Study of the effect of substitution by MnO₂, Ag₂O and CaO on the microstructure, electrical and dielectric characteristics of NiO ceramics

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Abstract
The effect of MnO$_2$, Ag$_2$O and CaO on the physical, microstructure and electrical properties of NiO were investigated in this work. Minimum values of water absorption were attained in specimens fired at 1200 °C for 2 hours lead better densification by minimizing the present of closed pores. Maximum values of firing shrinkage were attained in specimens fired at 1200 °C for 2 hours. Results of XRD show Nickel oxide and Nickel Manganese oxide – Ni$_6$MnO$_8$. SEM of mix (C$_1$), shows exsolution two liquid phase, grain growth, grains pelt shape, melt phase, crystalline phase, exsolution miscibility and Mn enter the lattice of Ni. The relation between I and V for the different mixes show very good plateau in (I-V) relation. Ac conductivity increase with increasing frequency at room temperature.

Key words: NiO, Microstructure, XRD, frequency, conductivity.
وأكسيد المنجنيز. وقد تم قياس الخواص الكهربائية للمجموعات المختلفة وال العلاقة بين شدة التيار و فرق الجهد، وقد تم أيضا قياس السعة و المقاومة النوعية والموصلية وثابت العازل لهذه العينات و وتبين نتائج العلاقة بين التوصيلة مع التردد بالعينات المختلفة أيضا تزداد بزيادة التردد لكل عينة.
Introduction

Now-a-days, lead free high dielectric materials are of great interest in the field of microelectronic and various technological applications such as; capacitors, memory devices, low field magnetoresistance etc. [15, 13]. Nickel oxide (NiO) is a Mott–Hubbard insulator at room temperature, but according to simple energy band theory, it should be a conductor. Hence, Verwey, De Boer and Mott were pointed out this problem and, explained the poor conductivity of NiO by using the Heitler–London approximation. The electrical conductivity and the dielectric constant of pure NiO at room temperature are the order of $10^{-13}$ ohm$^{-1}$ cm$^{-1}$ and 11.9 respectively [11]. The insulating property of NiO can be tuned to semiconducting nature by substituting lithium (Li+) ions [1]. Recently, semi-transparent p-type conducting films of the nickel oxide (NiO) have attracted considerable attention because of their importance in several scientific applications, including (i) material for electrochromic display devices [16,9], (ii) functional sensor layers in chemical sensors [10], (iii) transparent electronic devices [19] and (iv) the magnetic properties of nanoparticles [18,17,5,3]. Nan et al. [6,7,8] reported that Li and Ti co-doped NiO bulk materials had an extraordinarily high dielectric constant ($\varepsilon_s \approx 10^4 \sim 10^5$) and high temperature and frequency stabilities. The giant dielectric constant response of the doped NiO may be attributed to a grain boundary-layer mechanism as found in boundary-layer capacitors [6,7,8]. Gokul et. al.,[4] reported that NiO nanoparticles possess negative temperature coefficient resistance and the ac and dc conductivities depends on the temperature and the particles. In similar fashion, Marllick et. al.,[14] investigated the activation energy and frequency of NiO and Fe doped NiO, and they found that the activation energy and frequency depending on electrical conductivity. In this study, the effect of heat treatment such as annealing temperature on microstructures and dielectric properties of NiO doped MnO$_2$,Ag$_2$O and CaO were investigated in order to optimize the dielectric properties.

Materials and Methods:

The powder was prepared using the mixed oxide method in alcoholic medium. All the oxides used were analytical grade: NiO, MnO$_2$, Ag$_2$O and CaO. The molar compositions of the investigated systems were as shown in Table 1. In this study, these compositions were chosen to evaluate the phenomena involved on the physical and electrical properties of this system.
Two discs were used, the first one has 1.2 cm diameter and 0.2 cm thickness, and the second disc has 5 cm diameter and 0.2 cm thickness. These two discs were processed by a semi-dry press method under 70 KN. The pellets were sintered at (800 – 1200 0C) for 2 h in oxygen atmosphere and slowly cooled to room temperature (5 0C/min). The optimum firing temperature for each mix was deduced from the determination of the following parameters; firing shrinkage, and water absorption. The method given is according to the ASTM standard (C71, C72) [2]. The different mixes were examined by XRD. Using Philips apparatus type 170, a vanadium (λ =1.54 Å) and Ni-filter. In Metallurgy Research Center, Egypt. A continuous plot of intensity for 20 values 4 to 80 was made at a scanning speed of 1o / min, with a paper speed of 10 mm/min. Mean grain size was determined by analyzing the SEM micrographies (Joel-JEM. T 200). To perform the electrical measurements, silver contacts were deposited on the sample surfaces. The (I-V) measurements of these samples were made by using a DC power supply in a current range up to 2 mA and pulse technique (8×20 μs current pulses) for higher current ranges as described elsewhere . The non-linearity index (α) was calculated in a current range of 1 mA to 1 A using the following equation:

