

Table of contents

Certificate	ii
Declaration by the candidate	iii
Copyright transfer certificate	iv
Acknowledgments	v
List of figures	xiii
List of tables	xix
Preface	xxi
Chapter 1 Introduction and Motivation	25
1.1 General introduction to luminescence	27
1.2 Classification of Luminescence phenomenon	27
1.2.1 Electroluminescence	28
1.2.2 Chemiluminescence	28
1.2.3 Mechanoluminescence	29
1.2.4 Radioluminescence	29
1.2.5 Thermoluminescence	29
1.2.6 Photoluminescence	30
1.2.6.1 Fluorescence	31
1.2.6.2 Phosphorescence	31
1.3 Photoluminescence mechanism	32
1.3.1 Excitation process	33
1.3.2 Relaxation process	33
1.3.2.1 Radiative transition	34
1.3.2.2 Non-radiative transition	34
1.3.3 Photoluminescence Decay Mechanisms	35
1.4 Phosphor materials.....	36
1.4.1 SrMoO ₄ phosphor	37
1.4.2 Zn ₃ (VO ₄) ₂ phosphor	39
1.5 Rare-earth ions	41
1.5.1 4f-4f intra-configurational transition	44
1.5.2 5d-4f inter-configurational transition.....	45
1.5.3 Charge transfer transition.....	46
1.6 Trivalent Rare earth ions.....	46
1.6.1 Trivalent samarium ion	46
1.6.2 Trivalent dysprosium ion	46
1.6.3 Trivalent europium ion	47
1.6.4 Trivalent terbium ion	48
1.6.5 Trivalent holmium ion	48
1.6.6 Trivalent erbium ion	49

1.6.7 Trivalent neodymium ion.....	49
1.7 Application of phosphor materials.....	49
1.7.1 White Light Emitting Diodes.....	50
1.7.2 Optical Thermometry.....	53
1.7.2.1 Temperature sensing techniques.....	53
1.7.2.2 Fluorescence thermometry.....	55
1.7.2.3 FIR thermometry.....	56
1.8 Motivation of the thesis	59
Chapter 2 Synthesis and characterization techniques.....	63
2.1 Overview.....	65
2.2 Synthesis of the composition	65
2.2.1 Doped SrMoO ₄ compositions.....	65
2.2.1 Doped Zn ₃ (VO ₄) ₂ compositions.....	66
2.3 Characterizations techniques & their working principle	67
2.3.1 X-ray diffraction:	67
2.3.2 Scanning electron microscope (SEM) and Energy dispersive X-ray spectroscopy (EDS)	69
2.3.3 Fourier Transform Infrared (FTIR) Spectroscopy.....	71
2.3.3 X-ray photoelectron spectroscopy (XPS)	72
2.3.4 UV-Vis Spectroscopy	74
2.3.4.1 UV-Vis spectrophotometer.....	74
2.3.4.2 UV-Vis spectroscopy analysis.....	75
2.3.5 Photoluminescence Spectroscopy.....	76
2.3.5.1 PL spectrophotometer.....	77
2.3.5.3 Temperature-dependent PL measurement.....	78
Chapter 3 Study of Bi ³⁺ assisted luminescence in SrMoO ₄ :Sm ³⁺ red phosphor.....	79
3.1 Introduction.....	81
3.2 Materials and synthesis technique	83
3.2.1 Materials and preparation of Bi ³⁺ , Sm ³⁺ co-doped SrMoO ₄ phosphors.....	83
3.2.2 Characterizations.....	83
3.3. Results and discussion	84
3.3.1 X-ray diffraction analysis	84
3.3.2 Energy dispersive X-ray analysis.....	90
3.3.3 FT-IR study.....	90
3.3.4 Absorption study.....	91
3.3.5 Photoluminescence study.....	95
3.3.6 Decay curve analysis.....	101
3.3.6 CIE study	102
3.4 Conclusions.....	103

