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Synthesis and characterization of titanium dioxide doped nickel oxide dielectric materials

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Abstract

Nickel oxide (NiO) belongs to the transition metal oxide family, having good dielectric constant with the range of 10^3 – 10^5, but it has high dielectric loss. In this research, the effect of titanium dioxide (TiO_2) addition into NiO was investigated. Generally, TiO_2 was used in the application of electrical ceramic, catalysts, electric conductors and chemical intermediates. $Ni_{1-x}Ti_xO_{1+x}$ was prepared via solid-state reaction method with 6 different TiO_2 compositions. The preparation started with the powder mixing process for 24 hours and followed by calcination process at 950 °C for 4 hours. Then, the calcined powders were compacted into 6 mm pellet shape under pressure of 250 MPa pressure. Three pellets were made for each TiO_2 composition. Those pellets were sintered at 1250 °C for 5 hours. XRD results showed that pure NiO at 0.01 and 0.02 mole % of TiO_2 compositions produced single NiO crystalline phase, while 0.03, 0.05 and 0.10 mol % of TiO_2 showed the TiO_2, instead of NiO phases. SEM analysis showed that increasing TiO_2 concentration make the grain size increase, with 0.02 mole % of TiO_2 gave the largest grain size, shows that 0.02 mole % is the optimum TiO_2 concentration for grain size enlargement. Furthermore, the bulk density of $Ni_1xTi_xO_{1+x}$pellet was reduces at higher TiO_2 concentration. In dielectric test, the addition of 0.03 mole % of TiO_2 gave the highest dielectric constant with value of 4.51 x 10^{14} and 0.05 mole % of TiO_2 gives the result of lowest dielectric loss (0.53).

1. INTRODUCTION

The dielectric materials, which known as insulating materials can be in the form of solid, liquid or gas. Solid dielectrics are widely used in electrical engineering because of their excellent insulators such as mica, glass, rubber and ceramics. There are a few ceramics that commonly used in dielectric materials including calcium copper titanium oxide (CCTO), aluminium oxide (Al_2O_3), aluminium nitride (AlN), silicon carbide (SiC), fused silica (SiO_2) and nickel oxide (NiO). Among them, NiO has attracted much attention in dielectric materials due to its abundant of production. About 4000 tons of chemical grade NiO are produced annually (Lascelles et al., 2005). In the ceramic industry, NiO is used to make frits, ferrites, and porcelain glazes. Moreover, NiO is a very important material extensively used in catalysis, battery cathodes, gas sensors, electrochromic films, and magnetic materials (Motlagh et al., 2011). However, this material still needed for synthesizing high quality and ultra-fine powders with required characteristics in terms of their size, morphology, optical properties, magnetic properties (Marselin and Jaya, 2015) and dielectric properties. NiO is good in insulation, but it needs to be enhance its properties especially in dielectric. In this study, the solid-state was used to synthesis and characterize the TiO_2 doped NiO. By having various amount of TiO_2 added to the NiO, the improvement in phase composition, microstructure, density and dielectric properties will be seen.

2. MATERIALS AND METHODS

2.1. Materials

The materials used in this study were NiO powder (HmBG Chemicals brand); TiO_2 powder (Bendosen Laboratory Chemical brand); and ethanol (Bendosen Laboratory Chemical brand).

2.2. Methods

The aim of this experiment was to produce $Ni_{(1-x)}Ti_xO_{(1+x)}$, with the improvement of dielectric properties. This experiment was on $Ni_{(1-x)}Ti_xO_{(1+x)}$ ceramics where the dopants concentration was emphasized. The $Ni_{(1-x)}Ti_xO_{(1+x)}$ ceramics were prepared and synthesized using solid-state reaction method. The formula for $Ni_{(1-x)}Ti_xO_{(1+x)}$ is referred to the ratio of Ni and TiO_2 powder content in the sample mixtures. The whole ratio was 1 and 1-x was the total of Ni

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content. *x* is replaced by the amount of TiO_2 in the compound according to the composition stated which were 0, 0.01, 0.02, 0.03, 0.05 and 0.10 mol %. The samples were labelled as Sample 1, 2, 3, 4, 5 and 6 according to the increasing of TiO_2 content.

