SYNTHESIS AND DIELECTRIC PROPERTIES OF NANOCRYSTALLINE TITANATES, ZIRCONATES, NIOBATES AND TANTALATES: DISCOVERY OF AN UNUSUAL OSCILLATORY BEHAVIOUR OF THE DIELECTRIC PROPERTIES OF COMPOSITES OF NANO AND MICRON SIZED PARTICLES

by

VISHNU SHANKER

Department of Chemistry

Submitted
in fulfilment of the requirements of the degree of Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

INDIA

MAY 2007

Dielectrics ② Titanates
Zirconates

Dedicated

to

my Ma and Papa ......

CERTIFICATE

This is to certify that the thesis entitled, "**Synthesis and dielectric properties of nanocrystalline niobates and tantalates: Discovery of an unusual oscillatory behaviour of the dielectric properties of composites of nano and micron sized particles**", being submitted by **Mr. Vishnu Shanker**, 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. Vishnu Shanker 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 : 24-5-2007

Prof. A. K. Ganguli

Professor

Department of Chemistry

Indian Institute of Technology, Delhi

New Delhi – 110016.

INDIA

ACKNOWLEDGEMENTS

याकुन्देन्दु तुषारहारधवळा याशुभ्र वस्त्रान्विता यावीणा वरदण्डमण्डितकरा या श्वेत पद्मासना।
याब्रह्माच्युत शङ्करप्रभृतिभिर्देवैस्सदा पूजिता सामांपातु सरस्वती भगवती निश्शेषजाड्यापहा॥

I offer my thesis at the lotus feet of Ma Sarasawati, as without her blessings, this thesis would have not certainly seen the light of the day.

It is a great privilege to work with Prof. A. K. Ganguli, my thesis supervisor and I thank him from the depth of my heart for his constant encouragement and valuable suggestions towards the successful completion of this work and provide me a wonderful learning experience.

I am grateful to the Head, Prof. B. Jayaram, former Heads, Prof. H. M. Chawla and Prof. U. K. Nadir, Department of Chemistry, for providing me the necessary facilities in the department to carry out my research. I am extremely grateful to Prof. A. K. Singh and Prof. A. Ramanan for their encouragement.

I am also grateful to all the supporting staff of the department especially Mr. Aggrawal and Mr. Sharma for their kind help and cooperation. I render my thanks to all the staff members of the office of the Department of Chemistry and stores for their help and co-operation in last five years. I take this opportunity to thanks Prof. T. R. Rao and Dr. V. V. Krishnan (Chemical Engineering) and Mr. D. C. Sharma (Textile Technology) for providing the instrumentation facilities in their labs.

I fail to find words to express my immense gratitude to Dr. Rama Kant, Department of Chemistry, Delhi University, for his valuable scientific discussions and advice.

I am very much thankful to Prof. K. V. Ramanujachary, Professor of chemistry at Rowan University, USA for carrying out some thermal and electron microscopy measurements.

I am grateful to all my lab-colleagues, past and present, especially my senior, Dr. M. Thirumal, Dr. Gunjan, Dr. Pika and my present colleagues, Shalabh, Saroj, Sonalika, Aparna, Jai Prakash, Prathyusa and Jhangeer for providing me with an excellent and *friendly working environment. I express my heartfelt thanks to Saroj for his help and support whenever I needed.*

I wish to express my appreciation and immense love towards all my friends, especially, Dadu (Arunava), Purnendu, Shailesh, Hari, Vivek, Anirban, Prosenjit, Khatri, Anand....... for making my stay the most memorable one.

I express my deep gratitude and reverence to Prof. C. Bhakta without whose blessings I believe I would have not been able to achieve anything in my life. I am thankful to Nandani and Ashutosh for their constant support, inspiration, understanding and who have also been great friends.