Chapter 4 Effect of Zn ²⁺ co-doping on the luminescence of Sm ³⁺ doped SrMoO ₄ phosphor.....	105
4.1 Introduction.....	107
4.2. Methods.....	108
4.2.1 Preparation of phosphors	108
4.2.2 Characterization techniques	109
4.3. Results and discussion	110
4.3.1 XRD study	110
4.3.2 Morphology study.....	113
4.3.3 FT-IR study.....	114
4.3.4 XPS Study.....	115
4.3.5 Absorption study.....	117
4.3.6 Photoluminescence study.....	119
4.3.7 PL Decay analysis.....	124
4.3.8 CIE and CCT study.....	126
4.3.9 Temperature-dependent PL analysis.....	126
4.4 Conclusions.....	130
Chapter 5 Energy Transfer Dynamics, Emission Color Tuning, and Fluorescence Thermometry in Dy ³⁺ /Eu ³⁺ co-doped SrMoO ₄ phosphors.....	131
5.1 Introduction.....	133
5.2 Experimental.....	136
5.2.1 Chemicals.....	136
5.2.2 Synthesis Process.....	137
5.2.3 Characterisation	137
5.3 Results and Discussion	138
5.3.1 Structural and compositional properties	138
5.3.2 Absorption and bandgap study.....	143
5.3.3 PLE and PL analysis	144
5.3.4 Energy transfer dynamics	149
5.3.5 PL Decay study	151
5.3.6 Tunable color study of Dy ³⁺ /Eu ³⁺ co-doped SrMoO ₄	153
5.3.7 Fluorescence Thermometry	155
4.4 Conclusion	160
Chapter 6 Enhancement in greenish-white photoluminescence of Zn ₃ (VO ₄) ₂ phosphor by Bi ³⁺ doping.....	163
6.1 Introduction.....	165
6.2 Materials and synthesis technique	166
6.2.1 Materials for the synthesis	166

6.2.2 Preparation of Bi ³⁺ doped Zn ₃ (VO ₄) ₂ phosphors.	167
6.2.3 Characterizations.....	167
6.3 Results and discussion	168
6.3.1 Structural analysis.....	168
6.3.2 Morphological and elemental analysis.....	172
6.3.3 Infrared spectroscopy analysis.....	173
6.3.4 Absorption study.....	174
6.3.5 Photoluminescence study.....	175
6.3.6 Effect of Bi ³⁺ doping on the photoluminescence spectrum	178
6.3.7 CIE coordinates.....	179
6.4 Conclusions.....	180
Chapter 7 Greenish-yellow emission from rare-earth free Li ⁺ doped zinc vanadate phosphor.....	181
7.1 Introduction.....	183
7.2 Material and methods.....	186
7.2.1 Phosphor synthesis.....	186
7.2.2 Characterisation	186
7.3 Results and discussion	187
7.3.1 Structural analysis.....	187
7.3.1.1 XRD study	187
7.3.1.2 FTIR spectroscopy analysis	191
7.3.1.3 FE-SEM analysis	192
7.3.1.4 XPS analysis	193
7.3.2 Optical study	194
7.3.2.1 UV-Vis absorption analysis	194
7.3.2.2 Photoluminescence analysis.....	196
7.3.2.3 Role of Li ⁺ in enhancing the PL intensity.....	198
7.3.2.4 Decay curve analysis.....	199
7.3.2.5 CIE and CCT analysis.....	201
7.3.2.6 TDPL and quantum yield analysis.....	202
7.3.2.7 Configurational coordinate diagram	204
7.4 Conclusion	204
Chapter 8 Conclusion	207
8.1 Summary.....	209
8.2 Future Scope of the study	214
Bibliography	215
List of Publications	232

