

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**INVESTIGATION OF NANOMATERIAL
SUPPORTED FLUOROPHORE, PHOSPHOR OR
PHOSPHOR-BLENDS IN POLYMERIC
MATRICES FOR OPTOELECTRONIC
APPLICATIONS**

by
Utku ULUCAN

August, 2022
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**INVESTIGATION OF NANOMATERIAL
SUPPORTED FLUOROPHORE, PHOSPHOR OR
PHOSPHOR-BLENDS IN POLYMERIC
MATRICES FOR OPTOELECTRONIC
APPLICATIONS**

**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Degree of Philosophy in
Nanoscience and Nano engineering program.**

**by
UTKU ULUCAN**

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Ph.D THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**INVESTIGATION OF NANOMATERIAL SUPPORTED FLUOROPHORE, PHOSPHOR OR PHOSPHOR-BLENDS IN POLYMERIC MATRICES FOR OPTOELECTRONIC APPLICATIONS**” completed by **UTKU ULUCAN** under supervision of **PROF. DR. KADRIYE ERTEKİN** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of science in Nanoscience and Nanoengineering.

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INVESTIGATION OF NANOMATERIAL SUPPORTED FLUOROPHORE, PHOSPHOR OR PHOSPHOR-BLENDS IN POLYMERIC MATRICES FOR OPTOELECTRONIC APPLICATIONS

ABSTRACT

In this thesis we investigated the interactions between the commercially available LED phosphorus and nano-scale materials or dyes in terms of their emission abilities in polymers. In the first part of the thesis, photoluminescence of the Eu^{2+} doped Ca- α -Sialon ($\text{Ca-}\alpha\text{-SiAlON:Eu}^{2+}$), Ce^{3+} doped lutetium aluminum garnet (LuAG:Ce^{3+}) and their binary blends with the quinine sulphate (QS) were investigated by steady-state and decay time measurements. The $\text{Ca-}\alpha\text{-SiAlON:Eu}^{2+}$ exhibited 44% increase in the intensity when blended with the QS. Similarly, the binary blend of QS-LuAG:Ce^{3+} exhibited 98% enhancement in the intensity. Excited state lifetimes of the phosphors were also studied in nanosecond and microsecond time scales, respectively. Spectral data presented some evidence for the donor-acceptor relationship of the QS/ $\text{Ca-}\alpha\text{-SiAlON:Eu}^{2+}$ and QS/LuAG:Ce^{3+} counterparts where the QS was the donor. The offered phosphor blends, exhibited enhancement in the optical brightness without any spectral shift.

In the second part of the thesis, CO_2 sensitive HPTS dye was used along with the bioactive glasses and ionic liquid. The bioactive glasses equipped with the rare earths of Er^{3+} , Tb^{3+} and Er^{3+} and Tb^{3+} , were chosen due to their porous structure, optical transparency and intrinsic fluorescence. After spectral characterization steps we exposed the composites towards varying concentrations of the CO_2 and recorded the intensity based response both in steady-state and kinetic mode. We also determined the decay times in the absence and presence of the CO_2 . We obtained promising results from the studies performed by using the bio-compatible bioactive glasses in terms of enhanced optical brightness and CO_2 sensitivity.

Keywords: Fluorescence, bioactive glass, HPTS, carbon dioxide.

OPTOELEKTRONİK UYGULAMALARA YÖNELİK NANO MALZEME DESTEKLİ FLOROFOR, FOSFOR VEYA FOSFOR KARIŞIMLARININ POLİMERİK MATRİKSER İÇERİSİNDE İNCELENMESİ

ÖZ

Bu tez kapsamında, ticari olarak temin edilebilen bazı LED fosforları ile nano ölçekli malzemeler veya boyalar arasındaki etkileşimler, polimerik matriksde emisyon yetenekleri açısından araştırılmıştır. Tezin ilk bölümünde Eu^{2+} katkılı $\text{Ca-}\alpha\text{-SiAlON}$ ($\text{Ca-}\alpha\text{-SiAlON:Eu}^{2+}$) ve Ce^{3+} katkılı lutesyum alüminyum garnet (LuAG:Ce^{3+}) ve bunların kinin sülfat (QS) ile ikili karışımlarının fotolüminesansı, kararlı durum ve bozunma süresi ölçümleri ile incelenmiştir. ($\text{Ca-}\alpha\text{-SiAlON:Eu}^{2+}$) QS ile karıştırıldığında oluşan kompozit emisyon performansında %44 oranında bir artış sergilemiştir. Benzer şekilde, QS-LuAG:Ce³⁺ ikili karışımı, emisyon şiddetinde %98'e varan artış göstermiştir. Fosforların uyarılmış durum ömürleri de sırasıyla nanosaniye ve mikrosaniye zaman ölçeklerinde incelenmiştir. Spektral veriler, QS'nin verici (donor) olduğu QS/(Ca- α -SiAlON:Eu²⁺) ve QS/ (LuAG:Ce³⁺) karışımlarının donör-akseptör etkileşimleri için bazı kanıtlar sunmuştur. Önerilen fosfor karışımları, herhangi bir spektral kayma olmaksızın optik parlaklıkta umut verici gelişme sergilemiştir.

Tezin ikinci bölümünde, bioaktif camlar ve iyonik sıvı ile birlikte CO₂ duyarlı HPTS boyası kullanılmıştır. Er³⁺, Tb³⁺ ve Er³⁺ ve Tb³⁺ nadir toprak elementleri ile doplanmış bioaktif camlar, gözenekli yapıları, optik şeffaflıkları ve içsel floresansları nedeniyle seçilmiştir. Spektral karakterizasyon adımlarından sonra, kompozitler değişen CO₂ konsantrasyonlarına maruz bırakılmış ve hem kararlı durumda hem de kinetik modda emisyon yanıtı kaydedilmiştir. Ayrıca CO₂'nin yokluğunda ve varlığında luminesans bozunma süreleri de ölçülmüştür. Biyouyumlu bioaktif camlar kullanılarak yapılan çalışmalardan optik parlaklık ve CO₂ duyarlılığı açısından umut verici sonuçlar elde edilmiştir.

Anahtar kelimeler: Floresans, bioaktif cam, HPTS, karbon dioksit.

CONTENTS

	Page
PH.D THESIS EXAMINATION RESULT FORM	ii
ACKNOWLEDGMENTS	iii
ABSTRACT.....	iv
ÖZ	v
LIST OF FIGURES	ix
LIST OF TABLES	xv
CHAPTER ONE-INTRODUCTION	1
1.1 Luminescence.....	2
1.2 Mechanism of Luminescence	2
1.3 Quantum Yield	3
1.4 Decay Time	4
1.4.1 Time-Domain Decay Time Measurements by TCSPC Approach.....	5
1.4.2 Frequency Domain Lifetime Measurement	6
1.5 Fluorescence Resonance Energy Transfer (FRET)	7
1.5.1 Dexter and Forster Mechanisms	7
1.6 Florescence and Phosphorescence of Molecular Species	8
1.7 Molecules Exhibiting Fluorescence Characteristics.....	8
1.8 Fluorescence and Phosphorescence of Inorganic Materials.....	9
1.8.1 Yellow Phosphors.....	13
1.8.1.1 YAG:Ce ³⁺	13
1.8.1.2 Green Phosphors	14
1.8.1.3 Red Phosphors	14
CHAPTER TWO- QUININE SULPHATE.....	15

2.1 Enhancement of Optical Properties of $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ and $\text{Ca-}\alpha\text{-SiAlON}:\text{Eu}^{2+}$ by Quinine Sulphate	15
2.2 Introduction	15
2.3 Experimental Method and Instrumentation.....	19
2.3.1 Reagents.....	19
2.3.2 Instruments	19
2.3.3 XRD and XPS Spectra of the Utilized Particles.....	21
2.3.3.1 XRD and XPS Spectral Data of the LuAG.....	21
2.3.3.2 XPS Spectrum of the LuAG	22
2.3.4 XRD and XPS Spectral Data of the SiAlON.....	24
2.3.4.1 XRD Patterns of the SiAlON	24
2.3.4.2 XPS Spectrum of the SiAlON.....	25
2.3.5 Morphology and Size of the Utilized Particles.....	27
2.3.6 Composition, Spectral Results and Optical Properties of the Utilized Materials.....	28
2.3.7 Spectral Properties of the PMMA Embedded Quinine Sulphate (QS)....	29
2.3.8 Excitation-Emission Behavior of the SiAlON and the Binary Mixtures with Quinine Sulphate	31
2.3.9 Optical Properties of the $\text{LuAG}:\text{Ce}^{3+}$ and $\text{LuAG}:\text{Ce}^{3+}$ / Quinine Sulphate Binary Mixtures.....	34
2.3.9.1 Decay Time Measurements.....	38
2.3.9.2 Decay Characteristics of the QS in the PMMA	42
2.3.9.3 Decay Characteristics of the QS/ $\alpha\text{-SiAlON}:\text{Eu}^{2+}$ Binary Blends .	43
2.3.9.4 Decay Characteristics of the $\text{LuAG}:\text{Ce}^{3+}$ /QS Blends	44
2.4 Conclusion.....	46

CHAPTER THREE- CO_2 SENSING STUDIES..... 47

3.1 Bioactive Glasses	47
3.2 Experimental	50
3.2.1 Chemicals	50

3.2.2 Instruments	51
3.2.3 Gas Blender	51
3.3 Results and Discussions	52
3.3.1 Characterization of the Used Bioactive Glasses.....	52
3.3.2 Synthesis of Ion Pair of HPTS.....	53
3.3.3 Preparation and Chemistry of the Indicator Composite	54
3.3.4 Spectral Characterization of the Bioactive Glasses and HPTS	57
3.3.5 Combination of the HPTS Dye and Bioactive Glass Particles	59
3.3.6 Photoluminescence Spectra of the HPTS and 1% Er Doped Bioactive Glass Containing Composites	61
3.3.7 Photoluminescence Spectra of the HPTS and 5% Tb ³⁺ Doped Bioactive Glass Containing Composites	64
3.3.8 Photoluminescence Spectra of the HPTS and 3% Er ³⁺ -Tb ³⁺ Doped Bioactive Glass Containing Composites	67
3.3.9 CO ₂ Induced Response of the Composites	70
3.3.10 CO ₂ Induced Response of Er ³⁺ Doped Bioactive Glass and HPTS	71
3.3.11 CO ₂ Induced Response of Tb ³⁺ Doped Bioactive Glass and HPTS	74
3.3.12 CO ₂ Based Response of the Er ³⁺ -Tb ³⁺ Doped Bioactive Glass and HPTS	76
3.3.13 Decay Time Measurements of HPTS Equipped Bioactive Glasses	79
3.3.14 Kinetic Measurements: Response Time and Recovery Characteristics	86
3.4 Conclusion.....	89

REFERENCES.....	91
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LIST OF FIGURES

	Page
Figure 1.1 Jablosky diagram (was taken from: Lakowicz, 2006 and re-arranged).....	2
Figure 1.2 –Mono exponential decay of a luminescent material (was taken from: Terpetschnig & Jameson, 2005).....	5
Figure 1.3 Flow diagram of a TCSPC instrument (was taken from: Wolfbeis, 1991 and re-arranged).....	6
Figure 1.4 Phase shift in frequency domain lifetime measurement (was taken from: Wolfbeis, 1991 and re-arranged).....	7
Figure 1.5 Molecular structure of (a) quinine sulfate (QS), (b) fluorescein, (c) rose Bengal, (d) 8-Hydroxypyrene-1,3,6-trisulfonic acid, trisodium salt.....	9
Figure 1.6 Band Structure of Phosphor Materials (was taken from: Kasap & Capper, 2017 and re-arranged)	10
Figure 1.7 Crystal Structure of the YAG:Ce ³⁺ (was taken from: Lei, Chun-Che, Chiao- Wen & Ru-Shi, 2010)	13
Figure 1.8 Cubic Crystal Structure of the Ce ³⁺ activated LuAG (was taken from: Lei, Chun-Che, Chiao-Wen & Ru-Shi, 2010).	14
Figure 2.1 Photograph of the used spectrofluorometer instrument.....	21
Figure 2.2 XRD patterns of the LuAG:Ce ³⁺	22
Figure 2.3 XPS spectrum of the LuAG including binding energies and quantification information of the elements	23
Figure 2.4 High resolution XPS survey scans of LuAG:Ce ³⁺	24
Figure 2.5 XRD patterns of the used Ca- α -Sialon:Eu ²⁺ powders	25
Figure 2.6 XPS spectrum of the SiAlON including binding energies and quantification information of the elements	26
Figure 2.7 High resolution XPS spectrum of the SiAlON	27
Figure 2.8 SEM images of the LuAG:Ce ³⁺ and Ca- α -Sialon:Eu ²⁺ under different magnification were shown in figure -a, -b, -c and -d, respectively.....	28
Figure 2.9 Normalized excitation-emission spectra of quinine sulfate in thin film form in PMMA (a and a', λ_{ex} =354 nm, λ_{em} =390 nm, b and b': λ_{ex} =405 nm, λ_{em} =502 nm)	30

