

Study of physical properties of nanocrystalline nickel

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Abstract—The dielectric property of Nanocrystalline nickel is studied. Ni nanocrystal have been synthesized by the thermal decomposition of the Ni (acac)₂ [Nickel (acetylacetonate)₂], oleylamine complex as a precursor⁽¹⁻³⁾. Trioctylphosphine [CH₃(CH₂)₇]₃P was used as both solvent and surfactant for control the size of the nanoparticles. Characterization of the nanoparticles has been done by the XRD and TEM method, XRD suggests that particle size is about 1nm while it is about 1-10nm from TEM data. The dielectric properties of this sample are studied in a wide range of temperature (17K-300K and frequency (1Hz-1MHz). The dielectric constant decreases with increasing frequency which is described by polarization. The electrical conductivity increases with increasing frequency which is explained by considering the hopping mechanism. This is in addition to the size effect expected in these metal nanoparticles, which shall lead to semiconducting behavior. The AC-conductivity slowly increases with increasing temperature. The significant change in the dielectric constant for this Nanocrystalline nickel is observed as temperature is varied showing that conduction processes are thermally activated.

Keywords—Dielectric property; Nanocrystalline nickel; Electrical conductivity; Frequency

I. INTRODUCTION

Synthesized Monodispersed nanocrystalline nickel particles are significant importance of their application in magnetic storage devices, magnetic carriers for drug targeting and catalysis, ferrofluids, magnetic refrigeration system⁽⁴⁻⁵⁾. Nanostructured systems are useful in designing the electrical, magnetic and optical properties of materials⁽⁶⁻⁷⁾. It is clear that Nanostructured material will have an increased impact on electronics because the modern world require handy electronics device with better functionality. Nanocrystalline materials are reported to exhibit different and improved properties compared to their bulk counterpart and studies of the physical properties of nanomaterial are very important. The dielectric property of nanocrystalline materials exhibits unusual property that plays a vital role in the development of new materials. High dielectric materials are very important and attractive for their potential application as capacitors, memory devices and sensors. The studies on the effect of frequency in the dielectric behavior and ac conductivity give valuable information about the conduction phenomena of nanostructured materials. Here the variation of dielectric constant, dielectric loss, loss factor, and modulus and ac conductivity with frequency of applied field and temperature has been studied.

II. MATERIALS AND METHODS

Nickel nanocrystalline particles are prepared by thermal decomposition of Ni(acac)₂ and oleylamine mixture. The TOP (Tri Octyl Phosphine) is used as both solvent and surfactant for control the size of Ni nanoparticles. The Nickel oleylamine complex was prepared by allowing the reaction between 0.52gm nickel acetylacetonate [Ni(acac)₂ Aldrich Chemical Co., 95%] and 2 ml oleylamine reducing agent. [Aldrich Chemical Co., 80%]. This reaction mixture is heated on heating mantle until the temperature reaches up to 100°C. Sky blue color solution appeared at the end of reaction. Now take 5 ml capping agent Tri-octyl-phosphine (TOP, Aldrich Chemical Co., 99%) in a test tube and heat it up to 215°C. Then, it is added into Ni-oleylamine complex solution. After addition, dark green color solution appeared and within one or two minutes the solution turns into black solution. Appearance of black color indicates that colloidal nanoparticles were generated. For complete formation of nanoparticles the above black solution is heated at 200°C for 30 minutes. After this, the resulting solution was cooled at room temperature. In this way finally we get black precipitate of nickel nanoparticles in solution. In this step we got thickened colloidal nickel nanoparticles from black solution. The nickel nano particles were precipitated by adding excess of ethanol to the solution and with this process separated the greenish supernatant. Finally obtained nickel nanoparticles were dried in an oven range up to 150°C. The yield of overall synthesis was 50% of the amount of Ni(acac)₂. The nanoparticles could be easily dispersed in non polar organic solvent such as hexane or toluene. The size of nanoparticles can be controlled by using different type of capping agent such as Tri-Octyl-Phosphine (TOP, 5 ml Aldrich Chemical Co., 99%) form 2 nm sized nanoparticles while Tri-Phenyl-Phosphine (TPP, 5 gm Aldrich Chemical Co.99%) form 7 nm sized nanoparticles⁽⁸⁻¹⁰⁾. This capping agent acts as a solvent & surfactant both.

