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# The Comparison between Samarium Doped Nickel Oxide and Samarium Added Nickel Oxide on Dielectric Properties

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**Abstract.** In this research, the effect of Samarium Oxide (Sm) doped (mol%) NiO as a dopant and added (wt%) in NiO as ceramic composite were investigated. The comparison of both doped and added ceramic in their dielectric properties was studied. Both electroceramic  $\text{Ni}_{(1-x)}\text{Sm}_x\text{O}$  and  $\text{NiSmO}_3$  were prepared by using a solid-state reaction method. Samarium was added with five different concentrations, which are 0.01, 0.02, 0.03, 0.05, and 0.10 mol% for dopant and another five different concentrations which are 1, 2, 3, 4, and 5 wt% for addition in NiO. The XRD results show that both ceramic doped and added samples did not change the NiO cubic structure. Besides, a high concentration of  $\text{Sm}^{3+}$  causes the lattice parameter of NiO to increase. The dielectric behavior was observed in a frequency range of 100 to 100 000 Hz. The optimum composition for  $\text{Ni}_{(1-x)}\text{Sm}_x\text{O}$  and  $\text{NiSmO}_3$  was obtained at  $x = 0.01$  mol% and 5.0 wt% sample with highest  $\epsilon''$  ( $2.4 \times 10^4$  and  $9.3 \times 10^4$ ) respectively but at the same time, they exhibit high dielectric loss ( $\tan \delta$ ) with value 4.9 and 10.5 respectively.

## 1. Introduction

High dielectric materials are widely used in electro ceramic potential applications such as capacitor and memory devices. The most requirement demand is the materials that perform such high dielectric constant ( $\epsilon_0$ ) in high frequency and temperature resistance while having the lowest dielectric loss ( $\tan \delta$ ). The material with large dielectric constant generally in perovskite ferroelectric oxides. This is due to the distortion of structural at ferroelectric transition in ferroelectric and relaxor materials [1].

Recent studies find that the materials that exhibit high dielectric constant were  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO), lead zirconate titanate (PZT),  $\text{LaMnO}_3$ , and  $\text{BaTiO}_3$ . They usually exhibit a high dielectric constant at  $10^3$ - $10^5$  at room temperature due to the interfacial polarization mechanism [2].

Pure nickel oxide (NiO) acts as an insulator material at room temperature with non-perovskite, non-ferroelectric, and non-toxic (lead-free). It is classified as a 'Mott Hubbard insulator' due to its lower conductivities with the range of  $10$ - $13 \text{ S cm}^{-1}$  in room temperature in which the conduction is due to the holes of intermediate-mass. Many research found that this NiO material can exhibit high dielectric constant with a value of  $10^3$ - $10^5$  by doping NiO with monovalent and bivalent materials. These recent years, there have been many studies about the materials doped in NiO to increase its dielectric properties such as (Li, Ti)-doped NiO, (Li, Al)-doped NiO, and (Li, Si)-doped NiO. In this study,  $\text{Sm}^{3+}$  doped NiO (mol %) and  $\text{Sm}^{3+}$  added NiO (wt %) were synthesized to study the dielectric properties of both ceramics.



