

***Luminescence Study of Some Rare Earth Doped
CaMoO₄ Phosphors for Lighting Application***



*Thesis submitted in partial fulfilment for the
Award of Degree*

Doctor of Philosophy

in

Physics

by

Prashant Dixit

DEPARTMENT OF PHYSICS

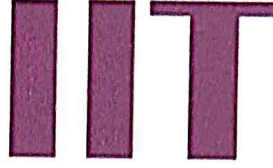
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI – 221005

Roll No. 17171019

2022



भारतीय
प्रौद्योगिकी
संस्थान
काशी हिन्दू विश्वविद्यालय



INDIAN
INSTITUTE OF
TECHNOLOGY
BANARAS HINDU UNIVERSITY

CERTIFICATE

It is certified that the work contained in the thesis titled “Luminescence Study of Some Rare Earth Doped CaMoO_4 Phosphors for Lighting Application” by Prashant Dixit has been carried out under my supervision and that this work has not been submitted else where for a degree.

It is further certified that the student has fulfilled all the requirements of the comprehensive examination, candidacy, and SOTA for the award of Ph.D. Degree.

Signature:

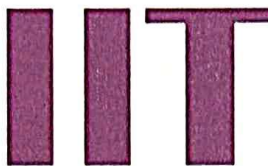

15/12/22

Supervisor

*Dr. Praveen Chandra Pandey
(Associate Professor)
Department of Physics
Indian Institute of Technology
(Banaras Hindu University)
Varanasi-221005 (U.P), India*



भारतीय
प्रौद्योगिकी
संस्थान
काशी हिन्दू विश्वविद्यालय



INDIAN
INSTITUTE OF
TECHNOLOGY
BANARAS HINDU UNIVERSITY

DECLARATION BY THE CANDIDATE

I, “Prashant Dixit”, certify that the work embodied in this thesis is my own bona fide work and carried out by me under the supervision of “Dr. Praveen Chandra Pandey” from “July 2017” to “December 2022”, at the “DEPARTMENT OF PHYSICS”, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, thesis, etc., or available on websites and have not included them in this thesis and have not cited as my work.

Date: 15 | 12 | 22

Place: IIT (BHU), Varanasi

Signature of the Student

(Prashant Dixit)

CERTIFICATE BY THE SUPERVISOR

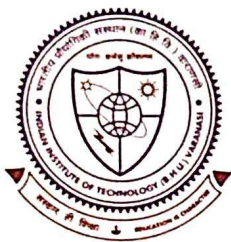
It is certified that the above statement made by the student is correct to the best of my knowledge.

15 | 12 | 22
Supervisor

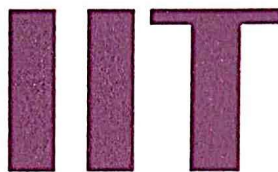
*Dr. Praveen Chandra Pandey
(Associate Professor)*

15 | 12 | 22
Signature of Head of Department

Prof. Sandip Chatterjee



भारतीय
प्रौद्योगिकी
संस्थान
काशी हिन्दू विश्वविद्यालय



INDIAN
INSTITUTE OF
TECHNOLOGY
BANARAS HINDU UNIVERSITY

COPYRIGHT TRANSFER CERTIFICATE

*Title of the Thesis: Luminescence Study of Some Rare Earth Doped CaMoO₄ Phosphors for
Lighting Application*

Name of the Student: Prashant Dixit

COPYRIGHT TRANSFER

The undersigned hereby assigns to the Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the "DOCTOR OF PHILOSOPHY".

Date: 15/12/22

Place: IIT (BHU), Varanasi

Signature of the Student

(Prashant Dixit)

Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for the author's personal use provided that the source and the Institute's copyright notice are indicated.

Acknowledgments

Foremost, I express my deep sense of gratitude to my research supervisor Dr. Praveen Chandra Pandey for his excellent guidance, motivation, and constant encouragement during my entire research work. The completion of this research work is indeed an outcome of his support, valuable ideas, and suggestions.

I express my gratitude to the Head of the Department for providing me required facilities. I am extremely thankful to my RPEC members Prof. Sandip Chatterjee and Dr. B. N. Pal for the invaluable inspiration, kind support, and numerous insightful suggestions during the entire course of this research. I am also grateful to Prof. S. B. Rai (BHU) and Dr. S. Satapathy (RRCAT) for their valuable support in the form of insightful discussions and sample characterizations.

