Study of Dielectric Properties of Non Stoichiometric Nickel Oxide

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Abstract. Thermal decomposition method was used to synthesis non stoichiometric nickel oxide at different sintering temperatures upto 1100 °C. X-ray diffraction method along with rtiyeld refinement is used for structure cauterization of synthesized compounds. The dielectric constant and dielectric loss was found to have dependency on stoichiometry. These results were interpreted as the decomposition temperature increases, which heals the defects present in the non-stoichiometric nickel oxide and Loss peak shifts to the higher frequency which is due to long-range hopping of charge carriers.

INTRODUCTION

Nickel oxide (NiO) is the most comprehensively investigated transition metal oxide over the decades [1]. NiO is one of the promising and environment friendly p-type semiconductors with wide band gap energy ranging from 3.6 to 4 eV (bulk form). NiO is a very interesting material due to its complex band structure. Stoichiometric NiO (NiO) is a Mott-Hubbard insulator with room temperature conductivity of less than $10^{-13}$ S cm$^{-1}$. Very low conductivity of NiO may be due to hopping of charge carriers associated with Ni$^{2+}$ vacancies [2]. NiO has been considered as a promising functional material for varieties of applications, such as, smart windows [3], spin valves giant magneto resistance (GMR) sensor [4], solar cells [5], gas sensors [6], high permittivity dielectric material and electrochromic material for displays [7], photoelectrolysis [8], etc. several efforts have been made to explain the insulating behavior of NiO, were in, appreciable conductivity can be achieved in NiO by creating Ni vacancies or substitution at nickel side, thereby creating Ni vacancies and the composition ratio of Ni and O changes and NiO becomes non-stoichiometric. Many optoelectronic and transport properties of the materials depends on dielectric constant and dielectric loss. This are two basic criteria that a material must match for the better applicability and efficiency Dielectric studies have been done on nonstoichiometric nickel oxide to investigate any variation of dielectric constant and dielectric loss with frequency and different oxygen content. Hence various property, including dielectric behavior changes in non stoichiometric nickel oxide, this can be attributed to presence of excess oxygen. However, when NiO is anti-ferro magnetically ordered or defect-rich, the dielectric loss increases significantly [9]. In the present work the dielectric property in non stoichiometric NiO, produced by thermal decomposition route, was studied.

EXPERIMENTAL PROCEDURE

Nickel nitrate hexa-hydrate [Ni(NO$_3$)$_2$.6H$_2$O] is sintered at different temperature [10, 11], which was decomposed to produced nickel oxide samples of various stoichiometries[12]. Nickel salt was heated in air for 3 hr. at temperatures range from 400 °C and 1100 °C. By sintering at two different temperature samples NiO400 and NiO700 and NiO1100were prepared at 400°C, 700°C and 1100°C. X-ray diffraction was conducted with the help of the Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (0.154 nm) in the angle range 10°–90°. The
dielectric measurement was performed with impedance analyzer model-Wayne Kerr 6500 V works in the frequency range of 20 Hz to 120 MHz and in the ac voltage range from 10 mV to 1 V.

<table>
<thead>
<tr>
<th>Intensity (%)</th>
<th>2θ</th>
<th>Sin²θ</th>
<th>(h^2 + k^2 + l^2)</th>
<th>C (hkl)</th>
<th>a(Å)</th>
<th>(\overline{a}(\text{Å}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>61.69</td>
<td>37.279</td>
<td>0.1022</td>
<td>3</td>
<td>0.034 (111)</td>
<td>4.1772</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>43.472</td>
<td>0.1365</td>
<td>4</td>
<td>0.034 (200)</td>
<td>4.1727</td>
<td></td>
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<tr>
<td>44.83</td>
<td>62.901</td>
<td>0.2722</td>
<td>8</td>
<td>0.034 (220)</td>
<td>4.1772</td>
<td></td>
</tr>
<tr>
<td>15.68</td>
<td>75.416</td>
<td>0.3741</td>
<td>11</td>
<td>0.034 (311)</td>
<td>4.1772</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 1.** Shows the crystallographic data using analytical analysis for NiO samples.

