

Synthesis, structure and dielectric properties of nanocrystalline $\text{SnO}_2\text{-CoO-Nb}_2\text{O}_5$ varistor doped with Cr_2O_3

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Abstract The effect of Cr_2O_3 on the microstructure and dielectric properties of SnO_2 varistors doped with Nb_2O_5 and CoO was investigated. The density of ceramic samples was calculated and found increases from 6.6819 to 6.8704 g cm^{-3} . It is observed in this figure that, independent of the Cr_2O_3 concentration, no other crystalline phase besides SnO_2 is observed indicating that the system is single phase within the detection precision of the X-ray diffraction. The average crystallite size of the prepared samples using was estimated Scherrer's equation. A scanning electron microscope (SEM) was utilized in order to study the effect of variation of Cr_2O_3 content and its impact on the microstructure and electric properties. The obtained results show that, as Cr_2O_3 concentration increases the dielectric permittivity increases and ac resistivity decreases and then increases and takes it maximum resistivity at 0.5 mol%. The compositional dependence of the dielectric permittivity and ac resistivity has been explained in the light of the SEM micrographs. The obtained results show also that the sample of 0.5 mol% of Cr_2O_3 has highest resistivity and consequently low dielectric loss. So, it can be used in some technological applications such as transformer and inductor cores.

1 Introduction

Varistors are very important materials used as voltage pulse suppressors and over voltage protectors in electronic systems and industrial equipment. SnO_2 ceramics are n-type semi-conductors with native oxygen vacancies compensated by electrons, it similar to ZnO , but it does not densify when sintered without additives. Dense SnO_2 -based ceramics can be achieved by introducing dopants such as CoO and MnO_2 or by hot isostatic pressing [1–3]. SnO_2 has very low densification rate due to its high surface diffusion at low temperatures and high pressure at high temperatures. Also, the addition of CoO and MnO_2 to SnO_2 produces high densification allowing for the development of other electronic devices [4–6]. The nonlinear electrical properties of SnO_2 ceramics and other systems have been reported by many authors [7–12]. On the other hand, the dopants such as Nb_2O_5 and Ta_2O_5 play an important role to enhance the degree of nonlinearity, which can be also described as varistor forming oxide as in the field of ZnO varistors [13, 14].

In SnO_2 ceramic system, Nb increases the electrical conductivity of grains and Co is extremely active in the promotion of Sn oxide densification. Addition of trivalent transition oxides such as Fe_2O_3 , Cr_2O_3 and rare earth oxides improves significantly the electrical characteristics of SnO_2 -based varistors [15–22]. In the previous works, the effects of CuO on the grain size, density, nonlinearity, and dielectric properties of the $\text{SnO}_2\text{-Ni}_2\text{O}_3\text{-Nb}_2\text{O}_5$ and $\text{SnO}_2\text{-Co}_2\text{O}_3\text{-Ta}_2\text{O}_5$ varistors were investigated [23, 24]. They shows that the breakdown electric field of the SnO_2 varistors decreases with increasing CuO content and the nonlinear coefficient possesses a peak value of 31 and the leakage current density has the minimum value of 21 A/cm^2 at 0.2 mol% CuO sintered at 1300 °C. So, 0.2 mol% is

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the optimum CuO content for SnO₂ varistors, and 1300 °C is the best sintering temperature for this system [25].

In the present work we study the effect of Cr₂O₃ concentration on the structure and dielectric properties of nanocrystalline SnO₂ varistors doped with Nb₂O₅ and CoO to determine the optimum concentration of Cr₂O₃ in this varistor for the technological applications.

