Studies on Dielectric, Electrical, Magnetic and Hetero-photocatalytic Properties of Bismuth Layered Aurivillius Oxides

Thesis submitted in partial fulfilment

For the Award of Degree

DOCTOR OF PHILOSOPHY

By

SHRUTI SINGH

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY

(BANARAS HINDU UNIVERSITY)

VARANASI-221005

Roll No.: 17051011 **2022**

CERTIFICATE

It is certified that the work contained in the thesis titled "**Studies on dielectric, electrical, magnetic and hetero-photocatalytic properties of Bismuth Layered Aurivillius Oxides**" by "**Shruti Singh**"has been carried out under my supervision and thatthis work has not been submitted elsewhere for a degree.

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23/6/2022

Prof. K. D. Mandal (Supervisor)
Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University) Varanasi

Dr. Asha Gupta (Co-Supervisor)
Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University) Varanasi

DECLARATION BY THE CANDIDATE

I, Shruti Singh, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of Prof. K. D. Mandal from 2017 to 2022, at the Department of Chemistry, Indian Institute of Technology (Banaras Hindu University), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma.

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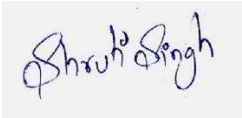

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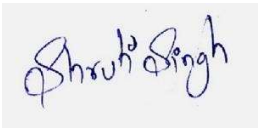

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It is certified that the above statement made by the student is correct to the best of my knowledge.

23/6/2022

Prof. K. D. Mandal
(Supervisor)
Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University)
Varanasi

Dr. Asha Gupta
(Co-supervisor)
Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University)
Varanasi

Prof. Y.C. Sharma
(Head)
Department of Chemistry
Indian Institute of Technology
(Banaras Hindu University)
Varanasi

विभागाध्यक्ष/HEAD
रसायन विज्ञान विभाग
Department of Chemistry
भारतीय प्रौद्योगिकी संस्थान (का.हि.वि.वि.)
Indian Institute of Technology (B.H.U.)
वाराणसी-२२१००५/Varanasi-221005

Dedicated To My Parents

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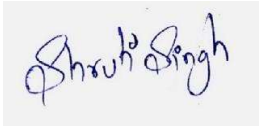
With regards to numerous questions about my future academic endeavours, I shall answer in the words of *Sir Winston Churchill*, "Now, this is not the end. It is not even the beginning of the end. But it is, perhaps, the end of the beginning."



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E	Permittivity or dielectric constant
ε^*	Complex Quantity of dielectric constant
ε'	real components of dielectric constant
ε''	Imaginary component of dielectric constant
i	Imaginary number
ε_0	Permittivity of free space
ε_r	relative dielectric constant
C	Capacitance
F	Farad
tan δ	tangent loss
σ	conductivity
f	frequency
λ	Wavelength
θ	Angle theta
°C	Degree centigrade
K	Kelvin
k_B	Boltzmann constant
T_B	Blocking temperature
χ	Magnetic susceptibility
C	Curie constant
M	Magnetization
H	Magnetic field
Oe	Oersted
ρ	Density

B	Induced magnetic field
E	Electric field
P	Net polarization
$P_{electronic}$	Electronic polarization
P_{ionic}	Ionic polarization
$P_{molecular}$	Molecular polarization
$P_{interfacial}$	Interfacial polarization
Hz	hertz
ω	angular frequency
t	tolerance factor
Å	angstrom
R	Resistance
C	Capacitance
R_b	Resistance of bulk
C_b	Capacitance of bulk
R_{gb}	Resistance of grain boundary
C_{gb}	Capacitance of grain boundary
eV	electron Volt

A surfeit of research work is carrying out on perovskites. The perovskite oxides with the general formula ABO_3 have been widely investigated for their excellent ferroelectric, dielectric, optoelectronic and piezoelectric properties. The materials having high dielectric constant and low dielectric loss has importance in material science due to its applications in electrical and electronic devices such as multilayer capacitor (MLCC), microwave devices, aircraft, dynamic random excess memory (DRAMs) and automobiles, gas sensors, capacitors, humidity sensors as well as memory devices. Ceramic capacitor materials sought more attention due to the increasing demand for high dielectric constant and good thermal stability. Thurnauer firstly reported in 1941 the high dielectric constant ($\varepsilon_r \sim 10^3$) of $BaTiO_3$ ceramic material but has limitation on temperature dependence of ε_r in industrial applications. Further, temperature independent dielectric constant materials have played a significant role in the ceramic capacitor industry. Its easy synthesis, stability in harsh conditions and easily modifiable crystal structure with a series of perovskite family keeps it in demand.

