

Synthesis, characterization and dielectric properties of nanocrystalline nickel

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Nickel nanoparticles were synthesized by thermal decomposition route. It was characterized by XRD, TEM and FTIR spectroscopy. Dielectric properties and *ac* electrical conductivity were measured by impedance spectroscopy. The particle sizes calculated from XRD and TEM measurement were about 1.22 and 10 nm, respectively. FTIR spectra showed the presence of organic elements. The variation of dielectric constant, dielectric loss and *ac* electrical conductivity with frequency and temperature, has been studied.

Keywords: Thermal decomposition, XRD, TEM, FTIR, Dielectric constant, Dielectric loss, Electrical conductivity

1 Introduction

The small grain size of nanomaterials has significant effect due to drastic change in the physical properties of the materials used for their interconnects and components¹. The issue of the dielectric property for nanomaterials is very important and attractive for their potential applications as capacitor, memory device and sensor²⁻⁶. The dielectric property of nanomaterials interestingly exhibits unusual property which will give rise to develop new materials². The frequency behaviour of dielectric materials gives the valuable information about the conduction phenomena of nanostructures materials with their capacitants⁷. It is to be noted that the dielectric properties in nanomaterials have some interesting aspects especially for metal nanoparticles in which the capacitants are basically insulating and the core is metallic. However, when they form such complex system of nanoparticles, the basically insulating capacitants would change their insulating state into more conductive phase, due their ionic form, while those of the metal turning into insulating phase as the particle size is reduced to that of a few atoms big (~1 nm), due to quantum size effect. How this situation influences their overall dielectric properties is of fundamental importance. In the present paper, the variation of dielectric constant, dielectric loss and *ac* electrical conductivity with frequency and temperature has been studied.

2 Experimental Details

Nickel nanoparticles were synthesized by thermal decomposition through complexation of nickel

(acetylacetonate)₂, Ni(acac)₂ with oleylamine (OA) and consequent reaction with triphenylphosphine⁸ (TPP). All reactions were carried out in Ar atmosphere. Typically, the Ni-OA complex was prepared by reacting 1.568 g Ni(acac)₂ and 6 ml of OA at 100°C under Ar atmosphere. In the resulting metal complex solution, 15.013 g of TPP pre-heated at 215°C was injected. The colour of the solution changed from green to black, indicating that colloidal nanoparticles were generated. The black solution was heated for 2 h at ~210°C. Then, the solution was cooled to room temperature. The nanoparticles were precipitated by adding excess ethanol to the solution. The precipitated nanoparticles were retrieved by centrifugation. The nanoparticles could easily be redispersed in non-polar organic solvents such as toluene. The XRD measurement was carried out using Bruker D8 advance X-ray diffractometer employing Cu-K α radiation in the 2 θ range 30° to 90° at 30 mA, 40 kV. In the present investigation, TEM measurements were carried out using TECHNAI-20-G², with resolution of 1.4Å, equipped with a CCD camera. Samples for TEM imaging were prepared by dispersing a few microgram of specimen in toluene and dropping the diluted solution over carbon coated copper grid. Fourier Transform Infrared Spectroscopy (FTIR) was carried out with a Bruker Model Vertex 70 spectrometer. The method for sample preparation was to grind a quantity of the sample with potassium bromide salt finely. In the powder mixture, there was 1% Ni nanoparticles powder and it was then pressed in a hydraulic press to form a transparent pellet (diameter-10 mm, thickness-0.5 mm) through which

the beam of the spectrometer can pass. The dielectric measurements were carried out in the temperature range 10-300K using a high frequency analyzer (Model: Alpha-A of NovoControl technologies), which has the frequency range of 1 μ Hz to 40 MHz and a constant (RMS) *ac* voltage of 1.5 V.