The raw materials were wet mixed with ethanol as wet media for 24 hours using zirconia ball as the mixing medium. Then, the mixture powder was calcined at 950 ºC for 4 hours using the furnace. The heating and cooling rate was 5 °C/min. Next, the mixture powders were grounded using agate mortar to be finer powder. The calcined powders were compacted into pellets with 6 mm diameter using the hydraulic hand press machine at 250 MPa. Then, the pellets were sintered at 1250 ºC for 5 hours using furnace with heating and cooling rate at 5 ºC/min. For analysis process, those samples were analysed and characterized using XRD, SEM, density and dielectric tests. The pattern numbers of sintered pellets were COD 4329323 (Ni O) and COD 9008749 (O Ti) for all samples.

3. RESULTS AND DISCUSSION

Figure 1 showed the XRD pattern of TiO_2 doped NiO sintered at 1250 °C. The XRD pattern at 2θ peaks gave values of 37.258°, 43.291°, 62.884°, 75.423° and 79.417° are indexed as $(\bar{1}\bar{1}\bar{1})$, $(\bar{2}00)$, $(\bar{2}\bar{2}0)$, $(\bar{3}\bar{1}\bar{1})$ and $(\bar{2}\bar{2}\bar{2})$. However, from Ponnusamy et al. (2015) studies, they found that the diffraction peaks at 2θ were 37.2°, 43.3°, 62.7°, 75.6° and 79.4° are indexed as (111), (200), (220), (311) and (222) planes of NiO.

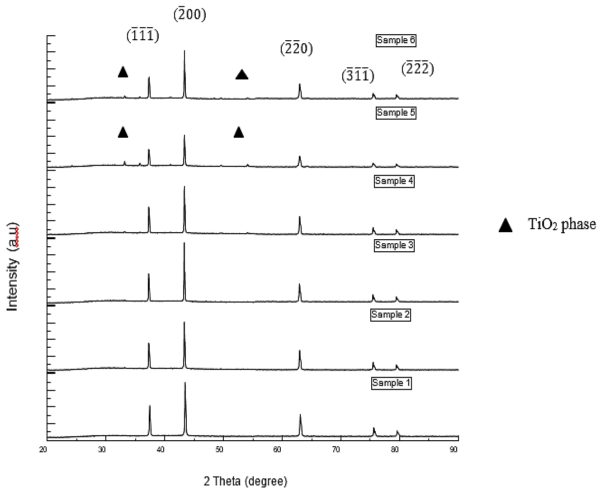

Figure 1: Sintered pellet XRD pattern (COD 4329323 (Ni O) and COD 9008749 (O Ti))

After sintering process, the TiO_2 reduced its intensity due to the heat treatment in sintering process caused the larger grain formation. Besides that, the graph in Figure 1 showed that the addition of TiO_2 up to 0.02 mole % which were Sample 1, 2, 3 and 4 did not changed the crystal structure. The TiO_2 phase only showed in Sample 5 and 6 after sintering process due to excess TiO_2 in the crystal structure.

As can be seen in Figure 2, there is decrement trend for the bulk density of $Ni_{1-x}Ti_xO_{1+x}$ pellet. Initially, the graph shows increment of bulk density value from 0 to 0.01 mole %, which translated from 3.42 to 5.41 g/cm^3 as the addition of TiO_2 had caused densification of the $Ni_{1-x}Ti_xO_{1+x}$ microstructure, resulting in the increase of bulk density value. However, the value decrease to 4.46 g/cm^3 as the composition of TiO_2 increase to 0.03 mole %. Then, the bulk density rises to 5.22 g/cm^3 at 0.05 mole % and decrease again when 0.10 mole % of TiO_2 added with the value of bulk density is 4.62 g/cm^3. This shows that there is inconsistent value of bulk density that might be caused by the error occurred during shaping process. The pressure applied was not well distributed throughout the pellets consistently. Besides that, the graph also shows the apparent porosity percentage of $Ni_{1-x}Ti_xO_{1+x}$ pellet. For pure NiO pellet, there was 47.22 % and dropped to 9.09 % when 0.01 mole % of TiO_2 doped NiO. Then, the percentage increase to 25.00 % at 0.03 mole % of TiO_2. But decrease to 17.39 % at 0.05 mole % and slightly increase to 19.23 % for 0.10 mole % of TiO_2. It can be concluded that the apparent porosity percentage decreased as the bulk density increased. According to Guo et al. (2006), the optimum amount of TiO_2 doped willemite ceramic, it implies that the increase of dielectric constant (ε_r) of willemite ceramic with sintering temperature is due to the increased of density and reduced porosity.