I use this opportunity to express my gratefulness to all the faculty members of the Department of Physics for their kind encouragement and motivation during my research period. I am also thankful to the entire non-teaching staff of the Department of Physics, and CIFC IIT (BHU) Varanasi for their assistance and for providing measurement facilities.

I wish to thank my lab companions and friends Vaibhav, Prashant Pandey, Raj, Hemant, and Umang, and my juniors Satyam and Sanket for providing me with a conducive environment to carry out my research work.

I would also like to express my sincere appreciation to my colleagues and dearest friends Nikesh, Rohit, Shweta, Akanksha, Neha, Digvijay, Vivek, Balbeer, and all research scholars of the department for their lively friendship and continuous support at all stages of my research.

I feel short of words to express my appreciation, gratitude, and indebtedness to my family members, my father Shri R. S. Dixit, and mother Smt. Shailaja Dixit, my bhaiya-bhabhi Shashank-Sneha, Sisters Varsha, Shobhana, and Rohini, my fiancée Rashmi, and my whole family for their unbounded love, blessings, encouragement, and support during my entire academics.

Many others that have been involved also deserve recognition. It is, however, not possible to list them all here. Their support in this effort is, however, greatly appreciated.

Sincerely
(Prashant Dixit)

Dedicated
To
My Beloved
Family

Table of contents

Certificate	ii
Declaration by the candidate	iii
Copyright transfer certificate	iv
Acknowledgments	v
.....	xii
List of figures	xiii
.....	xvi
List of tables	xvii
.....	18
Preface	19
Chapter 1 Introduction and Inspirations of thesis	23
1.1 Historical background of luminescence	25
1.2 Types of Luminescence	25
1.2.1 Mechanoluminescence (ML)	26
1.2.2 Chemiluminescence (CL)	27
1.2.3 Electroluminescence (EL).....	27
1.2.4 Radioluminescence (RL).....	27
1.2.5 Thermoluminescence (TL).....	28
1.2.6 Photoluminescence (PL)	28
1.2.6.1 Fluorescence	29
1.2.6.2 Phosphorescence	30
1.3 PL process mechanism.....	30
1.3.1 Excitation process	31
1.3.2 Emission process.....	32
1.3.2.1 Non-radiative emission	32
1.3.2.2 Radiative emission	33
1.3.3 PL decay mechanism	34
1.4 Phosphor materials.....	35
1.4.1 Requirements of phosphor materials	36
1.4.2 Comparative study of CaMoO ₄ with other alkaline earth metal molybdates.....	37
1.4.3 CaMoO ₄ phosphor as a host.....	38
1.5 Rare-earth ions	39
1.5.1 Ln ³⁺ configuration transitions	42
1.5.1.1 5d — 4f transitions.....	42
1.5.1.2 Intra 4f — 4f transitions.....	43
1.5.1.3 Charge transfer transitions	44
1.6 Rare-earth (Re ³⁺) ions used in research work	44
1.6.1 Europium (Eu ³⁺) ion	45
1.6.2 Dysprosium (Dy ³⁺) ion	46
1.6.3 Samarium (Sm ³⁺) ion	47
1.6.4 Terbium (Tb ³⁺) ion.....	47
1.7 Application of rare-earth doped phosphor materials	48
1.8 Chromaticity parameters.....	52
1.8.1 Commission Internationale de l'Elclairage (CIE) coordinates.....	52
1.8.2 Color rendering index (CRI).....	52
1.8.3 Correlated color temperature (CCT).....	53
1.8.4 Color purity (CP)	54