2 Experimental

Samples with chemical composition ((98.95 - x) SnO₂ + 0.05Nb₂O₅ + CoO + xCr₂O₃) mol% (x = 0, 0.1, 0.3, 0.5), namely C₁, C₂, C₃ and C₄ respectively were prepared using a conventional ceramic method. All the oxides were raw powders of analytical grade. At beginning, the raw powders were mixed in deionized water and ball-milled in polyethylene bottle for 4 h with 0.3 wt% of PVA as binder and highly wear-resistant ZrO₂ balls as grinding media. Subsequently, the obtained slurries were dried at 210 °C. After drying, the powder chunks were crushed into fine powders and sieved. Discs of 2 cm diameter and 0.2 cm thickness were obtained by a semi-dry press method under 70 KN. Finally the samples were sintered at 1300 °C for 2 h. The crystalline phases were identified by (XRD, using Philips apparatus type 170, Cu K_α and λ = 1.5418 Å) through a continuous scan mode with speed of 10°/min. The microstructure was examined on the fresh fracture surfaces of the samples via a scanning electron microscope (SEM Model Quanta 250 FEG) attached with EDAX unit, with accelerating voltage 30 kV, magnification 14× up to 10⁶ and resolution for Gun 1n. To measure the dielectric properties, silver electrodes were placed on both surfaces of the sintered disks. A programmable automatic R–C–L meter PM 6304 was used for the measurements of ac resistance and capacitance. From the measured values of ac conductivity and the dielectric constant at all frequency from 50 Hz to 5 MHz were calculated at constant temperature.

3 Results and discussion

The density and water absorption of the prepared samples were calculated using Archimedes method and the obtained shown in Fig. 1. This figure shows the addition of Cr₂O₃ results in an increase in the bulk density of the samples from 6.6819 to 6.8704 g cm⁻³. The increase of the density may be attributed to the difference between the molecular weight SnO₂ and Cr₂O₃. Also, when Cr³⁺ cation replaces Sn⁺⁴ in the lattice, it acts as an electron acceptor leading to the formation of oxygen vacancies, and consequently increasing the solid state diffusion rate. This diffusion

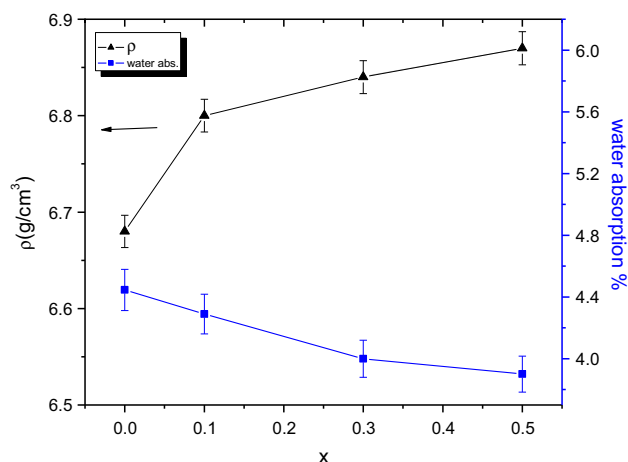


Fig. 1 Density and water absorption as a function of composition

promotes large densification and therefore the density increases. Water absorption of the material is defined as the amount of water absorbed by a material after immersion in water for a certain time. Figure 1 show also that, as density of the samples increases the water absorption decreases due to the decreases in the porosity of the samples. The calculated density of SnO₂ varistor sample was compared with the theoretical density of SnO₂ (6.95 g cm⁻³), this prefigures that SnO₂-based varistors are possible candidates for many dense industrial applications. Figure 2 illustrates the XRD of the as-prepared SnO₂-based varistor ceramics with different amounts of Cr₂O₃ doping. It was observed from the X-ray diffraction pattern that there is no appearance of any secondary phases produced by dopants in all samples except the SnO₂ phase (JCPDS card No. 77-0451). The absence of any diffraction line, Nb₂O₅, CoO and Cr₂O₃ is attributed to the complete dissolution of these dopants oxides in the lattice of SnO₂ and forming solid solution or the existence of Nb₂O₅, CoO and Cr₂O₃ in extremely small

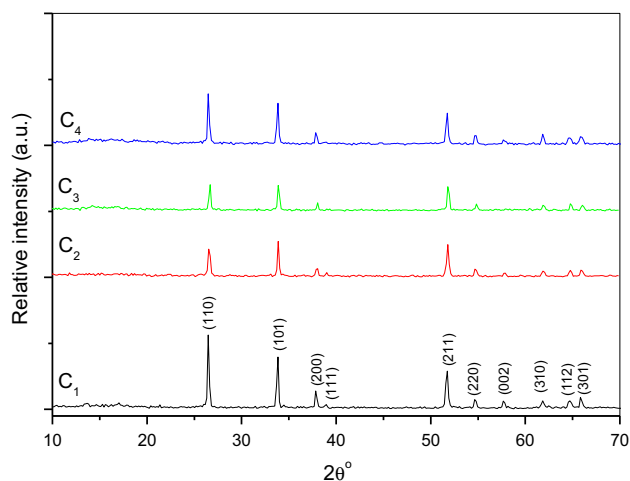


Fig. 2 XRD of all the prepared samples

size that could not be detected by XRD. Similar results were obtained in a previous work [25].

