LANTHANIDE BASED DOUBLE PEROVSKITES AND THEIR DIELECTRIC PROPERTIES

NIBEDITA DAS

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

JULY 2017

LANTHANIDE - BASED DOUBLE PEROVSKITES AND THEIR DIELECTRIC PROPERTIES

by

NIBEDITA DAS

Department of Chemistry

Submitted

in fulfillment of the requirements of the Degree of Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

JULY 2017

DEDICATED TO MY

FAMILY

CERTIFICATE

This is to certify that the thesis entitled, "Lanthanide based double perovskites and their dielectric properties", being submitted by **Mrs. Nibedita Das**, 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. Mrs. Nibedita Das has worked under our guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to our 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.

Professor A. K. Ganguli
Department of Chemistry
Indian Institute of
Technology, Delhi
New Delhi –110016
INDIA

Prof. M. Thirumal
Department of Chemistry
University of Delhi
New Delhi - 11007
INDIA

ACKNOWLEDGEMENTS

This thesis completed and became reality by the help of many people. It is a great pleasure for me to thank them who made my Ph.D. thesis possible. This completion would not have been possible without their help and support. I pay my sincere gratitude to all of them.

First of all, I am greatly indebted to my supervisor, ***Prof. Ashok Kumar Ganguli****, Department of Chemistry, IIT Delhi and Director, Institute of Nano Science and Technology, Mohali, for introducing me to the challenging world of research. I express my gratitude for the efforts he has made to groom me as a researcher. He taught me how to perceive a problem scientifically. He has an amazing way of teaching his students and solving the problems that they face during our research. His enthusiasm towards science has always inspired me and motivated me to love science. It is my great opportunity to do my doctoral program under his supervision. I thank him for his support, guidance, critical suggestions and for everything he taught me during my Ph.D. This thesis would not have been completed without the endless support provided by him. He is and will be always a source of inspiration for me.*

I feel a genuine pleasure to express my thanks to ***Prof L. C. Gupta*** *(Visiting scientist at the Dept. of Chemistry, IIT Delhi and retd. Professor at TIFR Mumbai) for his support and constant motivation to complete this thesis. I would like to thank him for sharing his knowledge and help in analyzing the data which led to fruitful results.*

I am grateful to my co supervisor ***Prof. M. Thirumal*** *(Professor at Dept. of Chemistry, Delhi University) for his help and motivation. He always encouraged me in my work and his constant scientific advices help me to complete my thesis.*

My heartfelt thanks to Prof. Ravi Shankar the Head, and Prof. A. Ramanan and Prof. A.K. Singh the former Heads of Department of Chemistry, IIT Delhi for providing all the facilities in the department. I am also grateful to all supporting staff of department of Chemistry, IIT Delhi and NRF, IIT Delhi for their kind help and cooperation. My special thanks Dr. Pramit Chowdhury for extending his help and kindness in the absence of my supervisor.

I am also thankful to my collaborators Dr. Amish G. Joshi (NPL, New Delhi) for XPS measurements, Dr. Satyendra Singh (JNU, New Delhi) for his help in ferroelectric measurements done in his lab, Dr. V. Raghavendra Reddy (DAE, Indore) for Mössbauer measurements. I would like to thank Dept. of Physics for PPMS facility.

I wish to express my gratitude for my seniors and colleagues, Dr. Jahangeer, Dr. Sonalika, Dr. Aparna, Dr. Menaka, Dr. Masood, Dr. Jaiprakash, Dr. Aditya, Dr. Debashree, Dr. Sunita, Dr. Soma, Dr. Bharat, Dr. Neha, Dr. Arabinda, Dr. Gohil, Dr. Kasinath, Dr. Parthsarthy, Dr. Sharmila, Dr. Ashima and my juniors Soumen, Sandeep, Zeba, Nitin, Vaishali, Jayanti, Soumen and Moumita for making the lab environment cordial and for helping me whenever required.

I am really grateful to my labmates and friends Dr. Manu, Dr. Mrinmoyee, Sanjit, Pintu and Vandana for their great support both professionally and personally and for making my stay at IIT Delhi fun and memorable. A special thanks to my friends Dr. Sarala and Dr. Jyotsna for being there whenever I needed their help.