List of figures

Fig. 1.1 Classification of luminescence processes based on Time duration and Excitation source.....	28
Fig. 1.2 (a) Bioluminescence in mushrooms (b) Watch face illuminated by tritium tubes (c) Thermoluminescence dating of ancient pots (d) Schematic representation of mechanoluminescence (ML) (e) Fluorescent LED bulbs.....	30
Fig. 1.3 Jablonski Diagram for explaining absorption, fluorescence, inter-system crossing, internal conversion, vibrational relaxation, and phosphorescence	32
Fig. 1.4 Crystal structure of SrMoO ₄ . ²²	38
Fig. 1.5 Typical photoluminescence excitation and emission spectra of SrMoO ₄ phosphor. ²²	39
Fig. 1.6 Crystal structure of Zn ₃ (VO ₄) ₂ . ²⁹	40
Fig. 1.7 Typical excitation and emission spectra of Zn ₃ (VO ₄) ₂ phosphor ³⁶	41
Fig. 1.8 Energy level structure of Ln ³⁺ in the range up to 40,000 cm ⁻¹ ⁴⁴	44
Fig. 1.9 Diverse applications of Phosphor materials	50
Fig. 1.10 (a) Fabrication of white LED based on yellow YAG:Ce ³⁺ phosphor and blue InGaN chip. (b) Emission spectra of the commercial wLED. ⁵³	51
Fig. 1.11 Desired characteristics of phosphors for lighting applications.....	53
Fig. 1.12 Various temperature sensing techniques based on contact and non-contact mode of operation.	54
Fig. 1.13 Energy level diagrams of some trivalent lanthanide ions having TCELs.	56
Fig. 2.1 Schematic of the auto-combustion synthesis process.....	66
Fig. 2.2 Schematic of the citrate sol-gel synthesis method.....	67
Fig. 2.3 (a) X-ray Diffractometer (b) Schematic representation of X-ray diffraction.	68
Fig. 2.4 Bragg's diffraction from atomic planes.....	69
Fig. 2.5 SEM- EDS set up.....	70
Fig. 2.6 (a) Working mechanism of a Michelson interferometer, configured for FTIR (b) JASCO 4600 FTIR spectrometer.....	71
Fig. 2.7 Illustration of the mechanism behind ATR setup.....	72
Fig. 2.8 Thermo scientific K- alpha XPS setup	74
Fig. 2.9 UV-Vis spectrophotometer (Jasco V-770) equipped with an integrating sphere setup.....	76
Fig. 2.10 (a) Components and working ray diagram of PL spectrophotometer setup (b) Horiba Photoluminescence spectrophotometer.....	77
Fig. 3.1 Rietveld refined XRD plots of SMO, SMS4 and SMB2.....	87
Fig. 3.2 The crystallite size and strain variation with samples obtained after their W-H plot analysis.....	89
Fig. 3.3 Energy dispersive X-ray spectra SMB2 phosphor.	90

