

**LANTHANIDE BASED DOUBLE PEROVSKITES
AND THEIR DIELECTRIC PROPERTIES**

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**DEPARTMENT OF CHEMISTRY
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**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.

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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. $\text{RE}_2\text{NiMnO}_6$, 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 , $\text{Bi}_2\text{NiMnO}_6$ 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 $\text{Pr}_2\text{ZnTiO}_6$ and $\text{Gd}_2\text{ZnTiO}_6$ 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 $\text{RE}_2\text{CoTiO}_6$ ($\text{RE} = \text{Pr}, \text{Nd}$) have synthesized by solid 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 $\text{RE}_2\text{NiTiO}_6$ ($\text{RE} = \text{Pr}, \text{Nd}, \text{Sm}$) 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 ($\text{M} = \text{Mn}$ and Fe). The compounds show ferromagnetic behavior below room temperature. XPS

Study shows the +3 oxidation state of cations. The magnetic structure of $\text{Pr}_2\text{FeCrO}_6$ was confirmed by variable temperature Mössbauer studies. Resistivity measurement of $\text{Pr}_2\text{CrMnO}_6$ 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 $\text{Pr}_2\text{FeCrO}_6$ was further confirmed by formation of electrical hysteresis loop at room temperature.

All the above materials have been synthesized by solid state method. Investigated 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 पेरोवस्केत 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 पेरोवस्केत 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 फेरामैग्नेटिक 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 मल्टीफ़ोरिक 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 एंटीफ़ोमैग्नेटिक 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 हिस्टैरिसिस 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 हिस्टैरिसिस लूप के गठन से भी पुष्ट किया गयाथा।

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

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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
Γ	Line width
ZFC	Zero Field Cooled
FC	Field Cooled
ϵ	Real part of dielectric constant
$\tan\delta$	dielectric loss tangent
d	lattice spacing
C	capacitance
F	frequency
H_C	Coercivity
P_r	Remanent Polarization
E_C	Coercive field