NANORODS AND NANOPARTICLES OBTAINED BY THE REVERSE MICELLAR ROUTE: DIELECTRIC AND MAGNETIC PROPERTIES

by

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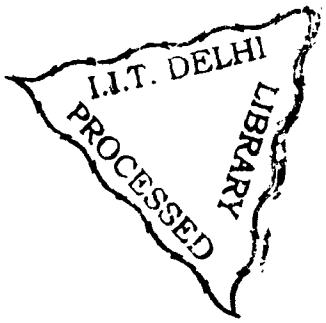
Submitted in accordance with the requirement for the Degree of Doctor of Philosophy

.to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

INDIA

DECEMBER, 2005



To

Abbu and Ammi .....

and

In loving memory of my grandparents

CERTIFICATE

This is to certify that the thesis entitled, **"Nanorods and nanoparticles obtained by the reverse micellar route: Dielectric and magnetic properties"**, being submitted by **Mr. Tokeer Ahmad**, to the Indian Institute of Technology, Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by him. Mr. Tokeer Ahmad has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full, to any other university or institute for award of any degree or diploma.

Date : 6/12/2005

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Acknowledgements

It is a great pleasure to extend my heart felt thanks to all those who made this thesis possible.

It is difficult to state my gratitude to my Ph.D. supervisor, Dr. A. K. Ganguli. With his enthusiasm, inspiration, and great efforts to explain things clearly and simply, he helped to make nano-chemistry fun for me. Throughout my entire Ph.D. and thesis-writing period, he provided encouragement, sound advice, good teaching, good company, and lots of good ideas. He has always brought out the best in me, and this period of working with him has been a wonderful learning experience. I would have been lost without him.

I am grateful to the Head, Prof. U. K. Nadir, and former heads, Prof. H. M. Chawla and Prof. M. N. Gupta, Department of Chemistry for providing me necessary facilities in the department. I also express my sincere thanks to Prof. A. K. Singh, Prof. B. R. Mehta and Dr. N. G. Ramesh for their encouragement. I am also grateful to all supporting staff of the department for their kind help and cooperation.

I would like to gratefully acknowledge Prof. A. Ramanan for his encouragement and help in absence of my supervisor as well as allowing me to stay in his house during drafting of my thesis.

It is difficult to find words to express my gratitude to Dr. Ramanujachary, Rowan University, U.S.A. for not only his help with the magnetic measurements; but also for his valuable suggestions and for his benevolent help which he unerringly provided whenever I needed it.

I take this opportunity to thank to Dr. G. U. Kulkarni (JNCASR, Bangalore), Dr Sukhbir Singh, Dr. A. K. Srivastava and Dr. Ram Kishore (NPL, Delhi) for TEM measurements

and Dr. S. M. Shivaprasad (NPL, Delhi) for XPS studies. I am very much thankful to Dr. S. Ghosh for the help and discussion in optical studies. I also acknowledge the help of Dr. K. Vijaymohanan, N.C.L. Pune, for the electrochemical studies.

I would also like to thank the Council of Scientific and Industrial Research (CSIR), New Delhi for providing the fellowship, which has supported me during my entire research period.

I express my sincere thanks to my lab-colleagues, past and present, especially Dr. Gunjan, Vishnu, Shalabh, Saroj, Sonalika, Jahangeer, Chandu, Nad, Poonam, Santosh and Debajit for their love, understanding and providing an excellent working environment. The company and help of Dr. Pika Jha during the toughest phase of my work is truly unforgettable. I extremely appreciate the help of Shalabh for carrying out some reactions under vacuum.

I would also like to thank Mrs. Jaya Ganguli for her moral and mental support. She was one of them who encourage me a lot towards the steps of successful work.

I sincerely appreciate and reciprocate the warm-heartedness, goodwill and love of my friends, especially, Tanveer, Farooq (bablu), Anees, Rahul, Anshu, Puja, Garima, Zaheer bhai, Jain, Sokhi and Nandu.