Fig. 3.4 FTIR spectra of SMO, SMS4 and SMB2.	91
Fig. 3.5 (a) Absorption spectra of all the prepared phosphors. (b) Urbach tail width plot for SMO. Inset shows variation of Urbach energy with samples.	92
Fig. 3.6 Tauc plot for all samples.	93
Fig. 3.7 Photoluminescence excitation and emission spectra for SrMoO ₄	95
Fig. 3.8 (a) PLE spectra for Sm ³⁺ doped SrMoO ₄ phosphors for 645 nm emission wavelength. (b) PLE spectra for Bi ³⁺ co-doped phosphors for 645 nm emission wavelength.	95
Fig. 3.9 Deconvoluted broadband PLE spectra of SMS4 in 250 – 310 nm wavelength range.	96
Fig. 3.10 (a) PL spectra for Sm ³⁺ doped SrMoO ₄ upon 404 nm excitation wavelength. (b) Comparative PL spectra of Bi ³⁺ co-doped SrMoO ₄ :4Sm ³⁺ and SrMoO ₄ :4Sm ³⁺ phosphors upon 404 nm excitation wavelength.	97
Fig. 3.11 (a) Comparative PL spectra of Bi ³⁺ co-doped SrMoO ₄ :4Sm ³⁺ and SrMoO ₄ :4Sm ³⁺ phosphors upon 308 nm excitation wavelength. (b) The energy level diagram showing energy transfer mechanism from Bi ³⁺ to Sm ³⁺ ions.	100
Fig. 3.12 Normalized logarithmic decay curves of (a) SMS4 and (b) SMB2 for ⁴ G _{5/2} → ⁶ H _{9/2} transition (645 nm) upon 404 nm excitation.	101
Fig. 3.13 CIE diagram for SMS4, SMB1, SMB2 and SMB3.	102
Fig. 4.1 Schematic describing the synthesis process.	109
Fig. 4.2 (a) Rietveld refined XRD patterns of (i) S0, (ii) S4, and (iii) Z1 phosphors. (b) The tetragonal crystal structure of SrMoO ₄ . (c) The linearly fitted W-H plots of S4, Z1, Z2, and Z3.	111
Fig. 4.3 SEM images of (a) S4 and (b) Z1 with histograms showing the particle size distribution.	113
Fig. 4.4 FTIR spectra of S0, S4, and Z1 samples in transmittance mode.	114
Fig. 4.5 (a) XPS Survey scan for S4 and Z1. XPS high resolution (b) Sr 3d, (c) Mo 3d, (d) O 1s, (e) Sm 3d spectra of S4 and Z1. (f) XPS spectra of Zn 2p for Z1 sample.	117
Fig. 4.6 (a) UV-Vis absorption graphs of SrMoO ₄ , Sm ³⁺ doped SrMoO ₄ , and Z1 phosphors. The Tauc plot is presented in the inset. (b) Urbach energy plot for S0. Inset showing the Urbach energy variation.	119
Fig. 4.7 (a) PLE spectrum of S0 recorded at 497 nm emission wavelength. (b) PL spectrum of S0 in the wavelength range 350-750 nm and monitored at 290 nm excitation wavelength.	119
Fig. 4.8 (a) Comparative PLE spectrum of Sm ³⁺ doped SrMoO ₄ phosphors. (b) Comparative PLE spectrum of S4 and Zn ²⁺ co-doped samples.	120
Fig. 4.9 (a) The comparative PL spectrum of Sm ³⁺ doped series in the wavelength range 525-750 nm. (b) The PL spectrum of Zn ²⁺ co-doped samples and S4 in 525-750 nm wavelength range.	122
Fig. 4.10 (a) The schematic of an energy transfer mechanism for MoO ₄ ²⁻ groups and Sm ³⁺ ions. (b) The deconvoluted broadband spectrum of S4. (c) CIE coordinates for S0, S4, and Z1 samples are marked in the CIE diagram.	123