The average crystallite size (t) of the prepared samples was estimated using Scherrer's equation [26],

$$t = (0.9\lambda / \beta \cos \theta) \tag{1}$$

where β is the peak width at half maximum, λ is wavelength and θ corresponds to the peak position. The obtained results shown in Fig. 3 indicate that the average crystallite size increase as Cr_2O_3 mol% increases.

SEM of the samples is shown in Fig. 4. The microstructure of the prepared ceramics consists of SnO_2 grains doped with Cr_2O_3 , CoO and Nb_2O_5 . It reveals that the surfaces of all as prepared samples possess a plain texture with the expected clear grain boundary for ceramic materials. A scanning electron microscope (SEM) was utilized in order to study the effect of variation of Cr_2O_3 content and its impact on the microstructure and electric properties, these microstructures are not greatly different with varistor ceramics doped with Er, Y and Dy oxides as reported previously [27–29]. It is clearly evident that by increasing the dopant level grain size becomes larger that is in good agreement with the calculated values using Scherrer's equation. EDAX of C_4 shows the distribution of Co, Cr and Nb between SnO_2 and SnO_2 grains as shown in Fig. 5.

Figure 6 shows the variation of the dielectric permittivity as a function of frequency for all samples. Obviously, the dielectric constant shows a decreasing trend for all the samples. The decrease is rapid at lower frequency and slower and stable at higher frequency. At low frequency range (50–1 kHz) the decrease of ϵ' value is more pronounced than at higher frequency due to the movement of charge carriers trapped at interfacial region which is caused

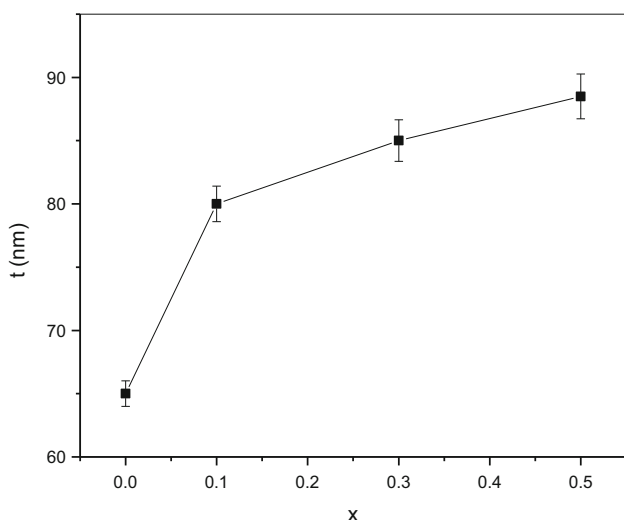


Fig. 3 Variation of the average crystallite size as a function of Cr_2O_3 content (x)

