


Dielectric Behaviour of Magnetic Nickel Nanoparticles Encapsulated in Silica

Radha M.^{1*}DOI: <https://doi.org/10.58260/j.nras.2202.0104>^{1*} M. Radha, Research Scholar, Bharat Institute of Higher Education and Research, Chennai, Tamil Nadu, India.

The impedance measurement showed activation energy of 1.3 eV and decrease in dc conductivity with temperature. The high dielectric constant over a wide frequency range is explained as a consequence of concentration of Ni much higher than the percolation threshold. The conductivity mechanism is dominated by tunneling at low frequency and electron hopping at high frequencies. The material suffers a low loss in high frequency range, making it suitable for high frequency magnetic applications.

Keywords: Nickel, Oxidation, Thermal Properties, Silica, Metal-Insulator Transitions, Electrical Measurements

Corresponding Author	How to Cite this Article	To Browse
M. Radha, Research Scholar, , Bharat Institute of Higher Education and Research, Chennai, Tamil Nadu, India. Email: radhalinga1984@gmail.com	M. Radha, Dielectric Behaviour of Magnetic Nickel Nanoparticles Encapsulated in Silica. Glo.Jou.Nov.Res.App.Sci. 2022;1(1):18-22. Available From http://nras.adsrs.net/index.php/nras/article/view/1	

Manuscript Received

Review Round 1

Review Round 2

Review Round 3

Accepted

Conflict of Interest
NilFunding
NilEthical Approval
YesPlagiarism X-checker
19%

Note



© 2022 by M. Radha and Published by ADSRS Education and Research. This is an Open Access article licensed under a Creative Commons Attribution 4.0 International License <https://creativecommons.org/licenses/by/4.0/> unported [CC BY 4.0].



Introduction

Nickel Nano forms attract continuing interest with their magnetic [1,2], optical [3,4], field emission [5], mechanical [6] and catalytic [7-9] properties. Nanocomposites of nickel with silica [10], carbon [11], polymer [12] and CNT [13] have been investigated for various applications. Nickel-silica nanocomposites have been obtained as Ni-embedded silica [14-17] and as core-shell structures with nickel at core [18-20] or as shell. Ni/SiO₂ nanocomposites have been shown to exhibit magneto-optical, magnetic and electrical [20] properties. In general, suitable encapsulation of nanoparticles is often preferred in nanotechnology in order to prevent grain growth or agglomeration and gain protection against oxidative or corrosive environments by surface passivation. In the case of ferromagnetic metal nanoparticles, their core-shell nanocomposites with the insulating silica further enhance their application potential by modification of their properties.

For example, nanocrystalline Ni despite its very good soft ferromagnetic properties and high Curie temperatures is not useful for high frequency magnetic applications due to unacceptably large eddy current losses. Silica coating of individual nanoparticles offer several advantages by protecting them against oxidative degradation and agglomeration and also increasing the resistivity several fold thus making them useful for high frequency magnetic devices.

Experimental Details

The Nano crystalline Ni powder was prepared by a hydrazine reduction method. Commercially available reagents of analytical grade were used without further purification in this synthesis. Typically, an aqueous solution of 0.2 M / 100 ml was first prepared by dissolving the precursor nickel chloride in water containing trace acetone (1 ml). Then, hydrazine hydrate solution (1 M, 5 ml) and NaOH solution in trace quantity (1 M, 2 ml) were added in sequence, following an earlier procedure [20]. Precipitation of ultrafine nickel particles was completed after 2 h on maintaining the reaction at 333 K. The black precipitate was recovered after repeated washing with double distilled water and ethanol. The synthetic Ni nanoparticles were annealed in air at 473, 573 and 673 K for 1 h.

The phase and microstructure of samples were characterized by X-ray Diffraction (XRD) using Cu-K 1 radiation on a high-resolution diffract meter from Huber Diffraktionstechnik. Magnetization measurements were carried out with an applied field up to 7 kOe on a EG&G Princeton applied research 4500 vibrating sample magnetometer (VSM). Thermal oxidation behavior of as-prepared nickel and Ni/SiO₂ powders were studied using a Perkin Elmer PC Series -7 thermo gravimetric analyzer (TGA) under oxygen atmosphere. Impedance characteristics in the frequency range of 1 Hz – 10 MHz were obtained for pellets of as-prepared and annealed Ni/SiO₂ powders using a Solectron SI 1260 impedance/gain phase analyzer. These experiments were also carried out for the as-prepared samples at temperatures from room temperature up to 363 K in steps of 10 K in normal atmosphere. JEOL EX2000 transmission electron microscopy (TEM) was used to study the microstructure of samples.