**TABLE 2.** Rietveld parameters of different NiO samples.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>a(Å)</th>
<th>(V_{\text{A}^3})</th>
<th>Rf factor</th>
<th>Bregg’s R-factor</th>
<th>(R_p)</th>
<th>(R_{wp})</th>
<th>(R_e)</th>
<th>(\chi^2)</th>
<th>L(nm)</th>
</tr>
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<tbody>
<tr>
<td>NiO400</td>
<td>4.176</td>
<td>72.82</td>
<td>2.39</td>
<td>3.94</td>
<td>24</td>
<td>16.7</td>
<td>14.9</td>
<td>1.261</td>
<td>240</td>
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<tr>
<td>NiO700</td>
<td>4.172</td>
<td>72.64</td>
<td>4.04</td>
<td>4.51</td>
<td>22</td>
<td>15.8</td>
<td>13.3</td>
<td>1.416</td>
<td>350</td>
</tr>
</tbody>
</table>

**FIGURE 1.** (a) X ray diffraction pattern of non stiochiometric Ni\(_{1-\delta}\)O. (b) Shows the Rietveld refinement fitting of XRD data.

**FIGURE 2.** Variation of real part of dielectric constant with frequency for NiO400, NiO500 and NiO1100 at room temperature.

**FIGURE 3.** Variation of imaginary part of dielectric constant with frequency for NiO400, NiO500 and NiO1100 at room temperature.
RESULT AND DISCUSSION

XRD analysis, which is the most useful technique for identification of crystalline structure, was employed to investigate the crystallinity and purity of the solid product obtained by thermal conversion in air of the poly-nuclear coordination compounds. The XRD data of nickel oxide sample prepared at different temperature is shown in Fig. 1(a), which shows the presence of the characteristic peaks for NiO at 2θ in the range of 10° – 90°, in accordance with JCPDF File 78-0643. The lattice parameters were obtained from the following relationship analytically: \( \sin^2 \theta = \frac{C}{(h^2+k^2+l^2)} \), where \( C = \frac{\lambda^2}{4a^2} \). The results of the X-ray structural analysis are given in Table 1 for one of the representative samples sintered at 400 °C. Our analysis indicates good agreement between Bragg’s reflection peaks obtained from analytical analysis data and the structural data of with JCPDF File 78-0643. This indicates that the NiO sample obtained by thermal conversion in air of the poly-nuclear coordination compounds, revealed the NiO with face-centered cubic phase, also known as the bunsenite structure (lattice constant \( a \) of cubic unit cell, 0.4177 nm). For others samples, there was also no appreciable deviation in structural data within the limit of accuracy of analytical method. No other additional peaks corresponding to other phases were emerged, suggested NiO phase is stable.

Further, the mean crystallite size of the NiO sample can be calculated using Sherrer formula: \( L = k\lambda/\beta\cos(\theta) \), where \( L \) is the crystallite size, \( k \) is the Sherrer constant, usually taken as 0.89, \( \lambda \) is the wavelength of the x-ray radiation (0.154056 nm for Cu Ka), and \( \beta \) is the full width at half maximum (FWHM) of diffraction peak measured at 2θ. The deduced values of crystallite size of the analyzed NiO samples are reported in Table 2, which indicates that as the sintering temperature of precursor increases the crystallite size of NiO also increases.

We have also performed Rietveld refinements for all the samples using Fullprof software. Fig. 1(b) shows the refinement profile of all the samples in which experimental data (circles), calculated pattern (continuous line) and their difference (continuous line at the bottom) are plotted; the positions of the Bragg reflections are indicated by vertical bars. The various parameters obtained from refinement data are given in Table 2. It can be concluded that the crystal parameters obtained from analytical calculation from XRD graph and fitting the curve by Rietveld refinement corroborates each other.

The dielectric properties of materials are characterized by the complex dielectric constant (\( \varepsilon \)) which is represented by \( \varepsilon = \varepsilon' - j\varepsilon'' \). The real part (\( \varepsilon' \)) of dielectric constant is the measure of the amount of energy stored in a dielectric due to the applied field and the imaginary part (\( \varepsilon'' \)) of dielectric constant describes the dissipated energy in dielectric. The value of real part of dielectric constant (\( \varepsilon' \)) is calculated by using \( \varepsilon = \frac{Ct}{A\varepsilon_0} \) where \( \varepsilon_0 \) is the permittivity of free space, \( t \) is the thickness of pellet, \( A \) is the cross sectional area and \( C \) is the capacitance of pellet.