I would like to thank everybody who taught me basic science and chemistry in particular in my early days: my high school teachers (especially Master Udai Singh), my undergraduate teachers (especially Sri Ram Dhall and Dr. P. N. Dua), and my post graduate teachers (especially Prof. V. K. Gupta, Prof. Kamaluddin, Dr. U. P. Singh and Dr. S. M. Sondhi) for their kind assistance with writing letters, writing chemical reactions, giving wise advice, chemical experiments, helping with various applications,

and so on. I wish to thank in addition Moulana Ashgar Ali (retired principle and my grandfather), Dr. Izhar Ahmad (my elder cousin) and advocate Shamshad Ali (my mamaji) who always encourage, inspire and providing me a light towards science.

I am also thankful to Aslam (Fufa), Dr Ameer Alam (Jiju), Safdar bhai, Ahmad mamu, Salman bhai, Boby, Tasaruf, Achchu, Asif, Dauod, Huma and my parents-in-law for their co-operation and providing me moral support.

I fall short of words to express my feelings for Farha (Hina) my wife whose constant motivation, support, inspiration, understanding, and unconditional love, helped me a lot to complete my work very smoothly. I have always found her standing by me in toughest phase of research. She has been a source of strength and courage to me and I hope this thesis will fulfill one of her cherished dreams.

Words cannot express my feelings towards my loving brothers (Jahangeer and Shariq), my sister (Dilnasheen) and my parents, who have done everything to enable me to concentrate on my research single-mindedly. They have been my constant source of inspiration, courage, support and eternal love. I hope that I have been able to live up to their expectations, at least in this respect.

Last, but not the least, I thank the Almighty for gifting me the life with such wonderful people. Without His blessings, this thesis would certainly have not been successesfully completed.

Tokeer Ahmad

Tokeer

Abstract

Nanoparticles and nanostructured materials have been fascinating the world of science in the last ten years. Nanomaterials are among the most challenging areas of current scientific and technological research because of interesting changes in their optical, magnetic, electrical and catalytic properties accompanied with improved physical properties like mechanical hardness, thermal stability or chemical passivity. These nanoscale materials can be defined as those whose characteristic length lies between one and hundred nanometers. Many physical properties of nanoparticles often differ drastically from those of single crystals with the same chemical composition. At nanometer size, crystallites are influenced by the presence of significant number of surface atoms and by the quantum confinement effect of the electronic states and this influences the property of nanomaterials as compared to their bulk phases. The properties of matter within this length scale are significantly different from individual atoms or molecules and from bulk materials. Nanoparticles exhibit unique electronic, magnetic, optical, photonic and catalytic properties and their size is ideal size for the use as nanomaterials building blocks which includes metals, semiconductors, core-shell nanostructures and organic polymeric materials. These materials play an important role in the selective surface modification of different substrates in the form of coatings. Several oxide nanoparticles are predicted to have tremendous applications in the future.

In chapter 1, a detailed survey of the background literature has been carried out for the state of knowledge existing in the area of nanoparticles with interesting dielectric, magnetic and electrochemical properties. We also discuss the synthesis of nanomaterials

using the reverse micellar route and its comparison with other synthetic methods with respect to the grain size, distribution and morphology.

In chapter 2, we discuss the synthesis of nano-structured dielectric oxides like barium, strontium and lead titanates ($BaTiO_3$, Ba_2TiO_4, $SrTiO_3$, Sr_2TiO_4, $PbTiO_3$) using the reverse micellar route. In our synthesis we have avoided the use of alkoxide for barium, strontium and lead as starting reagents, which are very expensive. Monophasic $BaTiO_3$ could be obtained after heating the precursor at 800°C and the X-ray pattern could be indexed satisfactorily on the basis of a tetragonal cell with the refined lattice parameters are '**a**' = 3.998(1) Å and '**c**' = 4.019(1) Å. Note that careful X-ray studies of the (200) reflection suggests a very weak tetragonal distortion at 800°C. The average grain size of the particles obtained from the X-ray line - broadening studies of the (111) reflection is found to be 20 nm. This is in accordance with the transmission electron microscopic studies (TEM), which show uniform, and monodisperse particles having grain size of 20 - 25 nm. The X-ray diffraction pattern indicates the presence of the tetragonal phase of $BaTiO_3$ at all sintering temperatures (900°C to 1100°C). TEM micrographs show uniform and monodisperse particles of grain size of the order of 30 – 35 nm for samples sintered at 900°C while after sintering at 1100°C (8h) the grains are agglomerated and have average grain size of 120 nm. In order to arrive at a definite answer regarding the distortion suggested by XRD studies in the 20-25 and 30-35 nm particles obtained at 800°C and 900°C temperatures respectively, we have carried out Raman spectroscopic studies. The Raman investigations suggest that both 20-25 and 30-35 nm nanoparticles of $BaTiO_3$ crystallize in the tetragonal phase. The dielectric constant was found to be 210 and dielectric loss was 0.02 for $BaTiO_3$ sintered at 900°C and at 100