A fundamental understanding of structure-property relationships is imperative in the rational design of new materials for tailored applications. The simple ABO_3 pervoskites have been modified to complex perovskite oxide represented by the general formula $(A'A'')(B'B'')O_3$ through doping. The indefinite possibility of configuration and structure of complex perovskite oxides is possible through vast opportunities of doping with homo or heteroatoms, which further open up the chance for a variety of technological applications.

Double perovskite and layered Perovskties are examples of complex perovskite oxide. This research work is focused on layered perovskites. The characteristics feature in the structure of Layered perovskites is the presence of infinite 2D slabs of the simplest ABO_3

pervoskite type structure separated by specific motif and layers having the general formula: $A_{(n-1)}B_{(n)}O_{(3n+1)}$.

Bismuth-layered perovskite ferroelectric materials belonging to aurivillius oxide semiconductors have lately evoked high curiosity because of their complex layered and unique electronic structure. The Aurivillius phases are composed of alternating layers of $(Bi_2O_2)^{2+}$ units with perovskite-like $(A_{n-1}B_nO_{3n+1})^{2-}$ blocks in between them, where A denotes mono, di- or tri-valent ions (K^+, Na^+, Ba^{2+}, Pb^{2+}, Sr^{2+}, Ca^{2+}, Bi^{3+}) and rare earth elements, B represents tetra, penta or hexa valent ions (Ti^{4+}, Ta^{5+}, Nb^{5+}, W^{6+}, Mo^{6+}, etc.) and m=1,2, 3, 4, 5 indicates to the number of BO_6 octahedral amid neighboring $(Bi_2O_2)^{2+}$ layers. The compound thus has polarization in two possible directions in which a small vector along the c-axis switches from the principal direction independently on the a-axis, generating anisotropy and resulting in a high dielectric constant.

This family of materials has fascinated enough owing to its photocatalytic activity in the removal of organic and inorganic pollutants from water and also eradication of bacteria and cancer cells, photoreduction of N_2 or CO_2 as well as acting as photovoltaic material for harvestation of solar energy. The layered arrangement not only allows better polarization of charge species but also provides a better possibility for the diffusion and separation of the photoexcited hole–electron pairs compared to other non-layered photocatalysts. The separation is possible as the reduction and oxidation lattice sites reside in an isolated manner on the edges and faces of the unit ultrathin sheets. The holes generated in the layered photocatalysts are trapped by water molecules present in the interlayer while diffusing to the sheet surface. This accelerated trapping method of holes causes electrons to diffuse easily and efficiently within the unit sheets before getting to the edges of the sheets. Additionally, bismuth (Bi) is a p-block element with a filled d orbital, and the s-orbital of the valence shell (Bi 6s) can hybridize with the p-orbital of

oxygen (O 2p), generating hybridized valence band (VB), which facilitate the mobility of holes in the VB generated by the photons and improves the photocatalytic efficiency of the Aurivillius oxide. Also, the introduction of Bi^{3+} lone pairs on the A site of the aurivillius structure could assist the distortion of perovskite that is responsible for ferroelectricity in the materials

Few physical properties of synthesized Bismuth Layered Aurivillius oxides such as dielectric, impedance, magnetic and hetero-photocatalytic were investigated at selected temperatures and frequencies. A brief description of the research work presented in the thesis, divided into five chapters, is given as follows:

Chapter I gives a brief description of Perovskites, its types and applications. Discussion on Perovskite Structure and Derivatives including cubic pervoskites and complex perovskite such as double pervoskites and layered Pervoskites(Ruddleson-Popper, Aurivillius and Dion-Jacobson phases), A general introduction of ceramic, composite materials, capacitors. An overview of dielectric material and type of polarization present in them along with the dielectric loss and impedance, with discussion on ferroelectric and magnetic properties interaction. Some light has also been shed on heterogeneous photocatalysis, its mechanism and the photocatalysts used in dye degradation. Details of bismuth layered aurivillius oxides and composite materials considered in the current study and the purpose of the thesis is mentioned in this chapter.