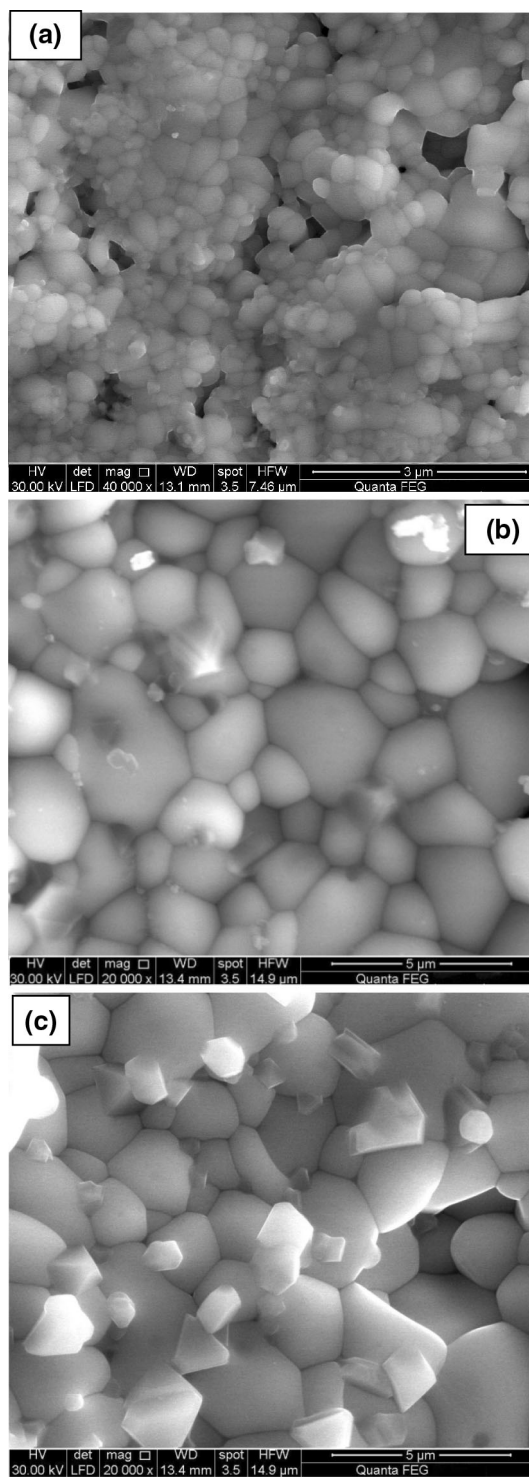


Fig. 4 SEM of the prepared samples **a** C_1 , **b** C_2 and **c** C_4

by inhomogeneous dielectric structure. At high frequency, the dominant mechanism contributing to dielectric constant is the hopping mechanism in their interstice under the influence of alternating field. The frequency of hopping between ions could not follow the frequency of applied

Fig. 5 EDAX of sample C₄ showing the distribution of Nb, Cr and Co between SnO₂ grains

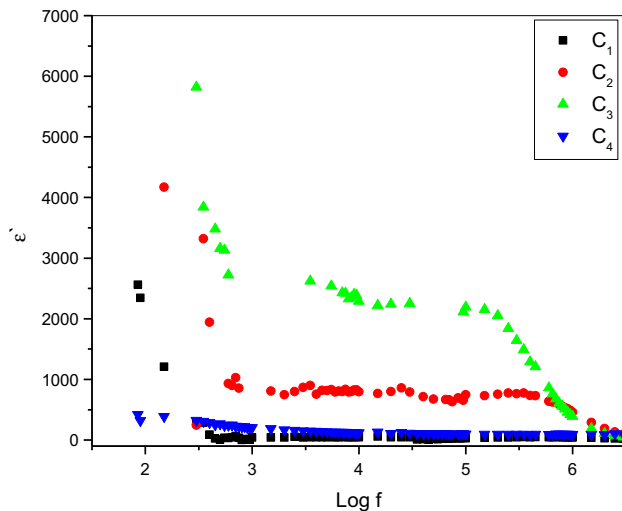
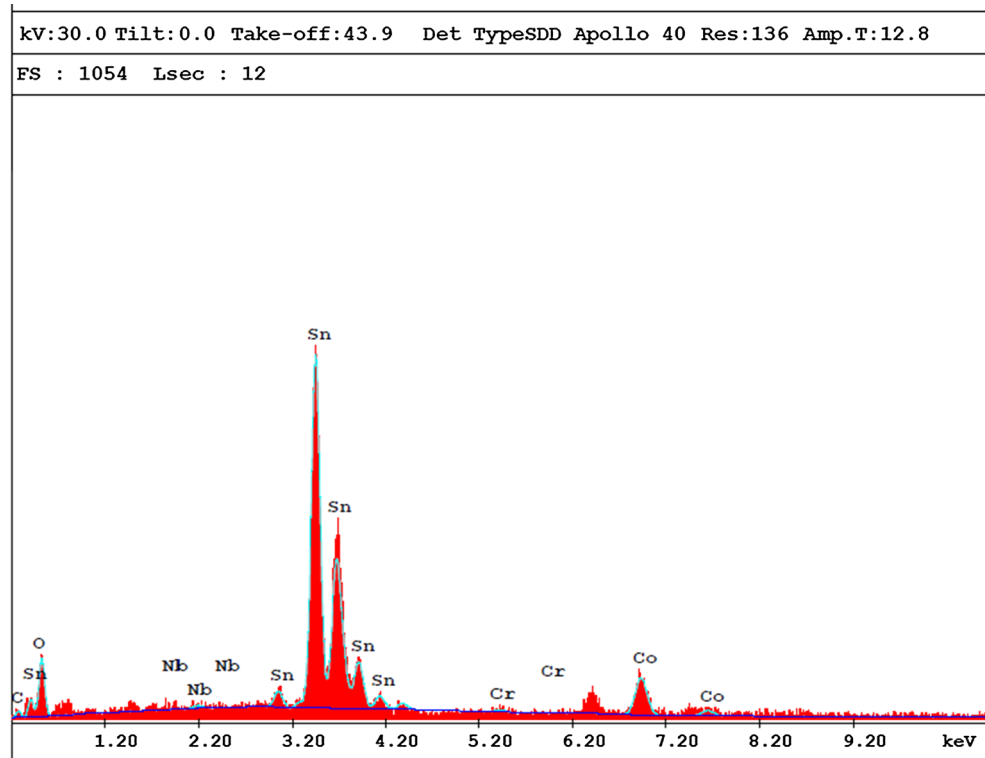