kHz frequency. The dielectric constant was found to be stable ($d\varepsilon/dF = 9.24 \times 10^{-7}$ Hz^{-1}) with frequency while dielectric loss showed a slight increase at higher frequencies. The dielectric constant is found to increase with sintering temperature being 520 after sintering at 1100°C.

Powder X-ray diffraction studies of nanoparticles of barium orthotitanate (Ba_2TiO_4) after calcining at 800°C result in a mixture of orthorhombic (70%) and monoclinic (30%) phases. The high temperature orthorhombic form present at 800°C is due to the small size of particles obtained by the reverse micellar route. Pure orthorhombic Ba_2TiO_4 was obtained on further sintering at 1000°C. Rietveld refinement of powder X-ray data was also carried out for Ba_2TiO_4 sintered at 1000°C. The refined cell parameters of the orthorhombic Ba_2TiO_4 are a = 6.0951(5) Å, b = 22.944(1) Å, c = 10.5425(8) Å. The structure refined to reasonable R-values in the space group $P2_1nb$. The values of Rp and wRp on refinement were found to be 0.085 and 0.113 respectively. The powder patterns showed a high background probably due to the small size of the particles. The particle size obtained from X-ray line broadening studies and transmission electron microscopic (TEM and HRTEM) studies is found to be 40-50 nm for the powder obtained after heating at 800°C. Sintering at 1000°C show increase in grain size upto 150 nm. Our studies corroborate well with the presence of a martensitic transition in Ba_2TiO_4. The dielectric constant is found to be 40 for Ba_2TiO_4 (at 100 kHz) for samples sintered at 1000°C. The dielectric loss obtained was low (0.06) at 100 kHz.

Monophasic nanoparticles of $SrTiO_3$, Sr_2TiO_4 and $PbTiO_3$ have also been obtained as observed by the powder X-ray diffraction studies. X-ray line broadening studies and transmission electron microscopic studies show spherical grains of 30-40 nm

size for strontium titanates, while, $PbTiO_3$ is obtained in the form of nanorods. The dielectric constant of $SrTiO_3$ and Sr_2TiO_4 is found to be 90 and 30 respectively (at 100 kHz) for samples sintered at 1000°C. $PbTiO_3$ shows a dielectric constant of 160 (at 100 kHz) after sintering at 900°C. The dielectric constant of Sr_2TiO_4 (with temperature) is highly stable. The temperature variation studies of the dielectric constant of $PbTiO_3$ show a ferroelectric phase transition at 490°C (1 kHz). The T_c varies with frequency and is found to decrease to 470°C at 100 kHz.

In chapter 3, we discuss the synthesis, characterization and dielectric properties of nanocrystalline zirconates of barium, lead and strontium using a modified reverse micellar route (avoiding Ba/Sr/Pb - alkoxide). The solid solutions of $Ba_{1-x}Pb_xZrO_3$ (x = 0.25, 0.50 and 0.75) have been synthesized for the first time. Powder X-ray diffraction studies show the monophasic nature of the powders of $BaZrO_3$, $PbZrO_3$, $SrZrO_3$ and the solid solution of $Ba_{1-x}Pb_xZrO_3$ (x = 0.25, 0.50, 0.75) after heating at 800°C. $BaZrO_3$ could be obtained after heating the precursor at 800°C and the X-ray pattern could be indexed satisfactorily on the basis of a cubic cell with the refined lattice parameter '**a**' = 4.1803(2) Å, however lead zirconate could be indexed on a orthorhombic cell with the refined lattice parameters of '**a**' = 5.8621(5) Å, '**b**' = 11.791(3) Å and '**c**' = 8.243(2) Å. We have also observed additional reflections in the PXRD pattern for the lead rich region $0.50 \leq x \leq 1.00$ which can be indexed in the orthorhombic unit cell known for $PbZrO_3$. We have found that the 'a', 'b' and 'c' parameters decrease slightly with Pb content in solid solution. Nanoparticles of $SrZrO_3$ could be obtained after heating at 800°C and the PXRD pattern could be indexed on the basis of a cubic cell as is known for $SrZrO_3$ with the refined lattice parameter of '**a**' = 4.0922(4) Å.