The silica coating of the Ni particles was carried out by hydrolysis of TEOS and its subsequent condensation as in Stöber process.

In order to prepare the Ni/SiO₂ Nano composite, the as-prepared Ni nanoparticles were re-dispersed in 25 ml of 4.2 vol% of ammonia (28% NH₃ in H₂O) in ethanol and immediately 25 ml of 10 vol% TEOS in ethanol was added slowly under vigorous stirring for 24 h and the product was then aged for 48 h. The resulting Ni/SiO₂ Nano composite powder was washed with acetone and dried by flash heating at 333 K. Portions of Ni/SiO₂ Nano composite powder were also annealed in air at temperatures of 573, 673, 773 and 873 K for 2 h.

Preparation of Cobalt Nanoparticles

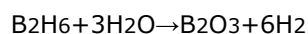
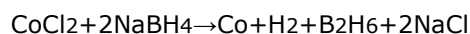
The chemical methods have been widely used to prepare nanostructured materials due to its potential to produce large quantity of final product and their control on particle size distribution and shape. Reduction of cobalt salts by strong reducing agents such as polyol [6], thermal decomposition, and hydrogenation [7] have been performed. In this work the simple sodium borohydride reduction method was used to prepare cobalt nanoparticles.

Laboratory reagent grade purified CoCl₂.6H₂O (98%) and NaBH₄ (97%) were obtained and used without further purification.

To prepare Co nanoparticles, 300ml of 0.3 of mol CoCl₂.6H₂O aqueous solution was prepared and stirred to get homogeneous solution. This original solution was pink in color. Then 100 ml aqueous solution of 1 M NaBH₄ was prepared and immediately added with the above solution. After addition of NaBH₄ solution, the solution color changed from pink color to black color. This color change indicates the reduction of cobalt cation into cobalt. The particles were allowed to precipitate. The precipitated particles were repeatedly washed using distilled water. Small amount of particles were separated from solution and stored in ethanol medium.

The remaining solution was separated into four parts and each part was annealed at 80°C in water bath for 60 min, 300 min, and 600 min respectively. The collected particles from each part of solution were stored in ethanol medium.

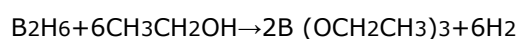
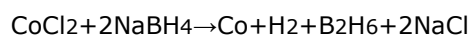
The reduction of cobalt chloride into cobalt in water medium involves following mechanism.



Similarly, cobalt nanoparticles were prepared with concentration of 0.1 mol of CoCl₂.6H₂O in 300 ml water. The particles were annealed at 80°C for 15 minutes and stored in ethanol medium.

To see the effect of capping ligands on structural and magnetic properties of cobalt nanoparticles, cobalt nanoparticles capped with trioctylphosphine oxide was prepared using same borohydride reduction method.

The preparation method involves following steps. Initially 0.5 mol of CoCl₂.6H₂O and 0.01 mol of TOPO were dissolved in 50 ml of ethanol and stirred to get uniform mixture of solution. Ethanol was chosen as a medium due to high solubility of TOPO in ethanol. Then 1M NaBH₄ in 50 ml ethanol solution was prepared and added to the above solution. The color change of solution from pink to black was observed. The precipitated particles were washed with ethanol. Particles were annealed at 80°C in water bath for 30 min, 60 min, and 120 min respectively. The reaction mechanism in ethanol medium is given below.



Results and Discussion

XRD patterns obtained for pure Ni nanoparticles as-prepared and annealed in air at 473, 573 and 673 K for 1 h are presented in Fig.1 and the patterns for the silica coated Ni particles as-prepared and annealed at 573, 673 and 873 K for 2 h are shown in Fig.2. The patterns correspond to diffraction from fcc-Ni. The estimated average grain size of the as-prepared Ni particles was 11 nm calculated for the (111) profile using the Scherrer formula. The onset of oxidation, as revealed by the first appearance of weak NiO peaks in Fig.1, is noticed at 573 K in the case of bare Ni nanoparticles and reaches completion at 673 K, whereas for the silica coated particles this onset occurs only at 673 K and oxidation proceeds slowly until 873 K (Fig.1). This establishes that silica coating provides increased thermal stability for these nanoparticles.