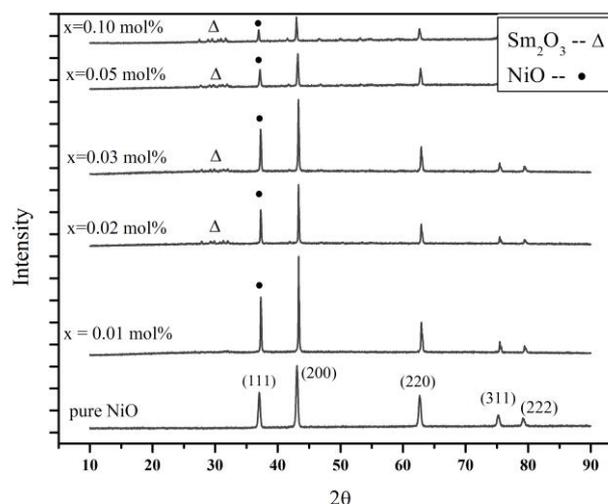
## 2. Material and Method

Both of the ceramics in this study were synthesized by using a solid-state reaction method. The starting material of NiO and Sm<sub>2</sub>O<sub>3</sub> powder have purity at least 99.9%. Two types of specimens (doped and added) with nominal compositions Ni<sub>(1-x)</sub>Sm<sub>x</sub>O for the doped specimens (x = 0.01, 0.02, 0.03, 0.05 and 0.1 mol%) and NiSmO<sub>3</sub> for the Sm<sup>3+</sup> added NiO (x = 1.0, 2.0, 3.0, 4.0 and 5.0 wt%) were prepared. The powders were mixed by dry mixing technique in aluminium oxide ball mill for 24 h. The mixed powder were dried and calcined at 950 °C for 4 h in air. The calcined powder were ground and pressed at 250 KPa with diameters 10-11 mm and thickness 2-3 mm. The green pellets were sintered in air at 1200 °C for 3 h. The phase formation of the samples were analyzed using X-ray diffraction (Bruker AXS D8 Advance). The dielectric constant ( $\epsilon'$ ) and tangent loss ( $\tan\delta$ ) were measured by using Impedance Analyzer from 10 Hz to 100 000 Hz.

## 3. Results and Discussion

Figure 1 shows the XRD pattern of the sintered SMNO Sm<sup>3+</sup> doped NiO with the chemical formula of NiO<sub>(1-x)</sub>Sm<sub>x</sub>O which different mol% of Sm<sup>3+</sup> (x = 0.01, 0.02, 0.03, 0.05 and 0.1 mol%). The presence of position sharp peak (2 $\theta$ ) was seen to be corresponded to (111), (200), (220), (311), and (222). It could be seen that those peaks do not change from identical crystalline phase of pure NiO. These results proved that the addition of Sm<sup>3+</sup> as a dopant in NiO at concentration x= 0.01 does not change the cubic structure of NiO. However, when the dopant concentration of Sm<sup>3+</sup> content equal to 0.02 mol% and more, the second phase was identified to present with a small peak. This phase is seemed to be the Sm<sub>2</sub>O<sub>3</sub> phase. This appearance phase is due to Sm<sup>3+</sup> has very small solid solubility in NiO. This low solid solubility of Sm<sup>3+</sup> makes the samples become a heterogeneous core/shell structure containing NiO as grains and Sm<sub>2</sub>O<sub>3</sub> rich in the boundary layer [3]. The presence of Sm<sup>3+</sup> has affected the morphology of NiO and altered the NiO-based material crystal orientation [4].

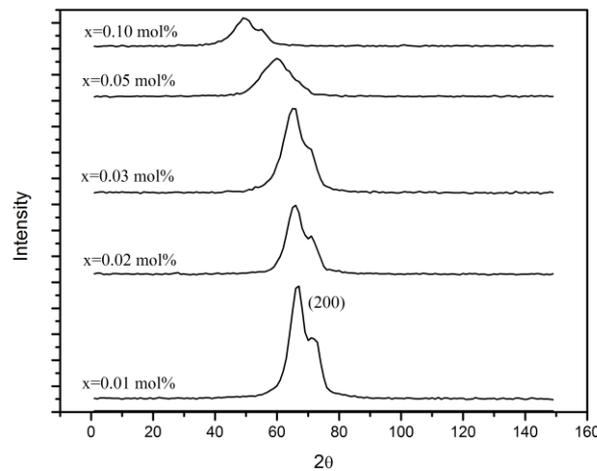
The results also show the decreasing of the diffraction peak intensity of NiO along with the addition of Sm<sup>3+</sup> as a dopant in NiO and it seems to be observed that the peaks were lower than the undoped NiO. These results indicated that the crystallinity of NiO becomes less with the increases of mol% in Sm<sup>3+</sup>. This is because of the incorporation of Sm<sup>3+</sup> concentration into NiO that disturbed the NiO lattice structure [2].



