

***Microemulsion based Synthesis of ternary/quaternary
Lanthanum oxide-based Nanomaterials and to study
their Electrochemical, Magnetic, and related properties***

**THESIS SUBMITTED IN THE PARTIAL FULFILMENT OF THE REQUIREMENT
FOR THE AWARD OF THE DEGREE OF**

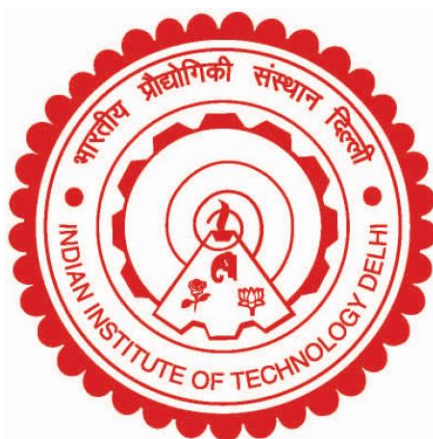
DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

By

KIRANDEEP



DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

NEW DELHI 110016

JULY 2023

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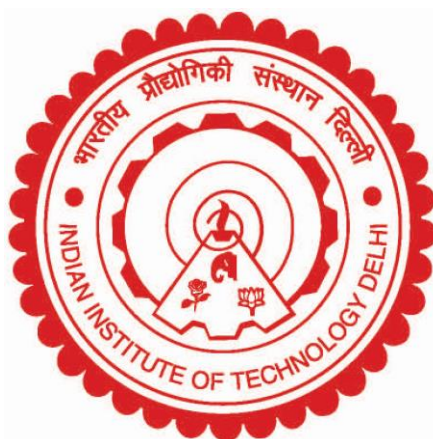
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Dedicated
To
My Dad

CERTIFICATE

This is to certify that the thesis entitled, “**Microemulsion based Synthesis of ternary/quaternary Lanthanum oxide-based Nanomaterials and to study their Electrochemical, Magnetic, and related properties**”, is being submitted by **Ms. Kirandeep**, 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. Kirandeep 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 the award of any degree or diploma.

Date:

Professor Ashok K. Ganguli

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INDIA

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Kirandeep

Abstract

Ruddlesden-Popper structures are a class of complex oxide materials with unique electronic and magnetic properties. These materials are composed of layers of transition metal oxides, such as perovskite oxides and rock salt-based metal oxide stacked on top of each other. The layers are held together by weak van der Waals forces, and the electronic properties of the material are determined by the interactions between the different layers. These materials can exhibit a wide range of electronic phases, including metallic, insulating, and superconducting phases. This makes them very interesting for potential electronic and magnetic applications. Ruddlesden-Popper structures are also known for their excellent electrocatalytic properties, especially for the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). This makes them potentially useful in technologies that store or convert energy, such as fuel cells and water splitting reactors.

The ideal RP structure has tetragonal symmetry, which, as with simple perovskites, deviates to lower symmetries as compositions or stoichiometries change. In addition to exhibiting a K_2NiF_4 -type structure, the essential electrical and magnetic characteristics of A_2BO_4 (with $n = 1$) type RP phases are sensitive to variations in oxygen stoichiometry. These layer-structured phases and characteristics are profoundly affected by the kind and size of the cations present at sites A and B. Properties of these compounds can be further altered by substitution of the lanthanide ion by alkaline earth metals like calcium, strontium leading to $AA'BO_4$ type structure.

The structural morphology and surface structure of Ruddlesden-Popper series oxides prepared by using traditional methods like solid-state and sol-gel synthesis lead to normally micron-sized particles. Since nanoparticles have different magnetic and electrical characteristics than their bulk counterparts, studying them has been a popular topic in recent years.

Our effort aims to reverse-micellar-route synthesise a variety of morphological forms of RP-type nanostructures. We have used reverse micellar route to obtain the nanostructures and have varied the surfactant/ co-surfactants and solvents to obtain varied morphology of the nanoparticles. With the aim of obtaining morphological and structural information relevant to their performance the prepared oxides have been thoroughly characterized by Powder X-ray Diffraction (PXRD) and FESEM-EDX studies. Lanthanum-based oxides La_2NiO_4 , LaNiO_3 , La_2CuO_4 and LaSrMO_4 ($M = \text{Co, Ni and Cu}$) have been studied to see effect of morphology on the magnetic, photoelectrochemical and other related properties.