III. RESULTS AND DISCUSSION

X-ray diffraction

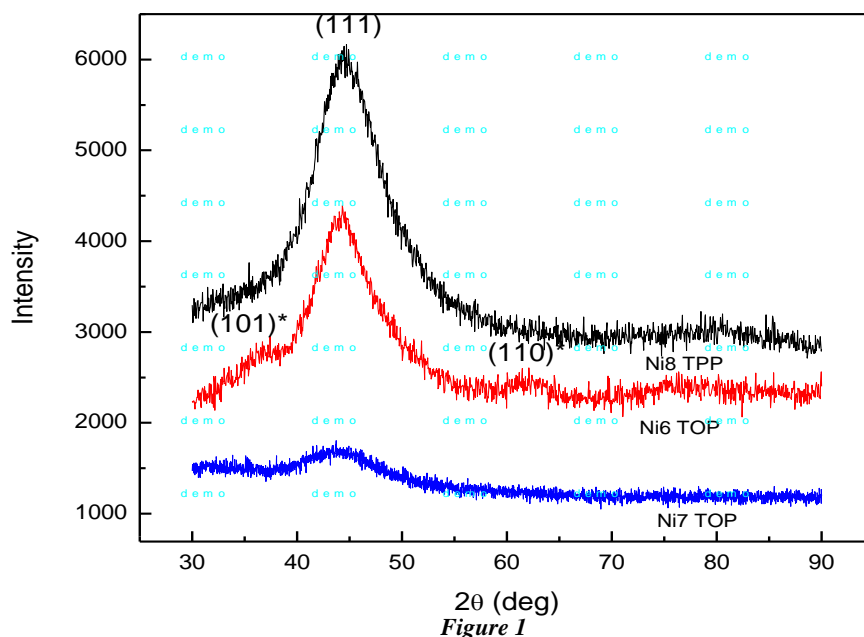


Figure 1

The curves show XRD patterns of the samples with different concentration of reactants and capping agents. From this XRD pattern of samples we have calculated the average grain size and their corresponding lattice parameter. The diffractograms exactly match the standard XRD pattern of face-centered cubic Ni, which proves the fcc structure of nanocrystalline nickel⁽¹¹⁾. The exhibition of a broad peak clearly indicates the formation of very small size particles, which is nearly amorphous. The peak corresponds to (111) plane. A close observation indicates that the peak position and width get change with concentration of reactant and concentration/ type of capping agent^(12,13). These are shown in Table.1. To see the stability in the storage of the nanoparticles, XRD of Ni6 samples was carried out (figure 1). It is clearly seen that there are two extra peaks (101) and (110). These shows the nanoparticles get oxidized in air, but not completely to oxide within 24Hr. We observed only partial oxidation, which too in two days.

TEM & SEM Result:

It is clear from the image that the particle size distribution exists such that it extends something like 100-500nm, which is extremely large compared to that found from XRD which is just nearly 1nm. This indicates that the image shown is the agglomerated particles⁽¹⁴⁾. It is however clear that for certain sizes, the particle sizes are uniform that is monodispersed⁽¹⁵⁾. It is interesting to note that particle sizes are highly uniform showing clear monodispersity as against that observed in SEM with different sizes. The particle size is approximately 10 nm, which is about ten times that observed in XRD. This is correlated with the shorter coherence length of X-rays in the medium and therefore related to the capping agent, which has perhaps a significant thickness. If this is correct, the capping agent will take a dominant role in the transport properties of the colloidal Ni.