**Figure 1.** XRD graph of sintered Ni<sub>(1-x)</sub>Sm<sub>x</sub>O with different mol% concentration

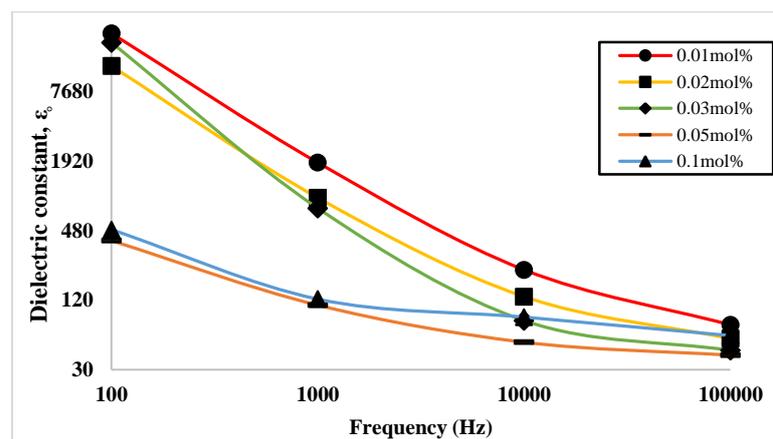
Figure 2 shows the peak of SMNO with different Sm<sup>3+</sup> which correspond to the peak (200). It is clearly shown that the peaks expand with the high content of the Sm<sup>3+</sup> dopant. The peaks were

correspond shifted to the left at a higher angle respectively. This is due to the changes in the lattice parameter of NiO. The lattice parameter has become bigger than pure NiO when  $\text{Sm}^{3+}$  concentration increased. This is because the number of defects increased when bigger ionic radii of  $\text{Sm}^{3+}$  (0.964nm) were substituted in the small NiO lattice (0.69nm). According to [5], the changes of the lattice parameter can be due to the differences in concentration of impurity atoms, defects, and the ionic radii of NiO and due to the external strain (temperature & pressures). In this research, the shifting was caused due to the bigger impurities and also strain induced in Ni atoms.



**Figure 2.** XRD pattern of sintered  $\text{Ni}_{(1-x)}\text{Sm}_x\text{O}$  focusing on the peak (200).

The dielectric constant ( $\epsilon_0$ ) and dielectric loss of sintered  $\text{Ni}_{(1-x)}\text{Sm}_x\text{O}$  measured at different frequencies ranging from 100 to 100 000 Hz were shown in figure 3 and figure 4 respectively. The dielectric constant was found to decrease when frequencies increase. The decrease in  $\epsilon_0$  takes place at range 100 Hz to 100 000 Hz. It was shown that SMNO-0.01 exhibits the giant reading of dielectric constant with a value of  $2.44 \times 10^4$  at 100 Hz. On the other hand, the SMNO-0.05 sample showed the lowest reading of  $\epsilon_0$  with a value of  $3.92 \times 10^2$ .

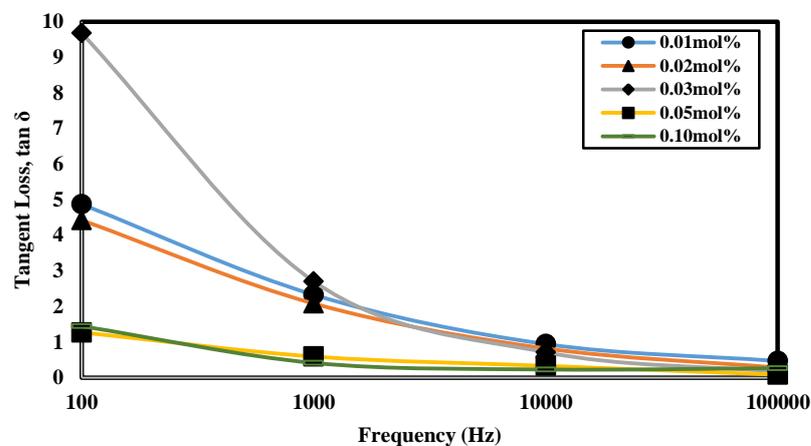


**Figure 3.** Dielectric constant of sintered  $\text{Ni}_{(1-x)}\text{Sm}_x\text{O}$  samples as a function of  $\text{Sm}^{3+}$  doping concentration

This result was the same as reported by [6] in their study that the materials exhibit giant dielectric  $\epsilon_0$  but it also showed the rapid decreased of  $\epsilon_0$  when frequency increased. Such behaviour is typical for the Maxwell-Wagner relaxation, which is generally employed to describe the observed high in  $\epsilon_0$  in electrically inhomogeneous material[7]. It was clear that the dielectric constant increased to higher

