NOVEL PEROVSKITE-BASED OXIDES: SYNTHESIS, STRUCTURAL CHARACTERIZATION, DIELECTRIC AND MAGNETIC PROPERTIES

by

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

to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

INDIA

JANUARY, 2004

- oxides
- synthesis

To

Ma and Baba .....

My pillars of Mental Strength,

Moral Support

and

Boundless Love

CERTIFICATE

This is to certify that the thesis entitled, **"Novel Perovskite-based Oxides: Synthesis, Structural Characterization, Dielectric and Magnetic Properties"**, being submitted by **Ms. Pika Jha**, 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 her. Ms. Pika Jha has worked under the guidance and supervision of Dr. A. K. Ganguli, 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 : 24.6.04

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ACKOWLEDGEMENTS

Over the past few years, I have come across many wonderful people, who, in someway or the other, have contributed to the successful completion of this thesis. A mere acknowledgement of their help is no match for their contribution. However, since that is the only recourse left to me, I hope it will partly suffice to repay the debts that I have incurred from them over the past few years.

It is a privilege to have been able to work with Dr. A. K. Ganguli, my thesis supervisor. I shall remain indebted to him for his constant enthusiasm, constructive criticism, valuable suggestions and enlightening discussions. He has always brought out the best in me, and this period of working with him has been a wonderful learning experience.

I am grateful to Prof. H. M. Chawla, The Head of the Department of Chemistry, and former Head, Prof. M. N. Gupta for providing me with the necessary facilities in the department. I am also grateful to all the supporting staff of the department for their kind help and cooperation. I am extremely grateful to Prof. A. K. Singh and Dr. A. Ramanan for their encouragement.

I take this opportunity to thank Dr. S. Bobev, of Los Alamos National Laboratory, USA, for the neutron diffraction data, and for his patient hearing and prompt reply of all the questions that I asked him. I am also thankful to Dr. P. Ramaswamy of CPRI, Bangalore, for her timely help in providing me with the EDX data.

I fail to find words to express my immense gratitude to Dr. K. V. Ramanujachary, of Rowan University, USA, for not only his help with the magnetic measurements; but also for his valuable suggestions and benevolent help, which he unerringly provided whenever I needed it.

I am grateful to all my lab-colleagues, past and present, especially my senior, Dr. M. Thirumal, and my present colleagues, Vishnu, Saroj, Maniprabha and Sonalika, for providing me with an excellent working environment. I am indebted to Dr. Gunjan, who always lent a helping hand and moral

support whenever I felt perturbed and shaken. I can never forget Tokeer, who was sure to bring a smile to my face during my gloomy and tough moments.

I sincerely appreciate and reciprocate the warm-heartedness, goodwill and love of my friends, especially, Pooja, Sulakshana, Garima, Rashmi, Jhili, Anshu, Arti, Minakshi, Sanjeev, Chandrani, Geeta, Suresh, Tirthada and Raji for making my stay a memorable one.

I am thankful to Chhotomama and Mami, Ananya, Santosh, Parul and Keshav for providing me with a home away from home, in Delhi.. I am grateful to Bhutada, who has been a great friend and a constant source support, inspiration and understanding. I am thankful to Tubu, who in his own way has done everything possible to shield me off from many a tension, which allowed me to focus on my work. I express my deep gratitude and reverence to Dida without whose blessings I believe I would not be able to achieve anything in life.

Words cannot express my feeling for Totan, my husband, whose constant support, inspiration, understanding, and unconditional love helped me sail through the toughest phase very smoothly. I have always found him standing by me in difficult times. I hope this thesis will fulfill one of his cherished dreams.

I fall short of vocabulary to express my feelings towards my parents, who have done everything to enable me to concentrate on my research single-mindedly. They bore with all my tantrums with a smiling face and endured everything to see me happy. They have been my constant source of inspiration, courage, support and eternal love. I am particularly indebted to my father, for it is he who laid the foundation, even before I was aware what research is all about. I hope that I have been able to live up to his expectations, at least in this respect.

Last, but not the least, I thank the Almighty for blessing my life with such wonderful people. Without His blessings, this thesis would certainly have not seen the light of the day.

ABSTRACT

The perovskite structure is one of the most versatile structures for tailoring the properties of materials. The range of properties of perovskites varies from superconductivity to ferroelectricity, magnetoresistance to magnetocapacitance, and laser host properties to name a few. In particular, the perovskite oxides have been explored for their dielectric and magnetic properties. Traditionally, titanium based oxides are known to show good dielectric properties. This thesis deals with synthesis of titanium-based oxides, in order to obtain new oxides with improved dielectric properties.