Scanning electron microscopy (SEM)

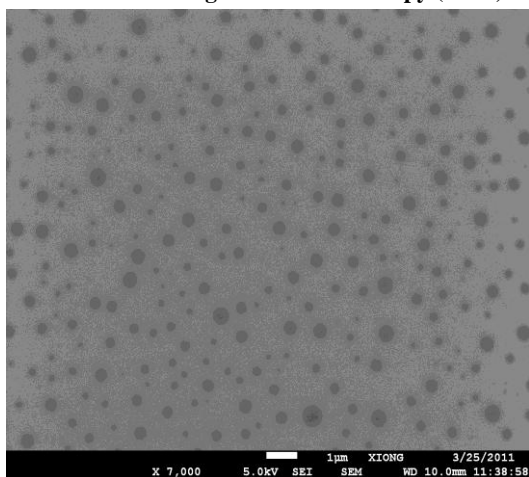


Figure: 2 SEM image of Ni7 sample.

Transmission electron microscopy (TEM)

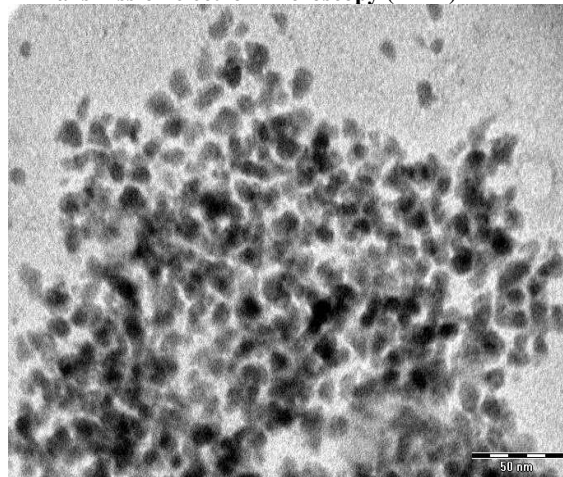


Figure: 3 TEM image of Ni7 sample

UV-Visible Spectroscopy

The UV-Visible spectrum of sample Ni6 is shown in Figure 14. Three peaks are seen at 317nm, 475nm and 524nm. They are assigned to the presence of the ionic form of ketone ($=C=O$)⁽¹⁶⁾ nickel(II) acetylacetonate, amine ($-NH_3$) of oleylamine⁽¹⁷⁾ and phosphorus (P) and phenyl ($-C_6H_5$) groups of trioctylphosphine⁽¹⁸⁾. It is because these functional groups are more stable when they are kept in this present order. That means that phosphorus and phenyl groups are the most stable groups and so on. This is in addition to the quantum size effect in this metallic state in bulk. In the quantized state, Ni can also become semiconductor. This makes the system interesting for investigation in its dielectric properties.

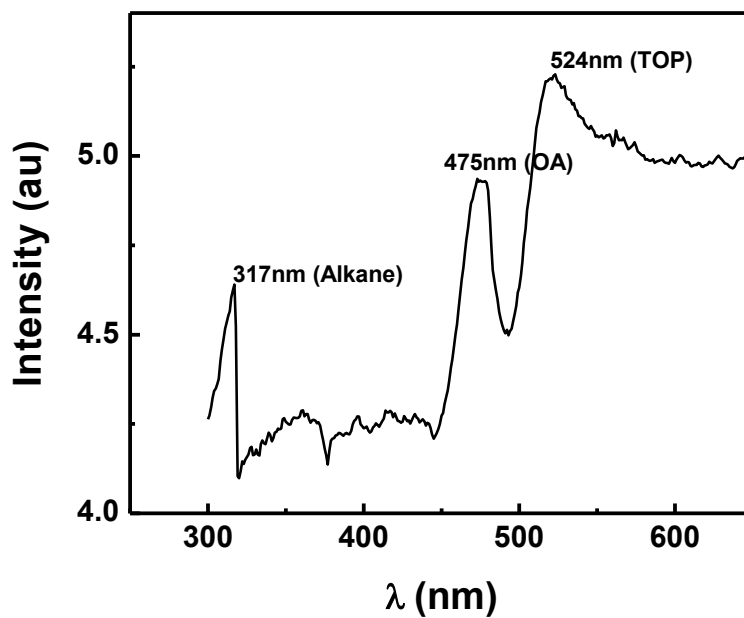


Figure 4 UV-Visible spectrum of sample Ni6.