I fall short of vocabulary to express my feelings towards my parents; Ma - Papa, who has done everything to enable me to concentrate on my research. They have been my constant source of inspiration, courage and support by showering their eternal love. I also wish to thank my sister Anju and my brothers, Sachchidanand and Satyam for providing an immense moral support and constantly inducing optimism during the tough phases especially during my last phase of research. Words fail to thank them for all that they have done for me.

The financial support of Department of Science and Technology and Indian Institute of Technology Delhi, as a scholarship is gratefully acknowledged.

Vishnu Shanker

VISHNU SHANKER

ABSTRACT

In the current era of advanced technologies, researchers especially materials scientists and solid-state chemists are involved in the synthesis of novel materials with unusual properties or with the discovery of new properties in earlier known materials. Oxide ceramics have a long tradition of being exploited in the electronic industry for their insulating properties. The dielectric ceramics are used in industrial applications as capacitors, ceramic engines, optical communications devices, electro-optic applications, laser materials, and as substrates in electronic or photo-electrochemical devices. Apart from the bulk materials consisting of micron-sized particles nanomaterials and their properties have become the most challenging areas of current scientific and technological research. In order to tune the dielectric properties with respect to the length scale we decided to look at the role of interfaces on addition of nanoscale particles to micron-sized particles of the same composition thus, keeping all parameters nearly similar (composition, crystallographic parameters etc) except reducing the grain size of the particles and hence varying the interfacial density. Since the microstructure is influenced by the nature and extent of sinteribility we have looked at the microscopic features carefully along with detailed thermal studies and surface area analysis. We have chosen the well-known dielectric oxide materials like $NaNbO_3$, $NaTaO_3$, $SrTiO_3$, $BaTiO_3$, $PbTiO_3$, $SrZrO_3$, $BaZrO_3$, and $PbZrO_3$ as our subject of investigation, since the variation of the nano-component leads to the changes in the microstructure would also be reflected in the variation of the dielectric properties. Our studies show that addition of nanoparticles to micron-sized particles leads to several interesting morphological changes (surface area, grain size) which result in an oscillatory variation of the dielectric

properties. We have observed an enhancement of the dielectric properties at an optimum concentration of micron and nano sized particles. In an attempt to understand the unusual effect of nanoparticles on the morphology and the dielectric properties of sintered compacts of such a mixtures of micron and nano sized particles, we embarked on the extensive study of the surface area and thermal properties along with microstructural investigation during the sintering process. **Henceforth such mixtures of nano and micron-sized particles would be identified with the prefix 'nμ' and referred as nμ-composites throughout this thesis.** This interesting oscillatory variation of the dielectric constant with increase in the amount of nanoparticles in the composites is observed for the first time. Our aim has been to understand the oscillatory behaviour of the dielectric constant and the generality of this behaviour in all the titanates, niobates, tantalates and zirconates studied by us.

Chapter I deals a brief introduction of nanomaterials and its synthetic methods, characterization techniques, dielectric property and fractal geometry. In addition, a brief survey of the research activity that has taken place in the area of advanced technological materials like thermoelectrics, ferroelectrics, piezoelectrics, dielectric insulators, etc.

Chapter II described the synthesis of nano-crystalline ($NaNbO_3$ and $Sr_{0.4}H_{1.2}Nb_2O_6.H_2O$) and submicron particles (Nb_2O_5, $SrNb_2O_6$, $Ba_3MgNb_2O_9$ and $Ba_3ZnNb_2O_9$) by the reverse micellar route and citrate polymeric precursor method respectively. These materials were characterized by using powder X-ray diffraction, FT-IR spectroscopy, thermo gravimetric and differential thermal analysis, scanning electron microscopy and transmission electron microscopy techniques. Enhancement of the dielectric constant is observed in the sintered disks of the micron sized (~ 0.75 μm) $NaNbO_3$ particles (obtained by the solid-state method) with addition of small amount of $NaNbO_3$ nanoparticles (~ 18 nm). Enhancement of the dielectric constant by 76 % and reduction of the dielectric loss by ~ 49 % is obtained at 1.5 wt % doping of $NaNbO_3$ nanoparticles. Oscillatory nature of dielectric constant is observed at lower wt % of nanoparticles (< 5 wt %). There is a significant change in the morphology of grains of the sintered disks leading to highly dense particles. These microscopic changes appear to be governed by the variation in the interfaces as introduced by the addition of the nanoscale dopants having high surface to volume ratio and are responsible for the oscillatory variation of the dielectric properties.

