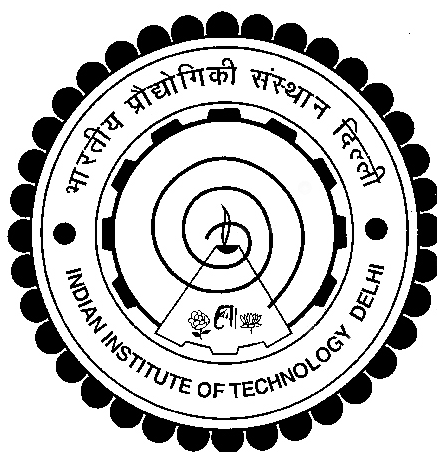


INVESTIGATION OF PEROVSKITE RELATED OXIDES: STRUCTURAL AND MAGNETIC PROPERTIES

ANTARA SARKAR



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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INVESTIGATION OF PEROVSKITE RELATED OXIDES: STRUCTURAL AND MAGNETIC PROPERTIES

by

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Submitted

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

to the



DEPARTMENT OF CHEMISTRY

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**This thesis is dedicated to my
parents and family.**

Indian Institute of Technology Delhi

Candidate's Declaration

I hereby certify that the work being presented in the thesis entitled, “**Investigation of perovskite related oxides: Structural and magnetic properties**”, in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy and submitted in the Department of Chemistry of the Indian Institute of Technology, Delhi. It is an authentic record of my own work carried out during a period of July 2018 to September 2021 under the supervision of Prof. Ashok K. Ganguli, Indian Institute of Technology, Delhi.

The matter presented in the thesis has not been submitted by me for the award of any other degree or in any other institute.

(Antara Sarkar)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

(Prof. Ashok K. Ganguli)

Supervisor

Date

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Abstract

Perovskites exist in varied structures and show structure dependent magnetic properties which is of great interest in the field of multiferroics, magnetocaloric and spintronic devices. Here we intend to study the various rare-earth(R) and transition metal (TM) ion interactions depending on their structures. Different Curie temperature, spin glass transition and spin reorientation transitions were observed depending on the degree of interactions and structural properties. It is interesting to study the role of orbital interactions, disorder in magnetic transitions leading to change in superexchange and double exchange interaction.

On substitution at A-site or B-site results in change in magnetic interactions, as well as creates structural distortions. We also obtained results where the spin interaction of the transition metal and rare-earth interaction, magnetic anisotropy, orientations of orbitals, disorder induced interactions were observed.

The structural investigation of various combinations of rare-earth and transition metal ions at A and B-site with La/Pr/Ho and Fe/Mn/Cr respectively were studied. The magnetic susceptibility measured at 1000 Oe, was found to decrease in $\text{Ho}_{1-x}\text{Pr}_x(\text{Mn}_{0.5}\text{Cr}_{0.5})\text{O}_3$ ($x = 0, 0.3, 0.5$ and 0.7), while in $\text{Ho}_{1-x}\text{Pr}_x(\text{Fe}_{0.25}\text{Mn}_{0.25}\text{Cr}_{0.5})\text{O}_3$ ($x = 0, 0.5$ and 1) it increased as the value of x increases, which could be attributed to increased Ho-Mn interaction and competing anisotropy of Pr and Fe orbitals in the first and second case respectively. $\text{Pr}(\text{Fe}_{0.25}\text{Mn}_{0.25}\text{Cr}_{0.5})\text{O}_3$ showed highest Curie temperature (247 K) and Curie-Weiss temperature (-58 K) and a maximum change in remanent magnetization at 5 K and 20 K amongst all the compositions, which suggests a stable spin structure and rare-earth spin reorientation taking place in this composition.