3 Results and Discussion

The XRD pattern of Ni-NP sample shows a broad peak at 44.92° (Fig. 1) indicating very small particle size and *fcc* structure. The *fcc* structure was confirmed from selected area diffraction pattern (Fig. 2d). The

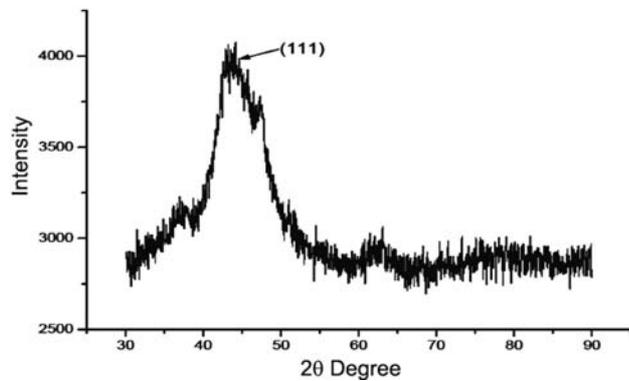


Fig. 1 — XRD pattern of Ni nanoparticles

particle size D of the synthesized Ni-NPs was calculated using Scherrer equation $D=0.9\lambda/\beta\cos\theta$ where β is the full width at half maximum and λ is 1.54\AA , θ is Bragg's angle. The particle size was 1.22 nm.

Bright field TEM image of Ni-NP sample (Fig. 2a) indicates that particle size is about 10 nm, which is much bigger than that estimated from XRD. However, the size seen from the dark field TEM image (Fig. 2c) almost matches that of XRD size. Therefore, on the face value capping thickness is rather large. The HRTEM image (Fig. 2b) shows that particles are spherical in shape and particles size about 10 nm. This is attributed to difference in the detection processes. The XRD actually determines the crystallite size of the metallic nickel while TEM determines the real sizes arose from the combined crystalline plus the capping (oleylamine and triphenylphosphine). This is supported by SAED pattern shown in the Fig. 2(d). For well-washed nanoparticles, FTIR spectra (Fig. 3) shows characteristic vibration bands particularly at 3401 , 2918 , 2326 - 2366 , 1590 - 1650 , 1552 , 1050 , 678 and 578 cm^{-1} . The band at 3401 cm^{-1} is due to N-H stretch and the band at 2918 cm^{-1} is due to C-H stretch. The band at 1590 - 1650 cm^{-1} is due to NH_2