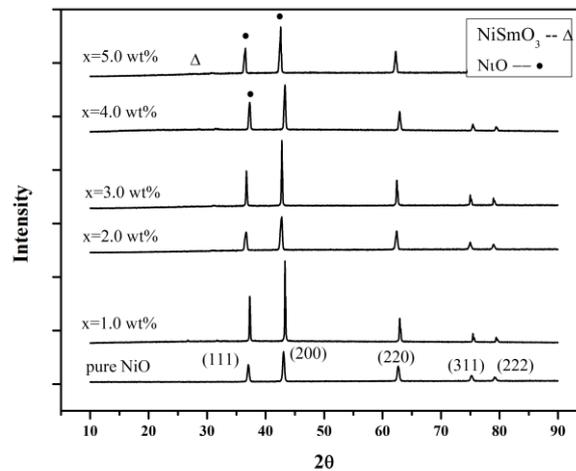
value due to the accumulation of  $\text{Sm}^{3+}$  atoms at the grain boundary when a low concentration of  $\text{Sm}^{3+}$  was used[8]. The higher concentrations of  $\text{Sm}^{3+}$  doped in NiO makes the  $\text{Sm}^{3+}$  abundant around NiO grains. This is because the big ionic radii of  $\text{Sm}^{3+}$  cannot substitute and accumulates at the grain boundaries of the samples therefore they produce heterogeneous core/shell around NiO grains.

Figure 4 shows the dielectric loss of  $\text{Ni}_{(1-x)}\text{Sm}_x\text{O}$  samples at different concentration dopant of  $\text{Sm}^{3+}$ . The lowest dielectric loss was exhibited by SMNO-0.10 at 10 000 Hz with a value of 0.2315. Furthermore, the dielectric loss seemed to be decreased when the frequency applied was increased. It can be seen that when samples contain high  $\epsilon_0$ , their dielectric loss ( $\tan\delta$ ) also at a higher value. On the other hand when the samples exhibit low  $\epsilon_0$ , their dielectric loss also lower. The lowest  $\tan\delta$  was recorded exhibits at a value of 0.2~ of samples SMNO-0.1 at 10 000 Hz. The  $\tan\delta$  seemed to decreased at frequency range 100 to 10 000 Hz and become constantly at 100 000 Hz.



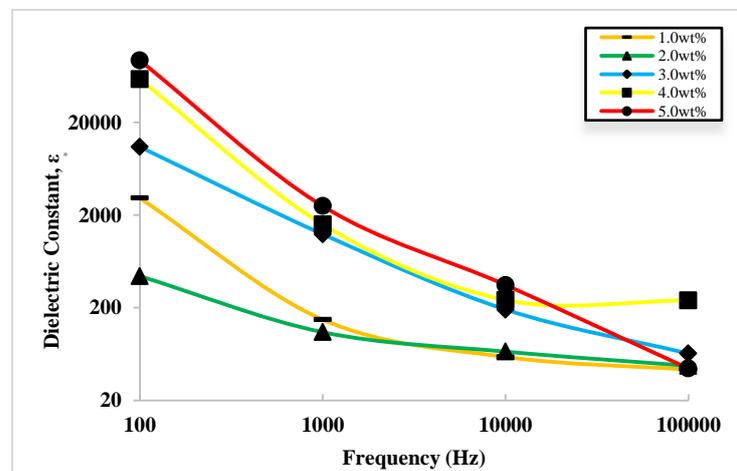
**Figure 4.** Dielectric loss of  $\text{Ni}_{(1-x)}\text{Sm}_x\text{O}$  with different  $\text{Sm}^{3+}$  doping concentration

Figure 5 shows the XRD pattern for the ceramic composite of  $\text{NiSmO}_3$  with different addition of  $\text{Sm}^{3+}$  (1.0, 2.0, 3.0, 4.0, and 5.0 wt%) in NiO. The pattern clearly showed as the same with the identical purity of NiO. This showed with NiO identical peak which corresponds to (111), (200), (220), (311), and (222) respectively. Those identical peaks mean that the cubic structure of NiO does not change. The grains of NiO were slightly affected by the impurity of  $\text{Sm}^{3+}$ . According to[3], the samples consist of the small undetectable of impurity in NiO grains become the heterogeneous core/shell structure in an amorphous state containing NiO that has no observable effect on the XRD pattern.



**Figure 5.** XRD pattern of sintered  $\text{NiSmO}_3$  with different wt% addition of  $\text{Sm}^{3+}$

Figure 6 shows the dielectric constant of  $\text{NiSmO}_3$  samples when the addition of  $\text{Sm}^{3+}$  increased. The  $\epsilon_0$  was improved with more addition of  $\text{Sm}^{3+}$ . It was apparent that the highest values of  $\epsilon_0$  were exhibited by SMNO-5 samples with a value of  $9.3 \times 10^4$  at 100 Hz. The value obtained in this study was higher if compared to the value reported by [9]. The dielectric constant in this study also exhibits the highest among the materials that have giant dielectric permittivity at a low frequency such as CCTO which has the  $\epsilon_0$  value of 80 000. According to [3], he claimed that a giant dielectric constant can be obtained by doping the rare earth with low concentrations.