The particle size obtained from X-ray line broadening studies and transmission electron microscopic studies is found to be in the range of 20-60 nm for all the oxides obtained after heating at 800°C. These oxides were monodisperse, spherical and nearly uniform as seen from TEM micrographs. Well-faceted, rhombic and cuboidal nanocrystals of $PbZrO_3$ could be obtained at 1000°C due to ease of grain growth in the presence of low melting lead oxide. The grain size is reasonably stable to sintering till 1000°C for all the oxides. The grain size of the solid solution of $Ba_{1-x}Pb_xZrO_3$ ($0 \leq x \leq 1$) was found to increase with the lead content. The dielectric properties of strontium zirconate and solid solutions of barium lead zirconate ($Ba_{1-x}Pb_xZrO_3$, x = 0.0, 0.25, 0.50, 0.75, 1.0) have been measured as a function of frequency and temperature. This is the first report on the dielectric properties of the above oxides synthesized using the reverse micellar route. The dielectric constant of the solid solution of $Ba_{1-x}Pb_xZrO_3$ ($0 \leq x \leq 1$) shows a maximum value of 93 at x = 0.50. Nanocrystalline $PbZrO_3$ shows the signature of the AFE-PE transition (though weak) with T_c of ~230°C as known for bulk $PbZrO_3$. The dielectric constant of 19.8 is observed for nanocrystalline $SrZrO_3$ sintered at 1000°C.

Chapter 4 describes a novel route for the synthesis of nanorods of transition metal (Cu, Ni, Mn, Co and Fe) and zinc oxalate by the reverse micellar route using CTAB (cetyltrimethyl ammonium bromide) as the surfactant. Powder X-ray diffraction studies and thermo gravimetric analysis confirms the formation of monophasic $CuC_2O_4.H_2O$, $NiC_2O_4.2H_2O$, $MnC_2O_4.2H_2O$, $ZnC_2O_4.2H_2O$, $CoC_2O_4.2H_2O$ and $FeC_2O_4.2H_2O$. The powder X-ray diffraction pattern of the light blue copper oxalate could be indexed on the basis of an orthorhombic cell reported for copper oxalate monohydrate. We have also obtained similar XRD patterns of pure copper oxalate monohydrate using iso-octane and

n-octane as the non-polar solvents. Powder X-ray diffraction pattern of nickel-based oxalate could be indexed on the basis of a monoclinic cell with the refined cell parameters of '**a**' = 11.77(2), '**b**' = 5.316(7), '**c**' = 9.814(9) and 'β' = 127.19°. Transmission electron microscopy shows that the as prepared nanorods of nickel and copper have diameter of 250 nm and 130 nm while the length is of the order of 2.5 μm and 480 nm respectively. The aspect ratio of the nanorods could be modified by changing the solvent. The nickel oxalate nanorods appear very smooth with uniform length while the copper oxalate nanorods appear to be corrugated. The nickel oxalate dihydrate nanorods show an antiferromagnetic transition at T_N = 45K, while the copper based nanorods show temperature independent paramagnetism.

We have obtained the nanorods of manganese oxalate dihydrate after drying at 60°C. Powder X-ray diffraction pattern of monophasic manganese oxalate dehydrate was indexed in the refined monoclinic lattice parameters of '**a**' = 12.023(2), '**b**' = 5.646(3), '**c**' = 9.968(7) and 'β' = 128.29°. We obtained the manganese oxalate (anhydrous) nanorods after heating at 150°C and the reflections could be indexed on the basis of an orthorhombic cell The systematic study of powder X-ray diffraction of manganese oxalate with temperature shows that manganese oxalate dihydrate at 60°C converts to the mixture of $MnC_2O_4.2H_2O$ and MnC_2O_4 at 100°C which finally change to anhydrous MnC_2O_4 at 150°C. We have carried out the TEM and DLS studies for anhydrous manganese oxalate. TEM studies show the formation of nanorods of manganese oxalate with average dimensions of 100 nm (diameter) and 2.5 μm (length). The DLS studies show an average size of ~1.0μm which supports the TEM studies. Magnetization studies

show a sharp magnetic transition (antiferromagnetic) for the nanorods of anhydrous manganese oxalate is observed near 15 K.