Figure 2 shows the variation of dielectric constant (\( \varepsilon' \)) with frequency for NiO400, NiO700 and NiO1100 at room temperature. At lower frequency the dispersion of dielectric constant was observed. The large value of dielectric constant at lower frequency observed is attributed to the grain boundary defects or the presence of excess oxygen. In addition to that, the excess oxygen content of the samples also affects the dielectric constant. Because the \( \text{Ni}_1.2\text{O} \) under the application of electric field act as dipoles. Due to change in the oxygen content, the particles per unit volume changes and thereby changes dipole moment per unit volume and hence the value of dielectric constant.

It is noticed that the dielectric constant is decreased in NiO400 as compared with NiO1100. The dielectric constant decreased in the whole applied frequency region as excess oxygen content of the sample increases. Because, the polarization is decreased due to the formation of grains by insulating grain boundaries. The excess oxygen may create many defects into NiO400, thus reduces the dielectric constant. Qualitatively this was observed in figure 2 that the dielectric constant at low frequency is rather high and found to decrease with the increase in frequency.

The imaginary part (\( \varepsilon'' \)) of dielectric constant of nonstoichiometric nickel oxide samples shows a normal dielectric behaviour as observed earlier. We note that the imaginary part of dielectric constant (\( \varepsilon'' \)) shows a decreasing trend with increase in frequency as shown in fig. 3, almost similar to real part of dielectric constant. This variation in imaginary part of dielectric constant (\( \varepsilon'' \)) with respect to frequency may be due to several factors; such as conduction mechanism, materials composition of sample, sintering temperature, grown technique and particle size.

The ratio of energy dissipated and energy stored in the material determines the dielectric loss factor (tan \( \delta \)) and variation of dielectric loss with frequency at room temperature is shown in fig. 4. It shows that the dielectric loss (tan \( \delta \)) decreases with the increase of frequency in all the samples. Small peaks are observed in samples which are believed to exist due to the resonance between the hopping frequency of charge carriers and applied frequency. Very
small peak is observed in NiO700 while no peak like behavior is observed in NiO1100 samples as their excess oxygen content is zero. Hence nonstoichiometry of the samples plays important role in dielectric property.

**Figure 4.** Variation of Dielectric Loss with frequency of NiO400, NiO700 and NiO1100 at room temperature.

**Figure 5.** Variation of ac conductivity as a function of frequency for NiO400, NiO700 and NiO1100 at room temperature.

We have observed that dielectric loss alters at higher frequency which is due to suppression of domain wall motion. The dielectric loss is maximum at lower frequencies and is due to nearly equal hopping frequency between different ionic sites and the frequency of the applied field. Dielectric loss of the NiO400, NiO700 and NiO1100 is different, which is due to the decrease in dielectric constant as, described earlier.

The ac conductivity of pure NiO400, NiO700 and NiO1100 is shown in fig. 5. It is found that the ac conductivity progressively increases with the increase in the frequency of the applied ac field. This is because rising in frequency would improve the electron hopping frequency. The ac conductivity is initially high for NiO400 and found to be less in NiO700 and NiO1100. The nonstoichiometry may initiate the defect ions; excess oxygen in the NiO400 tends to segregate at the grain boundaries due to the diffusion at the time of sintering. Due to presence of excess oxygen the flow of charge carriers at the grain boundaries increases and cause change in the conductivity initially there after the conductivity of decreases. NiO400 has highest value of ac conductivity both at low and high frequencies as compared to other samples.

In conclusion, nickel oxide of various stoichiometry were prepared by using a simple and inexpensive thermal decomposition technique at different sintering temperatures. The XRD studies show that all the nickel oxide samples were crystallize in cubic phase. The lowest and highest dielectric constant is observed at lower frequency are clearly indicates that nonstoichiometry of samples is an important feature while the dielectric loss (tan δ) decreases with increase in frequency having wide peaks in certain range of frequency, which is due to the resonance among the hopping frequency of charge carriers and applied frequency. Electric modulus spectra reflect the contributions from grain effects: the large resolved semicircle are caused by the grain effect.

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**REFERENCES**