The PXRD shows that La_2NiO_4 , LaSrMO_4 ($M = \text{Co, Ni and Cu}$) Crystallises in tetragonal system with space group of $I4/mmm$, whereas LaNiO_3 in rhombohedral system and La_2CuO_4 crystallises in orthorhombic crystal system.

Weak ferromagnetic interactions may be seen in the $M(H)$ curves recorded at 5 K in La_2NiO_4 . The samples of La_2NiO_4 have magnetic moments values varies from 2.73-3.08 μ_B respectively. For LaNiO_3 , the magnetic susceptibility data shows that the antiferromagnetic behaviour with the possible of weak ferromagnetic contribution at low temperatures. La_2CuO_4 shows no hysteresis and possesses antiferromagnetic behaviour. For LaSrCoO_4 no magnetic ordering at temperatures below 2 K, however one sample shows a modest increase at 250 K and bifurcation at lower temperatures, which may be due to deviation from exact composition. There is no long-range ordering for LaSrNiO_4 down to the observed temperature, which is 2 K. The spin-glassy behaviour has been observed in the majority of the bulk compound, and our observation are in agreement with reported literature since we found nonlinear variation in the plot of inverse susceptibility vs temperature.

Isothermal magnetization of LaSrCoO_4 at 10 K reveals that one sample has a ferromagnetic character, although none of the other samples exhibit hysteresis; this is also the case with LaSrNiO_4 , which has the same property.

The Mott-Schottky studies show that the La_2NiO_4 , La_2CuO_4 , LaNiO_3 , LaSrMO_4 ($M = \text{Co, Ni and Cu}$) have a p-type behaviour, with holes serving as the primary carriers. The all La_2NiO_4 nanocrystalline shows good photostability of photocurrent density via chronoamperometric measurements.

To investigate organic transformations, La_2CuO_4 and LaSrCuO_4 were utilised as catalysts. Catalytic reaction has been carried using copper-catalyzed one-pot $\text{C}(\text{sp}^2)\text{-H}$ bond scission of aldehydes for oxidative esterification.

Abstract (संक्षेप)

रूडल्सडेन -पॉपर संरचना अद्वितीय इलेक्ट्रॉनिक और चुंबकीय गुणों के साथ जटिल ऑक्साइड सामग्री का एक वर्ग है। ये सामग्रियां संक्रमण धातु ऑक्साइड की परतों से बनी होती हैं, जैसे कि पर्कोव्साइट ऑक्साइड और सेंधा नमक आधारित धातु ऑक्साइड एक दूसरे के ऊपर खड़ी होती हैं। परतें कमजोर वैन डेर वाल्स बलों द्वारा एक साथ रखी जाती हैं, और सामग्री के इलेक्ट्रॉनिक गुणों को विभिन्न परतों के बीच की बातचीत से निर्धारित किया जाता है। ये सामग्रियां धातु, इन्सुलेट और सुपरकंडक्टिंग चरणों सहित इलेक्ट्रॉनिक चरणों की एक विस्तृत श्रृंखला प्रदर्शित कर सकती हैं। यह उन्हें संभावित इलेक्ट्रॉनिक और चुंबकीय अनुप्रयोगों के लिए बहुत दिलचस्प बनाता है। रूडल्सडेन -पॉपर संरचनाएं अपने उत्कृष्ट इलेक्ट्रोकेटलिटिक गुणों के लिए भी जानी जाती हैं, विशेष रूप से ऑक्सीजन इवोल्यूशन रिएक्शन (OER) और ऑक्सीजन रिडक्शन रिएक्शन (ORR) के लिए। यह उन्हें उन तकनीकों में संभावित रूप से उपयोगी बनाता है जो ऊर्जा को संग्रहीत या परिवर्तित करती हैं, जैसे कि ईंधन सेल और जल विभाजन रिएक्टर।