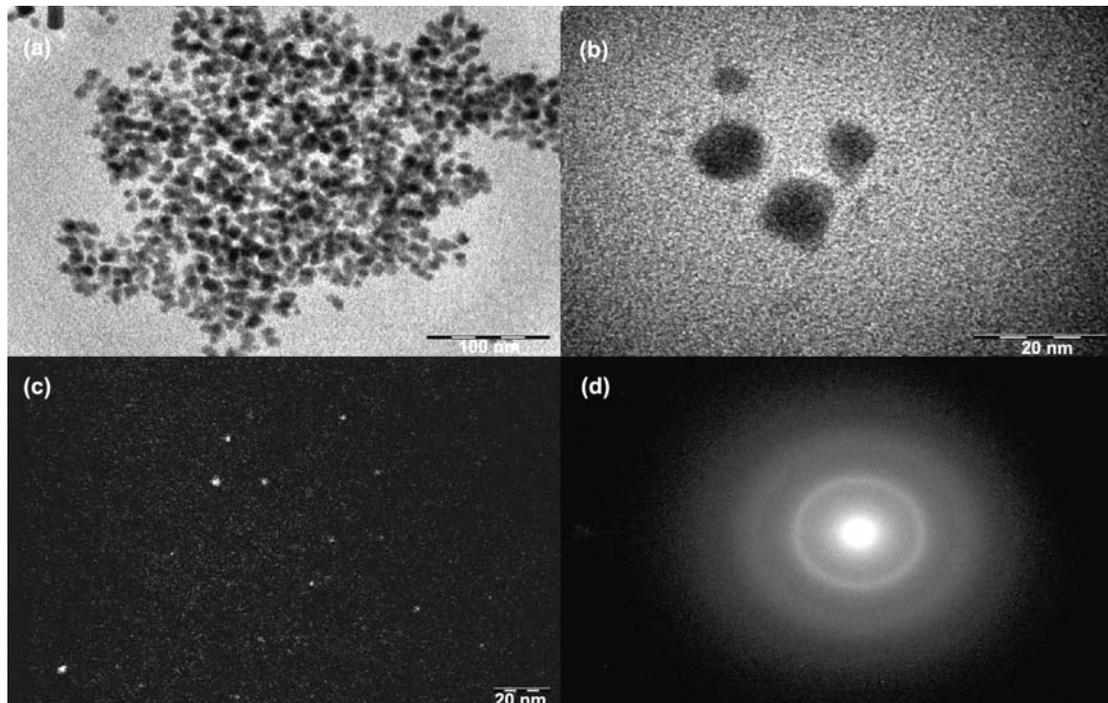


Fig. 2 — TEM (Transmission Electron Microscope) image of Ni nanoparticles. (a) Bright field TEM (Transmission Electron microscope) image of Ni nanoparticles. (b) HRTEM images of Ni nanoparticles. (c) Dark field TEM image of Ni nanoparticles. (d) SAED diffraction pattern of Ni nanoparticles

wag and the band at 1552 cm⁻¹ is due to C=C bond (benzene group). The bands at 1050 cm⁻¹, 678 cm⁻¹ and 578 cm⁻¹ are due to C-O bond, phenyl group, and acetylacetonate anion⁹, respectively.

Figure 4 shows the variation of dielectric constant with frequency at different temperature range between 20-300 K. The dielectric constant decreases rapidly with increase in frequency in the low frequency range and it reaches a constants value at high frequency range which is independent of frequency (Fig. 4). This behaviour can be explained by the polarization process present in the materials¹⁰. Basically, nanostructures samples contain large defects in their interfaces which can cause a positive and negative space charge distribution in these interfaces. Due to the applying of magnetic field, these space charges move and are trapped by these defects resulting a space charge polarization in the materials. The high value of dielectric constant at low frequency is due the space charge polarization¹⁰⁻¹². The dielectric constant is almost constant at high frequency which is due to hopping contribution¹².

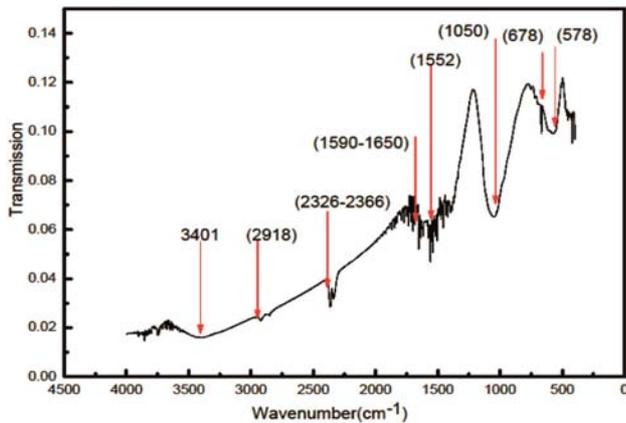


Fig 3-FTIR spectrum of Ni nanoparticles

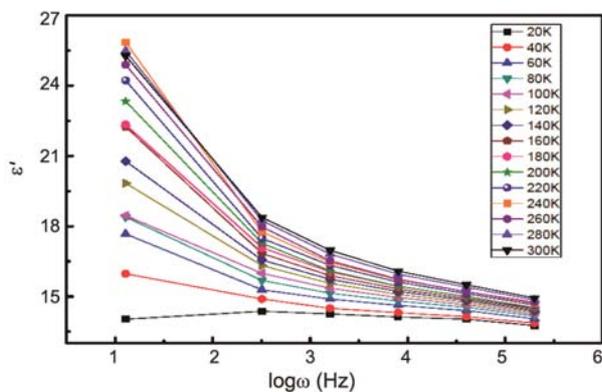


Fig. 4 — Variation of dielectric constant with frequency at different temperatures