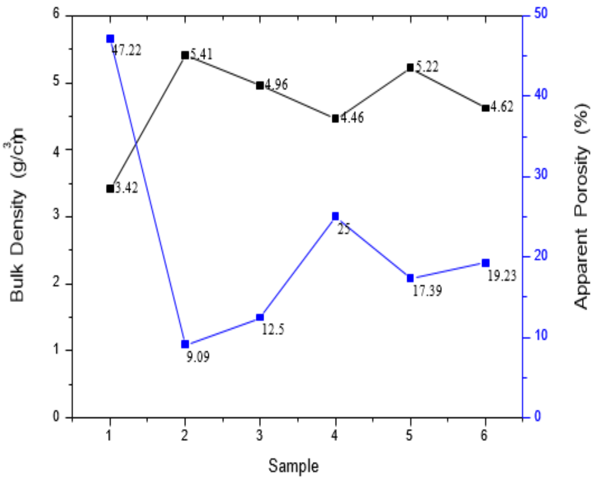

Figure 2: Value of bulk density and apparent porosity percentages of sintered pellets

Figure 3 showed the SEM analysis of $Ni_{1-x}Ti_xO_{1+x}$ pellet after sintering process. Figure 3(a) showed a microstructure with a lot of pores for the undoped NiO sample. The grain size increased as the TiO_2 content increased until the concentration of 0.02 mole % of TiO_2 but smaller when 0.03, 0.05 and 0.10 mole % of TiO_2 added. This showed that the 0.02 mole % of TiO_2 is the optimum TiO_2 concentration added into NiO to get the larger grain size. However, in Figure 3(e) and 3(f), there were unknown particle shapes in the pellet. They were some parts of pellet that melted due to heat treatment process.

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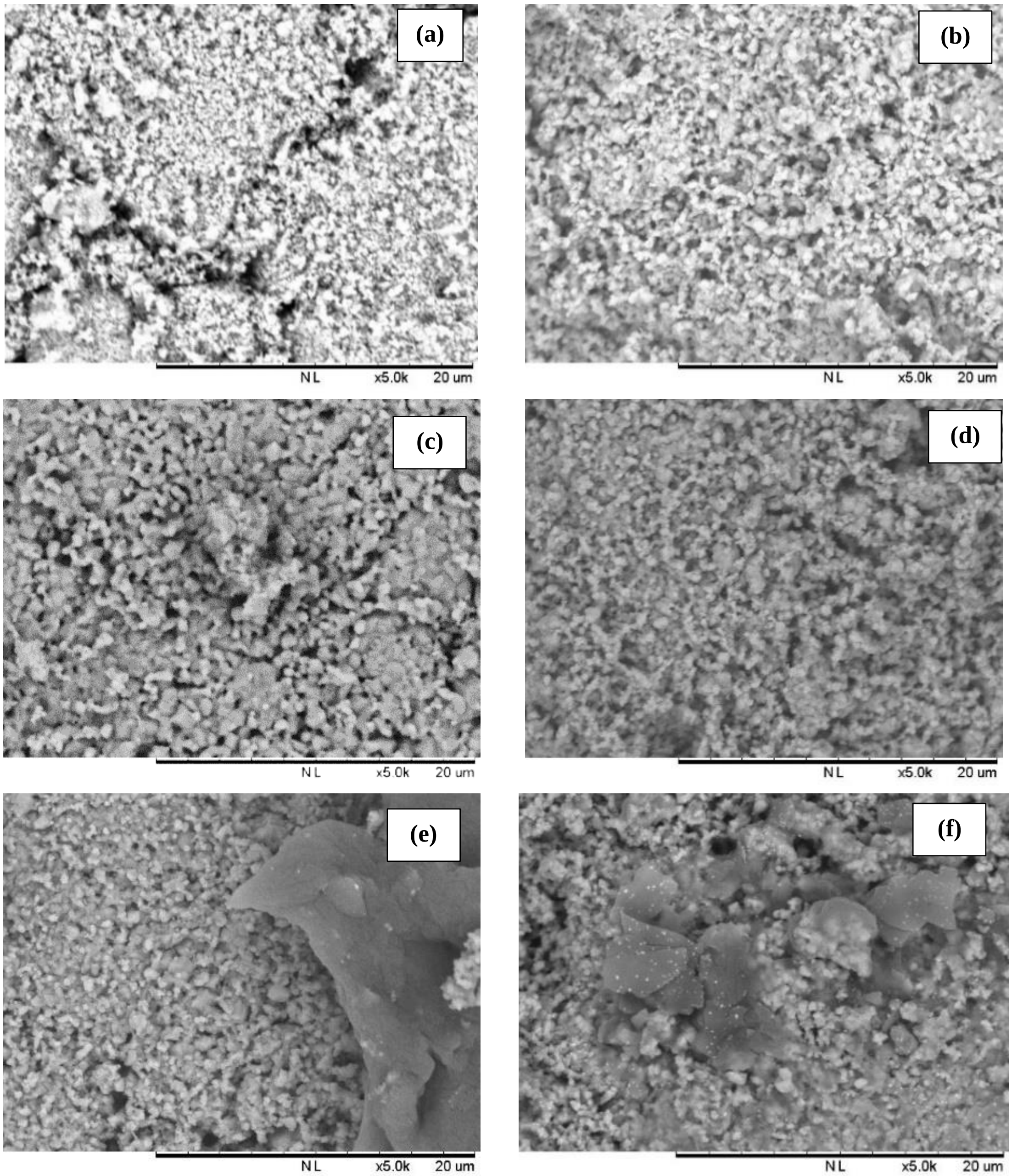