The investigation on Pr-Mn-Ru-O phase, on effect of structural disorder due to Ru-deficiency at B-site, as calculated from EDAX and XPS measurements by a stoichiometry of 0.15(2), which leads to enhanced spin glass like behavior at temperatures below 31 K, as evident from the bifurcation between the ZFC and FC curves. This pure Pr-Mn-Ru-O phase obtained was refined in the orthorhombic *Pnma* spacegroup, with greater octahedral distortion along the axial direction ($157.15(1)^\circ$) than in the equatorial ($168.88(1)^\circ$), along with a compression in the *b* lattice parameter, which further suggests greater Ru-vacancy along the axial *b* direction. The magnetic susceptibility increases at 18 K obtained from DC magnetic susceptibility data at 1000 Oe, suggests disorder induced ferromagnetic ordering, and that at 4.5 K which could said due to 'Pr' and Mn – O – Ru ordering. The non-saturation nature of isothermal magnetization at 2 K and 50 K, further suggests short range magnetic ordering.

To further investigate the competing magnetic interactions of rare-earth and transition metal ions, it was observed that the compound $\text{La}_{0.5-x}\text{Sm}_x\text{Pr}_{0.5}\text{CrO}_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5), showed negative magnetization at 100 Oe. The alignment of the rare-earth moment opposite to the net moment generated by the canted antiferromagnetic moment generated by the Cr ion resulted in negative magnetization for $x = 0.4$ and 0.5 at 100 Oe, ZFC. Pure phase of $\text{La}_{0.5-x}\text{Sm}_x\text{Pr}_{0.5}\text{CrO}_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) were refined in orthorhombic *Pnma* spacegroup, where the octahedral distortion increased as the value of *x* increased. This increase of anisotropy as the value of *x* decreased has resulted in $x = 0$ and 0.1 , to show magnetic reorientation in the temperature range 160 K to 25 K, from the bifurcation and recombination of FCC and FCW at 10,000 Oe. Exchange bias effect in ZFC and ZFW in the composition $\text{La}_{0.1}\text{Sm}_{0.4}\text{Pr}_{0.5}\text{CrO}_3$ was investigated, with the observation of negative exchange bias effect at

temperature below 230 K, which further suggests canted antiferromagnetic nature in the following compositions.

In order to inspect further the effect of structural distortion with the decrease in rare-earth radii was investigated in orthorhombic $R_{0.5}Sr_{0.5}Fe_{0.5}Mn_{0.5}O_3$ (R: Gd<Nd<Pr). Influence of increased octahedral distortion, primarily due to Jahn-Teller distortion, resulted in decrease of magnetic transition temperature due to increased hybridization between the transition metal and oxygen orbitals. The octahedral distortion decreases as the rare-earth size increases from Gd to Nd to Pr. $Gd_{0.5}Sr_{0.5}Fe_{0.5}Mn_{0.5}O_3$ shows canted antiferromagnetic ordering of Mn^{3+} spins at temperatures below 49 K followed by Gd antiferromagnetic ordering taking place at temperatures below 3 K. The compositions $Nd_{0.5}Sr_{0.5}Fe_{0.5}Mn_{0.5}O_3$ and $Pr_{0.5}Sr_{0.5}Fe_{0.5}Mn_{0.5}O_3$ showed spin glass like nature at 47 K and 58 K respectively, as $Nd_{0.5}Sr_{0.5}Fe_{0.5}Mn_{0.5}O_3$ showed greater octahedral distortion as compared to $Pr_{0.5}Sr_{0.5}Fe_{0.5}Mn_{0.5}O_3$.