Figure 2.10 I: Excitation-emission spectra of the Ca- α -SiAlON: Eu ²⁺ in thin film form in PMMA (λ_{ex} =405 nm, λ_{em} =600 nm) 3-II: Gathered excitation-emission spectra of the different forms in PMMA. A and a': QS (λ_{ex} = 354 nm), b and b': QS-Ca- α -SiAlON: Eu ²⁺ blend (λ_{ex} =405 nm), c, c': Ca- α -SiAlON: Eu ²⁺ (λ_{ex} = 405 nm), d, d'QS (λ_{ex} = 405 nm)	32
Figure 2.11 Normalized excitation and emission spectrum of the QS (a and a') and the Ca- α -SiAlON: Eu ²⁺ (b and b') upon excitation at 405 nm.....	34
Figure 2.12 I: Excitation-emission spectra of the LuAG:Ce ³⁺ in thin film form in PMMA (λ_{ex} =450 nm, λ_{em} =512 nm) II: Gathered excitation-emission spectra of the LuAG:Ce ³⁺ and LuAG:Ce ³⁺ / QS blend in the PMMA.....	36
Figure 2.13 Normalized excitation and emission spectrum of the QS (a and a') and the LuAG:Ce ³⁺ -upon excitation at 405 nm	37
Figure 2.14 Decay curve of the QS acquired in the PMMA matrix	38
Figure 2.15 Decay curve of the Ca- α -Sialon:Eu ²⁺ acquired in the PMMA matrix....	39
Figure 2.16 Decay curve of the LuAG:Ce ³⁺ acquired in the PMMA matrix	39
Figure 3.1 Basic SiO ₄ tetrahedron, crystalline form and amorphous glass structures (was taken from: https://www.slideshare.net/hzharraz/silica-sand-and-glass-industry and re-arranged).....	49
Figure 3.2 Gas humidification and gas blender systems used in the research lab	52
Figure 3.3 SEM micrographs of the bioactive glass powders synthesized in the study a) dopant-free bioactive glass 1393, b) 5% Er doped-1393, c) 5% Tb doped-1393, d) 5 % Er:Tb doped-1393 (Deliormanlı, Rahman, Oguzlar & Ertekin, 2021).....	53
Figure 3.4 Schematic chemical structure of the ion pair of the HPTS with tetraoctylammonium counter ion	54
Figure 3.5 The anion exchange scheme between TOAOH and EMIMBF ₄ and consequent interaction with H ₂ CO ₃ (was taken from: Oter, Ertekin & Derinkuyu, 2008) (Oter, Ertekin & Derinkuyu, 2008).....	56
Figure 3.6 Gathered excitation and emission spectra of the different concentrations of Er ³⁺ - containing bioactive glass particles (was taken from: Deliormanlı, Rahman, Oguzlar & Ertekin, 2021)	57

Figure 3.7 Gathered excitation and emission spectra of the different concentrations of Tb^{3+} - containing bioactive glass particles (was taken from: Deliormanlı, Rahman, Oguzlar & Ertekin, 2021)	58
Figure 3.8 Gathered excitation and emission spectra of the different concentrations of Eb^{3+} - Tb^{3+} co-doped bioactive glass particles (was taken from: Deliormanlı, Rahman, Oguzlar & Ertekin, 2021)	59
Figure 3.9 Overlay spectra of the IL-free EC doped HPTS, bare bioactive glass and their combination in form of thin film. (a, a': bare bioactive glass, b, b': HPTS only, c, c', HPTS and bioactive glass)	60
Figure 3.10 Overlay spectra of the IL-doped doped HPTS, bare bioactive glass and their combination in form of thin film. (red: bare bioactive glass, black: HPTS only, blue: HPTS and bioactive glass)	61
Figure 3.11 Overlay spectra of the IL-Free HPTS, 1% Er^{3+} doped bioactive glass and their combination in form of thin film in EC. (a, a': 1% Er^{3+} doped bioactive glass, b, b': HPTS only, c, c', HPTS and 1% Er^{3+} bioactive glass)	62
Figure 3.12 Overlay spectra of the IL-doped HPTS, 1% Er^{3+} doped bioactive glass and their combination in form of thin film. (red: 1% Er^{3+} doped bioactive glass, black: HPTS only, blue: HPTS and bioactive glass).....	63
Figure 3.13 Normalized overlay spectra of the HPTS and 1% Er^{3+} doped bioactive glass in form of thin film. (black: 1% Er^{3+} doped bioactive glass, red: HPTS only) (λ_{ex} for the HPTS: 466 nm., λ_{ex} for the bioactive glass: 374 nm)	64
Figure 3.14 Overlay spectra of the IL-free HPTS, 5% Tb^{3+} doped bioactive glass and their combination in form of thin film in EC. (red: 5% Tb^{3+} doped bioactive glass, black: HPTS only, blue: HPTS and 5% Tb^{3+} bioactive glass).....	65
Figure 3.15 Overlay spectra of the IL-doped HPTS, 5% Tb^{3+} doped bioactive glass and their combination in form of thin film. (red: 5% Tb^{3+} doped bioactive glass, black: HPTS only, blue: HPTS and bioactive glass).....	66
Figure 3.16 Normalized overlay spectra of the HPTS and 5% Tb^{3+} doped bioactive glass in form of thin film. (black: 5% Tb^{3+} doped bioactive glass, red:	

HPTS only) (λ_{ex} for the HPTS: 466 nm., λ_{ex} for the bioactive glass: 374 nm)	67
Figure 3.17 Overlay spectra of the IL-free HPTS, 3% Er^{3+} - Tb^{3+} doped bioactive glass and their combination in form of thin film. (red: 3% Er^{3+} - Tb^{3+} doped bioactive glass, black: HPTS only, blue: HPTS and 3% Er^{3+} - Tb^{3+} bioactive glass.).....	68
Figure 3.18 Overlay spectra of the IL-doped HPTS, 3% Er^{3+} - Tb^{3+} doped bioactive glass and their combination in form of thin film. (red: 3% Er^{3+} - Tb^{3+} doped bioactive glass, black: HPTS only, blue: HPTS and 3% Er^{3+} - Tb^{3+} bioactive glass.).....	69
Figure 3.19 Normalized overlay spectra of the HPTS and 3% Er^{3+} - Tb^{3+} co-doped bioactive glass in form of thin film. (black: 3% Er^{3+} - Tb^{3+} co-doped bioactive glass, red: HPTS only) (λ_{ex} for the HPTS: 466 nm., λ_{ex} for the bioactive glass: 376 nm).....	70
Figure 3.20 CO_2 induced excitation and emission spectra of the 1% Er^{3+} doped Bioactive glass and HPTS based composite for different concentrations of the CO_2 . a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g:20.0, h: 30.0, i: 40.0, j: 60.0, k:80.0, l:100.0% [CO_2]	71
Figure 3.21 CO_2 induced excitation and emission spectra of the 1% Er^{3+} doped Bioactive glass and HPTS based composite for different concentrations of the CO_2 in the presence of IL. a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g:20.0, h: 30.0, i: 40.0, j: : 60.0, k:80.0, l:100.0% [CO_2].....	72
Figure 3.22 Calibration plots of the composites for different concentrations the CO_2 : a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g: 20.0, h: 30.0, i: 40.0, j: 60.0, k: 80.0, l: 100.0% [CO_2]	73
Figure 3.23 CO_2 induced response of the 1% Er^{3+} doped Bioactive glass and HPTS based composite for 0.0-20.0% [CO_2]	74
Figure 3.24 CO_2 induced excitation and emission spectra of the 5% Tb^{3+} doped Bioactive glass and HPTS based composite for different concentrations of the CO_2 . a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g:20.0, h: 30.0, i: 40.0, j: 60.0, k:80.0, l:100.0% [CO_2]	75

Figure 3.25 CO ₂ induced excitation and emission spectra of the 5% Tb ³⁺ doped Bioactive glass and HPTS based composite for different concentrations of the CO ₂ in the presence of IL. a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g:20.0, h: 30.0, i: 40.0, j: 60.0, k:80.0, l:100.0% [CO ₂].....	75
Figure 3.26 Calibration plots of the IL-free and IL containing composites for different concentrations the CO ₂ : a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g: 20.0, h: 30.0, i: 40.0, j: 60.0, k: 80.0, l: 100.0% [CO ₂].....	76
Figure 3.27 CO ₂ induced excitation and emission spectra of the 3% Er ³⁺ -Tb ³⁺ doped Bioactive glass and HPTS based composite for different concentrations of the CO ₂ . a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g:20.0, h: 30.0, i: 40.0, j: 60.0, k:80.0, l: 100.0% [CO ₂]	77
Figure 3.28 CO ₂ induced excitation and emission spectra of the 3% Er ³⁺ -Tb ³⁺ doped Bioactive glass and HPTS based composite for different concentrations of the CO ₂ in the presence of IL. a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g:20.0, h: 30.0, i: 40, j: 60.0, k:80.0, l:100.0% [CO ₂].....	77
Figure 3.29 Calibration plots of the composites for different concentrations the CO ₂ : a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g: 20.0, h: 30.0, i: 40.0, j: 60.0, k: 80.0, l: 100.0% [CO ₂]	78
Figure 3.30 Decay curves of the IL-doped HPTS in the absence (0.0% pCO ₂) and presence (100.0% pCO ₂) of the CO ₂	80
Figure 3.31 Decay curves of the HPTS and 1393 BO containing composites in the absence (0.0% pCO ₂) and presence (100.0% pCO ₂) of the CO ₂	80
Figure 3.32 Decay curves of the IL, HPTS and 1393 BO containing composites in the absence (0.0% pCO ₂) and presence (100.0% pCO ₂) of the CO ₂	81
Figure 3.33 Decay curves of the IL-free, HPTS and 1% Er doped BO containing composites in the absence (0.0% pCO ₂) and presence (100.0% pCO ₂) of the CO ₂	81
Figure 3.34 Decay curves of the IL, HPTS and 1% Er doped BO containing composites in the absence (0.0% pCO ₂) and presence (100.0% pCO ₂) of the CO ₂ ...	82
Figure 3.35 Decay curves of the HPTS and 5% Tb doped BO containing composites in the absence (0.0% pCO ₂) and presence (100.0% pCO ₂) of the CO ₂ ...	82

Figure 3.36 Decay curves of the IL, HPTS and 5% Tb doped BO containing composites in the absence (0.0% pCO ₂) and presence (100.0% pCO ₂) of the CO ₂	83
Figure 3.37 Decay curves of the HPTS and 3% Er-Tb co-doped BO containing composites in the absence (0.0% pCO ₂) and presence (100.0% pCO ₂) of the CO ₂	83
Figure 3.38 Decay curves of the IL, HPTS and 3% Er-Tb co-doped BO containing composites in the absence (0.0% pCO ₂) and presence (100.0% pCO ₂) of the CO ₂	84
Figure 3.39 Kinetic response of the sensing composite prepared from the IL-Free HPTS- 1393 BO	87
Figure 3.40 Kinetic response of the sensing composite prepared from the IL-Free HPTS- 1% Er-1393 BO	88
Figure 3.41 Kinetic response of the sensing composite prepared from the IL-Free HPTS- 5% Tb-1393 BO	88
Figure 3.42 Kinetic response of the sensing composite prepared from the IL-Free HPTS- 3%Er- Tb-1393 BO	89