1.8.5 Luminous efficiency	54
1.9 Inspirations for thesis	55
Chapter 2 Synthesis process and Characterization tools	57
2.1 Outline.....	59
2.2 Synthesis process of undoped and doped CaMoO ₄ samples	59
2.3 Characterization tools	60
2.3.1 Structural study	60
2.3.1.1 X-ray diffraction (XRD) spectroscopy	60
2.3.1.2 Fourier transform infrared (FTIR) spectroscopy	62
2.3.1.3 X-ray photoelectron spectroscopy (XPS)	63
2.3.2 Morphological study: Scanning electron microscope (SEM) and Transmitted electron microscope (TEM)	65
2.3.3 Elemental study: Energy dispersive x-ray (EDX) spectroscopy.....	66
2.3.4 Absorbance study: UV-vis spectroscopy	66
2.3.4.1 Working principle	68
2.3.5 Photoluminescence (PL) spectroscopy	68
Chapter 3 Enhanced photoluminescence in CaMoO₄:Eu³⁺ red phosphor by Mn²⁺ co-doping.....	71
3.1 Introduction.....	73
3.2 Results and discussion	74
3.2.1 XRD analysis	74
3.2.2 TEM and EDX analysis	78
3.2.3 XPS analysis	80
3.2.4 FTIR analysis	83
3.2.5. Absorption analysis.....	84
3.2.6 Photoluminescence analysis.....	86
3.2.6.1 Excitation (PLE) spectra	86
3.2.6.2 Emission (PL) spectra	87
3.2.7 Chromaticity parameters.....	89
3.3 Conclusions.....	91
Chapter 4 Thermally stable bismuth-activated Tb³⁺ doped CaMoO₄ green phosphor	93
4.1 Introduction.....	95
4.2 Results and discussion	97
4.2.1 XRD analysis	97
4.2.2 SEM and EDX analysis	100
4.2.3 XPS analysis	102
4.2.4 FTIR analysis	104
4.2.5 Absorption analysis.....	105
4.2.6 Photoluminescence analysis.....	108
4.2.6.1 Excitation (PLE) spectra	108
4.2.6.2 Emission (PL) spectra	109
4.2.6.3 Energy transfer mechanism and PL decay analysis	113
4.2.7 Chromaticity parameters.....	115
4.2.8 Temperature-dependent PL (TDPL) analysis	116
4.3 Conclusions.....	119
Chapter 5 Realization of neutral white light emission in CaMoO₄:4% Dy³⁺ phosphor via Sm³⁺ co-doping	121
5.1 Introduction.....	123
5.2 Results and discussion	126

5.2.1 XRD analysis	126
5.2.2 SEM images analysis	129
5.2.3 XPS analysis	130
5.2.4 FTIR analysis	132
5.2.5 Absorption analysis.....	133
5.2.6 Photoluminescence analysis.....	135
5.2.6.1 Excitation (PLE) spectra	135
5.2.6.2 Emission (PL) spectra	137
5.2.6.3 PL decay analysis.....	142
5.2.7 Chromaticity parameters	144
5.3 Conclusions.....	146
Chapter 6 Improvement in white light emission of Dy³⁺ doped CaMoO₄ via Zn²⁺ co-doping.....	149
6.1 Introduction.....	151
6.2 Results and discussion	154
6.2.1 XRD analysis	154
6.2.2 SEM Images analysis.....	158
6.2.3 EDX analysis	158
6.2.4 TEM images analysis.....	160
6.2.5 XPS analysis	161
6.2.6 FTIR analysis	164
6.2.7 Absorption analysis.....	165
6.2.8 Photoluminescence analysis.....	167
6.2.8.1 Excitation (PLE) spectra	167
6.2.8.2 Emission (PL) spectra	169
6.2.8.3 PL decay analysis.....	172
6.2.9 Chromaticity parameters	174
6.2.10 Temperature-dependent PL (TDPL) analysis	176
6.3 Conclusions.....	179
Chapter 7 Conclusion	181
7.1 Summary	183
7.2 Future Scope	187
Bibliography	189
List of Publications	207