XRD patterns obtained for pure Ni nanoparticles as-prepared and annealed in air at 473, 573 and 673 K for 1 h are presented in Fig.1 and the patterns for the silica coated Ni particles as-prepared and annealed at 573, 673 and 873 K for 2 h are shown in Fig.1. The patterns correspond to diffraction from fcc-Ni. The estimated average grain size of the as-prepared Ni particles was 11 nm calculated for the (111) profile using the Scherrer formula. The onset of oxidation, as revealed by the first appearance of weak NiO peaks in Fig.1, is noticed at 573 K in the case of bare Ni nanoparticles and reaches completion at 673 K, whereas for the silica coated particles this onset occurs only at 673 K and oxidation proceeds slowly until 873 K (Fig.1). This establishes that silica coating provides increased thermal stability for these nanoparticles.

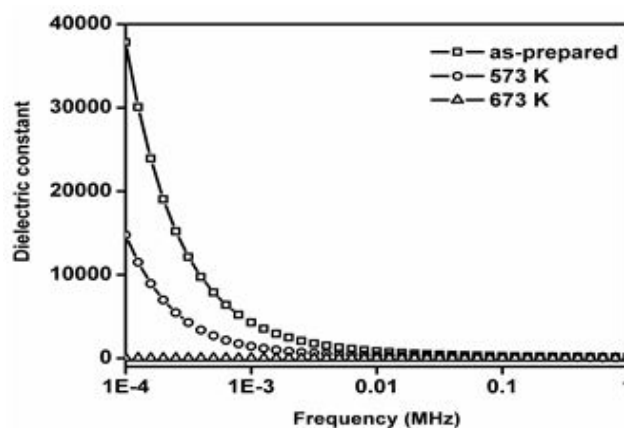


Fig-1: The real part (ε') of the dielectric constant at RT as a function of frequency for the as-prepared and annealed.

The oxidation behavior and thermal stability of Ni/SiO₂ particles were further investigated by thermo gravimetric analysis. The oxidative weight gain was measured in a thermo gravimetric analyzer by taking equal quantities by weight of the bare Ni particles as well as silica coated Ni particles (annealed at 573 K) through a heating program at the rate of 10 K /min in flowing oxygen. Figure 3 shows the weight gain TGA plot as a function of temperature. The onset temperature of 550 K for oxidation, as inferred from the start of weight gain, for the bare Ni particles agrees very well with similar result from XRD. The net weight gain of ~24% is marginally less than the theoretically expected weight gain of 27.3% for the NiO stoichiometry, perhaps due to the inevitable presence of oxide even in the starting material due to surface oxidation of the nanoparticles. TGA of silica coated Ni particles under similar heating program, shown by the dashed curve in Fig.3, shows an onset at 700 K and proceeds to a saturation at ~940 K showing a smaller weight gain. In addition, an apparent initial weight loss is also noticed for this case. For the chemically achieved silica coating, such a weight loss represents the removal of adsorbed water till about 450 K and desorption of chemically bonded water and DE hydroxylation beyond this temperature. From a comparison of the net weight gain of 11.3% for the coated particles with the 24% net weight gain for bare Ni, the weight ratio of Ni : SiO₂ is estimated as 1:1. This is verified by the energy dispersive X-ray analysis EDX data.

The complex impedance plane plot of as-prepared and annealed nickel-silica nanocomposites are shown in Fig.6. The graph shows a single semicircle at high frequencies due to the silica coated nickel and an arc in the low frequency region, which is attributed to the interface polarization effect. The depressed semicircular-arc can be defined by a parallel combination of resistance (R_p) and constant phase element (CPE) capacitor. The impedance of CPE is expressed as $Z_{CPE} = B / (j\omega)^a$. The parameter B is a constant for given experimental data. The exponent a gives the degree of energy dissipation and varies between 0 and 1. The impedance of CPE is purely capacitive for a = 1 and purely resistive for a = 0. A non-linear least squares fitting of the high frequency data using a parallel R_p-CPE equivalent circuit yielded 7.4x10⁴ 2.2x10⁵ and 2.8x10⁸ Wcm for the resistivity's of the as prepared, annealed

At 573 and 673 K samples respectively. Large resistivity for the annealed sample could mainly be due to the densification of silica around the nickel nanoparticles. The depressed semicircle observed in our sample can be explained as due to presence of surface charge states due to chemisorbed functional groups and moisture. Thus, the depression of semicircle is less after annealing the sample.