To study the effect on disruption of long range ordering of orbitals on increased Curie –Weiss (θ_{CW}) temperature and on photoelectrocatalytic properties were investigated in monoclinic $Sr_2YbRu_{1-x}Ta_xO_6$ ($x = 0, 0.25, 0.5, 0.75$ and 1) system. The long range ordering of Yb – O –Ru was found to be maximum in Sr_2YbRuO_6 , which decreased on substituting Ta in place of Ru, as evident from the maximum θ_{CW} obtained in Sr_2YbRuO_6 (-148 K), which decreased substantially for $x = 0.75$ (-125 K) to $x = 0.5$ (-118 K), and $x = 0.25$ (-102 K). On increasing Ta concentration, the bandgap was found to increase linearly from 1.78(1) eV ($x = 0$) to 2.08(1) eV ($x = 0.75$) however with a slight decreased deviation (0.04(1) eV) observed in case of Sr_2YbRuO_6 . Photoelectrocatalytic measurement showed maximum oxygen evolution current density of $17 \mu A/cm^2$ in light and dark ($12 \mu A/cm^2$), in Sr_2YbRuO_6 . XPS showed Ru and Ta were majorly in +5 and +4 oxidation states.

सारांश

पेरोव्स्काइट्स विभिन्न संरचनाओं में मौजूद हैं और संरचना पर निर्भर चुंबकीय गुण दिखाते हैं जो कि मल्टीफेरिक्स, मैग्नेटोकैलोरिक और स्पिंट्रॉनिक उपकरणों के क्षेत्र में बहुत रुचि रखते हैं। यहां हम विभिन्न दुर्लभ-पृथ्वी (आर) और संक्रमण धातु (टीएम) आयन इंटरैक्शन का अध्ययन करने का इरादा रखते हैं जो उनकी संरचनाओं पर निर्भर करता है। विभिन्न क्यूरी तापमान, स्पिन ग्लास संक्रमण और स्पिन पुनर्विन्यास संक्रमणों को अंतःक्रियाओं और संरचनात्मक गुणों की डिग्री के आधार पर देखा गया। कक्षीय अंतःक्रियाओं की भूमिका का अध्ययन करना दिलचस्प है, चुंबकीय संक्रमण में विकार जिसके कारण सुपरएक्सचेंज और डबल एक्सचेंज इंटरैक्शन में परिवर्तन होता है।

ए-साइट या बी-साइट पर प्रतिस्थापन पर चुंबकीय अंतःक्रियाओं में परिवर्तन होता है, साथ ही संरचनात्मक विकृतियां भी पैदा होती हैं। हमने ऐसे परिणाम भी प्राप्त किए जहां संक्रमण धातु और दुर्लभ-पृथ्वी की बातचीत, चुंबकीय अनिसोट्रॉपी, ऑर्बिटल्स के उन्मुखीकरण, विकार प्रेरित बातचीत की स्पिन बातचीत देखी गई।

ए और बी-साइट पर क्रमशः ला/पीआर/हो और फे/एमएन/सीआर के साथ दुर्लभ-पृथ्वी और संक्रमण धातु आयनों के विभिन्न संयोजनों की संरचनात्मक जांच का अध्ययन किया गया। 1000 Oe पर मापी गई चुंबकीय संवेदनशीलता, $\text{Ho}_{1-x}\text{Pr}_x(\text{Mn}_{0.5}\text{Cr}_{0.5})\text{O}_3$ ($x = 0, 0.3, 0.5$ और 0.7) में घटती पाई गई, जबकि $\text{Ho}_{1-x}\text{Pr}_x(\text{Fe}_{0.25}\text{Mn}_{0.25}\text{Cr}_{0.5})\text{O}_3$ ($x = 0, 0.5$ और 1) यह x के मान के बढ़ने के साथ बढ़ता है, जिसका श्रेय क्रमशः पहले और दूसरे मामले में पीआर और फे ऑर्बिटल्स की बढ़ी हुई हो-एमएन इंटरैक्शन और प्रतिस्पर्धी अनिसोट्रॉपी को दिया जा सकता है। $\text{Pr}(\text{Fe}_{0.25}\text{Mn}_{0.25}\text{Cr}_{0.5})\text{O}_3$ ने उच्चतम क्यूरी तापमान (247 K) और क्यूरी-वीस तापमान (-58 K) और सभी रचनाओं के बीच 5 K और 20 K पर अवशेष चुंबकीयकरण में अधिकतम परिवर्तन दिखाया, जो सुझाव देता है कि इस संरचना में स्थिर स्पिन संरचना और दुर्लभ-पृथ्वी स्पिन पुनर्रचना हो रही है।