$$\alpha = \frac{\log I_2 - \log I_1}{\log V_2 - V_1}$$

Where I1 and I2 are the currents at the voltages V1 and V2. The connection of semiconductor sample in electric circuit is show in Fig. 1.

The PM 6304 programmable automatic RCL meter was used for precise measurements of resistance, capacitance and inductance. From the measured values of capacitance, the dielectric constant at all frequency from 1 KHz-20 KHz was calculated at constant temperature. The capacitance and resistance at constant temperature were measured at different between (1-30) KHz and the respective permittivity [ε'] was calculated according to the following relations :

$$\varepsilon' = \frac{C \cdot d}{\varepsilon_o \cdot A}$$

Where C = capacitance In farad. d = thickness of specimen in m.

$$\varepsilon_o = \text{dielectric constant of vacuum } 8.85 \times 10^{-12} \text{ F/m.}$$

A = area of specimen in m².

Also, from the values of resistance [R], the resistivity [ρ] and conductivity [σ] were calculated from the following relation:
Resistivity \([ \rho ] = \frac{RA}{d} \),

Conductivity \(( \sigma ) = \frac{1}{\rho} \).

Table (1): Composition of different mixes in mol %

<table>
<thead>
<tr>
<th>oxides</th>
<th>NiO</th>
<th>MnO2</th>
<th>CaO</th>
<th>Ag2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>98.1</td>
<td>0.9</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>C2</td>
<td>98.3</td>
<td>0.7</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>C3</td>
<td>98.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Fig. 1. The position of semiconductor sample in electric circuit

Results and Discussion:

Minimum water absorption appears in samples (C2) and (C3) equal to 1.088 and 1.261 fired at 1200 °C for 2 hours, respectively. It is evident that better densification and less water absorption are achieved in all mixes fired at 1200 °C for 2 hours as shown in Fig. 2. Therefore, this temperature was the selected as the proper maturing temperature for all mixes. Above 1200 °C all samples were start of deformation. Results of firing shrinkage as a function of temperature of different are graphically plotted in Fig. 3, showed increase of shrinkage with rise in temperature. Maximum values of firing shrinkage were attained in specimens fired at 1200 °C for 2 hours. Higher sintering temperature and longer sintering times give rise to a reduction in bulk densities due to increased amount of porosity between the large grains of NiO resulting from the rapid grain growth induced by the liquid phase sintering.
Fig. (2): Water absorption of mixes C1, C2 & C3

Fig. (3): Firing % shrinkage of C1, C2 and C3

Fig. (4) shows the X-ray diffraction pattern of sample C2 annealed at 1050 °C for 10 min in oxygen atmosphere in which, Nickel – NiO , Hexagonal phase (RH) a=2.954 b=2.954 c= 7.236 at about 2θ=43.429 d=2.082Å, 2θ= 37.398 d= 2.40273Å, 2θ=63.008 d= 1.47410Å , 2θ=75.521 d= 1.25792 Å, 2θ=79.486 d= 1.20483Å.[PDF
number is (166)-3-54.6827]. Nickel Manganese oxide – Ni₃MnO₈ – Cubic phase –(a=8.324 b=8.324  c = 8.324 ) at about 2θ=37.398  d= 2.40273Å, 2θ=43.429  d= 2.082Å, 2θ=63.008  d= 1.47410 Å [PDF number is 9225]).