आदर्श आरपी संरचना में टेट्रागोनल समरूपता होती है, जो कि साधारण पर्कोव्साइट्स की तरह, रचनाओं या स्टोइकोमेट्रीज़ में परिवर्तन के साथ कम समरूपता के लिए विचलित होगी। K_2NiF_4 -प्रकार की संरचना को प्रदर्शित करने के अलावा, A_2BO_4 ($n = 1$ के साथ) प्रकार RP चरणों की आवश्यक विद्युत और चुंबकीय विशेषताएं ऑक्सीजन स्टोइकोमेट्री में भिन्नता के प्रति संवेदनशील हैं। ये परत-संरचित चरण और विशेषताएं साइट ए और बी पर मौजूद उद्धरणों के प्रकार और आकार से गहराई से प्रभावित होती हैं। इन यौगिकों के गुणों को कैल्शियम, स्ट्रोंटियम जैसे क्षारीय पृथ्वी धातुओं द्वारा लैथेनाइड आयन के प्रतिस्थापन द्वारा और अधिक बदला जा सकता है। $AA'BO_4$ प्रकार की संरचना के लिए अग्रणी।

सॉलिड-स्टेट और सोल-जेल संश्लेषण जैसे पारंपरिक तरीकों का उपयोग करके तैयार किए गए रूडल्सडेन -पॉपर श्रृंखला ऑक्साइड की संरचनात्मक आकृति विज्ञान और सतह संरचना सामान्य रूप से माइक्रोन आकार के कणों की ओर ले जाते हैं। चूंकि नैनोकणों में उनके थोक समकक्षों की तुलना में अलग-अलग चुंबकीय और विद्युत विशेषताएं हैं, उनका अध्ययन हाल के वर्षों में एक लोकप्रिय विषय रहा है। हमारे प्रयास का उद्देश्य रिवर्स-माइकलर-रूट आरपी-टाइप नैनोस्ट्रक्चर के विभिन्न प्रकार के रूपात्मक रूपों को संश्लेषित करना है। हमने नैनोसंरचना प्राप्त करने के लिए रिवर्स माइकलर मार्ग का उपयोग किया है और नैनोकणों के विभिन्न आकारिकी प्राप्त करने के लिए सर्फैक्टेंट / सह-सर्फैक्टेंट्स और सॉल्वेंट्स में विविधता लाई है। उनके प्रदर्शन के लिए प्रासंगिक रूपात्मक और संरचनात्मक जानकारी प्राप्त करने के उद्देश्य से तैयार ऑक्साइड को पाउडर एक्स-रे विवर्तन (पीएक्सआरडी) और एफईएसईएम-ईडीएक्स अध्ययनों द्वारा पूरी तरह से चित्रित किया गया है। लेण्टेनियम-आधारित ऑक्साइड La_2NiO_4 , LaNiO_3 , La_2CuO_4 और LaSrMO_4 ($\text{M}=\text{Co}$, Ni और Cu) का चुंबकीय, फोटोइलेक्ट्रॉनिक और अन्य संबंधित गुणों पर आकारिकी के प्रभाव को देखने के लिए अध्ययन किया गया है।

PXRD से पता चलता है कि La_2NiO_4 , LaSrMO_4 ($\text{M}=\text{Co}$, Ni और Cu) $I4/mmm$ के अंतरिक्ष समूह के साथ चतुष्कोणीय प्रणाली में क्रिस्टलीकृत होता है, जबकि LaNiO_3 विषमकोणीय प्रणाली में और

La_2CuO_4 ऑर्थोरोम्बिक क्रिस्टल प्रणाली में क्रिस्टलीकृत होता है।

La_2NiO_4 में 5 K पर रिकॉर्ड किए गए M(H) वक्रों में कमजोर फेरोमैग्नेटिक इंटरैक्शन देखे जा सकते हैं। La_2NiO_4 के नमूनों में चुंबकीय क्षण मान क्रमशः $2.73\text{--}3.08 \mu_B$ से भिन्न होते हैं। LaNiO_3 के लिए, चुंबकीय संवेदनशीलता डेटा से पता चलता है कि कम तापमान पर कमजोर फेरोमैग्नेटिक योगदान की संभावना के साथ एंटीफेरोमैग्नेटिक व्यवहार।