Fig. 6 AC dielectric permittivity as a function of frequency for different mixes

field and hence it lags behind, therefore the values of dielectric constant decreases at higher frequency [30]. Figure 7 shows the variation of the dielectric loss ϵ'' as a function of frequency for all samples. The dielectric loss shows a decreasing trend with the increase of the frequency for all the samples due to the decreasing in the electrical resistivity.

The relation between ac conductivity and frequency for different mixes are shown in Fig. 8. Figure 8 shows that,

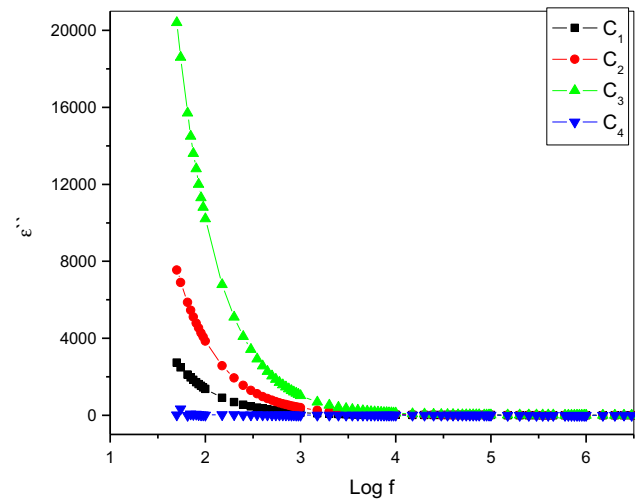


Fig. 7 Dielectric loss as a function of frequency for different mixes

the electrical conductivity increases with increasing the frequency at room temperature. The conductivity increased slowly in low frequency region but sharply in high frequency region. This behavior can be explained in the light of hopping model of charges [31]. According to this model, the increase in frequency of the applied field enhances the hopping of charges between the charge carriers Sn^{4+} and Sn^{2+} and hence the conductivity increases. Moreover, the increasing frequency of the applied field liberates the charges trapped in deep traps.