LIST OF TABLES

	Page
Table 1.1 Different type of phosphorus, and their potential applications depending on the excitation wavelength and dopant (was taken from: Kasap & Capper, 2017 and re-arranged)	12
Table 2.1 Composition of the utilized phosphors and additives	29
Table 2.2 Decay times of the composites prepared by donor; Quinine Sulphate and their blends including varying amounts of the acceptor counterparts; α -SiAlON:Eu ²⁺ and LuAG:Ce ³⁺	41
Table 3.1 Composition of the utilized test materials.....	55
Table 3.2 I ₀ /I ₁₀₀ parameters of the utilized composites (I ₀ =emission intensity at the 0.0% pCO ₂ I ₁₀₀ = emission intensity at the 100.0% pCO ₂).....	79
Table 3.3 Bi-exponential decays and related statistics (decay time, standard deviation and abundance %) of the IL-free composites.....	85
Table 3.4 Bi-exponential decay times, standard deviation and abundance % of the IL-doped composites	86

CHAPTER ONE

INTRODUCTION

In this thesis we have intended to investigate fluorophore, phosphor or phosphor-blends along with nano-materials in polymeric matrices. Since the phosphorus can find a wide variety of applications from screen technologies and sensors to lighting we focused on this aspect of these materials. We investigated some of the optical properties of phosphors, or phosphor blends along with dyes and or nanomaterials in appropriate polymeric matrices.

In the first part of the thesis, we investigated excitation and emission-behavior of orange and green phosphors of Eu^{2+} activated Ca- α -Sialon (Ca- α -Sialon: Eu^{2+}) and Ce^{3+} doped lutetium aluminum garnet (LuAG: Ce^{3+}) in polymethylmethacrylate (PMMA) matrix along with; quinine sulphate (QS) which is a well-known dye for the fluorescence specialists due to the excellent emission performance, and acceptable stability. We obtained promising results with the blended materials, which may be used for the fabrication of LEDs, smartphone and televisions screens, monitors, and panels of other electronic devices.

In the second part of the thesis, we studied ion-pair form of 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium-salt (HPTS) in an ethyl cellulose (EC) matrix along with ionic liquid and the nano-scale biocompatible-bioactive glasses. When the acid base indicator of HPTS dye used together with the nano-scale bioactive glasses, exhibited enhanced optical brightness as well as high acid-base and carbon dioxide sensitivity. Therefore, we evidenced better CO_2 sensitivity of the proposed material compromising the HPTS and nano-scale bioactive glasses with spectroscopic measurements as well as excited state life times.

1.1 Luminescence

Luminescence can simply be defined as the emission of energy by the excited state electrons of a material either at room temperature or below the room temperature. The luminescence defined here is different from the black body radiation which arises from the thermal spontaneous radiation of ordinary objects heated up to very high temperatures. The luminescence phenomenon can be explained by the Jablonsky's diagram (Lakowicz, 2006).

1.2 Mechanism of Luminescence

Jablonsky diagram explains the excitation (absorption) and emission behavior of the molecules via singlet ground and excited states (S_0 , S_1 and S_2). In all cases, in singlet states the electrons are in paired form. The vibrational states lie between the singlet states. Triplet state on the other hand, bears the excited state electron on a parallel spin with the ground state, which is less possible with respect to the singlet state transitions and therefore called as “forbidden transitions”.

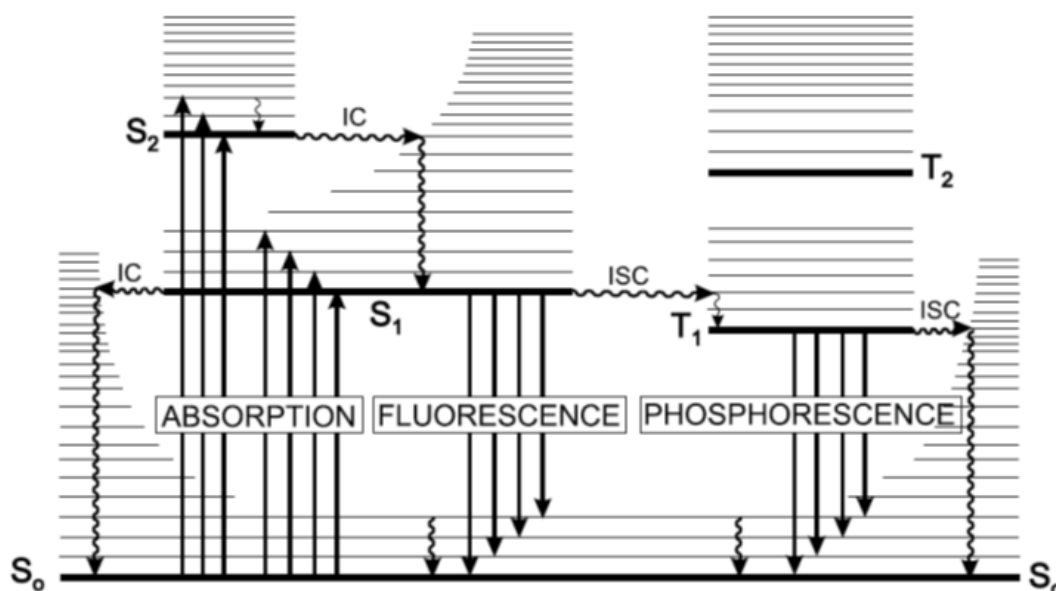


Figure 1.1 Jablonsky diagram (was taken from: Lakowicz, 2006 and re-arranged)

“Internal conversion” can be defined as transition of an electron from a higher to a lower electronic state in molecular structures or atoms, and results in radiationless de-activation where the energy of the excited electron is given off to vibrational levels of the molecule, or to the solvent in form of heat (Lakowicz, 2006).

When a singlet state electron passes to a triplet state converting its spin **“intersystem crossing”** occurs. The radiative transition from an excited triplet level to a singlet is known as **“phosphorescence”**.

1.3 Quantum Yield

Fluorescence quantum yield (Q) is a characteristic property of a fluorophore or phosphor and can be defined as the ratio of photons absorbed by the molecule to the photons emitted. The fluorescence quantum yield can simply be defined by the equation 1.1.

$$Q = \frac{photons_{em}}{photons_{abs}} \quad (1.1)$$

However, for the phosphor type of materials the quantum yield has generally been mentioned as “internal” and “external” quantum efficiency. The internal quantum efficiency is very similar to the former definition and can be explained as the “ratio of the number of photons emitted to the number of photons” absorbed by the sample. The correct measurement of the QY however, relies on the measurement of decay times, and the radiative and non-radiative rate constants. In terms of equation 1.2, it can be written as

$$\Phi = \frac{k_r}{k_{nr} + k_r} \quad (1.2)$$

Where , k_r and k_{nr} are the rate constants for the radiative and non-radiative decays, respectively.

$$k_r = \Phi/\tau \quad (1.3)$$

$$k_{nr} = (1 - \Phi)/\tau \quad (1.4)$$

Φ and τ were extracted from the experiments and k_r and k_{nr} were calculated from the decay time data (Lakowicz, 2006).

1.4 Decay Time

Fluorescence lifetime measurements are informative about on the excited-state reactions, deactivation processes, and energy transfer rates. Lifetime measurements can be performed by two different approaches including “time” and “frequency” domain measurements, respectively.

In time-domain mode a pulsed light source is used and the time-dependent behavior of fluorescence is recorded. In the case of frequency-domain method, a modulated light source is used for excitation of the sample. Lifetime information comes from the difference of the excitation light wave and the emission as a function of time.

For a luminescent material, emission intensity is proportional to the number of the excited molecules in an exponential manner. Depending on mechanism of the quenching the decay may be -mono, -bi or -three exponential.

Figure 1.2 indicates –mono exponential decay form. Herein, the lifetime “ τ ” is the time required for the concentration of emitting species to decrease to $1/e$ (0.37) of its original number.

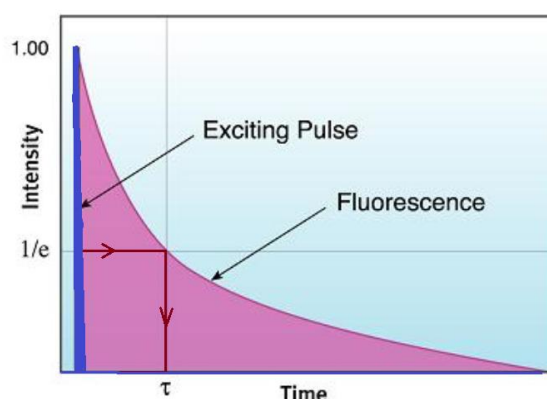


Figure 1.2 –Mono exponential decay of a luminescent material (was taken from: Terpetschnig & Jameson, 2005)

The decays can also be expressed by the following equations.

$$I(t) = I_0 A_1 \exp(-t/\tau_1) \quad (1.5)$$

$$I(t)/I_0 = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1.6)$$

Where equations 1.5 and 1.6 indicate -mono and -bi exponential decays, respectively. I_0 and I are the emission intensities in the beginning of the excitation and at any time after excitation. τ_1 and τ_2 are decay times of the bi-exponential decay, respectively. A_1 and A_2 are the corresponding amplitudes of the decays (Lakowicz, 2006).

1.4.1 Time-Domain Decay Time Measurements by TCSPC Approach

Time-correlated single photon counting (TCSPC) technique uses photons of the excited samples or molecules by a pulsed laser source. When a single photon from the sample arrived at the photomultiplier tube (PMT) of the instrument, the PMT converts the arrived photon to the electron. Meanwhile, the electron pulse is converted to a current. This pulsed current arrives at the Time Amplitude Converter (TAC) which stops and counts the time, where the difference between start and the stop times or “the time delay” has been calculated by the signal processor of the instrument. The

resulting histogram “counts” versus “channels” represents the fluorescence intensity versus time. Decay times can be extracted by using these histograms. Flow diagram of a TCSPC instrument is shown in Figure 1.3.