Figure 3: SEM microstructures of surface sintered pellets for (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4, (e) Sample 5 and (f) Sample 6

Next, the sintered pellets were broken into pieces in order to examine the fracture surface morphology. Figure 4 showed the SEM microstructure of cross section of each sample. It can be observed that the grain sizes are quite homogeneous and the bigger the grain size, the composition of TiO_2 increase. The optimum TiO_2 content for improving $Ni_{1-x}Ti_xO_{1+x}$ grain was found at 0.02 mole %.

Previous study by Bari et al. (2013) showed that the addition of TiO_2 nanoparticles to the lead zirconate titanate (LZT) ceramics significantly improved the density and a dense and uniform microstructure and also abnormal grain growth were observed by SEM. The use of TiO_2 nanoparticle reduces porosity and leads to an increase in green density.

The electrical properties of dielectric materials are mainly depending on dielectric constant and loss. Furthermore, the higher ε_r and lower tan δ will produce a good electroceramic product. This test is very useful in order to investigate the effect of TiO_2 dopant on the dielectric constant and dielectric loss of $Ni_{1-x}Ti_xO_{1+x}$.

Figure 5 shows the frequency dependence of dielectric constant (ε_r) of $Ni_{1-x}Ti_xO_{1+x}$ samples as a function of TiO_2 doping concentration. It was observed that ε_r can decreased with the increasing of the frequencies. A decrease ε_r values took place at the frequencies in the range of 6 – 8.25 MHz and become almost linear between 8.25 – 9.0 MHz. The ε_r was improved by the addition of TiO_2 doping. The ε_r of undoped NiO is 2.37 x 10^{14} at 6 MHz, while the ε_r of 0.03 mole % TiO_2 doped NiO gave the result of 4.51 x 10^{14} dielectric constant, which is the highest value among other doping content. The result obtained was a good agreement and comparable with the previous study of Mallick and Mishra (2012) that studied the doping of transition metals on NiO. They observed that the giant dielectric responded when (Li, Fe) and (Li, V) doped NiO ceramic. This study proved that doping technique could increased the dielectric constant of NiO.