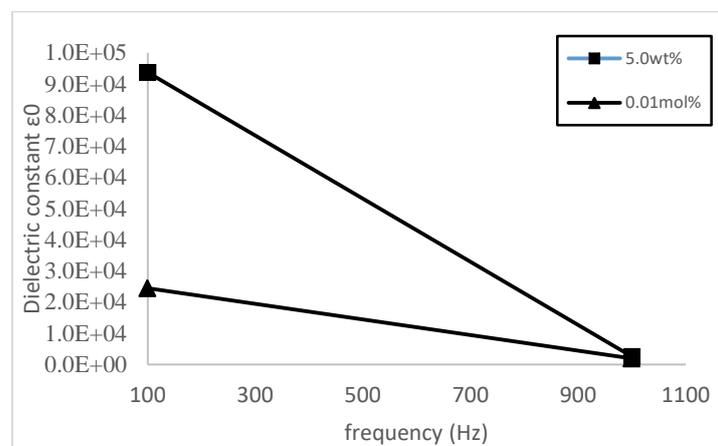


**Figure 6.** Dielectric constant of  $\text{NiSmO}_3$  samples with different addition of  $\text{Sm}^{3+}$  (wt%)

Figure 7 shows the differences between the highest values exhibits in both ceramic samples in dielectric constant at frequency range 100 to 1000 respectively. The values SMNO-0.01 doped and SMNO-5 were chosen to be compared as they both exhibit the highest values among other samples. It seemed that SMNO-5 of added NiO exhibits more giant  $\epsilon_0$  values than SMNO-0.01 doped NiO. Their value was extremely high which nearly reached towards value up to  $\sim 10^5$ . The mass of raw materials at 5.0wt% addition concentration was the nearly the same value of the mass obtained from the 0.01mol% of Sm doping concentration. It showed that the low concentrations of

$\text{Sm}^{3+}$  either in doped or added in NiO seemed to accumulate on the grain boundary in oxide form that can be caused by the increases of dielectric constant.

Hence, from the obtained mass by 5.0wt% of  $\text{Sm}^{3+}$  concentrations, the number of mol% can be obtained where the mol% percent becomes the optimum mol% to  $\text{Sm}^{3+}$  doped in NiO structure can exhibit a high dielectric constant. From the obtained mol%, we can prove that  $\text{Sm}^{3+}$  doped in NiO lattice at an optimum point 0.014 mol% exhibits the highest value of  $\epsilon_0$  among other doping concentrations. It was proved that the small values of  $\text{Sm}^{3+}$  concentrations in doping the NiO lattice can produce the end products with extremely high  $\epsilon_0$  in low frequency, the same level as the materials that perform giant dielectric constant at low frequency. In a further study, the NiO needs to be doped with something monovalent atoms materials such as the common formula  $\text{A}_x\text{B}_y\text{Ni}_{1-x-y}\text{O}$  that makes  $\text{Sm}^{3+}$  as co-doped in doping the NiO to produce the giant dielectric constant with low loss factor.



**Figure 7.** The comparison between the dielectric constant of 0.01 mol% and 5.0 wt% at 100 and 1000 Hz

#### 4. Conclusions

Both samples of  $\text{Ni}_{(1-x)}\text{Sm}_x\text{O}$  and  $\text{NiSmO}_3$  were successfully synthesized by using solid-state techniques. The XRD shows that both of the samples does not change the cubic structure of NiO. There is a small second phase of  $\text{Sm}_2\text{O}_3$  that appears when doping concentration increased. The dielectric was observed in four different frequencies (100-100 000Hz). The optimum composition of dopant sample  $\text{Ni}_{(1-x)}\text{Sm}_x\text{O}$  was obtained which at 0.01 mol% exhibits the highest dielectric constant ( $2.4 \times 10^4$ ). Besides, for samples  $\text{NiSmO}_3$ , an optimum composition that exhibits giant dielectric constant was 5.0wt% with vale of  $9.3 \times 10^4$ . From this, both compositions, the optimum mol% composition were obtained to get the highest dielectric constant were at 0.014mol%  $\text{Sm}^{3+}$  concentration doped NiO.

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