Chapter 1 provides a brief introduction to synthetic strategies, the perovskite structure and dielectric and magnetic properties. In addition, a brief survey of the research activity that has taken place in the area of perovskite oxides, particularly, in the area of ordered structures and dielectric and magnetic properties, has been presented.

In chapter 2 we have discussed two new families of perovskite-based oxides, namely, $(Ln_{2/5}Ba_{2/5}Ca_{1/5})(Zn_{2/5}Ti_{3/5})O_3$ and $(Ln_{1/3}Ba_{1/3}Ca_{1/3})(Zn_{1/3}Ti_{2/3})O_3$ (Ln = rare-earth). We have discussed the synthesis and structural characterization of the oxides. Detailed structural analysis of the oxide $(Ln_{2/5}Ba_{2/5}Ca_{1/5})(Zn_{2/5}Ti_{3/5})O_3$ (Ln = Nd) has been carried out using powder X-ray and neutron diffraction. It is found from Rietveld refinement of powder neutron data that the oxide crystallizes in cubic symmetry with space group $Pm\bar{3}m$ and lattice parameter ~ 3.95 Å. Electron diffraction confirmed the cubic structure. Powder X-ray diffraction patterns of other rare-earth containing oxides

(La and Pr) confirm that they have the same structure. There is a slight increase in lattice parameter as we move from the La-based oxide to that of the Pr containing oxide, depending on the size of the rare-earth cation. Annealing under various atmospheres, like air and oxygen was done to promote cation ordering, but without any positive results. The exact composition of the oxides was verified using electron probe microanalysis and energy dispersive X-ray (EDX) analysis. Dielectric measurements were carried out on sintered pellets of the compounds (Ln = La, Pr and Nd) in the frequency range of 50 Hz to 500 kHz and in the temperature range of 35°C to 300°C. All these compounds have been found to exhibit high dielectric constant (ε) and low loss (D). These compounds also show high stability with respect to frequency and temperature. The dielectric constant for these oxides are 70, 57 and 59 for the La, Pr and Nd based oxides respectively. Their respective dielectric losses are 0.003, 0.013 and 0.0049.

Pure phases were obtained for the oxides $(Ln_{1/3}Ba_{1/3}Ca_{1/3})(Zn_{1/3}Ti_{2/3})O_3$ in case of Ln = La, Pr and Nd. These oxides too crystallized in the cubic structure, as observed from powder diffraction studies. There is a slight decrease in lattice parameter in each of the oxides as compared to the $(Ln_{2/5}Ba_{2/5}Ca_{1/5})(Zn_{2/5}Ti_{3/5})O_3$ oxides. This is expected, as the average size of the cations in the A and B sites is less in the $(Ln_{1/3}Ba_{1/3}Ca_{1/3})(Zn_{1/3}Ti_{2/3})O_3$ oxides. There has been no ordering of the cations in this case. It is seen that there is a considerable increase in the dielectric constant when compared to the oxides of the type $(Ln_{2/5}Ba_{2/5}Ca_{1/5})(Zn_{2/5}Ti_{3/5})O_3$ with the same rare-earth ion. All these three compounds exhibit highly stable dielectric properties, with respect to frequency (in the range 50 to 500 kHz) and temperature (35°C to 300°C). The dielectric constant depends on the size of the cations and varies from 81 for the La-based oxide to

70 for the Nd-based oxides. The dielectric loss is in the range of 0.003 to 0.004 for all the three oxides.

In chapter 3 we have attempted to substitute zinc by cadmium (the higher group member of Zn) to obtain oxides of the type, $(Ln_{2/5}Ba_{2/5}Ca_{1/5})(Cd_{2/5}Ti_{3/5})O_3$ and $(Ln_{1/3}Ba_{1/3}Ca_{1/3})(Cd_{1/3}Ti_{2/3})O_3$ (Ln = rare-earth). Powder X-ray diffraction of the oxides $Ln_{2/5}Ba_{2/5}Ca_{1/5})(Cd_{2/5}Ti_{3/5})O_3$ shows the oxides to be cubic. Rietveld refinement of powder X-ray and neutron diffraction data confirms the cubic structure. The lattice parameters obtained is around 4.00 Å. In case of the oxides of the family $(Ln_{1/3}Ba_{1/3}Ca_{1/3})(Cd_{1/3}Ti_{2/3})O_3$ powder X-ray diffraction shows cubic phases with lattice parameters slightly lower than those of $(Ln_{2/5}Ba_{2/5}Ca_{1/5})(Cd_{2/5}Ti_{3/5})O_3$. Annealing of the oxides in oxygen and air was carried out to promote cation ordering. The oxides retained their cubic structure even after annealing as in the case of analogous zinc based oxides. Compositional analysis was carried out by energy dispersive analysis of x-rays (EDX). It is found in these oxides very little amount of cadmium is present due to high volatility cadmium. The appropriate formula for $(Ln_{2/5}Ba_{2/5}Ca_{1/5})(Cd_{2/5}Ti_{3/5})O_3$ (Ln = La) was $(La_{0.52}Ba_{0.48}Ca_{0.25})(Cd_{0.04}Ti_{0.65})O_{2.85}$. Dielectric measurements of these oxides have been carried out with respect to variation in temperature and frequency. The dielectric constant (ε) is 35 for $(La_{2/5}Ba_{2/5}Ca_{1/5})(Cd_{2/5}Ti_{3/5})O_3$ and 50 for $(Nd_{2/5}Ba_{2/5}Ca_{1/5})(Cd_{2/5}Ti_{3/5})O_3$. The dielectric loss for the two oxides are 0.0021 and 0.0017 respectively. These measurements were carried out at 100 kHz and at 35°C. Both these oxides show high stability of both the dielectric constant and the dielectric loss with temperature ($d\varepsilon / dT \sim 10^{-3}$). In case of the oxides of the family $(Ln_{1/3}Ba_{1/3}Ca_{1/3})(Cd_{1/3}Ti_{2/3})O_3$, the dielectric