I pay my gratitude to my parents Mr. Bhimasen Das and Mrs. Pramila Das and my sisters Mrs. Madhusmita Parida and Mrs. Sasmita Das, my brother Mr. Sambit Das my brothers-in-law Mr. Manoj Parida and Mr. Sudhir R. Das, My sister-n-law Mrs. Akasmika

Behera made me what I am. They are the constant source of inspiration for me. I would thank them for the sacrifices they made for me. I thank them for their love, care and patients to listen to me and help me to make my decision fruitful. I always found them standing by my side and supporting me whenever I felt it necessary. They taught me the discipline of life and always helped me and guided me to take right decisions in life. I specially thank to my nieces Ms. Pallavi Parida and Ms. Arna Das, my nephews Saswat Das and Divyajyoti Parida for their love and affection and for being the part of my journey. I will also thank my in-laws Mr. Dinabandhu Das, Mrs. Sebati Das, My brothers-in-law Mr. Khsirod Ch. Das and Mr. Prashant Das, my sisters-in-law Mrs. Hemalata Das and Mrs. Swapna Das for their constant inspiration and motivation. I thank all my near and far family members.

My words are short and I am not able to find words to explain my thanks and gratitude to my husband Mr. Pravat Das a great friend, a constant pillar and a motivator to help me to complete my Ph.D. at IIT Delhi. His encouragement, inspiration and moral support gave me strength to overcome from every drastic situation and he never let me feel helpless and alone in my life. Again I feel my words are limited to express thanks to my little son Prateek Das who is the source of my life. I thankful to him for his love and care during the tough days of my Phd. Being an independent child he always encouraged me and supported me to complete my work successfully. I owe everything to Pravat and Prateek.

I acknowledge the financial support of BRNS and Nanoscale Research Facilities IIT Delhi for fellowship.

Nibedita Das

Abstract

Mankind is always in a search for new materials with unusual properties. Perovskites with range of structure and property interplay makes them an excellent research field for researchers. In past few decades, people have discovered several new double perovskites with interesting properties which has scope for wide ranging applications. Ferroelectric $BaTiO_3$ and dielectric $SrTiO_3$ are examples of perovskite compounds which are widely used in communication Industry. RE_2NiMnO_6, Y_2FeCrO_6 are examples of double perovskites where the B-site is ordered between B, B' elements. These compounds are known due to their fascinating properties. Interest of researchers has been focused on novel perovskite based multifunctional materials for the fabrication of memory device which have distinct features of nonvolatile, fast, robust and less energy efficiency. Magnetodielectric materials are of great interest due to the combination of magnetic as well as dielectric behavior in the single component. $BiFeO_3$, $BiMnO_3$, Bi_2NiMnO_6 are examples of magnetoelectrics with very high ferroelectric and ferromagnetic transition temperature while orthorhombic $GdFeO_3$ and $RMnO_3$ (R = Tb-Lu and Y) have strong magnetic and ferroelectric coupling. Ferroelectric materials have the unique property of switchable polarization when an electric field is applied. We are focusing on the synthesis of dielectric, ferroelectric and multiferroic materials.

In the present work we are concerned with the synthesis and properties of some new dielectric materials with double perovskite structure. We have synthesized some lanthanide based zinc titanates Pr_2ZnTiO_6 and Gd_2ZnTiO_6 and investigated their structure and dielectric properties. They show high dielectric constant and nearly zero dielectric loss.

We synthesized a series of new dielectric materials Pr_2MTiO_6 M = Mg, Ca and Sr. The structure as well as the properties of these materials varies depending upon the cation. The

structure of these compounds were investigated through Powder X-ray diffraction method and Raman spectroscopic study.

New dielectric materials RE_2CoTiO_6 (RE = Pr, Nd) have synthesized by soild state method. The structure of the compound was investigated through Powder X-ray diffraction method. The compounds are antiferromagnetic with T_C below 17 K.