List of figures

Fig. 1.1 Types of luminescence depend on modes of excitation and time duration.	26
Fig. 1.2 (a) Mechanoluminescence process, (b) Chemiluminescence in a chemical solution, (c) Electroluminescence process, (d) Tritium-based watch dial (radioluminescence), (e) Thermoluminescence process, (f) Photoluminescence phenomenon.	29
Fig. 1.3 Jablonski diagram for explaining the Fluorescence and Phosphorescence phenomenon.	31
Fig. 1.4 Crystal structure of CaMoO_4 phosphor.	38
Fig. 1.5 The PLE and PL spectrum of CaMoO_4 phosphor.	39
Fig. 1.6 Energy levels of different Ln^{3+} ions.	42
Fig. 1.7 Jablonski diagram, excitation and emission transitions of Eu^{3+} , Dy^{3+} , Sm^{3+} and Tb^{3+} ion.	48
Fig. 1.8 (a) White light emitting diode chip, (b) Phosphor use for fingerprint detection technique, (c) As a photocatalysis, (d) Bio-imaging application and (e) Optical thermometry application.	49
Fig. 1.9 Advantages of wLEDs over other traditional light sources.	50
Fig. 1.10 (a) Fabrication of commercial wLED and (b) Luminescence spectrum of commercial wLED.	51
Fig. 2.1 Schematic diagram for synthesis process of CaMoO_4 phosphor.	60
Fig. 2.2 (a) XRD instrument setup, and (b) Working principle of Powder-XRD.	61
Fig. 2.3 (a) FTIR instrument setup, and (b) Working principle of FTIR.	62
Fig. 2.4 (a) XPS instrument setup and (b) Mechanism of emitting photoelectrons.	64
Fig. 2.5 Instrument setup of (a) Scanning Electron Microscope (SEM) and (b) Transmitted Electron Microscope (TEM).	65
Fig. 2.6 UV-Visible spectroscopy setup with the internal part.	67
Fig. 2.7 Whole setup of Horiba PL spectroscopy.	69
Fig. 3.1 Rietveld refined XRD patterns of (a) CMO, (b) E4, and (c) EM0.3 samples.	76
Fig. 3.2 (a) Variation in the volume of a unit cell and lattice parameters (inset) with Mn^{2+} co-doping, and (b) Variation in crystallite size and lattice strain (inset) with Mn^{2+} co-doping.	77
Fig. 3.3 TEM images of (a) CMO, (b) EM0.3, and (c) SAED pattern of EM0.3 sample.	78
Fig. 3.4 EDX spectra of (a) CMO, (b) E4, and (c) EM0.3 samples.	79
Fig. 3.5 XPS survey scan of CMO and EM0.3 samples.	81
Fig. 3.6 High-resolution XPS scan of Ca2p, Mo3d, and O1s for CMO and EM0.3 samples.	82
Fig. 3.7 High resolution of XPS scan of Eu3d and Mn2p for EM0.3 sample.	82
Fig. 3.8 FTIR spectra of CMO, E4, EM0.1, EM0.3 and EM0.5 samples.	84

Fig. 3.9 (a) Absorption spectra of Eu^{3+} doped CaMoO_4 . Inset: Tauc plot for obtaining bandgap and (b) Absorption spectra of Mn^{2+} co-doped Eu^{3+} doped CaMoO_4 .	85
Fig. 3.10 PL excitation spectra of (a) Eu^{3+} doped CaMoO_4 and (b) Mn^{2+} co-doped Eu^{3+} doped CaMoO_4 phosphors.	87
Fig. 3.11 PL emission spectra of (a) Eu^{3+} doped CaMoO_4 and (b) Mn^{2+} co-doped Eu^{3+} doped CaMoO_4 phosphors.	88
Fig. 3.12 Chromaticity diagram for E4 and EM0.3 phosphors.	91
Fig. 4.2 Rietveld refined XRD patterns of (a) T0, (b) T5, (c) B4 samples, and (d) crystal structure of the B4 sample.	99
Fig. 4.3 SEM images of (a) T0, (b) T5, and (c) B4 samples.	101
Fig. 4.4 EDX spectra for (a) T0, (b) T5, and (c) B4 samples.	101
Fig. 4.5 (a) High-resolution XPS survey, XPS spectra of (b) Ca2p, (c) Mo3d, (d) O1s, (e) Tb3d and (f) Bi4f for B4 and T5 samples.	103
Fig. 4.6 FTIR spectra for T0, T5, and B4 samples.	105
Fig. 4.7 (a) Absorption spectra for T0, T5, B2, B3, B4, and B5 samples. Inset: Tauc plot for calculation of band gap and (b) Plot of Urbach energy for T0 sample. Inset: Variation in Urbach energy with Bi^{3+} co-doping.	107
Fig. 4.8 (a) PL excitation spectra for all Tb^{3+} doped phosphors and (b) PL excitation spectra for all Bi^{3+} co-doped phosphors.	109
Fig. 4.9 (a) PL emission spectra for all Tb^{3+} doped phosphors and (b) PL emission spectra for all Bi^{3+} co-doped phosphors.	111
Fig. 4.10 $\log(I/x)$ versus $\log(x)$ plot for multi-polar interaction.	112
Fig. 4.11 (a) PL excitation, (b) Energy transfer mechanism, and (c) PL emission for T5 and B4 under Bi^{3+} excitations.	113
Fig. 4.12 (a) PL decays curves and (b) Chromaticity diagram for T5 and B4 phosphors.	115
Fig. 4.13 (a) TDPL spectra for B4, (b) CIE coordinates variation with temperature, (c) Bar diagram depicting intensity variation, (d) Normalized integrated intensity versus temperature, (e) Configurationally diagram for explaining thermal quenching and (f) $\ln [(I_0/I_T)-1]$ versus $1/KT$ graph for required activation energy calculation.	119
Fig. 5.1 Rietveld refined the XRD pattern of (a) CMO, (b) D4, (c) S3, and (d) crystal structure of the S3 sample.	127
Fig. 5.2 (a) Variation in unit cell volume and lattice parameters (inset) with Sm^{3+} co-doping and (b) Variation in crystallite size and lattice strain (inset) with Sm^{3+} co-doping.	129
Fig. 5.3 SEM images of (a) CMO, (b) D4, and (c) S3 samples.	130
Fig. 5.4 (a) High-resolution XPS survey, XPS spectra of (b) Ca2p, (c) Mo3d, (d) O1s, (e) Dy3d, and (f) Sm3d for S3 sample.	132
Fig. 5.5 (a) FTIR spectra of CMO, D4, and S3 samples, (b) Absorption spectra of Sm^{3+} co-doped phosphors, Inset: Tauc plot for calculating bandgap (c) Variation in Urbach energy with Sm^{3+} co-doping. Inset: calculating Urbach energy for CMO sample.	133