Variation of Dielectric Constant with Frequency

Figure 5 and 6 shows the variation of dielectric constants with frequency at different temperatures for nanocrystalline nickel. It can be seen from the figure that the real part of dielectric constant initially decreases rapidly with increase in frequency and as frequency increases, ϵ' takes a constant value. In dielectric nanostructured samples, interfaces with a large volume fractions containing a large number of defects, such as dangling bonds, vacancies, vacancy clusters and micro porosities, which can cause a change of positive and negative space charge distribution in interfaces. When subjected to an electric field, these space charges move. When they are trapped by defects several dipole moments are formed. At low frequency region these dipole moments easily follow the change of the electric field and hence dielectric loss and the dielectric constant show large values at low frequency⁽¹⁹⁾. In an overlapped potential well, at least a few holes executing interwell hopping reverse the direction of motion when the electric field direction reverses. Thus interwell hopping contributes to dielectric relaxation at low frequencies. In normal dielectric behavior, the dielectric constant remains almost constant at high frequency because beyond a certain frequency of electric field, intrawell hopping becomes prominent, and the charge carriers do not get enough time for long range hopping before field reversal. As a result at high frequency region only intrawell hopping exists, because the average hopping distance for intrawell hopping is one lattice spacing while that for interwell hopping is of the order of few nanometers. As a result polarization decreases as the signal frequency is increased. In MHz region, the charge carriers would barely have started to move before the field reversal occurs and ϵ' falls to a small value at higher frequencies in nanocrystalline nickel of this sample⁽²⁰⁾. It is thus amply clear that in spite of the fact the nickel in bulk is metallic in nature; the present colloidal nanocrystalline nickel has very large dielectric constant showing its good dielectric properties. This characteristic might be of immense importance in electronics and other applications.

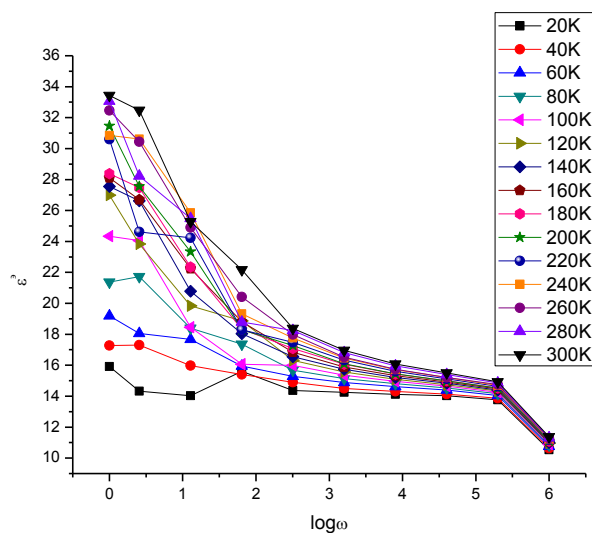


Figure 5 Variation of dielectric constant with frequency of nanocrystalline nickel.

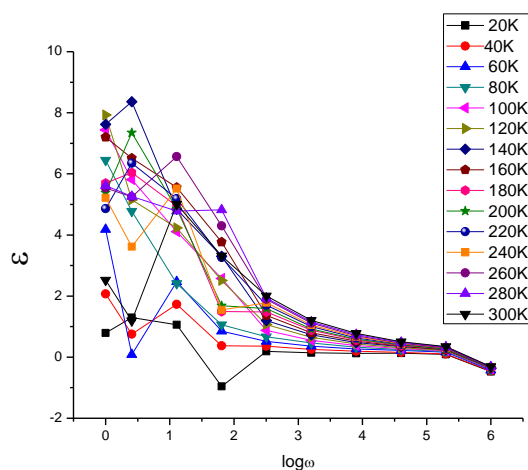


Figure 6 Variation of imaginary part of dielectric constant with frequency of nanocrystalline nickel