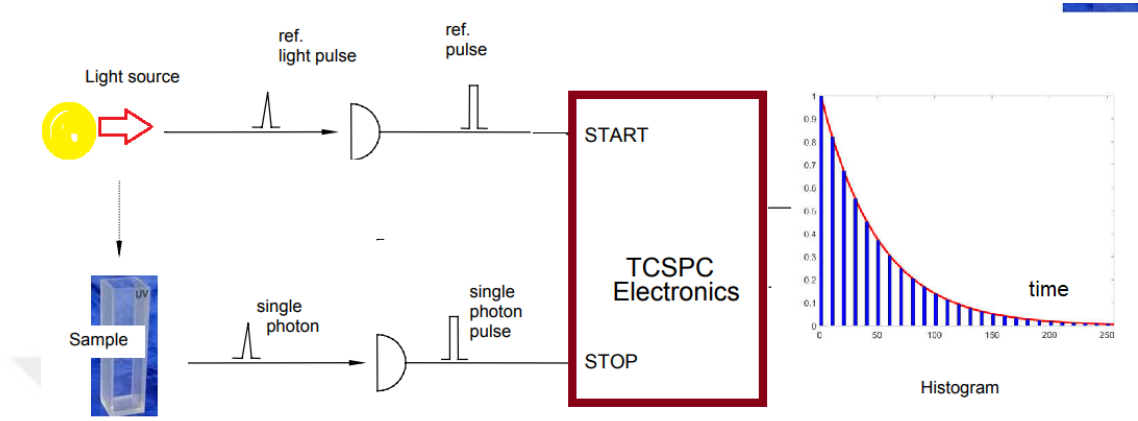


Figure 1.3 Flow diagram of a TCSPC instrument (was taken from: Wolfbeis, 1991 and re-arranged)

1.4.2 Frequency Domain Lifetime Measurement

In frequency-based decay time measurement approach, excitation light is modulated with “angular frequency of ω ” and then, the phase angle was recorded versus time. Fluorescence lifetimes can easily be calculated from the phase shift Φ by using the Equation 1.8 where f and τ are the frequency and decay time, respectively (Wolfbeis, 1991). Figure 1.4 indicates the variation of the phase shift with the time.

$$\tan \Phi = 2\pi f\tau \quad 1.7$$

$$\tau = \frac{\tan \Phi}{2\pi f} \quad 1.8$$

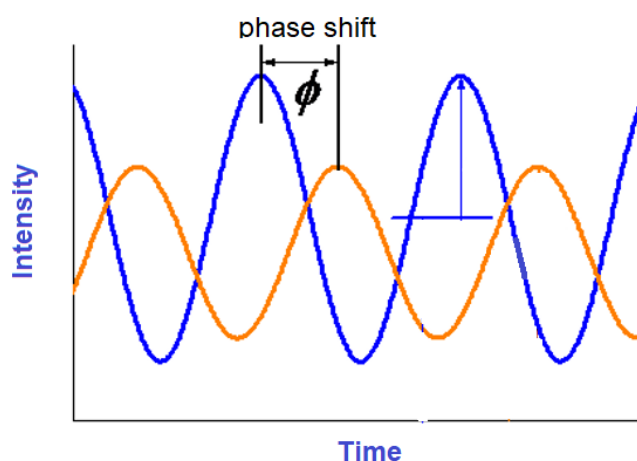


Figure 1.4 Phase shift in frequency domain lifetime measurement (was taken from: Wolfbeis, 1991 and re-arranged)

1.5 Fluorescence Resonance Energy Transfer (FRET)

Fluorescence resonance energy transfer (FRET) is a phenomenon that involves transfer of energy from a donor to an acceptor species (Mahanwar, Patil, Naik & Wakshe, 2019). This kind of energy transfer may take place between molecules in solution or in crystal lattice in solid state.

1.5.1 Dexter and Forster Mechanisms

Fluorescence resonance energy transfer can be explained by Dexter and Forster mechanisms. Dexter energy transfer relies on transfer of an electron from donor to acceptor molecule and requires an overlap between the emission spectrum of the donor and the excitation spectrum of the acceptor. This kind of an overlap is only possible at short distances between the donor and acceptor species; typically, within 10 Å (Libretexts, 2021).

In case of Förster resonance energy transfer (FRET), two chromophores; a donor and an acceptor should take place. The donor species initially should be in excited state. If the donor molecule transfers its energy to an acceptor through a non-radiative dipole-dipole coupling this is the “Förster resonance energy transfer”. The efficiency

of the energy transfer is related to the distance between the donor and acceptor and is inversely proportional to the sixth power of the distance.

Energy transfer reveals itself through quenching of the donor fluorescence and an accompanying decrease of the fluorescence lifetime. Therefore, variation of decay time can be used as an evidence of the FRET (Lakowicz, 2006).

1.6 Florescence and Phosphorescence of Molecular Species

Fluorescence is a process, where excitation of atoms or molecules by electromagnetic radiation results in a radiation when they return to ground state. In case of fluorescence, the excited molecules or atoms yield their energy in a short time range. Probably the most important parameter to differentiate florescence and phosphorene from each other is the duration of the decay which is also known as “decay time”. The radiative decay from an excited singlet state back to ground state (Fluorescence) occurs in the order of 10^{-10} - 10^{-9} nano seconds. On the other hand, the duration of the intersystem crossing and following phosphorescence occurs in the order of 10^{-8} to 10^{-3} seconds (Lakowicz, 2006).

1.7 Molecules Exhibiting Fluorescence Characteristics

There are a lot of molecules exhibiting fluorescent properties. Probably the most common future of these molecules is to have conjugated double bounds in their structure. When they excited, electrons lying on these levels efficiently absorb the light and then the emission occurs. Efficiency of the florescence increases with the number of conjugated double or triple bounds and degree of their condensation. Presence of molecular rigidity enhances the florescence. In case of flexible structures, molecular florescence decreases. There are a lot of external parameters effecting the fluorescence, and in most cases efficiency of the fluorescence decreases with increasing temperature due to the increasing collisions and consequent deactivation processes. Solvents, including heavy atoms like iodide and bromide also decrease the

fluorescence. However, increase in viscosity of the microenvironment of the fluorescent molecule enhances the performance of the emission.

Some examples of the fluorescent molecules are listed below. Some of them are also known as fluorescence quantum yield and lifetime standards.

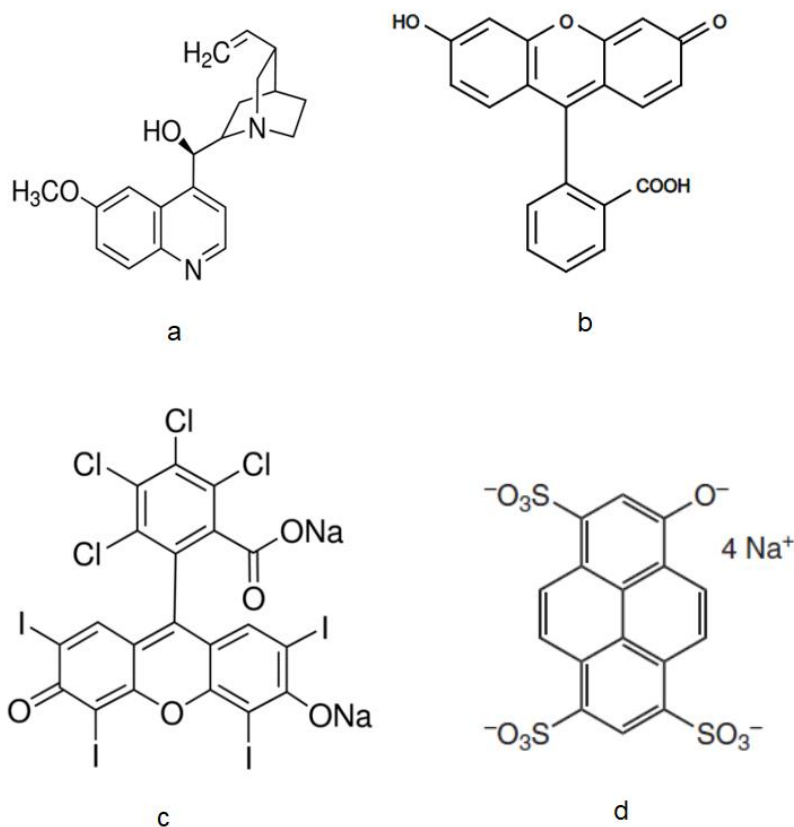


Figure 1.5 Molecular structure of (a) quinine sulfate (QS), (b) fluorescein, (c) rose Bengal, (d) 8-Hydroxypyrene-1,3,6-trisulfonic acid, trisodium salt

1.8 Fluorescence and Phosphorescence of Inorganic Materials

Fluorescence and Phosphorescence are mainly defined for molecular structures dissolved in specific solvents and sometimes in water. However, there are inorganic materials exhibiting fluorescence and more specifically, phosphorescence. Among them phosphors used in color TV screens, LCD displays, laser materials, detectors and scintillators can be encountered. These materials generally exhibit phosphorescence rather than fluorescence. Phosphorescence observed in such kind of materials can be

explained by band structure consisting of a valance and a conduction band. The valance band which is rich from electrons, and the conduction band is empty from electrons with respect to the valance band. The gap lying between these two bands is known as the “band gap”. Donor and acceptor levels within the band gap structure can be created by using specific dopants. The dopant atoms mainly consisting of rear earths or transition metals are located in a crystal lattice which may have different types of geometries.

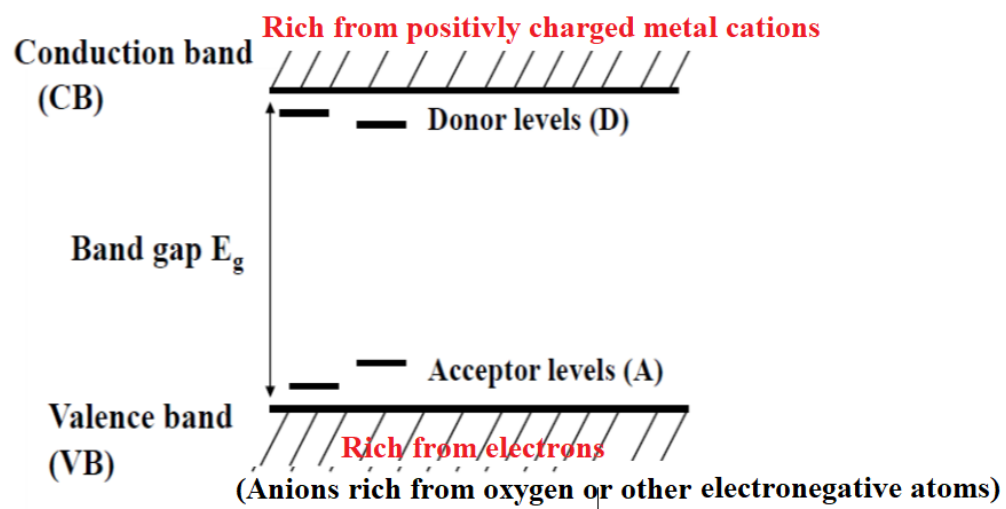


Figure 1.6 Band Structure of Phosphor Materials (was taken from: Kasap & Capper, 2017 and re-arranged)

Energy levels in phosphor-type materials consists of a valance and a conduction band, respectively. Anions containing the electronegative atoms in an augmented manner are located in the valance band. The conduction band however is made up of positively charged metal cations which are lack of electrons. Upon excitation such a material by light, electrons lying in the valance band passes to the conduction band. Meanwhile, dopants taking place in the lattice may also be excited by the same radiation. Energy levels of the acceptors or activators are within the band gap. All these energy uptake is known as absorption. Following the absorption, the excited electrons turn back emitting a radiation generally at longer wavelengths than the excitation the light. A list of representative phosphorus is given below.

Different types of phosphors may exhibit different emission characteristics, for almost all regions of the electromagnetic spectrum from the UV and visible part to the red wavelengths. Phosphors may be fabricated in a variety of formulations for different purposes. Maybe packaged in form of powders and generally micrometer scale particles. They may be in form of Silicates, Garnets, Aluminates or Nitrides and may be doped with appropriate rare-earth according to the purpose. Silicates and garnets may be candidate for display and white light applications. On the other hand, Aluminates, and Nitrides can be used in warm color production. A list of different type of phosphorus, and their potential applications depending on the excitation wavelength and dopant was shown in Table 1.1.