बी-साइट पर आरयू-कमी के कारण संरचनात्मक विकार के प्रभाव पर पीआर-एमएन-आरयू-ओ चरण पर जांच, जैसा कि ईडीएक्स और एक्सपीएस माप से 0.15 (2) के स्टोइकोमेट्री द्वारा गणना की जाती है, जिससे स्पिन ग्लास को बढ़ाया जाता है। 31 K से नीचे के तापमान पर व्यवहार, जैसा कि ZFC और FC वक्रों के बीच विभाजन से स्पष्ट है। प्राप्त इस शुद्ध Pr-Mn-Ru-O चरण को ऑर्थोरोम्बिक Pnma स्पेसग्रुप में परिष्कृत किया गया था, जिसमें अक्षीय दिशा (157.15(1)°) के साथ भूमध्यरेखीय (168.88(1)°) की तुलना में अधिक ऑक्टाहेड्रल विरूपण होता है। बी जाली पैरामीटर में, जो आगे अक्षीय बी दिशा के साथ अधिक से अधिक आरयू-रिक्ति का सुझाव देता है। 1000 Oe पर DC चुंबकीय संवेदनशीलता डेटा से प्राप्त 18 K पर चुंबकीय संवेदनशीलता बढ़ जाती है, विकार प्रेरित फेरोमैग्नेटिक ऑर्डरिंग का सुझाव देता है, और 4.5 K पर जो 'Pr' और Mn - O - Ru ऑर्डरिंग के कारण कहा जा सकता है। 2 K और 50 K पर इज़ोटेर्मल चुंबकत्व की गैर-संतृप्ति प्रकृति, आगे छोटी दूरी के चुंबकीय क्रम का सुझाव देती है।

दुर्लभ-पृथ्वी और संक्रमण धातु आयनों की प्रतिस्पर्धी चुंबकीय बातचीत की जांच करने के लिए, यह देखा गया कि यौगिक $\text{La}_{0.5-x}\text{Sm}_x\text{Pr}_{0.5}\text{CrO}_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ और 0.5) ने 100 पर नकारात्मक चुंबकत्व दिखाया। ओ.ई. Cr आयन द्वारा उत्पन्न कैन्ड एंटीफेरोमैग्नेटिक मोमेंट द्वारा उत्पन्न नेट मोमेंट के विपरीत रेयर-अर्थ मोमेंट के संरेखण के परिणामस्वरूप $x = 0.4$ और 0.5 के लिए 100 Oe, ZFC पर नेगेटिव मैग्नेटाइजेशन हुआ। $\text{La}_{0.5-x}\text{Sm}_x\text{Pr}_{0.5}\text{CrO}_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ और 0.5) के शुद्ध चरण को orthorhombic Pnma स्पेसग्रुप में परिष्कृत किया गया, जहां x के मान में वृद्धि के साथ ऑक्टाहेड्रल विरूपण में वृद्धि हुई। एक्स के मूल्य में कमी के रूप में अनिसोट्रॉपी की इस वृद्धि के परिणामस्वरूप $x = 0$ और 0.1 , तापमान सीमा 160 K से 25 K में चुंबकीय पुनर्विन्यास दिखाने के लिए, FCC और FCW के 10,000 Oe पर द्विभाजन और पुनर्संयोजन से हुआ है। संरचना में ZFC और ZFW में विनिमय पूर्वाग्रह प्रभाव $\text{La}_{0.1}\text{Sm}_{0.4}\text{Pr}_{0.5}\text{CrO}_3$ की जांच की गई, जिसमें 230 K से नीचे के तापमान पर नकारात्मक विनिमय पूर्वाग्रह प्रभाव का अवलोकन किया गया, जो आगे निम्नलिखित रचनाओं में कैन्ड एंटीफेरोमैग्नेटिक प्रकृति का सुझाव देता है।