Ferroelectric materials RE_2NiTiO_6 (RE = Pr, Nd, Sm) with double perovskite structure have been synthesized. T_c of these compounds is well above room temperature. All these compounds display P-E hysteresis loop at room temperature.

We have successfully synthesized new double perovskites Pr_2MCrO_6 (M = Mn and Fe). The compounds show ferromagnetic behavior below room temperature. XPS

Study shows the +3 oxidation state of cations. The magnetic structure of Pr_2FeCrO_6 was confirmed by variable temperature Mössbauer studies. Resistivity measurement of Pr_2CrMnO_6 shows the semi-conductor behavior of the compound up to 160 K. Dielectric transition at certain temperature indicates ferroelectric nature of the compounds. The ferroelectric behavior of Pr_2FeCrO_6 was further confirmed by formation of electrical hysteresis loop at room temperature.

All the above materials have been synthesized by solid state method. Invstigated the structure of the compounds by Powder X-ray method. We have measured their dielectric as well as magnetic properties.

सार

मानव जाति हमेशा असामान्य गुणों के साथ नई सामग्रियों की खोज में होती है श्रेणी के साथ पेरोवाक संरचना और संपत्ति परस्पर क्रिया का उन्हें शोधकर्ताओं के लिए एक उत्कृष्ट शोध क्षेत्र बनाता है | अतीत में कुछ दशकों से, लोगों ने दिलचस्प गुणों के साथ कई नए डबल पेरोस्कोट की खोज की है जो व्यापक अनुप्रयोगों के लिए अवसर है | फेरोइलेक्ट्रिक $BaTiO_3$ और डायलेक्ट्रिक $SrTiO_3$ हैं प्रतिवस्कर मिश्रित यौगिकों के उदाहरण जो व्यापक रूप से संचार उद्योग में उपयोग किए जाते हैं | RE_2NiMnO_6, Y_2FeCrO_6 डबल परोवस्केत के उदाहरण हैं जहां बी साइट के बीच आदेश दिया जाता है बी, बी 'तत्व ये यौगिक उनके आकर्षक गुणों के कारण जाने जाते हैं। का ब्याज शोधकर्ताओं के लिए उपन्यास परोवस्केत आधारित बहुविध सामग्री पर ध्यान केंद्रित किया गया है | मेमोरी डिवाइस का निर्माण जो कि गैर- वाष्पशील, तेज, मजबूत और कम की विशिष्ट विशेषताएं हैं | ऊर्जा दक्षता मैग्नेटोडिलेक्ट्रिक सामग्री के संयोजन के कारण बहुत रुचि है एक घटक में चुंबकीय और ढांकता हुआ व्यवहार। $BiFeO_3$, $BiMnO_3$, Bi_2NiMnO_6 बहुत उच्च फेरोइलेक्ट्रिक और फेरामेग्नेटिक संक्रमण के साथ मैग्नेटोएक्ट्रिक्स के उदाहरण हैं | तापमान जबकि orthorhombic $GdFeO_3$ और $RMnO_3$ (R = Tb-Lu and Y) मजबूत चुंबकीय है | और फेरोइलेक्ट्रिक युग्मन फेरोइलेक्ट्रिक सामग्री में स्विच करने योग्य की अद्वितीय विशेषता है | ध्रुवीकरण जब एक विद्युत क्षेत्र लागू किया जाता है। हम ढांकता हुआ के संश्लेषण पर ध्यान केंद्रित कर रहे हैं |

फेरोइलेक्ट्रिक और मल्टीफ्रोरिक सामग्री वर्तमान कार्य में हम कुछ के संश्लेषण और गुणों से चिंतित हैं | डबल पेरोवस्की संरचना के साथ नई ढांकता हुआ सामग्री हमने कुछ लैंटनैड को संश्लेषित किया है | आधारित Pr_2ZnTiO_6 और Gd_2ZnTiO_6 और उनकी संरचना और ढांकता हुआ गुण। वे उच्च ढांकता हुआ निरंतर और लगभग शून्य ढांकता हुआ हानि दिखाते हैं।