constant was found to be higher than the analogous oxides with nominal composition $(Ln_{2/5}Ba_{2/5}Ca_{1/5})(Cd_{2/5}Ti_{3/5})O_3$ having the same rare-earth.

In chapter 4 we have attempted to synthesize new solid solutions in order to study the effect of substitution of the structure and properties of the oxides. Starting from the nominal composition of oxides described in the previous studies (chapters 2 and 3) we have further substituted the A and B sites to obtain new families of oxides with tunable dielectric properties, depending on the amount of substitution. We have thus investigated oxides of the type $Nd_2Ba_2CaCu_{2-x}Zn_xTi_3O_{14}$, $(La_{2/5}Ba_{2/5}Ca_{1/5})(Cd_{(2-x)/5}Zn_{x/5}Ti_{3/5})O_3$, $(Nd_{(2-x)/5}La_{x/5}Ba_{2/5}Ca_{1/5})(Zn_{2/5}Ti_{3/5})O_3$ $(0 \leq x \leq 0.4)$ and $Nd_2Ba_2CaCu_{5-x}Ti_xO_{14}$ $(0 \leq x \leq 5)$. It is observed from powder X-ray diffraction that pure phases are obtained for all the compounds in the first three families mentioned above. However, for the family $Nd_2Ba_2CaCu_{5-x}Ti_xO_{14}$, pure phase has been obtained only when x = 0 and 3. In case of $Nd_2Ba_2CaCu_{2-x}Zn_xTi_3O_{14}$ it is seen that the copper rich compounds crystallize in the tetragonal structure, where the '**c**' parameter is roughly 5 times the '**a**' parameter. This suggests an ordering of 'Cu' and 'Ti' ions along the **c**-axis. However, for the zinc-rich phases ordered structures are not formed and the formula can be written as $(Nd_{2/5}Ba_{2/5}Ca_{1/5})(Cu_{(2-x)/5}Zn_{x/5}Ti_{3/5})O_3$ It is seen that there is an increase in the lattice parameter with increase in zinc substitution from '**a**' = 3.913(8) and '**c**' = 19.63(1) at x = 0 to '**a**' = 3.925 (1) Å and '**c**' = 19.64 (1) Å for x = 0.2. For the oxides $(La_{2/5}Ba_{2/5}Ca_{1/5})(Cd_{(2-x)/5}Zn_{x/5}Ti_{3/5})O_3$ we find from Rietveld refinement and EDX analysis that the cadmium content is much lower than that expected. The oxides, $(Nd_{(2-x)/5}La_{x/5}Ba_{2/5}Ca_{1/5})(Zn_{2/5}Ti_{3/5})O_3$ crystallize in the disordered cubic structure for all the

compositions. There is a steady decrease in the lattice parameter with increase in lanthanum content as is expected from the higher ionic radius of lanthanum than that of neodymium. However, in case of the oxides of the family $Nd_2Ba_2CaCu_{5-x}Ti_xO_{14}$ pure phases are formed only for x = 0 and x = 3. The oxide with x = 3 has a quintupled perovskite structure, while that with x = 0 has a triple layered structure. The dielectric properties of all the families of oxides have been studied with respect to frequency and temperature, except for the oxide $Nd_2Ba_2CaCu_5O_{14}$, which gave low resistivity values from two probe measurements. In case of the family of oxides $Nd_2Ba_2CaCu_{2-x}Zn_xTi_3O_{14}$ there is a sharp fall in dielectric constant and a corresponding rise in dielectric loss with increase in copper. The dielectric constant falls from 59 for x = 0.4 to 8 for x = 0. The dielectric constant increases steadily with increase in zinc for the oxides $(La_{2/5}Ba_{2/5}Ca_{1/5})(Cd_{(2-x)/5}Zn_{x/5}Ti_{3/5})O_3$. The dielectric loss shows a marginal variation from 0.002 to 0.006. For the oxides $(Nd_{(2-x)/5}La_{x/5}Ba_{2/5}Ca_{1/5})(Zn_{2/5}Ti_{3/5})O_3$, the dielectric constant shows a regular decrease with increase in neodymium content till x = 1.5. The pure oxides (x = 0 and 2) show higher values of the dielectric constant compared to oxides with mixed rare-earth ions.