La_2CuO_4 कोई हिस्टैरिसीस नहीं दिखाता है और एंटीफेरोमैग्नेटिक व्यवहार रखता है। LaSrCoO_4 के लिए 2 K से नीचे के तापमान पर कोई चुंबकीय क्रम नहीं है, हालांकि एक नमूना 250 K पर मामूली वृद्धि और कम तापमान पर द्विभाजन दिखाता है, जो सटीक संरचना से विचलन के कारण हो सकता है। देखे गए तापमान, जो कि 2 K है, के नीचे LaSrNiO_4 के लिए कोई लंबी दूरी का आदेश नहीं है। बल्क कंपाउंड के बहुमत में स्पिन-ग्लासी व्यवहार देखा गया है, और हमारा अवलोकन रिपोर्ट किए गए साहित्य के अनुरूप है क्योंकि हमने पाया कि यह अरैखिक है। व्युत्क्रम संवेदनशीलता बनाम तापमान की साजिश में भिन्नता। 10 K पर LaSrCoO_4 के इज़ोटेर्मल मैग्नेटाइजेशन से पता चलता है कि एक नमूने में फेरोमैग्नेटिक कैरेक्टर है, हालांकि अन्य नमूनों में से कोई भी हिस्टैरिसीस प्रदर्शित नहीं करता है; LaSrNiO_4 के साथ भी यही स्थिति है, जिसकी समान संपत्ति है।

Mott-Schottky अध्ययनों से पता चलता है कि La_2NiO_4 , La_2CuO_4 , LaNiO_3 , LaSrMO_4 ($M = \text{Co}, \text{Ni}$ और Cu) का p-प्रकार का व्यवहार है, जिसमें छिद्र प्राथमिक वाहक के रूप में कार्य करते हैं। सभी La_2NiO_4 नैनोक्रिस्टलाइन क्रोनोएम्परोमेट्रिक माप के माध्यम से फोटोकंट घनत्व की अच्छी फोटोस्टेबिलिटी दिखाते हैं।

कार्बनिक परिवर्तनों की जांच करने के लिए, La_2CuO_4 और LaSrCuO_4 उत्प्रेरक के रूप में उपयोग किए गए थे। ऑक्सीडेटिव एस्टरीफिकेशन के लिए एल्लिहाइड के कॉपर-उत्प्रेरित एक-पॉट $\text{C}(\text{sp}^2)\text{-H}$ बॉन्ड विखंडन का उपयोग करके उत्प्रेरक प्रतिक्रिया की गई है।

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Abbreviations and Symbols

Å	Angstroms
°C	Centigrade
µm	Micrometer
nm	Nanometer
min	Minutes
sec	Seconds
h	Hours
mL	milliliter
eV	Electron-Volt
K	Kelvin
°	Degree (angle)
λ	Wavelength
C	Curie constant
θ	Weiss temperature
PXRD	Powder X-ray diffraction
TEM	Transmission Electron Microscopy
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-ray Spectroscopy
UV	Ultraviolet -visible
DRS	Diffuse reflectance spectroscopy
PEC	Photoelectrochemical
OER	Oxygen Evolution Reaction

ORR	Oxygen Reduction Reaction
LSV	Linear sweep voltammetry
M-S	Mott-Schottky
EIS	Electrochemical Impedance spectroscopy
RSE	Resistance Switching Effect
CW	Curie-Weiss
RP	Ruddlesden-Popper
PPMS	Physical Property Measurement System
AFM	Antiferromagnetism
SOFC	Solid Oxide Fuel Cells
SOEC	Solid Oxide Electrolysis Cells
NPs	Nanoparticles
NBs	Nanobamboo
FE	Faradaic efficiency
NRR	Nitrogen Reduction Reaction
MIT	Metal-Insulator transition
HTS	High Temperature Superconductors
CN	Coordination Number