Fig. (4): XRD of mixes C2

SEM of mix (C₁), which containing NiO, (1.0337) mol % MnO₂ and (0.295) mol % CaO, present in Fig. (5), shows exsolution two liquid phase, grain growth, grains pelt shape, melt phase, crystalline phase, exsolution miscibility and Mn enter the lattice of Ni. The scanning electron (SEM) micrographs of the Mn- doped NiO sample are present in Fig.(5). It is seen in figures that the microstructure has the certain type grain and also the voids take place between the grains. It is also found that the Mn, Ca, and Ag atoms are diffused into the NiO grains. In addition to NiMnO₃ and Ni₃Mn grains are observed Fig.(5). The grains in microstructure may have an important effect on electronic properties of the sample.
Fig. (5): SEM of mix (C1)

(a) Thermally etched surface, general view $X = 500$.

(b) Thermally etched surface, showed two phases NiO grains and intergranular phase at triple point $X = 1000$. 
SEM of mix (C₂) which containing NiO, (1.4510) mol % MnO₂ and (0.295) mol % CaO, present in Fig. (6), showed grain growth of NiO grains in preferred orientation Mn enter the lattice of NiO, grain plet shape and crystalline phase.

**Fig. (6): SEM of mix (C₂)**

(a) Thermally etched surface, general view X = 500.

(b) Thermally etched surface growth in preferred orientation in NiO grains, X = 1000.

The relation between I and V for the different mixes C1,C2 and C3 show very good plateau in (I-V) relation as shown in Fig.(7). The non-lineare behavior in NiO base materials is
attributed to the formation of interface states in the band gap of NiO which lead to the development of potential barriers to electrical conduction at NiO grain boundaries.

Fig. (7) : (I – V ) Characteristics of mixes C1,C2, and C3

Fig. (8) shows Variation of Capacitance (pf) with Frequency (KHz) at room temperature of mixes C1,C2 and C3 which contain NiO, CaO, MnO₂ and Ag₂O. The measured data show that the capacitances decrease generally with increasing frequencies. The measured data are also very small due to the presence of Ag₂O. The capacitance was increased with decreasing the mol% MnO₂ in present of Ag₂O and CaO, become more conducting in the presence of Ag₂O in comparison with insulating sample.

Fig (8) Variation of capacitance (pf) with frequency of mixes C1,C2 and C3
The results of dielectric constant as a function of frequency (1-20) KHz at room temperature for prepared samples NiCaMnAgO$_4$ of mixes C1,C2 and C3 are graphically plotted in Fig.(9). It is clearly observed from this Fig. that the dielectric constant $\varepsilon$ decreases with increase frequency for NiCaMnAgO$_4$ samples, in a behavior similar to that exhibited by most semiconducting materials [12]. For mixes which contain NiO, CaO, MnO$_2$ and Ag$_2$O, the measured data show that the dielectric constants decrease generally with increasing frequencies. But the measured data is also very small due to the presence of Ag$_2$O. The dielectric constant was increased with decreasing the mol% MnO$_2$ in present of Ag$_2$O and CaO. In the presence of Ag$_2$O, the samples become more conducting, dielectric constants are maintained at constant values as frequency increases up to 5 KHz. But at 5KHz abrupt change in dielectric constant which is caused dielectric relaxation is shown for all the powder amounts of mixes. The relation is presumably due to change of polarization mode of NiCaMnAgO$_4$ powders with frequency, transferring from dipole polarization to ionic polarization region.

Fig.(9). Dielectric constant as function of frequency of mixes C1,C2 and C3

Fig. (10) shows Ac conductivity plots of conductivity versus frequency of Mn-Ca –doped NiO . It is apparent from the figure that the conductivity exhibits a semiconductor behavior with frequency . This suggests that the activation energy required for the hopping process in
the Mn- Ca-Ag-doped NiO is low. This activation of charge carrier is indicative of a hopping conduction mechanism. The activation energy decreases with increasing frequency. Also the conductivity increases with increasing frequency at room temperature, may be attributed to the increase in the number of dipoles. The increase of frequency raised the conductivity because it increases the ionic response to the field again this is related to intergranular material at the field again this is related to intergranular material at any particular temperature. These effects are associated with polarization currents arising from trapping states of various kinds and densities. The increase in frequency raised the conductivity as a result of the increase in ionic response to the field again this is related to inter-granular material.

Fig (10) AC Conductivity as a function of frequency of mixes C1, C2 and C3.
Reference