Chapter III provides the synthetic methodologies for the synthesis of mono-dispersed and uniform nanoparticles of $NaTaO_3$ (~ 40 nm) and $SrTa_2O_6$ (~ 36 nm) by using the reverse micellar technique. However, tantalates like Ta_2O_5, $SrTa_2O_6$, $Ba_3MgTa_2O_9$ and $Ba_3ZnTa_2O_9$ were obtained by the citrate polymeric precursor method in submicron range. These materials were characterized by using powder X-ray diffraction, FT-IR spectroscopy, thermo-gravimetric analysis (TGA), differential thermal analysis (DTA), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. The dielectric constant is enhanced by the addition of small amount of nanoparticles of $NaTaO_3$ to the micron sized (~ 1 μm) particles of $NaTaO_3$ (obtained by the solid-state method). The dielectric constant is increased by 120 % and the dielectric loss is reduced by ~ 40 % is obtained by the addition of 5 wt % nanoparticles of $NaTaO_3$ to the micron-sized $NaTaO_3$. Oscillatory nature of dielectric constant is observed at lower wt % of nanoparticles (< 5 wt %). There is a significant change in the morphology of grains of the sintered disks leading to highly dense particles. These microscopic changes appear to be governed by the variation in the interfaces as introduced by the addition of the nano-scale dopants which are responsible for the oscillatory variation of the dielectric properties.

Chapter IV described in detail the studies of nμ-composite of titanates ($SrTiO_3$, $BaTiO_3$ and $PbTiO_3$) with respect to their morphology, thermal, surface area, dielectric property and fractal geometry. **An interesting oscillatory variation of the dielectric constant and dielectric loss with increase in the amount of nanoparticles is observed for the first time in the nμ-composite of all titanates.** A significant linear relation is observed in the surface area and dielectric characteristics with varying the concentration of nano-additive. Enhancement of the dielectric constant by greater than 50% and reduction of the loss by ~ 20 % is observed at 0.5, 1 and 2 wt % doping of nanoparticles of $SrTiO_3$, $BaTiO_3$ and $PbTiO_3$ respectively. There is a significant change in the morphology of the grains beyond 2 wt % of nano-additive, where coalescence of small particles on the surface of the large grains is observed, leading to fractal geometry of grains in the sintered disk of $SrTiO_3$. Below the critical dopant concentration (3 wt % of nanoparticles) there appears to be a rough surface geometry of the micron-sized grains. The microscopic changes (surface roughness, fractal geometry) appear to be governed by the variation in the interfaces as introduced by the addition of the nanoscale dopants and seem to be responsible for the oscillatory variation of the dielectric properties. Sintered disks of nμ-composites of $BaTiO_3$ show sharp ferroelectric transition and high dielectric constant at specific compositions. The variation in the dielectric constant at T_c is also reflected in the behaviour of the ferroelectric transition as studied by differential scanning calorimetry (DSC). The variation of the dielectric properties and the ferroelectric transition of the $BaTiO_3$ composites could be related to subtle changes in the microstructure. Similar behaviour is also observed for $PbTiO_3$ nμ-composites.

Chapter V deals the synthesis and dielectric properties of nμ-composites of zirconates ($SrZrO_3$, $BaZrO_3$ and $PbZrO_3$). Significant variation is observed in the dielectric constant with optimal properties at lower wt % (< 5 %) of nano-dopant. Enhancement of the dielectric constant by greater than 50 % and reduction of the loss by ~ 20 % is observed at 1, 5 and 0.5 wt % doping of nanoparticles of $SrZrO_3$, $BaZrO_3$ and $PbZrO_3$ respectively at room temperature. There is a significant change in the morphology of the grains observed in the sintered disk of nμ-zirconates.