Fig. 5.6 PL excitation spectra for (a) Dy ³⁺ doped phosphors, (b) Sm ³⁺ doped phosphors, and (c) Sm ³⁺ co-doped CaMoO ₄ :4%Dy ³⁺ phosphors.....	137
Fig. 5.7 PL emission spectra for (a) Dy ³⁺ doped phosphors, (b) Sm ³⁺ doped phosphors, (c) Sm ³⁺ co-doped CaMoO ₄ :4%Dy ³⁺ phosphors, and (d) PL emission in the range from 600 nm to 680 nm for Sm ³⁺ co-doped CaMoO ₄ :4%Dy ³⁺ phosphors.....	139
Fig. 5.8 log (I/x) versus log(x) plot for calculating multipolar interaction.....	141
Fig. 5.9 (a) Energy transfer mechanism of [MoO ₄] ²⁻ , Dy ³⁺ and Sm ³⁺ , (b) PL decay curves of D4 and S3 phosphors.....	144
Fig. 5.10 Chromaticity diagram of Sm ³⁺ co-doped phosphors.....	146
Fig. 6.1 Rietveld refined XRD patterns for (a) CMO, (b) Dy4, (c) Z0.25 samples, and (d) crystal structure of the Z0.25 sample.....	156
Fig. 6.2 (a) Variation of unit cell volume and lattice parameters (Inset) with Zn ²⁺ co-doping and (b) Variation of Crystallite size and lattice strain (Inset) with Zn ²⁺ co-doping.....	157
Fig. 6.3 SEM images of (a) CMO and (b) Dy4 and (c) Z0.25 samples.....	158
Fig. 6.4 EDX spectra for (a) CMO, (b) Dy4 and (c) Z0.25 samples.....	159
Fig. 6.5 TEM images of (a) Dy4, (b) Z0.25 samples, (c) SAED pattern for Z0.25 sample and (d) High-resolution TEM of Z0.25 sample.....	161
Fig. 6.6 XPS scan of (a) Ca2p, (b) Mo3d, and (c) O1s for CMO, Dy4 and Z0.25 samples, XPS scan of (d) Dy3d, (e) Zn2p for Dy4 and Z0.25, and (f) XPS survey for CMO, Dy4, and Z0.25 samples.....	163
Fig. 6.7 (a) FTIR spectra for CMO, Dy4, and Z0.25 samples, (b) UV-Vis absorption spectra, and (c) Tauc plot for CMO, Dy4, Z0.1, Z0.25, Z0.5, and Z1 samples.....	165
Fig. 6.8 Absorbance at 314 nm with time for Z0.25 phosphor.....	167
Fig. 6.9 PL excitation spectra for (a) CMO, (b) Dy4, (c) Z0.25, (d) (x% = 0, 2, 3, 4, 5) Dy ³⁺ doped CaMoO ₄ , and (e) (y% = 0, 0.1, 0.25, 0.5, 1) Zn ²⁺ co-doped CaMoO ₄ :4%Dy ³⁺ phosphors.....	169
Fig. 6.10 PL emission spectra for (a) CMO, (b) (x% = 0, 2, 3, 4, 5) Dy ³⁺ doped CaMoO ₄ phosphors, (c) Energy level diagram of [MoO ₄] ²⁻ and Dy ³⁺ , (d) Emission spectra for (y% = 0, 0.1, 0.25, 0.5, 1) Zn ²⁺ co-doped CaMoO ₄ :4%Dy ³⁺ phosphors. Inset represents intensity variation of 574 nm peak.....	172
Fig. 6.11(a) PL decay curve and exponential fitted line of Dy4, Z0.1, Z0.25, Z0.5, and Z1 phosphors, (b) Chromaticity diagram for Dy4 and Z0.25. Inset shows the image of Z0.25 phosphor under 352 nm UV exposure.....	174
Fig. 6.12 (a) TDPL spectra of Z0.25 phosphor. Inset: Bar diagram depicting intensity variation with temperature, (b) Chromaticity diagram depicting variation in CIE coordinates with temperature, and (c) Normalized integrated intensity versus T (K) for Z0.25 phosphor.....	177
Fig. 6.13 (a) Configurational coordinate diagram, and (b) The determination of activation energy for Z0.25 phosphor.....	179