Figure 5 shows the variation of tangent dielectric loss with frequency at different temperatures. The dielectric loss (tanδ) or χ_ω^{''} is defined as the imaginary component of the complex dielectric susceptibility¹³:

$$\chi_{\omega} = \chi'_{\omega} - \chi''_{\omega} = \left[\frac{\epsilon_{\omega}}{\epsilon_0} \right] - 1 \quad \dots(1)$$

The corresponding *ac* conductivity is

$$\sigma_{\omega} = \epsilon_0 \omega \chi''_{\omega} \quad \dots(2)$$

The observed frequency dependence of dielectric loss in a wide range of materials may be expressed by the empirical relation¹³

$$\chi''_{\omega} = \Lambda(T) \omega^{n-1} \quad \dots(3)$$

where $\Lambda(T)$ is a temperature dependent function and the value of n lies in the range $0 < n < 1$. According to Eq. (3), the variation of loss tangent with frequency should be flat in nature. In nickel nanoparticles, dielectric loss becomes flat at high frequency region due the contribution of hopping mechanism and at low frequency region it decreases very rapidly due to the space charge polarisation¹¹⁻¹³.

The temperature dependence of dielectric constant and dielectric loss with different frequency is shown in Figs 6 and 7. The dielectric constant and dielectric loss both are found to be increasing with increasing temperature. With increasing temperature, there will be orientation of much more dipoles which results into an increased value of dipole moment. It is also observed that dielectric constant and dielectric loss increase more rapidly at lower frequencies than higher frequencies. At low frequencies, the rapid increase of

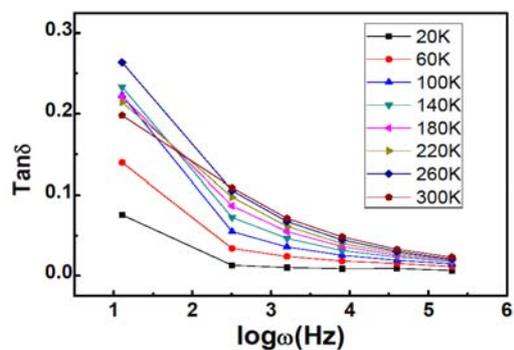


Fig. 5 — Variation of dielectric loss (tangent) with frequency at different temperatures

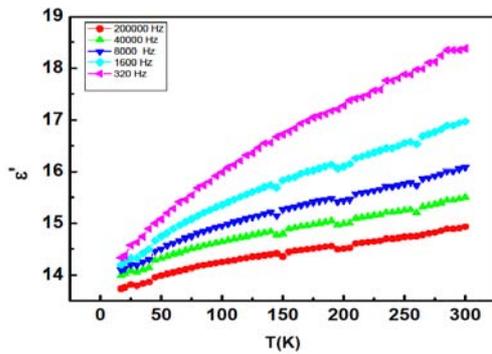


Fig. 6 — Variation of dielectric constant with temperature at different frequencies

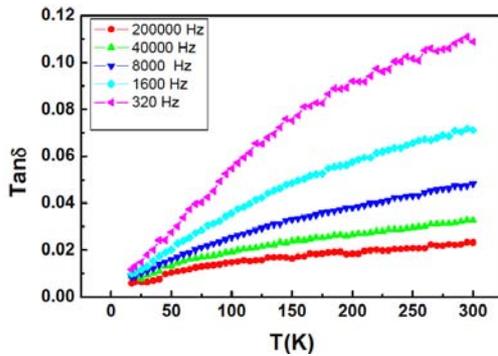


Fig. 7 — Variation of dielectric loss (tangent) with temperature at different frequencies

dielectric constant and dielectric loss is due the interfacial and dipolar polarization¹⁴.