TABLE OF CONTENTS

CERTIFICATE		i
ACKNOWLEDGEMENTS		ii
ABSTRACT		iv
LIST OF FIGURES		xvi
ABBREVIATIONS AND SYMBOLS		xl
CHAPTER I	**INTRODUCTION**	
I.1	Background	1
I.2	Synthesis of nanomaterials	2
I.2.1	Co-precipitation method	4
I.2.2	Solvothermal method	5
I.2.3	Sol-gel method	5
I.2.4	Hydrothermal method	6
I.2.5	Microemulsion method; Reverse micellar route	7
I.2.5.1	Reverse micelles as Nanoreactor	8
I.2.5.2	Mechanism for the formation of nanoparticles in microemulsions	9
I.2.5.3	Surfactants	10
I.2.5.4	Co-surfactants	12

I.2.5.5	Size of the Reverse Micelle (W_o ratio)	12
I.3	Characterization of Materials	13
I.3.1	Powder X-ray diffraction	13
I.3.2	Infrared spectroscopy	15
I.3.3	Thermogravimetric analysis	16
I.3.4	Differential Thermal Analysis (DTA) and Differential Scanning Calorimetery (DSC)	17
I.3.4 (a)	Heat Flux DSC	19
I.3.4 (b)	Power Compensated DSC	20
I.3.5	Dynamic Light Scattering	22
I.3.6	Scanning Electron Microscopy (SEM)	23
I.3.7	Transmission Electron Microscopy (TEM)	25
I.3.8	Surface Area Analysis (BET)	26
I.4	Dielectric Properties	28
I.4.1	Dielectric Constant	28
I.4.1.1	Electronic polarization	30
I.4.1.2	Ionic polarization	31
I.4.1.3	Dipolar polarization	32
I.4.1.4	Space charge polarization	32
I.5	Fractal geometry	37
I.6	Motivation for the research work embodied in this thesis	39
I.7	References	41

CHAPTER II **Synthesis, characterization and dielectric properties of fine-particles of niobates: Nanocrystalline $NaNbO_3$, $Sr_{0.4}H_{1.2}Nb_2O_6.H_2O$; sub-micron Nb_2O_5, $SrNb_2O_6$, $Ba(B'_{1/3}Nb_{2/3})O_3$ (B' = Mg, Zn); and nμ-composites of $NaNbO_3$**

II.1	Introduction	51
II.2	Experimental	57
II.2.1	Synthesis	57
II.2.1.1	Synthesis of nanoparticles	57
II.2.1.2	Synthesis of submicron particles of Nb_2O_5, $SrNb_2O_6$, $Ba(Mg_{1/3}Nb_{2/3})O_3$ and $Ba(Zn_{1/3}Nb_{2/3})O_3$	61
II.2.1.3	Synthesis of nμ-composites of $NaNbO_3$	62
II.2.2	Characterization	64
II.2.2.1	Powder X-ray Diffraction	64
II.2.2.2	TG-DTA measurements	65
II.2.2.3	Electron microscopy	65
II.2.2.4	Dielectric properties	66
II.3	Results and discussion	66
II.3.1	Phase analysis	66
II.3.2	FT-IR analysis	73
II.3.3	TG-DTA analysis	80
II.3.4	Crystallite and Grain Size Analysis	82
II.3.5	Dielectric properties	91
II.3.5.1	Dielectric properties of $NaNbO_3$ nanoparticles	91

II.3.5.2	Dielectric properties of submicron particles	93
II.3.5.3	Dielectric properties of nµ-composites	99
II.4	Conclusions	103
II.5	References	104