Variation of AC Electrical Conductivity with Frequency

The ac conductivity which is found to be high for higher frequency shows a trend necessary for small polaron hopping⁽²¹⁾. It is seen from figure 7 that conductivity increases with increase in frequency for all temperatures. The nature is similar for all other temperature but the value is shifted upward as temperature is raised. The conductivity increases with frequency at all temperatures⁽²²⁾. The real ac conductivity σ_{ac} , consists of two parts

$$\sigma_{ac} = \sigma_T + \sigma_{\omega} \quad (1)$$

The first term σ_T which is frequency dependent and temperature dependent

is due to the drift mobility of electric charge carriers. The second term σ_{ω} related to the dielectric relaxation caused by the localized electric charge carrier. It can be expressed as,

$$\sigma_{\omega} = B\omega^n \quad (2)$$

where ω is the angular frequency. The exponent n is a dimensionless constant while B is a constant having the unit of conductivity $((\Omega \text{ cm})^{-1})$ and is temperature dependent. When an electric field is applied either the long-range interwell hopping or a short range intrawell hopping may occur. The long-range interwell hopping of holes occurs between sites located in adjacent defect-potential wells, and short range intrawell hopping of holes occurs within one defect-potential well. The interwell hopping contributes to the dc part of the total conductivity while intrawell hopping contributes to the pure ac conductivity⁽²³⁾.

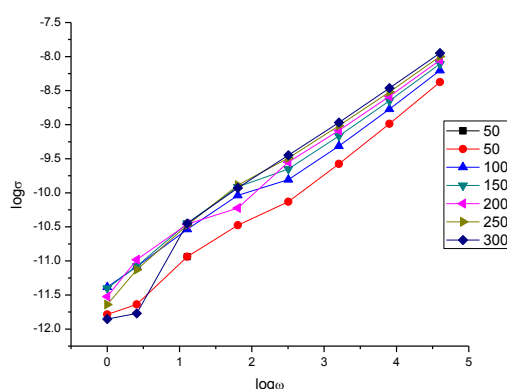


Figure 7 Variation of ac conductivity with frequency of nanocrystalline nickel

Variation of Ac Electrical Conductivity with Temperature

It is seen from the figure 8 that ac conductivity increases with increase in temperature as well as increase in frequency. It should be noted that these conductivity values are nine orders of magnitude smaller (10^{-9}) than its bulk counterpart ($\sim 0.14 \times 10^6 \text{ S/cm}$). This is remarkable.

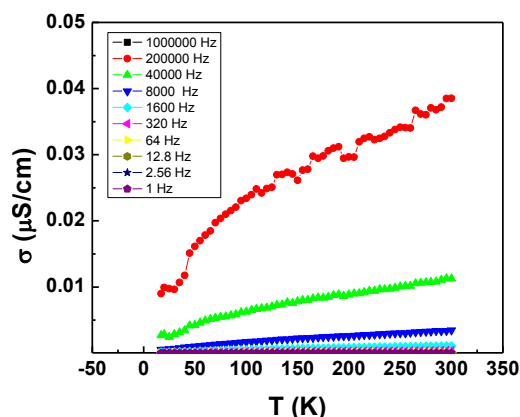


Figure 8 Variation of ac conductivity with temperature

IV. CONCLUSION

Nanocrystalline nickel sample have been made by thermal decomposition method⁽²⁴⁾. XRD suggest that particle size is about 1nm while it is about 10nm from TEM data. This means that the actual particle size nickel is about 1nm and the remaining part might be the capping, which is dielectric or insulating medium. This is in addition to the size effect expected in these metal nanoparticles, which shall lead to semiconducting behavior. The dielectric properties of this sample are studied in a wide range of temperature (17K-300K) and frequency (1Hz-1MHz). The dielectric constant decreases with increasing frequency which is described by polarization. The electrical conductivity increases with increasing frequency which is explained by considering the hopping mechanism. The ac conductivity slowly increases with increasing temperature. The significant change in the dielectric constant for this nanocrystalline nickel is observed as temperature is varied showing that conduction processes are thermally activated. These properties may find applications in electronics and other areas⁽²⁵⁾.

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