From Fig. 8, it is seen that *ac* conductivity increases with increasing frequency for all temperature. The conductivity is higher for higher frequency, is due the presence of polaron hopping in the sample¹⁵. The *ac* electrical conductivity of dielectrically materials consists of two parts¹⁶.

$$\sigma_{ac} = \sigma_T + \sigma_\omega \quad \dots(4)$$

the first term σ_T , which is frequency independent and temperature dependent, is due to the drift mobility of charge carriers. The second term σ_ω is related to the dielectric relaxation due to the localized electric charge carriers^{17,18}. It can be expressed as:

$$\sigma_\omega = A\omega^n \quad \dots(5)$$

where the constants *A* and *n* are both temperature and composition dependent parameter, where *A* has the units of conductivity and ω is the angular frequency. The *ac* conductivity increases with increasing frequency which is due the small polaron hopping.

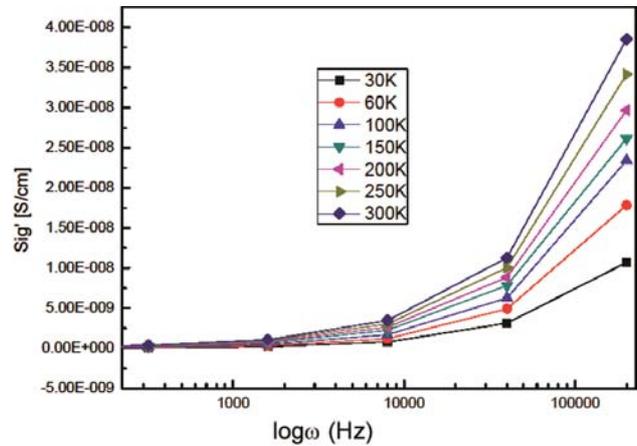


Fig. 8 — Variation of *ac* electrical conductivity with frequency at different temperatures

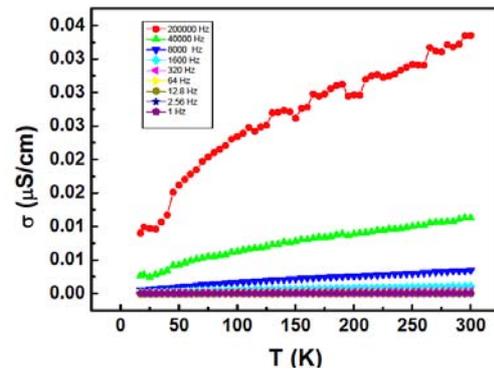


Fig. 9 — Variation of *ac* electrical conductivity with temperature at different frequencies

Figure 9 shows that *ac* conductivity increases with increasing temperature which is rapidly increasing for higher frequency. This means that the confined carriers started hopping between the interwells due the vibrations from *ac* signal. This enhances gradually as the frequency increases which leads to significantly larger slope in the conductivity.

4 Conclusions

Nanocrystalline nickel samples have been synthesized by thermal decomposition method. XRD pattern suggests that particle size in the range about 1nm. It was, however, about 10nm as obtained from TEM. The dielectric properties of this sample have been studied in a wide range of temperature (17-300 K) and frequency (1 Hz-1 MHz). The dielectric constant and dielectric loss decrease rapidly with increase in frequency in the low frequency range and it reach a constants value at high frequency range which is independent of frequency. The high value of dielectric constant at low frequency region is due to

the space charge polarization and almost constant value at high frequency region is due to the hopping contribution. The dielectric constant and dielectric loss both increase with increasing temperature. At low frequencies, the rapid increase of dielectric constant and dielectric loss is due the interfacial and dipolar polarization. The *ac* conductivity increases with increasing frequency for all temperature and is higher for higher frequency which is due the presence of polaron hopping. The *ac* conductivity also increases with increasing temperature.

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