CHAPTER III **Synthesis, characterization and dielectric properties of fine-particles of tantalates: Nanocrystalline $NaTaO_3$, $SrTa_2O_6$; sub-micron Ta_2O_5, $SrTa_2O_6$, $Ba(B'_{1/3}Ta_{2/3})O_3$ (B' = Mg, Zn); and nµ-composites of $NaTaO_3$**

III.1	Introduction	111
III.2	Experimental	118
III.2.1	Synthesis	118
III.2.1.1	Synthesis of nanoparticles of $NaTaO_3$ and $SrTa_2O_6$	118
III.2.1.2	Synthesis of submicron particles of Ta_2O_5, $SrTa_2O_6$, $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Ta_{2/3})O_3$	120
III.2.1.3	Synthesis of nµ-composites of $NaTaO_3$	121
III.2.2	Characterization	122
III.2.2.1	Powder X-ray Diffraction	123
III.2.2.2	FT-IR Spectroscopy	123
III.2.2.3	TG-DTA measurements	124
III.2.2.4	Electron microscopy	124
III.2.2.5	Dielectric property measurements	124
III.3	Results and discussion	125

III.3.1 Phase analysis 125

III.3.2 FT-IR analysis 131

III.3.3 TG-DTA analysis 138

III.3.4 Crystallite and Grain Size Analysis 139

III.3.5 Dielectric properties 149

III.3.5.1 Dielectric properties of $NaTaO_3$ and $SrTa_2O_6$ nanoparticles 149

III.3.5.2 Dielectric property of tantalates synthesized by the polymeric citrate precursor route 153

III.3.5.3 Dielectric properties of nμ-composites 159

III.4 Conclusions 163

III.5 References 163

CHAPTER IV Synthesis, characterization and dielectric properties of nμ-composites of $ATiO_3$ (A = Sr, Ba and Pb)

IV.1 Introduction 170

IV.2 Experimental 174

IV.2.1 Synthesis of nμ-composites 174

IV.2.2 Characterization 175

IV.3 Results and discussion 177

IV.3.1 Phase Analysis 177

IV.3.2 Microstructural Analysis 181

IV.3.2.1 Microstructural Analysis of $SrTiO_3$ 181

IV.3.2.2 Microstructural Analysis of $BaTiO_3$ 190

IV.3.2.3 Microstructural Analysis of $PbTiO_3$ 194

IV.3.3 Thermal Studies 198

IV.3.4 Surface area measurement 202

IV.3.5 Dielectric Properties measurements 203

IV.3.5.1 Dielectric Properties of $SrTiO_3$ 203

IV.3.5.2 Dielectric properties of $BaTiO_3$ 207

IV.3.5.3 Dielectric properties of $PbTiO_3$ 212

IV.3.6 Fractality and dielectric constant 215

IV.4 Conclusions 227

IV.5 References 229

CHAPTER V Synthesis, characterization and dielectric properties of nμ-composites of $AZrO_3$ (A = Sr, Ba and Pb)

V.1 Introduction 237

V.2 Experimental 240

V.2.1 Synthesis of nμ-composites 240

V.2.2 Characterization 241

V.3 Results and discussion 241

V.3.1 Phase Analysis 241

V.3.2 Microstructural Analysis 245

V.3.2.1 Microstructural Analysis of nμ-composites of $SrZrO_3$ 245

V.3.2.2 Microstructural Analysis of nμ-composites of $BaZrO_3$ 248

V.3.2.3 Microstructural Analysis of nμ-composites of $PbZrO_3$ 251

V.3.3 Dielectric Properties measurements 253

V.3.3.1 Dielectric Properties of $SrZrO_3$ 253

V.3.3.2 Dielectric Properties of $BaZrO_3$ 258

V.3.3.3 Dielectric Properties of $PbZrO_3$ 263

V.4 Conclusions 268

V.5 References 269

LIST OF PUBLICATIONS 275

BIO-DATA OF THE AUTHOR 277