Table 1.1 Different type of phosphorus, and their potential applications depending on the excitation wavelength and dopant (was taken from: Kasap & Capper, 2017 and re-arranged) (Kasap & Capper, 2017)

Host	Dopants	Colour	Excitation	Application
$\text{Bi}_4\text{Ge}_3\text{O}_{12}$	—	Blue	Ionising radiation	Scintillator
Sr_3SiO_5	Eu^{2+}	Blue	UV	White LED
SrGa_2S_4	Eu^{2+}	Green	UV	White LED
SrAl_2O_4	Eu^{2+} , Dy^{3+}	Green	UV, violet	Persistent phosphor
CaAl_2O_4	Eu^{2+} , Nd^{3+}	Blue	UV, violet	Persistent phosphor
BaFBr	Eu^{2+}	UV/blue	X-rays	X-ray imaging
CsBr	Eu^{2+}	Blue	X-rays	X-ray imaging
$\text{BaMgAl}_{10}\text{O}_{17}$	Eu^{2+}	Blue	UV	Fluorescent lamps, plasma displays
SrY_2S_4	Eu^{3+}	Red	UV	White LED
Y_2O_3	Eu^{3+}	Red	Electrons, UV	Plasma displays, fluorescent lamps
Sr_2SiO_4	Eu^{3+}	Yellow	UV	White LED
$(\text{Y}, \text{Gd})\text{BO}_3$	Eu^{3+}	Red	UV	Plasma displays
LaBr_3	Ce^{3+}	UV	Ionising radiation	Scintillator
$\text{Y}_3\text{Al}_5\text{O}_{12}$	Ce^{3+}	Yellow	Blue, violet	White LED
Gd_2SiO_5	Ce^{3+}	UV	Ionising radiation	Scintillator
$\text{Lu}_3\text{Al}_5\text{O}_{12}$	Ce^{3+}	Green	Ionising radiation	Scintillator
$\text{CeMgAl}_{11}\text{O}_{19}$	Tb^{3+}	Green	UV	Fluorescent lamps
LiF	Mg^{2+} and Ti^{4+}	UV/blue	Ionizing radiation	TL dosimetry
$\text{Gd}_2\text{O}_2\text{S}$	Tb^{3+}	Green	X-rays	Intensifying screens
Zn_2SiO_4	Mn^{2+}	Green	UV	Plasma displays
ZnS	Mn^{2+}	Yellow	Electric field	Panel displays

1.8.1 Yellow Phosphors

1.8.1.1 YAG:Ce³⁺

ZnS:Mn²⁺, Y₃Al₅O₁₂, Sr₂SiO₄, YAG:Ce³⁺ and (Sr,Ba)SiO₄:Eu²⁺ are the examples of yellow phosphorus. Among them cerium-activated yttrium aluminum garnet (YAG:Ce³⁺) is probably the most intensively used phosphor for the LED applications together with another phosphor component to generate white light. Different synthetic routes, including, sol-gel, co-deposition, spray pyrolysis, and combustion, were proposed for the synthesis of these kind of garnets (Lei, Chun-Che, Chiao-Wen & Ru-Shi, 2010). A cubic lattice structure has been proposed for the Y₃Al₅O₁₂ where some of the Ce³⁺ ions are replaced by the Y³⁺ ions with in the lattice. The offered structure, and tetrahedral and octahedral sites for the YAG:Ce³⁺ has been shown in Figure 1.7.

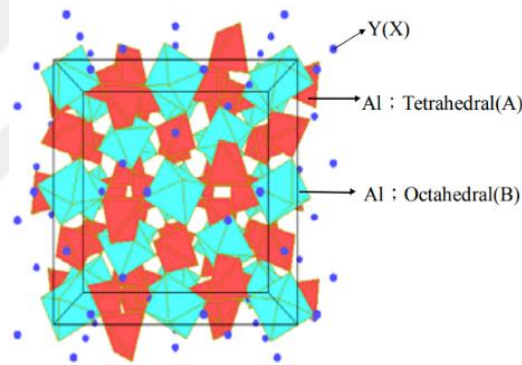


Figure 1.7 Crystal Structure of the YAG:Ce³⁺ (was taken from: Lei, Chun-Che, Chiao-Wen & Ru-Shi, 2010)

In case of Ce³⁺ activated YAG phosphors 4f⁰-5d¹ electrons of the Ce³⁺ undergoes ²D term split (²D_{3/2} and ²D_{5/2}), and, the ground-state 4f¹ configuration splits to ²F_{7/2} and ²F_{5/2} states via spin-orbit coupling due to the different effects of the crystal field parameters of the YAG. Therefore, the broad-band emissions observed for the YAG can be attributed to the presence of the two overlapping sub-bands.

1.8.1.2 Green Phosphors

The formulations including, (Ba,Sr)SiO₄: Eu²⁺, Lu₃Al₅O₁₂: Ce³⁺, Gd₂O₂S: Tb³⁺, SrGa₂S₄: Eu²⁺, SrAl₂O₄: Eu²⁺, Dy³⁺, Zn₂SiO₄: Mn²⁺, and CeMgAl₁₁O₁₉: Tb³⁺ can be listed as examples of the green phosphorus (Kasap & Capper, 2017). Among them, the Ce³⁺ activated LuAG attracts more attention due to the availability of LED applications. Crystal Structure of the Ce³⁺ activated LuAG which is same as the YAG, is shown in Figure 1.8.

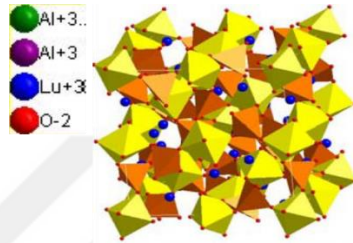


Figure 1.8 Cubic Crystal Structure of the Ce³⁺ activated LuAG (was taken from: Lei, Chun-Che, Chiao-Wen & Ru-Shi, 2010).

The difference in the emission color can be assigned to the parity-allowed 4f¹-4f⁰ 5d¹ transition of Ce³⁺ and differences of the microenvironment of the dopant ion; Ce³⁺ in the lattice.

1.8.1.3 Red Phosphors

Y₂O₃:Eu³⁺, (Y,Gd)BO₃:Eu³⁺, SrY₂S₄:Eu³⁺ and SiN₄-based phosphors can be encountered as the examples of red phosphors. Among them, the nitride-aluminosilicates, nitride-silicates, sialons, and nitrides, can find more application for the design of the LEDs. In most of the red phosphors the Eu³⁺ has been used as the dopant ion. Excitation and Emission Characteristics of the Ca-α-SiAlON:Eu²⁺ has been discussed into detail in further chapters.

CHAPTER TWO

QUININE SULPHATE

2.1 Enhancement of Optical Properties of $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ and $\text{Ca-}\alpha\text{-Sialon}:\text{Eu}^{2+}$ by Quinine Sulphate

In this chapter, photoluminescence properties of green and orange phosphors of Ce^{3+} doped lutetium aluminum garnet ($\text{LuAG}:\text{Ce}^{3+}$) and Eu^{2+} activated $\text{Ca-}\alpha\text{-Sialon}$ ($\text{Ca-}\alpha\text{-Sialon}:\text{Eu}^{2+}$) have been studied in the entrapped form in Polymethyl methacrylate (PMMA) matrix. On the other hand, Quinine sulphate (QS), which is known as a quantum yield standard with excellent emission performance, has been investigated many times, for different purposes. Herein, we investigated excitation and emission-behavior of quinine sulphate-phosphor blends consisting of $\text{LuAG}:\text{Ce}^{3+}/\text{QS}$ and $\text{Ca-}\alpha\text{-Sialon}:\text{Eu}^{2+}/\text{QS}$ in polymethylmethacrylate matrix; for the first time. The $\text{Ca-}\alpha\text{-Sialon}$ exhibited approximately 44% increase in the emission intensity when encapsulated along with the Quinine sulphate in the solid state. Similarly, the $\text{LuAG}:\text{Ce}^{3+}$ exhibited 98% increased brightness when used in QS containing PMMA matrix. Decay time measurements performed in nanosecond and microsecond time scales supported a potential energy transfer from QS to the phosphors. The promising results obtained in this study may open a cost-effective way to enhance the optical performance of the both phosphors, which are basic materials for the fabrication of LED bulbs, smartphone and televisions screens, monitors, and panels of other electronic devices.

2.2 Introduction

Today, phosphors in a wide spectrum of colors have been used in a variety of manufacturing processes, including display technologies, LED lighting, scintillators, and detectors. Among them, the orange-colored Eu^{2+} doped $\text{Ca-}\alpha\text{-Sialon}:\text{Eu}^{2+}$ and green-colored Ce^{3+} activated lutetium aluminum garnet; $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$; have been extensively studied due to their broad-band and efficient emission characteristics. The

Ca- α -Sialon has a high importance due to its potential warm-luminescence producing ability when coupled to a blue light-emitting diode. After the discovery of β -Sialon (Oyama & Kamigaito, 1971) and α -Sialon in 1971 and 1972 (Jack & Wilson, 1972), the first report indicating the structure of Ca- α -Sialon, has been published by Hampshire and co-workers (Hampshire, Park, Thompson & Jack, 1978). In the following years, its structure and optical properties have been studied many times (Liu, et al., 2006; Shioi, Hirosaki, Xie, Takeda & Li, 2010; Sakuma, Hirosaki, Xie, Yamamoto & Suehiro, 2007; Shioi, Hirosaki, Xie, Takeda & Li, 2010; Van Krevel, Van Rutten, Mandal, Hintzen & Metselaar, 2002; Xie, Hirosaki, Mitomo, Sakuma & Kimura, 2006; Xie, Hirosaki, Sakuma, Yamamoto & Mitomo, 2004; Xie, et al., 2005). Most of the efforts were focused on manipulation of the physical properties of the phosphors by modifying cations of general sialon structure; $[M_x(\text{SiAl})_{12}(\text{ON})_{16}]$; where “M” may be Ca, Mg, Li or Y, or sometimes lanthanide metals. The purely nitride or nitrogen-rich Ca- α -SiAlONs have been synthesized, exhibiting an increased red-shift compared to their oxygen-containing counterparts (Li, Hirosaki, Xie, Suehiro & Mitomo, 2007; Park, Song, Moon, Kang & Yoon, 2010; Xianqing, Machida, Horikawa & Hanzawa, 2008; Yang, Song, Bian & Liu, 2012). Over the years, spectral properties of the nitrogen-rich and oxygen-containing Ca- α -Sialon, have been widely researched by changing the doping elements and their concentration (Jian-Jun, 2012). Chen and co-workers published synthesis and optical properties of Ca- α -Sialons including different concentrations of Eu^{2+} emitting between 500 -700 nm, covering the yellow and orange spectral bands of the electromagnetic spectrum (Chen, Xu, Yu, Chen & Zeng, 2015). Pawlik et al. (Pawlik et al., 2016) and then, Wu and co-workers (Wu et al., 2014) presented different synthesis approaches for the fabrication of Eu-activated Ca- α -Sialons. In two different recent works, persistent or long persistent luminescence of the oxynitrides (Wang et al., 2020) and broad band emission of single-crystal $\text{CaAl}_2\text{Si}_4\text{N}_8\text{:Eu}^{2+}$ were discussed, respectively (Suda et al., 2020). Due to the increasing commercial importance, intensive studies on the red-emitting phosphors to enhance their spectral properties in terms of brightness, stability, and cost-effective production, are still ongoing.

Similar to the Sialon-type phosphors, the green-emitting Ce^{3+} -activated lutetium aluminum garnets ($\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$) have also widely been utilized in general lighting as LED phosphors, backlights of LCD display and smartphones, for lighting purposes in the automotive industry, monitors, televisions and, in any field requiring intense-broadband visible emission. Two maximum observed around 340 nm and 445 nm in the excitation spectrum of the $\text{LuAG}:\text{Ce}^{3+}$ can be assigned to the electron transitions from the lower energy 5d bands of the Ce^{3+} . The excitation potential at 450 nm, and following emission between 480 and 600 nm makes it a highly potential coupling material to blue light-emitting diodes (Kim, Kim, Lee & Kang, 2012; Ogiegło et al., 2012). Similar to the SiAlONs, the lutetium aluminum garnets have also been subject of the efforts in terms of compositional substitution to manipulate the excitation or emission maximum to shorter or longer wavelengths or to enhance the internal and external quantum efficiency of the phosphor (Dorenbos, 2002; Mateika, Völkel & Haisma, 1990; Wu, Gundiah & Cheetham, 2007).