In chapter 5, we have substituted the B-sites (Zn and Cd sites) with transition metal ions. Our aim was to see the effect of the magnetic ions on the dielectric properties as well as on the structure of the oxides. In the process, we have obtained bi-functional oxides that are magnetic and have high dielectric constant. Perovskite based oxides of the type $(Ln_{2/5}Ba_{2/5}Ca_{1/5})(M_{2/5}Ti_{3/5})O_3$ (Ln = La, Nd and M = Mn, Fe, Ni) have been synthesized by the solid state route. All these oxides crystallize in the (disordered) cubic

perovskite structure, as observed from powder X-ray diffraction patterns, with lattice parameter ~ 3.95 Å depending on the rare-earth and transition metal ion. No sign of ordering of the cations to give a tetragonal structure were observed even after annealing the compounds in air and oxygen for several days. EDX analysis confirms the composition of these oxides. Iodometric studies show that a small part of the Mn is present as Mn^{4+}, the remaining being present as Mn^{3+}. In case of the iron based oxides, about 80 % of the iron was in the divalent state, the remaining being in the trivalent state. It is found from the plot of χ_M against temperature at 10 kOe that the oxide $Ln_{2/5}Ba_{2/5}Ca_{1/5}Mn_{2/5}Ti_{3/5}O_3$ shows antiferromagnetic ordering at around 5 K. This oxide shows an unusually high dielectric constant of around 6000 at 1 kHz. It is seen that the dielectric constant decreases sharply with frequency showing a value of 592 at 100 kHz. Both the dielectric constant and dielectric loss decrease with frequency. Also there is a sharp increase in dielectric constant and loss with increase in temperature, which is possible due to electron hopping between adjacent trivalent and tetravalent states of Mn. In case of the solid solutions of the type $(Ln_{2/5}Ba_{2/5}Ca_{1/5})(Mn_{2/5-x}Ni_xTi_{3/5})O_3$, a shift from antiferromagnetic to paramagnetic behaviour is observed as the Ni content increases. The compound with x = 0.4 (in the nickel based oxide) is paramagnetic and has a moment of 1.81 μ_B. The dielectric constant (ε) of $(La_{2/5}Ba_{2/5}Ca_{1/5})(Ni_{2/5}Ti_{3/5})O_3$ was found to be 78 and the loss (D) was 0.21 at room temperature and 100 kHz. The dielectric constant shows a decrease with frequency (ε = 59 at 500 kHz). Similar Ni-substituted oxide is not obtained as a pure phase for the Nd-based systems. In case of Ln = Nd, only the Mn-substituted oxide is formed as a pure phase. This oxide is paramagnetic and has a magnetic moment of 6.92 μ_B. The dielectric constant for the composition

$(Nd_{2/5}Ba_{2/5}Ca_{1/5})(Mn_{2/5}Ti_{3/5})O_3$ was found to be 192 and the loss was 0.14 at room temperature at 100 kHz. The oxides $(Ln_{2/5}Ba_{2/5}Ca_{1/5})(Fe_{2/5}Ti_{3/5})O_3$ (Ln = La and Nd) have been found to be paramagnetic with effective magnetic moments of 4.07 μ_B and 5.16 μ_B for Ln = La and Ln = Nd respectively. The dielectric constant of these oxides have been found to be 84 and 89 for Ln = La and Nd respectively. Their respective dielectric losses were 0.43 and 0.39. The dielectric constant was found to be frequency dependent and decreases with rise in frequency and increases with rise in temperature. The dielectric loss however, shows opposite behaviour, that is, it rises with frequency and falls with temperature.

To summarize, the thesis has examined the possibility of a wide range of substitutions in the A and B-sites of the perovskite structure and has obtained several new oxides which have been characterized in detail with respect to their composition, cation occupancy, structure and dielectric properties. In addition, the effect of a magnetic ion in predominantly dielectric structure has been studied in detail for the first time. The large data generated from the above studies will hopefully serve as a source of information to solid-state scientists interested in dielectric properties of materials and their applications.

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