List of tables

Table 1.1 Number of terms, multiplicity, number of levels, ground states and configurations for different Lanthanide (Ln^{3+}) elements	41
Table 3.1 Structural parameters obtained after Rietveld refinement XRD patterns.	77
Table 3.2 Comparative study of weight % and atomic % obtained from EDX with the taken amount used in synthesis.	79
Table 3.3 Binding energies of all the elements obtained from XPS analysis.	82
Table 3.4 Vibrational band of CMO, E4, EM0.1, EM0.3 and EM0.5 samples	84
Table 3.5 Comparison table of chromaticity parameters of EM0.3 red phosphor to reported other red phosphors.	90
Table 4.1 Structural parameters obtained from Rietveld refinement XRD patterns.	99
Table 4.2 Comparative study of weight % and atomic % obtained from EDX with the taken amount used in synthesis.	102
Table 4.3 Comparison of CIE coordinates and color purity with Tb^{3+} doped other phosphors.	116
Table 5.1 Structural parameters obtained from Rietveld refinement XRD patterns.	129
Table 5.2 Obtained vibrational modes of CMO, D4, and S3 samples.	133
Table 5.3 Chromaticity parameters of D4, S1, S2, and S3 phosphors.	146
Table 6.1 Various applications of Dy^{3+} doped phosphors.	152
Table 6.2 Structural parameters obtained from Rietveld refinement XRD patterns.	157
Table 6.3 Comparison of EDX results with stoichiometric amount.	159
Table 6.4 Vibrational modes of CMO, Dy4, and Z0.25 samples.	165
Table 6.5 Fast and slow decay time and their corresponding amplitude.	174
Table 6.6 Chromaticity parameters for Dy4, Z0.1, Z0.25, Z0.5, and Z1 phosphors.	175
Table 6.7 Comparison table for chromatic parameters with Z0.25 phosphor.	176

Preface

The major motivation for my thesis work came from the study of rare-earth doped phosphors for various applications such as white light-emitting diodes (wLEDs), monochromatic phosphors used in display devices, and other applications based on their luminescence properties. CaMoO_4 phosphors have been doped with various rare-earth elements to produce excellent red, green and near-white emitting phosphors that are readily transferable to the host lattice matrix. CaMoO_4 represents a better host for luminescence-based applications because of its properties such as eco-friendly and low-cost synthesis, excellent thermal and chemical stability, good solubility for rare-earth elements, and near-UV absorption.