Herein, we investigated luminescence properties of the Eu^{2+} activated Ca- α -sialon and Ce^{3+} doped lutetium aluminum garnet, in the presence of quinine sulphate (QS) in embedded form in polymethyl methacrylate matrix for the first time considering applications made by blue LEDs, mobile phones, monitors, televisions, and other indoor and outdoor lighting requirements. Up to now, the QS has widely been used as an accepted quantum yield standard for fluorescence spectroscopy in the solution phase due to excellent properties, robust molecular structure, efficient emission performance, and reliable results (Fletcher, 1969; Himel & Mayer, 1970; Kristoffersen, Erga, Hamre & Frette, 2014). There are also many experimental studies where the quinine sulphate has been used as an energy transfer agent along with molecules or quantum dots (Mahanwar et al., 2019; Li, Zhang, Du & Lu, 2003; Singh, Iyer & Giri, 2012; Patil, Bhattar, Kolekar & Patil, 2011). However, utilization of this molecule in a solid-state along with phosphors is very rare. Rohwer and Martin proposed a method for determination of the quantum efficiency of conventional phosphor powders and quinine sulphate relying on the absorption of diffuse light in an integrating sphere. In this work, they reported quantum efficiency of the QS as $51.34\% \pm 0.605\%$ (Rohwer & Martin, 2005). Similarly, Osawa et al. used the QS in solid form

in a quantum efficiency measurement system for powder samples (Osawa, Haruta & Ohkubo, 2013). There are a few earlier reports indicating the utilization of the QS as a reference standard (Osawa, Haruta & Ohkubo, 2013; Rohwer & Martin, 2005). However, to the best of our knowledge, this is the first study in which phosphors and quinine sulphate were used together in a solid state to make a new and brighter phosphor blend.

The PMMA was chosen as matrix material due to excellent optical transparency in visible region, high light guidance, high resistance to sunlight exposure, and potential applications in optics, electronics and photonics. The commercially available Ca- α -Sialon: Eu^{2+} and LuAG: Ce^{3+} along with quinine sulphate were used in form of binary mixtures in the PMMA where the phosphor particles can exactly be considered as individual swimmers in the QS sea. Utilization of the PMMA was also important for the successful preparation of the homogeneous mixtures of high-density phosphors of Ca- α -Sialon: Eu^{2+} and LuAG: Ce^{3+} (4.7 and 6.73 g/cm³). The phosphors were used without further grinding considering the former studies indicating at the particle size of 20 μm the quantum efficiency of the phosphor reaches its maximum value (Liu, 2012). In this work average diameter of the phosphors was found to be 15 μm . Herein, we referred to the Ca- α -Sialon: Eu^{2+} and cerium-doped lutetium aluminum garnet ($\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$) as SiAlON and LuAG, respectively.

When the Eu^{2+} activated Sialon was embedded along with the QS in the PMMA, the brightness of the phosphor was enhanced 48 % in comparison to its individual form. Similarly, the LuAG: Ce^{3+} exhibited 98 % enhancement in emission intensity, in the same moiety. In this study, nano- and micro-second regime decay times have been measured and reported. Interestingly, when the SiAlON dusts are encapsulated in a QS-doped PMMA matrix, exhibited increased average decay time from 313 to 410 ns, with respect to their bare form. The excitation capability of the offered system by a blue LED and computability with fiber optics look like further advantages. Additionally, light-induced interactions between the SiAlON and quinine sulphate, and, the LuAG and QS are promising and may provide a cost-effective way to enhance

the optical properties of the both phosphors, other than co-doping with another transition metal or rare-earth.

2.3 Experimental Method and Instrumentation

2.3.1 Reagents

In this part of the study, we used two different phosphors along with an organic dye, which were all commercially available chemicals. The green phosphor; Ce³⁺-equipped lutetium aluminum garnet (LuAG:Ce³⁺) was provided from Mitsubishi Chemicals. The orange phosphor; Ca- α -Sialon:Eu²⁺ (NIMS standard) was purchased from Sialon Corporation Ltd. The polymeric matrix material of Polymethyl methacrylate (PMMA), and its solvent; tetrahydrofuran (THF), the quinine sulphate (QS) and absolute ethanol (EtOH) were provided from Sigma-Aldrich Company. Ethanolamine, isopropyl alcohol and acetic acid, were from Merck.

2.3.2 Instruments

Excitation-emission based spectral data of the samples were acquired by a spectrofluorometer (Edinburgh Inst., FLS920) which was equipped with a 150 W Xe lamp as the light source. Steady-state measurements were performed under xenon lamp excitation.

The excited-state lifetime data were acquired by using time correlated single photon counting mode (TCSPC) of the instrument which measures fluorescence decays in the time domain.

In this technique, time of arrival of each photon was correlated to the laser pulse and this was used for the excitation of the sample. This process can be repeated many times using a pulsed laser with a high repetition rate, therefore the photon distribution over the time and the spatial coordinates is formed.

In this thesis, we used femtosecond pulsed laser sources of 367 nm and 467.8 nm for the nanosecond time regime measurements. A microsecond flash lamp was used for the “microsecond time zone”. The instrument was working in the time-correlated single-photon counting (TCSPC) mode. The excitation and emission slits were adjusted to 1.5 and/or 5.0 nm, during the steady-state mode studies. A commercially available colloidal silica suspension in water (LUDOX 30%, Sigma-Aldrich) was used in order to avoid the scattering. Instrument Response Function (IRF) records was performed by the Ludox and recorded data were de-convoluted from the real decay time data.

Crystal structures of the used phosphorus of LuAG:Ce³⁺ and Ca- α -Sialon:Eu²⁺ were recorded by a “Cu K α source equipped X-ray diffraction spectrometer” from Thermo-Scientific. Zeiss Sigma-500 scanning electron microscope was used for clarification of the particle morphologies of the samples and the average particle diameters were found to be 9.8 and 15.9 micrometer for the LuAG:Ce³⁺ and Ca- α -Sialon:Eu²⁺, respectively. The X-Ray Photoelectron Spectroscopy analysis of the phosphor powders was carried out with a Thermo-Scientific XPS instrument; bearing an Al-K α source. A photograph of the spectrofluorometer was shown in Figure 2.1.

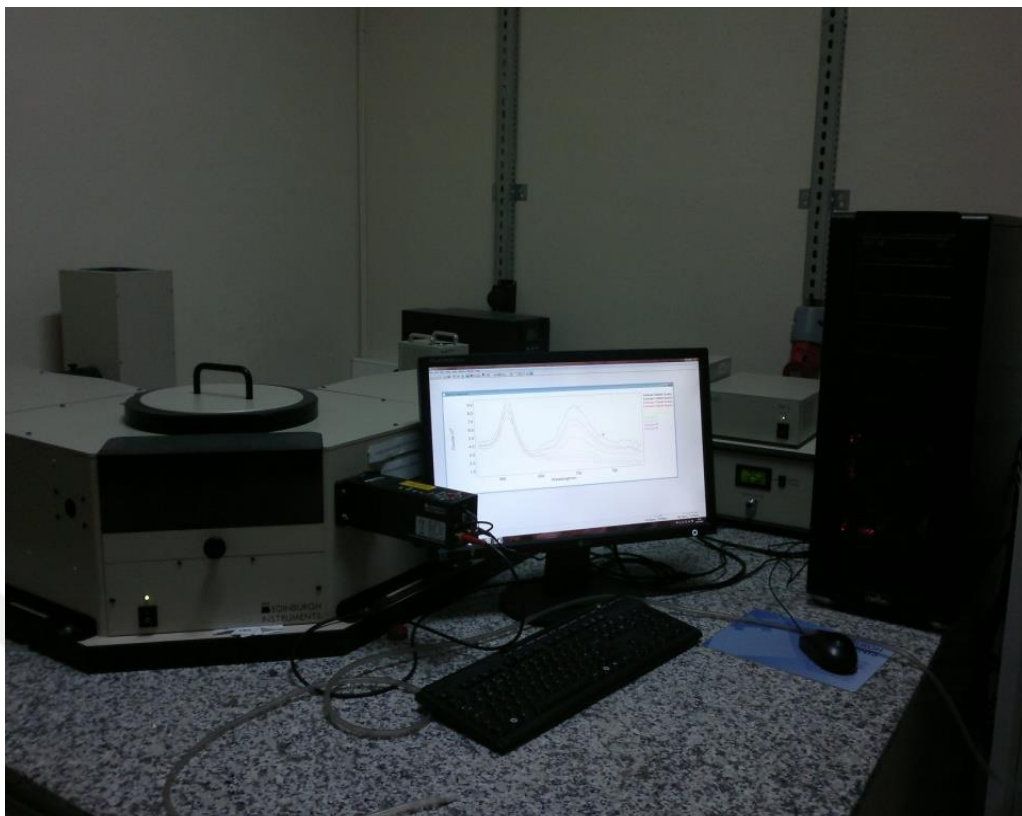


Figure 2.1 Photograph of the used spectrofluorometer instrument

2.3.3 XRD and XPS Spectra of the Utilized Particles

2.3.3.1 XRD and XPS Spectral Data of the LuAG

The XRD patterns of the matrix-free LuAG powders revealed presence of the single phase, indicating Aluminum Lutetium Oxide ($\text{Lu}_3\text{Al}_5\text{O}_{12}$) structure. The recorded data was in accordance with the JCPDS card number of 73-1368. Figure 2.2 reveals XRD patterns of the used LuAG powders. No visible impurity phases were detected in the XRD patterns of the phosphor.

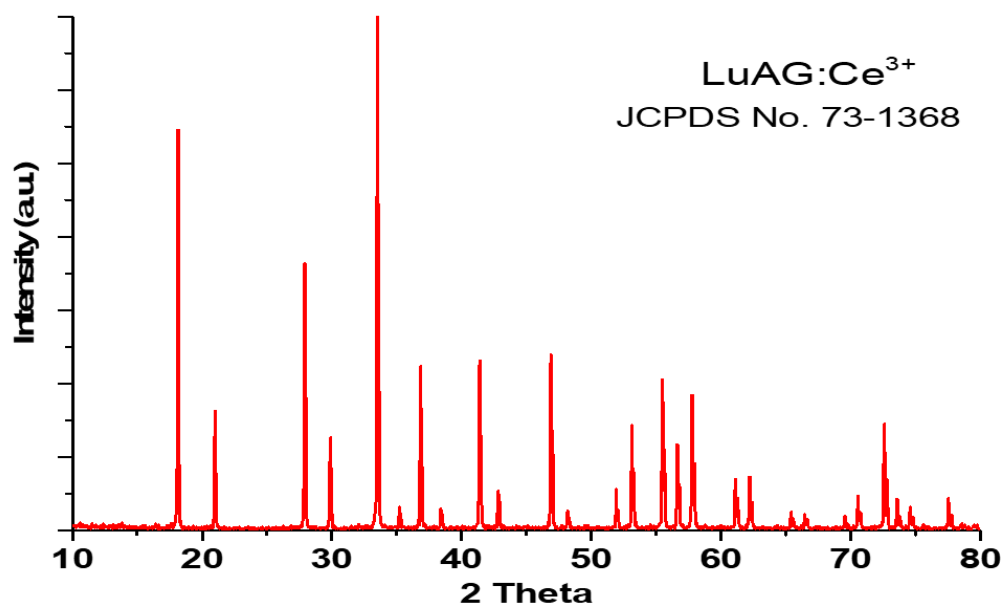
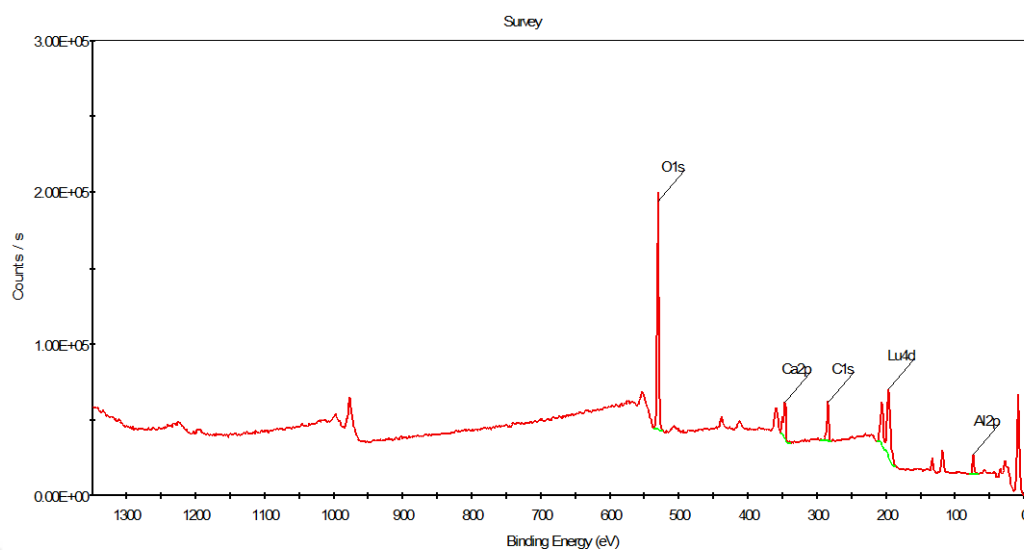


Figure 2.2 XRD patterns of the LuAG:Ce³⁺

2.3.3.2 XPS Spectrum of the LuAG

XPS spectrum of the LuAG was recorded by using an Al K Alpha source and is shown in Figure 2.3. Elemental ID analyses of the spectra indicated existence of the Oxygen, Lutetium and Aluminum by O1s, Lu4d and Al2p excitation peaks in the phosphor.