आगे का निरीक्षण करने के लिए दुर्लभ-पृथ्वी त्रिज्या में कमी के साथ संरचनात्मक विकृति के प्रभाव की जांच ऑर्थोरोम्बिक $\text{R}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (R: Gd<Nd<Pr) में की गई थी। बढ़े हुए ऑक्टाहेड्रल विरूपण का प्रभाव, मुख्य रूप से जाह्न-टेलर विरूपण के कारण,

संक्रमण धातु और ऑक्सीजन ऑर्बिटल्स के बीच संकरण में वृद्धि के कारण चुंबकीय संक्रमण तापमान में कमी आई। ऑक्टाहेड्रल विरूपण कम हो जाता है क्योंकि दुर्लभ-पृथ्वी का आकार जीडी से एनडी से पीआर तक बढ़ जाता है। $Gd_{0.5}Sr_{0.5}Fe_{0.5}Mn_{0.5}O_3$ 49 K से नीचे के तापमान पर Mn^{3+} स्पिन के कैन्ड एंटीफेरोमैग्नेटिक ऑर्डरिंग को दिखाता है, इसके बाद Gd एंटीफेरोमैग्नेटिक ऑर्डरिंग 3 K से नीचे के तापमान पर होता है। रचनाएँ $Nd_{0.5}Sr_{0.5}Fe_{0.5}Mn_{0.5}O_3$ और $Pr_{0.5}Sr_{0.5}Fe_{0.5}Mn_{0.5}O_3$ ने क्रमशः 47 K और 58 K पर स्पिन ग्लास जैसी प्रकृति दिखाई, क्योंकि $Nd_{0.5}Sr_{0.5}Fe_{0.5}Mn_{0.5}O_3$ ने $Pr_{0.5}Sr_{0.5}Fe_{0.5}Mn_{0.5}O_3$ की तुलना में अधिक ऑक्टाहेड्रल विरूपण दिखाया।

बढ़े हुए क्यूरी-वीस (θ_{CW}) तापमान पर ऑर्बिटल्स के लॉन्ग रेंज ऑर्डरिंग के विघटन पर प्रभाव का अध्ययन करने के लिए और मोनोक्लिनिक $Sr_2YbRu_{1-x}Ta_xO_6$ ($x = 0, 0.25, 0.5, 0.75$ और 1) सिस्टम में फोटोएलेक्ट्रोकेटलिटिक गुणों की जांच की गई। Sr_2YbRuO_6 में Yb - O -Ru की लंबी दूरी का क्रम अधिकतम पाया गया, जो कि Ru के स्थान पर Ta को प्रतिस्थापित करने पर कम हो गया, जैसा कि Sr_2YbRuO_6 (-148 K) में प्राप्त अधिकतम θ_{CW} से स्पष्ट है, जो $x =$ के लिए काफी कम हो गया है। 0.75 (-125 के) से $x = 0.5$ (-118 के), और $x = 0.25$ (-102 के)। टा सांद्रता बढ़ने पर, बैंडगैप 1.78 (1) eV ($x = 0$) से 2.08(1) eV ($x = 0.75$) तक रैखिक रूप से बढ़ता हुआ पाया गया, हालांकि मामले में मामूली कमी हुई विचलन (0.04(1) eV) के साथ देखा गया। Sr_2YbRuO_6 का। Photoelectrocatalytic मापन ने Sr_2YbRuO_6 में प्रकाश और अंधेरे ($12 \mu A/cm^2$) में $17 \mu A/cm^2$ की अधिकतम ऑक्सीजन विकास वर्तमान घनत्व दिखाया। XPS ने दिखाया कि Ru और Ta मुख्य रूप से +5 और +4 ऑक्सीकरण अवस्थाओं में थे।

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