हमने नई ढांकता हुआ सामग्री Pr_2MTiO_6 M = Mg, Ca, Sr की एक श्रृंखला संश्लेषित की। संरचना और साथ ही इन सामग्रियों के गुण कटियन के आधार पर अलग-अलग होता है। इन यौगिकों की संरचना की जांच पाउडर एक्स-रे विवर्तन पद्धति तथा रमन स्पेक्ट्रोस्कोपिक अध्ययन माध्यम से की गई है |

नई ढांकता हुआ पदार्थ RE_2CoTiO_6 (RE = Pr, Nd) ठोस स्थिति द्वारा संश्लेषित किया गया है | कंपाउंड की संरचना पाउडर एक्स-रे विवर्तन के माध्यम से जांच की गई है | इस पदार्थ एंटिफ्रोमैग्नेटिक होते हैं जो कि T_C 17 K से नीचे होता है।

डबल पेरोवस्की संरचना के साथ फेरोइलेक्ट्रिक सामग्री RE_2NiTiO_6 (RE = Pr, Nd, Sm) संश्लेषित किया गया है। इन यौगिकों का टीसी कमरे के तापमान से ऊपर है। ये सभी यौगिक कमरे के तापमान पर P-E हिस्टैरिसीस के पाश प्रदर्शित है ।

हमने सफलतापूर्वक नए डबल पेरोवैक्ट्स Pr_2MCrO_6 (M = Fe, Mn) को संश्लेषित किया है। ये यौगिक कमरे के तापमान के नीचे T_C दिखाते हैं। एक्सपीएस अध्ययन से पता चलता है कि सब कटियन +3 ऑक्सीडेशन स्टेटेश में है। Pr_2FeCrO_6 का चुंबकीय ढांचा तापमान आधारित अध्ययन द्वारा पुष्टि गयी है। Pr_2CrMnO_6 के प्रतिरोधकता माप क्यूम्यक के अर्द्ध कंडक्टर व्यवहार से पता चलता है कि 160 K तक निश्चित रूप से ढांकता हुआ संक्रमण तापमान यौगिकों के फेरोइलेक्ट्रिक प्रकृति को इंगित करता है । का फेरोइलेक्ट्रिक व्यवहार Pr_2FeCrO_6 को कमरे के तापमान पर बिजली के हिस्टैरिसीस लूप के गठन से भी पुष्ट किया गयाथा।

सभी उपरोक्त सामग्री को सॉलिड स्टेट विधि द्वारा संश्लेषित किया गया है। इनवेस्टिवेटेड पाउडर एक्स-रे विधि द्वारा यौगिकों की संरचना हमने उनके ढांकता हुआ, चुंबकीय गुणों के भी मापा है।

TABLE OF CONTENTS

Chapter 5: Ferroelectric compound RE_2NiTiO_6 (RE = Pr, Nd, Sm) with Double perovskite structure.

Chapter 6: Structure, magnetic, dielectric study of Pr_2CrMnO_6 and Pr_2CrFeO_6.

Figure caption

ABBREVIATIONS AND SYMBOLS

Å	Angstrom
° C	Centigrade
μm	Micrometer
Cm	centimeter
h	Hours
PXRD	Powder X-ray diffraction
SAED	Selected Area Electron Diffraction
FSEM	Field Scanning Electron Microscopy
μ	Magnetic Moment
H	Magnetic Field
μB	Bohr−magneton
eV	Electron – Volt
K	Kelvin
°	Degree (angle)
λ	Wavelength
Ω	Ohm
T	Tesla
G	Gauss
Oe	Oersted
χ_M	Molar Magnetic susceptibility (dc)
χ_M^{-1}	Inverse Molar Magnetic susceptibility (dc)

ρ	Resistivity
γ	Sommerfeld coefficient
θ	Weiss constant and Bragg's diffraction angle
GPa	Gega Pascals
V	Electric field gradient
δ	Isomer shift
Γ́	Line width
ZFC	Zero Field Cooled
FC	Field Cooled
ε	Real part of dielectric constant
tanδ	dielectric loss tangent
d	lattice spacing
C	capacitance
F	frequency
H_C	Coercivity
P_r	Remanent Polarization
E_C	Coercive field