Fig. 4.11 PL decay curves of (a) S4 and (b) Z1 samples, recorded upon 404 nm excitation and 645 nm emission.	125
Fig. 4.12 (a) Temperature-dependent PL spectra of Z1 phosphor. (b) Configurational coordinate diagram for understanding thermal quenching phenomenon in Z1 phosphor.	128
Fig. 4.13 (a) Bar diagram depicting intensity variation of three major peaks with increasing temperature. (b) Normalized integrated intensity plot as a function of temperature for Z1 phosphor. (c) $\ln((I_0/I_T)-1)$ vs. $1/kT$ plot for the determination of activation energy. (d) CIE chromaticity diagram depicting variation in CIE coordinates with temperature for Z1 phosphor.....	129
Fig. 5.1 (a) XRD patterns of (i) E4, (ii) D4, and (iii) D0 phosphors along with their Rietveld refinement profile. (b) SrMoO ₄ crystal structure with SrO ₈ dodecahedron and MoO ₄ tetrahedron.	138
Fig. 5.2 FTIR spectra of D0, D4, and E3 phosphor.....	140
Fig. 5.3 XPS Survey scan (a) and XPS graph of (b) Sr 3d, (c) Mo 3d, (d) O 1s, (e) Dy 3d spectra for E4 and D4. (f) XPS spectrum of Eu 3d for E4 sample.	142
Fig. 5.4 (a) UV-Visible Absorption spectrum of the phosphors. (b) Tauc plot of all the phosphors. Inset shows the variation of Bandgap.....	144
Fig. 5.5 PLE (in violet) and PL (in green) spectrum of D0 phosphor examined at 500 nm emission wavelength and 297 nm excitation wavelength, respectively.	144
Fig. 5.6 PLE spectrum of (a) Dy ³⁺ doped phosphors, and (b) Eu ³⁺ co-doped phosphors.	145
Fig. 5.7 PL spectrum of Dy ³⁺ doped phosphors recorded at (a) 297 nm and (b) 352 nm emission wavelength.....	146
Fig. 5.8 (a) Comparative PL spectra of D4 and E series examined at 297 nm excitation wavelength. (b) The normalized intensity variation of ⁴ F _{9/2} → ⁶ H _{13/2} and ⁵ D ₀ → ⁷ F ₂ peaks as a function of Eu ³⁺ doped samples. (c) Comparative PL spectra of D4 and E series monitored at 352 nm excitation wavelength. (d) Comparative PL spectra of E series monitored at 464 nm excitation wavelength.	147
Fig. 5.9 (a) I ₀ /I as a function of (1) C ^{6/3} , (2) C ^{8/3} , and (3) C ^{10/3} (b) Schematic of the energy transfer phenomenon in SrMoO ₄ :Dy ³⁺ , Eu ³⁺	151
Fig. 5.10 PL decay curve of (a) D4 and (b) E4 phosphors.	152
Fig. 5.11 CIE chromaticity diagram of (a) Dy ³⁺ /Eu ³⁺ co-doped SrMoO ₄ phosphors under 297 nm excitation, (b) Dy ³⁺ doped SrMoO ₄ phosphors examined at 352 nm excitation, and (c) E4 phosphor under different excitation wavelengths.	155
Fig. 5.12 Temperature-dependent PL of D4 phosphor examined at (a) 297 nm, (b) 352 nm. Temperature-dependent PL of E4 phosphor examined at (a) 464 nm, (b) 297 nm. Inset shows the variation of 372 nm and 615 nm peaks in E4 phosphor with temperature.	156
Fig. 5.13 (a) The FIR variation with temperature, (b) plot of $\ln(\text{FIR})$ vs. $1/T$, (c) absolute sensitivity (S _a), and (d) relative sensitivity (S _r) as a function of temperature for E4 phosphor.....	158