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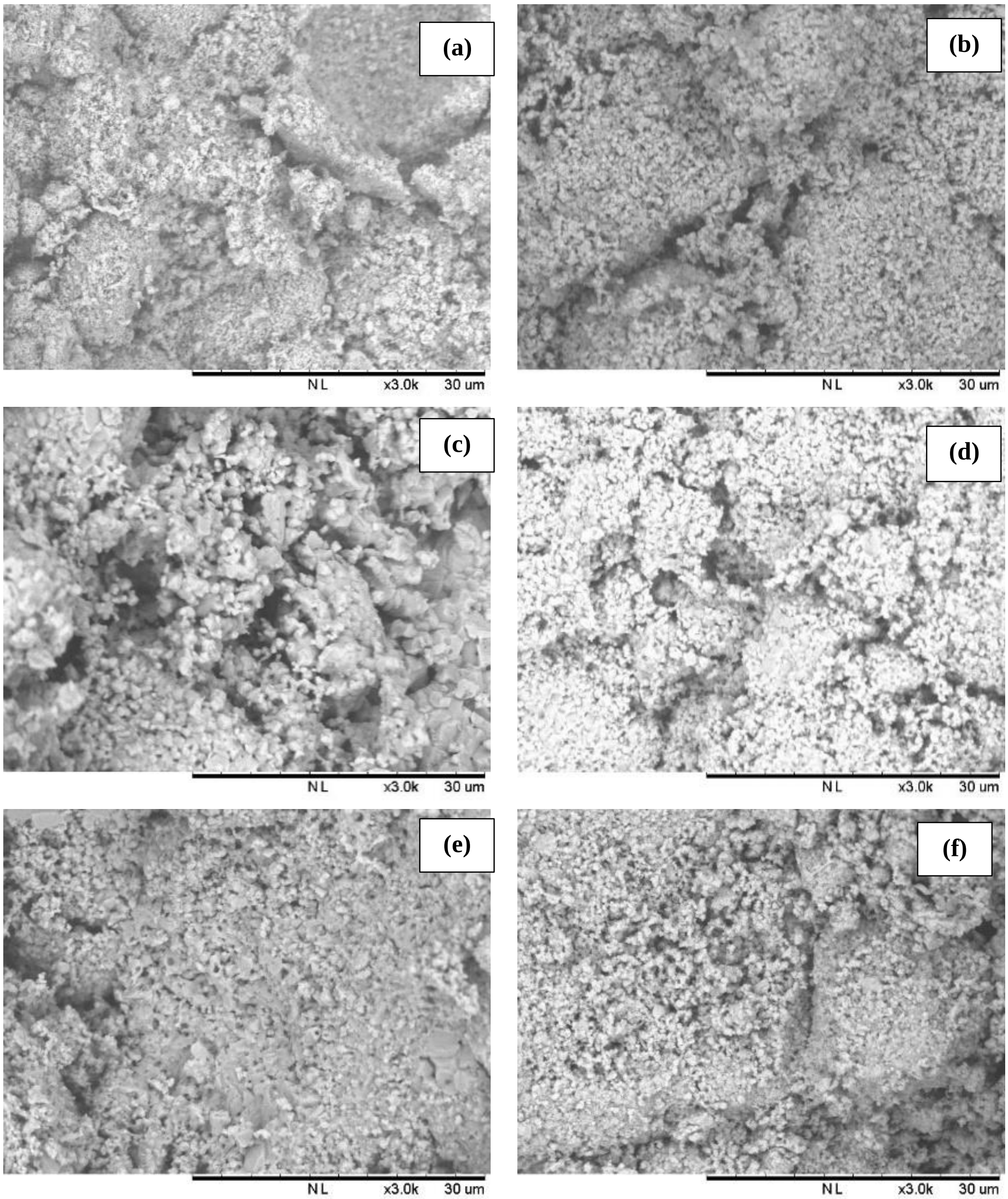

Figure 4: SEM microstructures of cross section surface sintered pellets for (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4, (e) Sample 5 and (f) Sample 6

Next, Figure 6 showed that dielectric loss (tan δ) for all concentrations of TiO_2 doped into NiO. However, when the frequency at 6 MHz, the lowest tan δ was at 0.05 mole % of TiO_2 with the value of 0.53, compared to undoped NiO with the value 0.71. The highest tan δ was 0.99 in Sample 3 with 0.02 mole % of TiO_2. \In addition, based on the previous study by Surendran et al. (2005), the microwave dielectric properties of $MgAl_2O_4$ spinels were tailored by the addition of different mole fractions of TiO_2. The ε_r of the mixed phases were increased with the molar addition of TiO_2 into the spinel to form mixtures based on $(1\text{-}x)MgAl_2O_4\text{-}xTiO_2$ (x = 0.0 - 1.0). This study proved that TiO_2 dopant was able to improve the dielectric properties.