Chapter II described the experimental procedure used for the preparation and characterization of the perovskite oxides and their composites. The modified solid stae route and the chemical route were used for the preparation of materials. X-ray diffraction(XRD) and transmission electron microscope (TEM) have been studied for the determination of crystalline size and particle size, respectively. Scanning electron

microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) analysis have been used for microstructural studies and elemental analysis of materials, respectively. The oxidation state of the ceramics was to be examined by X-ray photoelectron spectroscopy, study of surface roughness and the maximum peak height of the materials have been determined by atomic force microscopy (AFM). The mean particle size and distribution, as well as the zeta potential of the material was determined by a dynamic light scattering technique using a Zetasizer Nano-ZS. The Brunauer–Emmett–Teller (BET) surface area was investigated by nitrogen adsorption-desorption isotherm. The magnetic properties of the materials were measured by a superconducting quantum interference device with the temperature and applied field. Dielectric properties of materials were measured on a LCR meter with the variation of temperature and frequency.

Chapter III described the synthesis, characterization $Bi_4Ti_3O_{12}$-$BaTiO_3$ (BTO-BT) nanocomposite, a Aurivillius oxide, which is synthesised by modified solid-state route, and characterised by various techniques like FTIR, XRD, TEM, UV-DRS, Zetasizer Nano-ZS, AFM, BET, SEM-EDX and XPS for the phase identification, microstructural analysis, bandgap determination, elemental analysis and oxidation state of the material. Formation of BTO-BT nanocomposite (orthorhombic and cubic) confirmed by Le-Bail fitting analysis with the help of XRD data. The electrical measurement of the material showed the existence of semiconducting grains and insulating grain boundaries responsible for Maxwell relaxation and a high dielectric constant of value 4.75×10^3 at 368 K was observed. The Magnetic behavior studied by SQUID indicates it to be magnetically frustrated materials. The material was found to be applicable in photocatalytic degradation of Rhodamine B under UV light through major reactive species, i.e. $OH^{\cdot}$ radicals and $O2^{\cdot -}$ generated during the photocatalytic reaction proved to be following the first-order kinetics.

Chapter IV contains $Bi_4BaTi_4O_{15}$ (BBTO), an Aurivillius oxide, which is mixed metal bismuth–layered based oxide fabricated by chemical route, has shown highly efficient photocatalytic activity in degradation of organic dye besides possessing high dielectric constant. The obtained material was characterised by various techniques like Fourier Transform Infrared (FTIR), transmission electron microscope, Scanning Electron Microscopy-Energy Dispersive X-rays Spectroscopy (SEM-EDX) X-ray powder diffraction (XRD), Zetasizer Nano-ZS, Ultraviolet- differential reflectance spectroscopy (UV-DRS), Brunauer–Emmett–Teller, Atomic Force Microscopy (AFM) and X-ray photoelectron spectra for the phase identification, microstructural analysis, bandgap determination, elemental analysis and oxidation state of the material. XRD data confirm the presence of single-phase BBTO ceramic, corroborated by Le-Bail fitting analysis. A high dielectric constant value of 3.08×10^3 was obtained for the BBTO ceramic at 368 K. The material is stable in suspension form in solution and is a highly efficient photocatalyst. BBTO degraded 80% of RhB dye within 1 h of time period under UV light via major reactive species $OH^{\cdot}$ radicals and $O2^{\cdot -}$, generated during the photocatalytic reaction, which is proved to be following the first-order kinetics.

Chapter V contains $Bi_4SrTi_4O_{15}$ (BSTO), which is mixed metal bismuth–layered based Aurivillius oxide synthesized by the chemical route. Besides possessing high dielectric constant, it also shows much efficient photocatalytic activity in the degradation of organic dye. The obtained material was characterized by various techniques like Fourier Transform Infrared (FTIR), transmission electron microscope (TEM), Scanning Electron Microscopy-Energy Dispersive X-rays Spectroscopy (SEM-EDX) X-ray powder diffraction (XRD), Zetasizer Nano-ZS, Ultraviolet- differential reflectance spectroscopy (UV-DRS), Brunauer–Emmett–Teller, Atomic Force Microscopy (AFM) and X-ray photoelectron spectra for the phase identification, microstructural analysis,

bandgap determination, elemental analysis and oxidation state of the material. XRD data confirm the presence of single-phase BSTO ceramic. A high dielectric constant value of 2.76×10^3 was obtained for the BSTO ceramic at 368 K. The material is stable in suspension form in solution and is a highly efficient photocatalyst. BSTO degraded 84% of RhB dye within 1 h of the time period under UV light via major reactive species $OH^{\cdot}$ radicals and $O2^{\cdot-}$, generated during the photocatalytic reaction, which is also proved to be following the first-order kinetics.