The temperature dependence of dc conductivity of as-prepared Ni/SiO₂ nanocomposite in the temperature range from 323 to 363 K were analyzed. The conductivity is found to decrease with increasing temperature. The activation energy for the thermally activated hopping process was obtained by fitting the dc conductivity data with the Arrhenius relation,

$$\sigma T = \sigma_0 \exp\left(-E_a/kT\right) \quad (1)$$

Where, σ_0 is the pre-exponential factor with the dimensions of (Ωcm)⁻¹ K, E_a is the activation energy for dc conductivity and k is the Boltzmann constant. The activation energy was calculated for the as-prepared Ni/SiO₂ nanocomposite as 1.31 eV. Szu et have reported an activation energy of 1.04 eV for Cu₁₀(SiO₂)₉₀ nanocomposite.

Reference

1. Chen Y, Peng DL, Lin D, Luo X (2007) Nanotechnology 18:505703
2. He L, Zheng W, Zhou W, Du H, Chen C, Guo L (2007) J. Phys.:Condens. Matter. 19:036216
3. Zamorskiia MK, Nounehb K, Kobayashic K, Oyamac M, Ebothed J, Reshak AH (2008) Optics & Laser Technology 40:499
4. Liu CC, Lue JT (2007) Optics Communications 280:477
5. Joo J, Lee SJ, Park DH, Kim YS, Lee Y, Lee CJ, Lee SR (2006) Nanotechnology 17:3506
6. Rinaldi A, Peralta P, Friesen C, Sieradzki K (2008) Acta Mater. 56:511
7. Kim H, Cho MS, Kim SY, Kim YJ, Woo HG, Kim DH, Sohn H, Li H (2007) J. Nanosci. Nanotechnol. 7:3964

8. Pan YX, Liu CJ, Shi P (2008) *J. Power Sources* 176:46
9. Liu G, Li Y, Chu W, Shi X, Dai X, Yin Y (2008) *Catal. Commun.* 9 :1087
10. Das S, Panda SK, Nandi P, Chaudhuri S, Pandey A, Ranganathan R (2007) *J. Nanosci. Nanotechnol.* 7:4447
11. Cao Y, Cao J, Zheng M, Liu J, Ji G, Ji H (2007) *J. Nanosci. Nanotechnol.* 7:504
12. Tomita S, Jönsson PE, Akamatsu K, Nawafune H, Takayama H (2007) *Phys. Rev. B* 76:174432
13. Sun Y, Sun J, Liu M, Chen Q (2007) *Nanotechnology* 18:505704
14. Yeshchenko OA, Dmitruk IM, Alexeenko AA, Dmytruk AM (2008) *J. Phys. Chem. Solids* 69:1615
15. Amekura H, Takeda Y, Kishimoto N (2004) *Thin Solid Films* 464–465:268
16. Nandy S, Mallick S, Ghosh PK, Das GC, Mukherjee S, Mitra MK, Chattopadhyay KK (2008) *J. Alloy. Compd.* 453:1
17. Yan Z, Yu-Qing K, Xiao-Yong F, Jie Y, Xiao-Ling S, Wei-Li S, Mao-Sheng C (2008) *Chin. Phys. Lett.* 25:1902.
18. Fonseca FC, Goya GF, Jardim RF, Muccillo R, Carreño NLV, Longo E, Leite ER (2002) *Phys. Rev. B* 66:104406
19. Fu W, Yang H, Chang L, Li M, Bala H, Yu Q, Zou G (2005) *Colloids and Surfaces A: Physicochem. Eng. Aspects.* 262:71
20. Iwamoto M, Kosugi Y (2007) *J. Phys. Chem. C.* 111L:13