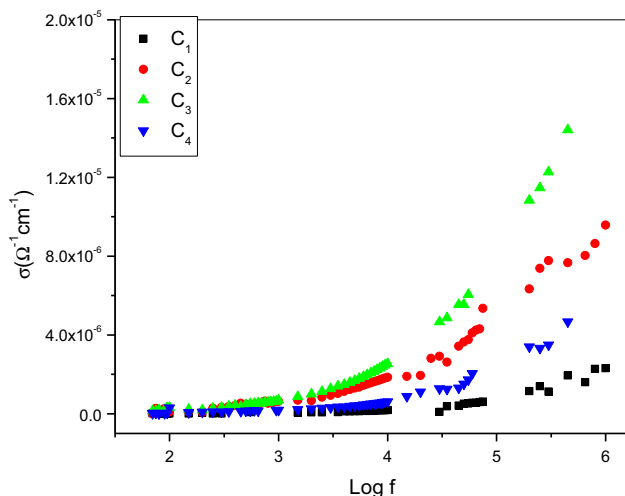


Fig. 8 Ac conductivity as a function of frequency for different mixes

The compositional dependence of the dielectric constant, dielectric loss and ac resistivity is shown in Table 1. Table 1 shows that, as Cr₂O₃ concentration increases the dielectric permittivity increases and ac resistivity decreases and then increases and takes it maximum resistivity at 0.5 mol%. When a Cr³⁺ cation replaces Sn⁺⁴ in the lattice it acts as an electron acceptor leading an increasing in the dielectric permittivity, ac conductivity and consequently the resistivity decreases. The increases in the resistivity at x = 0.5 mol% can be explained in the light of SEM micrographs. The increase in the resistivity at x = 0.5 mol% is attributed to the segregation of ions at the grain boundaries as shown in the SEM micrographs which acts as scattering centers that oppose the electron flow [32] and consequently increases the electrical resistivity for the investigated system which reduces the occurrence of the eddy currents. The samples also show high nonlinear coefficient in the range of 29–41.

The electrical resistivity of the varistor system can be improved with the addition of pentavalent ions such as Sb₂O₅, Nb₂O₅ and V₂O₅ which act as electron donors to the crystal lattice according to the following equation [33–35]

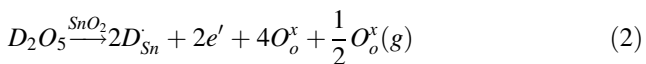
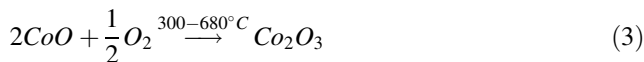


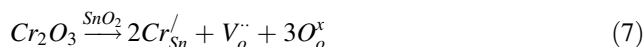
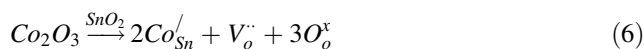
Table 1 Compositional dependence of the dielectric permittivity (ε'), dielectric loss (ε'') and the ac resistivity (ρ) of the prepared samples

x	ε'	ε''	ρ (Ω cm)
0	28	1.48	8.7 × 10 ⁵
0.1	748.22	4.14	1.6 × 10 ⁵
0.3	2110	10.6	1 × 10 ⁵
0.5	103	1.4	3.33 × 10 ⁵

Trivalent cations such as chromium, ytterbium and scandium that act as acceptors of electrons are added to SnO₂ crystal lattice which used to improve the varistor system [35–39]. There are change in the oxidation state of CoO and Cr₂O₃ by increasing temperature, according to the following reactions: [40]



when a Cr³⁺ cation replaces Sn⁺⁴ in the lattice, it acts as an electron acceptor leading to the formation of oxygen vacancies, thus increasing the solid state diffusion rate through the SnO₂ lattice, according to the equations below: [41]



The segregation of these ions in the grain boundary increase the resistivity values and causes the improvement of nonlinear coefficient due to the higher absorption of electron acceptor species on the grain boundary surface, increasing the barrier height potential and decreasing the conductivity, as demonstrated in the above Eqs. (5–7) [42–44]. Bueno et al. [45] reported that, the mechanisms responsible for the formation of the potential barrier are related to the presence of oxygen species adsorbed on the grain boundary region such as O⁻ and O⁻, which donate electrons for the oxygen, providing the formation of a region with negative charge density. CoO and Cr₂O₃ are also responsible for the formation of barrier in SnO₂ varistors. The obtained results show that the sample of 0.5 mol% of Cr₂O₃ has highest resistivity, low dielectric loss and consequently reduces the energy loss as heat. Accordingly they can be used in many applications such as transformer cores and memory cores.

4 Conclusions

The substitution by Cr₂O₃ improves the microstructure of SnO₂ varistors where the density increases from 6.6819 to 7.2803 g cm⁻³. SEM of the prepared samples sintered confirming the presence of particles of non-uniform structure having single almost spherical particles of small diameter ranged from 51 to 83 nm. The dielectric permittivity, dielectric loss and ac resistivity show a decreasing trend with the frequency for all the prepared samples. The

obtained results show that, as Cr_2O_3 concentration increases the dielectric permittivity increases and ac resistivity decreases and then increases and takes its maximum resistivity at 0.5 mol%. The compositional dependence of the dielectric constant and ac resistivity has been explained in the light of SEM micrographs. The obtained results show also that the sample of 0.5 mol% of Cr_2O_3 has highest resistivity and consequently low dielectric loss. So, it can be used in some technological applications such as transformer and inductor cores.

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