LuAG:Ce ³⁺		
Name	Peak BE(eV)	Weight %
O1s	530.32	30.83
C1s	285.14	12.99
Ca2p	347.16	5.48
Al2p	74.98	17.41
Lu4d	197.08	33.12
Ce3d	880.01	0.17

Figure 2.3 XPS spectrum of the LuAG including binding energies and quantification information of the elements

Further HR-XPS scans of the LuAG over Lu4d, Al2p, and O1s are given in Figure 2.3-b. The peaks of the Al, Lu, and O located at the binding energies of 74.98, 197.08, and 530.32 eV (see Table 2), evidences the oxidation states of the metals and

oxygen in the LuAG is in the form of Lu^{3+} , Al^{3+} , and O^{2-} , respectively (Yildirim, Dalmis, Ertekin, Birlik & Azem, 2020).

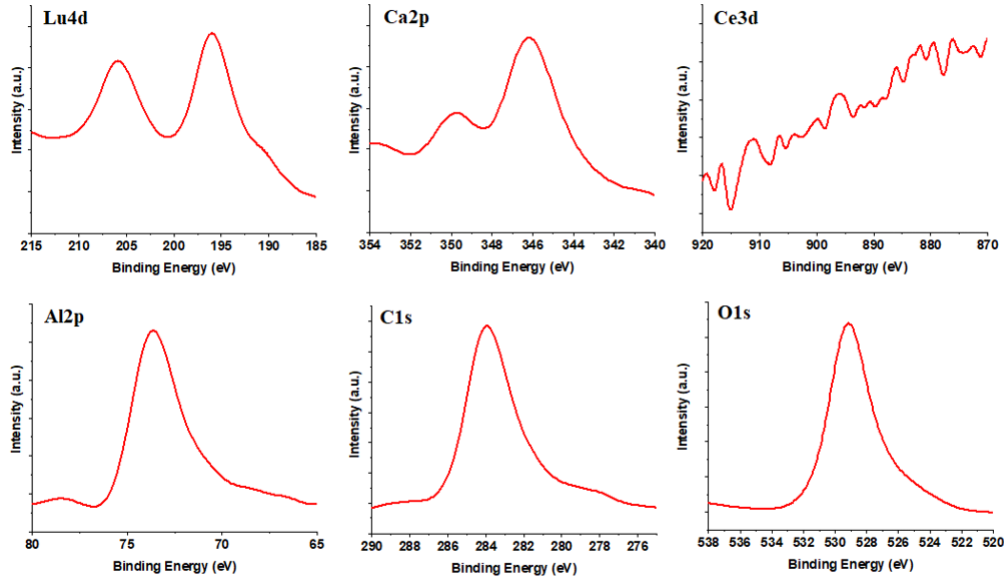


Figure 2.4 High resolution XPS survey scans of LuAG:Ce³⁺

2.3.4 XRD and XPS Spectral Data of the SiAlON

2.3.4.1 XRD Patterns of the SiAlON

The XRD patterns of the matrix-free Ca- α -Sialon: Eu²⁺ powders revealed presence of the single phase. The recorded data was in accordance with the JCPDS card number of 33-0261. Figure 2.5 reveals XRD patterns of the used Ca- α -Sialon:Eu²⁺ powders. No visible impurity phases were detected in the XRD patterns of the phosphor.

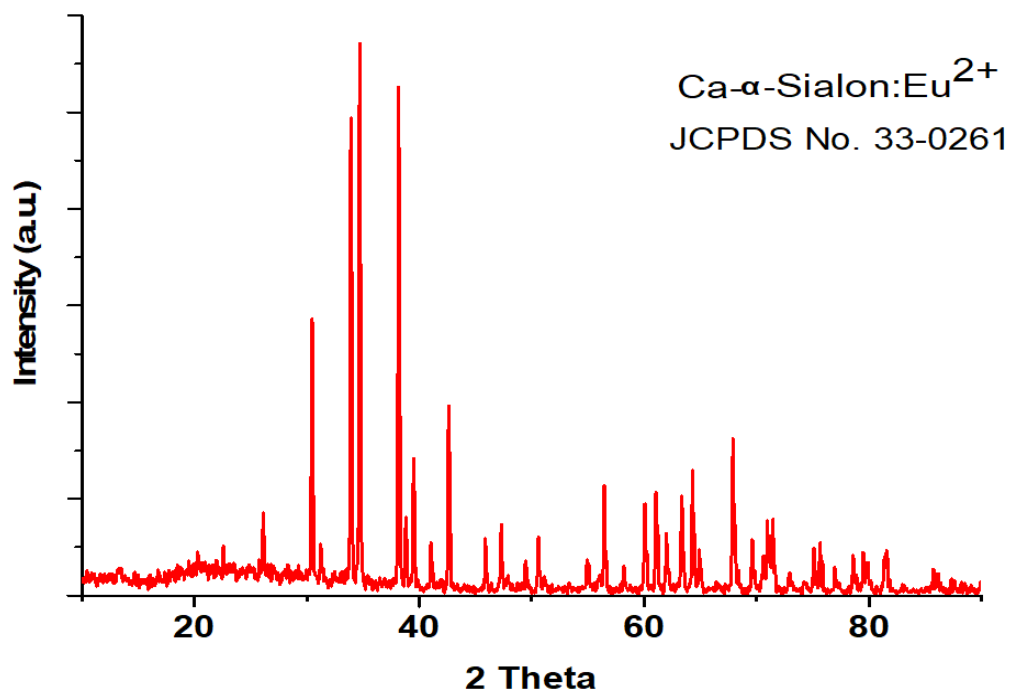
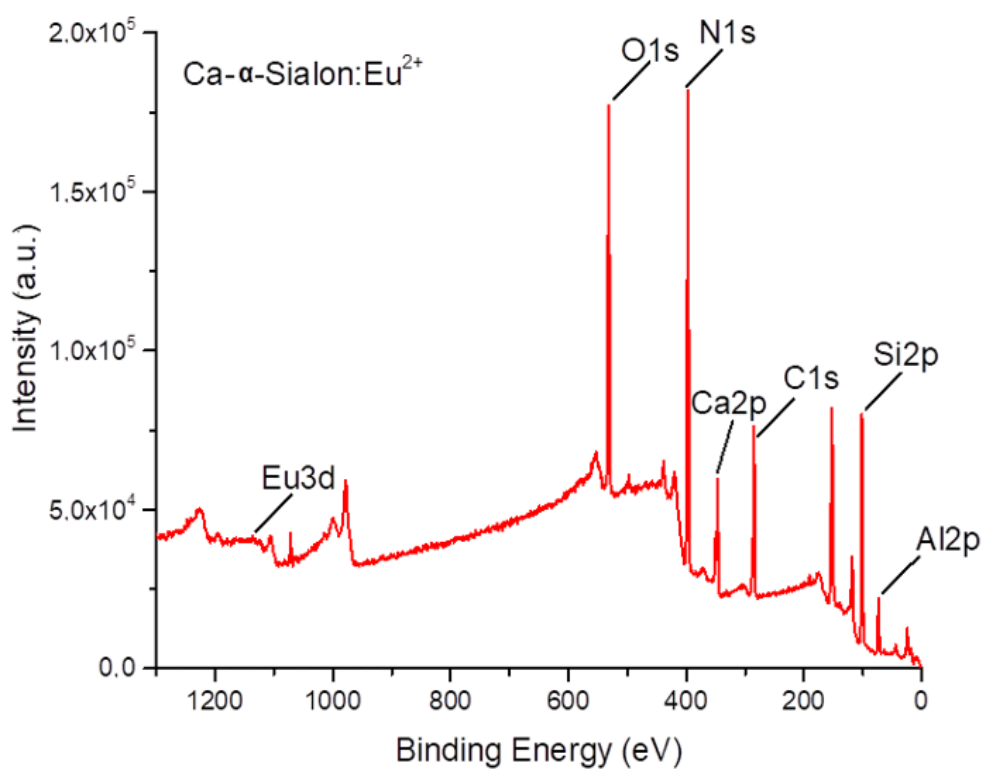


Figure 2.5 XRD patterns of the used Ca- α -Sialon:Eu²⁺ powders

2.3.4.2 XPS Spectrum of the SiAlON

XPS scans of the matrix-free SiAlON supported the presented formulation Figure 2.6 indicates binding energies and percentage composition of the related peaks. The peaks of 1122.08, 531.88, 397.23, 347.06, 285.05, 101.88, and 73.85 eV, reveals presence of the elements of Eu, O, N, Ca, C, Si and Al, for the SiAlON phosphor, respectively. The high-resolution XPS scans, over O1s, C1s, Ca2p, Al2p, Eu3d, Si 2p and N1s revealed the oxidation states of the O²⁻, C⁴⁺, Ca²⁺, Al³⁺, Eu²⁺, Si⁴⁺ and N³⁻, respectively.



Ca- α -SiAlON:Eu ²⁺		
Name	Peak BE(eV)	Weight %
O1s	531.88	15.08
C1s	285.05	11.23
Ca2p	347.06	5.31
Al2p	73.85	12.21
Eu3d	1122.08	1.03
Si2p	101.88	32.63
N1s	397.23	22.50

Figure 2.6 XPS spectrum of the SiAlON including binding energies and quantification information of the elements

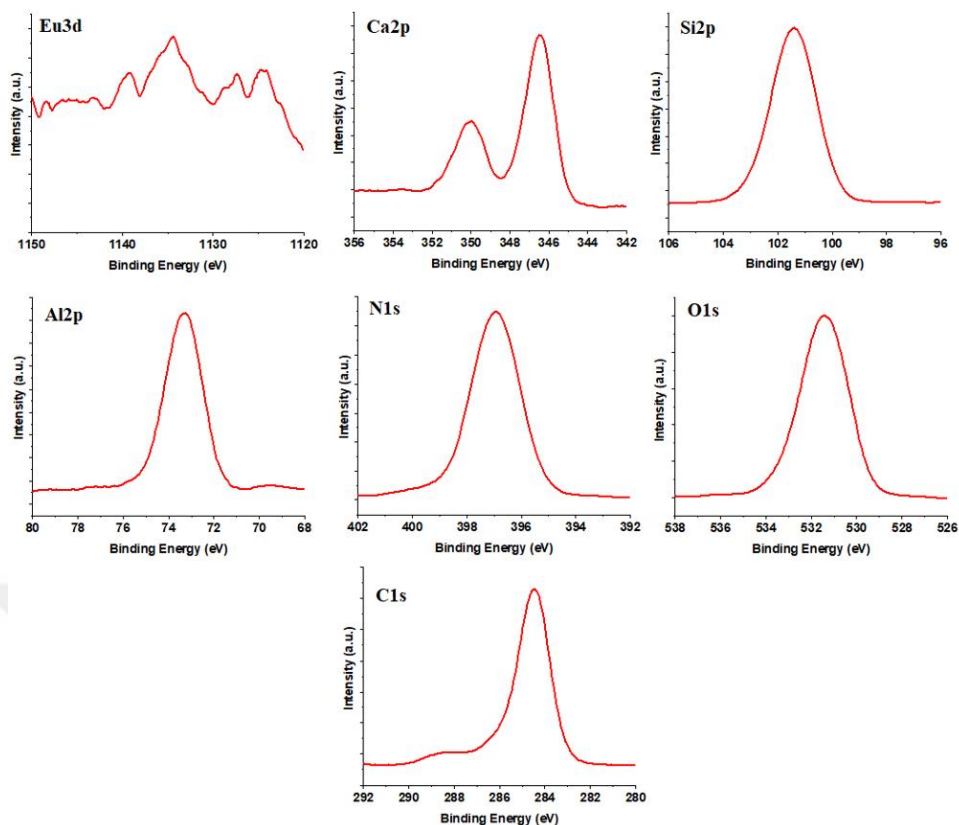


Figure 2.7 High resolution XPS spectrum of the SiAlON

2.3.5 Morphology and Size of the Utilized Particles

SEM images clarified morphologies and average sizes of the phosphors. The LuAG exhibited a micro-scale size distribution and well-shaped spherical morphology. However, the SiAlON exhibited equiaxed grains with elongated morphology. SEM images of the LuAG:Ce³⁺ and Ca- α -Sialon:Eu²⁺ under different magnification were shown in Figure 2.8 -a, -b, -c and -d, respectively.

