdf No: 75.419. No additional reflections by the CoO were observed in Figure 3 [18]. This result suggests that the dopant is well substituted in the ZnO lattice and the wurtzite structure is not tailored by the addition of Co into the ZnO matrix at least up to the detection level of XRD [19]. This behaviour is possible due to the small difference in radii between divalent, high-spin Co in tetrahedral coordination (0.58 Å) and divalent Zn in tetrahedral coordination (0.60 Å) [20-22]

3.2 FTIR

FTIR analysis in Figure 4 shows the complexation of ZnO-$CaMnO_3$ compound before sintering, while ZnO-$CaMnO_3$–CoO compound before and after sintered.

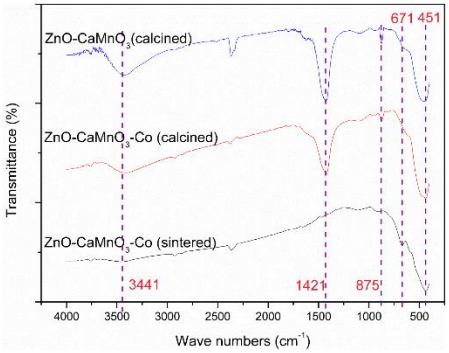


Figure 4 FTIR analysis of compounds

It was found that non sintered compound contained ZnO and Ca, Mn, Co complexes. In phase pure ZnO very intense peak are observed in wavenumber range of 600 cm^{-1} to 400 cm^{-1}. This intense peak also reported by [23-27] in their works. Besides the ZnO bonding, CoO bond also indicated by the appearance week peak at 671 cm^{-1} [28]

The loss of several characteristic peaks in region of 600-2500 cm^{-1} in calcined compound, were associated to removing of carbonyl (C=O), carboxylate and alkyl regarding to high temperature during sintering process [11]. The obviously disappearance of peak at 1421 cm^{-1} and peak 875 cm^{-1}, shows the removing of carbonate group (-CO_3)

[11, 28, 29]. Removing of this –CO_3 aligned with the XRD results in this work.

The boarding peaks in range of 2750-3750 cm^{-1} represents the OH bond with the free ion in 3600-3650 cm^{-1} and H bonded at 3200-3500 cm^{-1} [30, 31]. The removing of OH bond are related with change to highly crystalline of ceramic after sintered as shown by XRD results in Figure 2 and Figure 3.

3.3 I-V

Table 1 shows the value of non-linear coefficient (α) for ZnO-$CaMnO_3$–CoO and ZnO-$CaMnO_3$ compounds.

Table 1 Comparison of α

compound	Non-inear coefficient (α)	Standard error
ZnO-$CaMnO_3$	1.3530	0.00237
ZnO-$CaMnO_3$–CoO	1.6212	0.00256

Additive of $CaMnO_3$ on the compound system shown obviously change regarding to breakdown voltage of this varistor. This $CaMnO_3$ shows an a good agreement with the [9] in order to produces low voltage varistor. The value of α slightly increase by the effect of small doping Co into the samples [32].

4.0 CONCLUSION

Structure and complexation of both ceramics and its precursor powder were examined by XRD shows the change in crystallite size through decreasing of peaks broadening, change of inhomogeneous crystallize size and also microstrain in the compound are suggested occurs. FTIR analysis confirmed the chemical changes during citrate gel reaction and elimination of organic functional groups during calcination or sintering to produce dense ZnO-$CaMnO_3$-CoO ceramics. The nonlinear coefficient (α) ZnO-$CaMnO_3$-CoO ceramics as a function of sintering time was monitored using *I-V* characteristic measurement. The α value increased proportionally with the doping of Co contents. The value slightly increased in the range of 1.0-2.0.

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