Fig. 5.14 (a) Configurational coordinate diagram for explaining the temperature-induced fluorescence processes in E4 phosphor. (b) CIE color coordinates of E4 sample examined at 297 nm excitation wavelength and different temperatures presented in CIE diagram.	159
Fig. 6.1 Rietveld refinement of the room temperature XRD patterns of ZVO and ZVB1 phosphors. The ‘*’ denotes $Zn_2V_2O_7$ having a $C2/m$ (12) space-group.	168
Fig. 6.2 Crystal structure of ZVO, drawn based on Rietveld refinement.	169
Fig. 6.3 SEM images for all samples.	172
Fig. 6.4 EDS spectra of $Zn_3(VO_4)_2:Bi(1\%)$ phosphor.	173
Fig. 6.5 FTIR spectrum of all phosphors.	174
Fig. 6.6 (a) Absorbance spectrum of all prepared phosphors. (b) Urbach energy plot for ZVB1, where the blue line shows a linearly fitted portion of the graph. The inset in figure b shows the variation of Urbach energy with prepared phosphors.	175
Fig. 6.7 (a) Photoluminescence excitation spectrum of prepared phosphors for 542 nm emission wavelength. (b) Peak fitting of ZVB1 excitation spectra.	176
Fig. 6.8 (a) Photoluminescence emission spectrum of prepared phosphors for 340 nm excitation wavelength. (b) Peak fitting of ZVB1 emission spectra.	177
Fig. 6.9 (a) Schematic of energy transfer among $[VO_4]^{3-}$ energy levels and from $[VO_4]^{3-}$ to MMCT band. (b) CIE coordinates for all the prepared phosphors.	179
Fig. 7.1 Schematic of the synthesis process.	186
Fig. 7.2 (a) Rietveld refined XRD patterns of samples. (b) Crystal structure of the samples based on refinement data. (c) The alteration in the peak intensity and FWHM of (020) peak in 2θ for all prepared samples.	188
Fig. 7.3 Williamson-Hall plot for all the prepared phosphors.	189
Fig. 7.4 FTIR spectra of all prepared phosphors.	192
Fig. 7.5 FE-SEM micrographs of (a) L0 and (b) L2	192
Fig. 7.6 (a) XPS survey scan for L2. XPS spectra of (b) V 2p, (c) Li 1s, (d) Zn 2p, (e) O 1s for L2.	194
Fig. 7.7 (a) Absorbance spectrum of the samples. Inset shows Tauc plot and bandgap of all the phosphors. (b) Urbach energy plot for L0. The fluctuation of Urbach energy with Li^+ doped phosphors is depicted in the inset of (b).	196
Fig. 7.8 (a) PLE spectra of the phosphors examined at 542 nm emission wavelength. Inset shows the variation of PLE spectrum intensity. (b) PL spectra of the prepared phosphors monitored at 360 nm excitation wavelength. Inset shows the variation of PLE spectrum intensity.	197
Fig. 7.9 Deconvoluted excitation peak (a) and emission peak (b) for L0. Deconvoluted excitation peak (c) and emission peak (d) for L2. (e) Configurational coordinate diagram for understanding absorption, fluorescence, and thermal quenching phenomenon.	198
Fig. 7.10 PL decay curves of (a) L0 and (b) L2 samples, recorded upon 360 nm excitation and 542 nm emission.	200
Fig. 7.11 Chromaticity diagram depicting CIE coordinates of L0 and L2 phosphors.	201

Fig. 7.12 (a) TDPL spectra of L2 phosphor, (b) Normalized integrated intensity plot as a function of temperature, (c) $\ln ((I_0/I_T)-1)$ vs. $1/kT$ plot, and (d) CIE chromaticity diagram depicting variation in CIE coordinates with temperature for L2 phosphor.203

List of tables

Table 1.1. The total number of terms, degeneracy, no of levels, ground level, and λ/cm^{-1} for f^n electronic configuration.	43
Table 3.1 Structural parameters obtained after Rietveld refinement of Sm^{3+} doped SrMoO_4	85
Table 3.2 Structural parameters obtained after Rietveld refinement of Bi^{3+} doped $\text{SrMoO}_4:4\text{Sm}^{3+}$	86
Table 3.3 Crystallite size (D) and strain (ϵ) values for all samples.	89
Table 3.4 Calculated optical bandgap (E_g) and Urbach energy (E_u) for all samples.	94
Table 4.1 Atomic positions, lattice parameters, Unit cell volume, and bond angles obtained after rietveld refinement for S0, S4, and Z1.	112
Table 4.2 The crystallite size values of S4, Z1, Z2, and Z3 phosphors.	112
Table 4.3 The obtained binding energies of all the elements present in S4 and Z1 samples from their respective XPS spectrums.	116
Table 5.1 Atomic positions, unit cell volume, and lattice parameters of D0, D4, and E4 phosphors.	139
Table 5.2 The B.E of the elements present in D4 and E4 samples based on their XPS spectra.	142
Table 5.3 CIE coordinates, CCT value, and CP of prepared phosphors.	154
Table 5.4 Comparison of relative sensitivity for reported phosphors and synthesized E4 phosphor.	160
Table 6.1 Structural parameters after Rietveld refinement of ZVO and ZVB1 for the orthorhombic phase.	170
Table 7.1 Structural parameters for all the phosphors derived after Rietveld refinement of their individual XRD patterns.	190
Table 7.2 Vibrational modes assigned to different wavenumber bands observed in FTIR spectrum of samples.	191
Table 8.1 Some major highlights of the work done and its comparison with reported work.	213