We have also characterized the nanorods of zinc, cobalt and iron oxalate using powder X-ray diffraction, TEM, AFM and DLS studies. The average dimensions of these nanorods were 120 nm, 300 nm and 2 μm respectively in diameter and 600 nm, 6.5 μm and several microns respectively in length. The aspect ratio of the cobalt oxalate nanorods could be modified by controlling the temperature. We have also carried out the magnetic measurements of cobalt and iron oxalate dihydrate nanorods which show an antiferromagnetic ordering at 21 K and 27 K respectively.

In chapter 5, we discuss the synthesis of nanoparticles of CuO, NiO, MnO, Mn_2O_3, Mn_3O_4, ZnO, Co_3O_4, Co, Fe_2O_3 and Fe_3O_4 by thermal decomposition of the nanorods of metal (Cu, Ni, Mn, Zn, Co and Fe) oxalates obtained by the reverse micellar method at 450-500°C under varying atmospheric conditions. The monophasic nature of all the oxide nanoparticles is shown by powder X-ray diffraction and their grain size are obtained by X-ray line broadening and transmission electron microscopy (TEM). Copper oxide nanoparticles were obtained by decomposing oxalate nanorods synthesized from two different apolar solvents, (isooctane and n-octane). Our studies show that the grain size of CuO nanoparticles is highly dependent on the nature of non-polar solvent used to initially synthesize the oxalate rods (25-30 nm and 80-90 nm sized nanoparticles with isooctane and n-octane respectively). CuO nanoparticles show onset of weak ferromagnetism (80 K and 220 K) depending on the size of nanoparticles. Our studies lay down a convenient procedure for the synthesis of homogenous nanoparticles of NiO (~ 25 nm) with a narrow size distribution which show interesting magnetic and

electrochemical characteristics. All the commonly known manganese oxides could be obtained as single phases from the manganese oxalate precursor by decomposing in different atmosphere (air, vaccum or nitrogen). Both MnO (28 nm) and α-Mn_2O_3 (50 nm) are stabilized in cubic phases. α-Mn_2O_3 shows a weak antiferromagnetic transition (T_N = 80 K), while the spinel Mn_3O_4 (100 nm) particles show a ferrimagnetic transition at 43K. The ZnO nanoparticles obtained from zinc oxalate rods are ~ 55 nm in diameter. The photoluminescence studies show two peaks at 370nm and 403 nm which can be ascribed to free excitonic transition and donor - acceptor pair transition respectively. The temperature dependent PL intensity of ZnO shows an anomalous non-monotonous temperature dependence probably due to two different optical processes. The grain size was ~35 nm for Co_3O_4, however Co nanoparticles were highly monodisperse and uniform of sizes 20-25 nm. Co_3O_4 nanoparticles show an antiferromagnetic ordering at ~35K, however, Co nanoparticles are magnetically ordered even at room temperature. Fe_3O_4 nanoparticles (~60-70 nm) are faceted in shape, however Fe_2O_3 nanoparticles (~50 nm) are spherical and show a transition from a weakly-ferromagnetic to weakly anti-ferromagnetic transition ~225 K which is reminiscent of a Morin-like transition.

In annexure, we discuss the synthesis of nanoparticles of complex manganites (viz. $LaMnO_3$, $La_{0.67}Sr_{0.33}MnO_3$ and $La_{0.67}Ca_{0.33}MnO_3$) using the reverse micellar route. The monophasic complex manganites are obtained at 800°C. The TEM studies show a grain size of 68 nm, 80 nm and 50 nm for $LaMnO_3$, $La_{0.67}Sr_{0.33}MnO_3$ and $La_{0.67}Ca_{0.33}MnO_3$ respectively. We have observed the ferromagnetic onset at around 250K for $LaMnO_3$, 350K for $La_{0.67}Sr_{0.33}MnO_3$ and 200K for $La_{0.67}Ca_{0.33}MnO_3$.

TABLE OF CONTENTS