The research work presented in this thesis has been divided into **seven** chapters.

Chapter 1 gives a brief overview of the phenomena of luminescence, its types, photoluminescence mechanism, phosphor materials, and the characteristics of rare-earth elements. The limits and difficulties of phosphors used in industrial wLED and its dependent parameters are covered in this chapter. The structural and luminescent characteristics of the CaMoO_4 phosphor employed in the thesis work are also specifically examined in this chapter. At the end of this chapter, the thesis's rationale is described. It is based on research on numerous phosphors utilized in various optoelectronic applications.

Chapter 2 discusses the synthesis methods used for the preparation of phosphors and the analytical techniques used for the structural and luminescent properties of phosphors, the study of which explains the various structural and luminescence properties of phosphors in subsequent chapters.

Chapter 3 shows the enhancement of the luminescence of $\text{CaMoO}_4:4\text{Eu}^{3+}$ red phosphors with doping of limited concentrations of the transition ion Mn^{2+} ions. In this chapter, pure

CaMoO₄, Eu³⁺ (2% to 5%) doped CaMoO₄, and Mn²⁺ (0.1%, 0.3%, and 0.5%) co-doped 4% Eu³⁺ doped CaMoO₄ phosphors were synthesized by urea assisted combustion method. Structural analysis has been studied for crystal structure, phase identification, and calculation of crystallite size and microstrain. Some results of absorption spectra such as red-shift in doped and co-doped samples are discussed. This chapter discusses the effects of Mn²⁺ co-doping on the red-orange emission of Eu³⁺-doped CaMoO₄. The correlation of the changed crystal field with Mn²⁺ co-doping and the luminescence of Eu³⁺ ions is discussed.

Chapter 4 describes the role of Bi³⁺ ions in the green luminescence of CaMoO₄:5%Tb³⁺ phosphors. CaMoO₄, Tb³⁺ (2% to 6%) doped CaMoO₄ and Bi³⁺ (2% to 5%) co-doped 5% Tb³⁺ doped CaMoO₄ samples prepared by urea-assisted combustion synthesis method. Structural and morphological analysis of all the samples has been studied and their crystalline phase, lattice strain, crystalline size and particle size have been discussed. In this chapter, the improvement in crystallinity due to doping of Bi³⁺ ions is explained and correlated with the luminescence of CaMoO₄:5%Tb³⁺ green phosphor. This chapter discusses the charge transfer between the energy levels of Bi³⁺ ion to Tb³⁺ ion. Moreover, the thermal stability of the best Bi³⁺ co-doped phosphor has also been investigated.

Chapter 5 discusses the study of energy transfer dynamics in Sm³⁺/Dy³⁺ co-doped CaMoO₄ phosphors for single-component white light emitters. The chapter deals with the conversion of cold white light to neutral white light by precisely controlling the Sm³⁺ dopant concentration, which is a major drawback for commercial wLEDs. The chapter deals with the study of crystalline structure, particle shape and size through structural and morphological analysis. The energy transfer process between Dy³⁺ ions and Sm³⁺ ions from the host as well as from Dy³⁺ ion to Sm³⁺ ion is discussed. In the PL decay lifetime section

of this chapter, the energy transfer between Dy^{3+} to Sm^{3+} is explained in detail and the energy transfer efficiency is also determined.

Chapter 6 presents the enhancement of the photoluminescence properties of Dy^{3+} doped CaMoO_4 phosphors with co-doping of Zn^{2+} ions. The chapter presents the structural and elemental properties investigated by XRD, SEM, TEM, FTIR and XPS. The Zn^{2+} co-doping improves the crystallinity of the $\text{CaMoO}_4:4\%\text{Dy}^{3+}$ phosphor by reducing the defect levels which is explained in detail in the XPS section. The chapter shows the correlation between the change in crystallinity and the improvement in luminescence by Zn^{2+} co-doping. Moreover, the thermal stability of 0.25% Zn^{2+} co-doped $\text{CaMoO}_4:4\%\text{Dy}^{3+}$ phosphor has also been investigated. Therefore, this chapter opens new avenues for development as excellent single-component white light emitters for various optoelectronic applications.

Chapter 7 discusses a brief description of the thesis and presents a further plan for further studies including improving the work presented in the thesis and studying it with other applications.