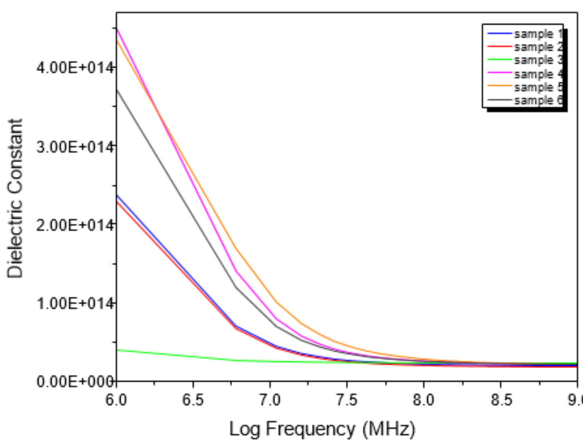

Figure 5: Frequency dependence of dielectric constant of $Ni_{1-x}Ti_xO_{1+x}$ samples as a function of TiO_2 doping concentrations

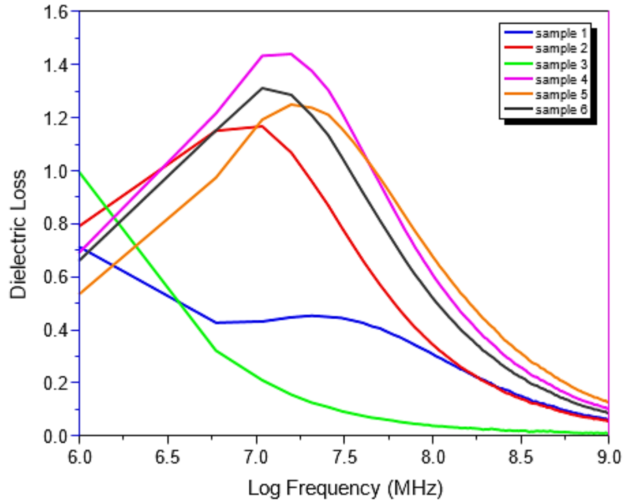

Figure 6: Frequency dependence of dielectric loss of $Ni_{1-x}Ti_xO_{1+x}$ samples as a function of TiO_2 doping concentrations

4. CONCLUSION

$Ni_{1-x}Ti_xO_{1+x}$ first time introduce in conclusion and never found in previous pages were synthesized and characterized using solid-state method. XRD results of sintered samples produced a single NiO crystalline phase from Sample 1 to 3, which were represented pure NiO, 0.01 and 0.02 mole % of TiO_2 respectively, but there were small secondary phases of TiO_2 showed in Sample 4 to 6 as they represented the addition of 0.03, 0.05 and 0.10 mole % of TiO_2. SEM analysis showed that the largest grain sizes among those samples is 0.02 mole % as the optimum TiO_2 content. Besides that, the amount of grain boundaries was increased as the TiO_2 content increased. Thus, this showed that the TiO_2 concentration increased, the bulk density decreased. For the dielectric test, the results come out with improvement of dielectric constant, ε_r by the addition of TiO_2 doping. The ε_r of undoped NiO is 2.37^{14} at 6 MHz, while the ε_r of 0.03 mole % TiO_2 doped NiO gave the result of 4.51^{14} dielectric constant, which was the highest value among other doping content. In addition, the lowest dielectric loss, tan δ was at 0.05 mole % of TiO_2 with the value of 0.53, compared to undoped NiO with the value 0.71 and the highest tan δ was 0.99 when 0.02 mole % of TiO_2 was added. These results showed that different TiO_2 dopants gave the different effect in improving dielectric constant and dielectric loss. However, throughout this study, overall can be concluded that the doping of TiO_2 was able to improve dielectric properties of NiO ceramic.

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