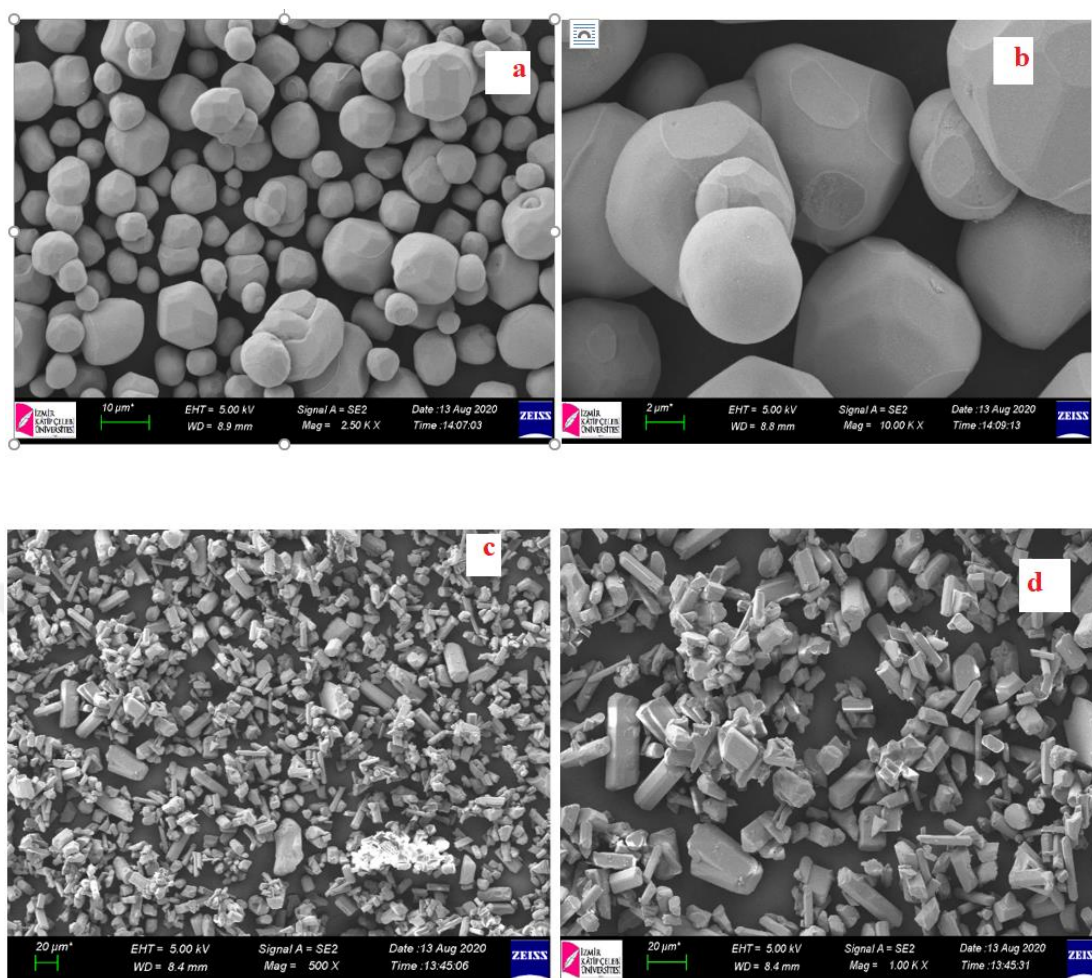


Figure 2.8 SEM images of the LuAG:Ce³⁺ and Ca-α-Sialon:Eu²⁺ under different magnification were shown in figure -a, -b, -c and -d, respectively

2.3.6 Composition, Spectral Results and Optical Properties of the Utilized Materials

Photoluminescent properties of the quinine sulphate (QS) and phosphors were examined when they are individually encapsulated and, in form of their binary mixtures with the QS in the PMMA, respectively. Composition of the utilized phosphors and additives were shown in Table 2.1. The presented composition given in Table 2.1 was prepared in 25 mL of glass vials under magnetic string until a homogeneous mixture was obtained.

Table 2.1 Composition of the utilized phosphors and additives

Phosphor (5 mg)	Matrix (mg)	Additive (5 mg)	Solvent (mL)
LuAG:Ce ³⁺ 5mg	PMMA 120	-	THF 1 mL
LuAG:Ce ³⁺ +QS 2.5 mg+2.5 mg	PMMA 120	QS	THF 2 mL
Ca- α -SiAlON:Eu ²⁺ 5mg	PMMA 120	-	THF 1mL
Ca- α -SiAlON:Eu ²⁺ + QS 2.5mg+2.5 mg	PMMA 120	QS	THF 2mL

The excitation wavelength of the QS and phosphors were quite different from each other. While, the QS; alone could be excited at short wavelengths (λ_{ex} =305 nm), the green and orange phosphors were suitable for excitation at longer wavelengths (405 and 450 nm). Therefore, we examined the excitation abilities at different wavelengths for their blends considering their potential utilization in LED applications or screen technologies.

2.3.7 Spectral Properties of the PMMA Embedded Quinine Sulphate (QS)

Quinine sulphate (QS); has frequently been used as a standard for evaluation of luminescence quantum efficiency and the calibration of spectrofluorimeter due to its high fluorescence intensity and stability in solutions of sulphuric acid. Despite a reported ascending forward red -shift in the emission maximum of quinine sulfate dihydrate as the excitation energy increases from 230 to 360 nm; the NIST has been accepted the QE value of the 0.01 M quinine sulfate dihydrate in 1 N H₂SO₄ as 52% (Rohwer, Martin & Lumin, 2005). Herein, the QS has been chosen as an additive as well as reference material due to its resistivity towards oxygen, and, almost constant quantum efficiency over a range of excitation wavelengths. In this work, during the preparation of the phosphor-free QS-based thin films and composites, the quinine sulphate has completely been solved in THF and then added into the viscous solution

of the PMMA. The spectral data were acquired after the solidification of the thin films. In preparation of the binary mixtures, phosphor powders were added into the QS containing PMMA matrix. Therefore, the microenvironment of each phosphor particle was surrounded by evenly distributed QS molecules. In order to understand the issue of which chromophore have the potential to transfer energy to each other, we investigated spectral properties of the fluorescent materials, individually and, in form of binary mixtures, respectively. We also tested the spectral response of the QS at three different excitation energies; 354, 405, and 450 nm, to evaluate its behavior when tested along with the phosphors.

Normalized excitation-emission spectra of the PMMA encapsulated quinine sulphate acquired from a thin film were shown in Figure 2.9.

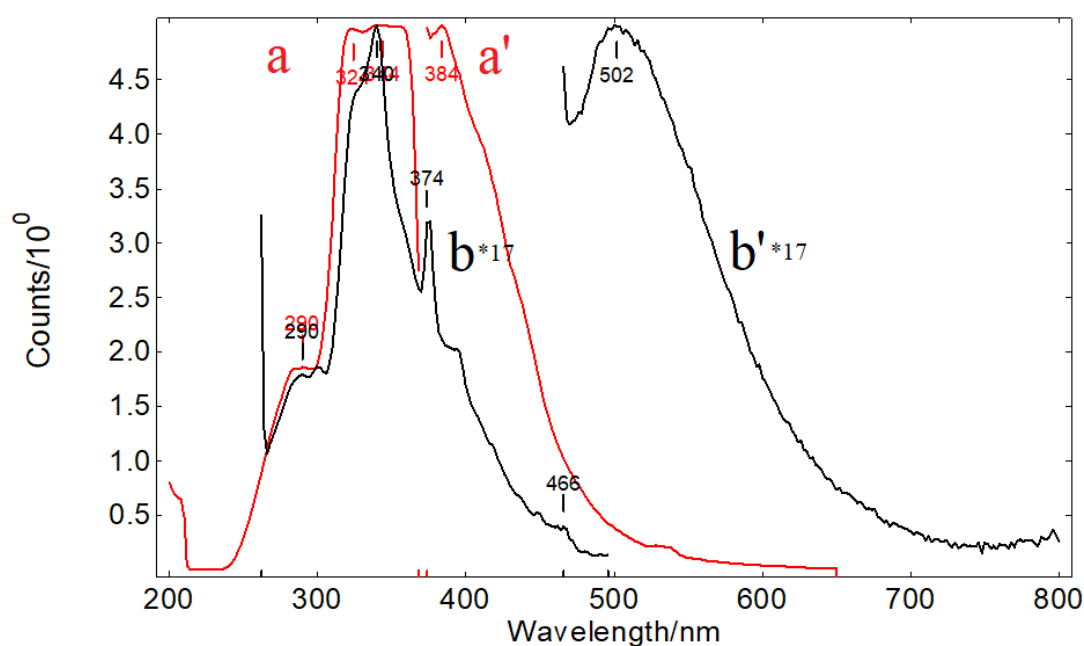


Figure 2.9 Normalized excitation-emission spectra of quinine sulfate in thin film form in PMMA (a and a', $\lambda_{ex}=354$ nm, $\lambda_{em}=390$ nm, b and b': $\lambda_{ex}=405$ nm, $\lambda_{em}=502$ nm)

The PMMA embedded QS exhibited an intense emission maximum at 384 nm, upon excitation at 354 nm. When excited by 405 nm of radiation, the broad band emission maximum shifted to longer wavelengths and centered around 502 nm,

exhibiting an increase in the Stokes shifts and a decrease the emission intensity. Similar observations were recorded for the excitation performed at 450 nm. In the case of 405 nm excitation, the intensity of the emission band was about one in 17th of the emission intensity obtained by the 354 nm excitation (See Fig. ..). The enhancement of Stoke's shift from 30 to 148 nm, can be attributed to the effective transition of the excited state electrons within the vibrational sub-orbitals of the QS and following strong internal conversions due to the different structural perturbation of the vibronic levels by different excitation energies. In both cases, the observed excitation spectrum can be attributed to the $\pi-\pi^*$ and $n-\pi^*$ transitions of the QS molecule along with the other two higher electronic-state transitions lying between the 200 and 300 nm range. Conjugation in the asymmetric QS molecule and internal charge transfer contributes to the bright emission of the QS.

2.3.8 Excitation-Emission Behavior of the SiAlON and the Binary Mixtures with Quinine Sulphate

To realize the light-induced interactions between the SiAlON and the quinine sulphate; spectral behavior of both forms has been studied when they are encapsulated separately and together in form of binary mixtures, in the PMMA respectively (See Figure 2.10-I and -II). The two excitation maximum recorded at 324 and 396 nm for the PMMA-embedded SiAlON, corresponds to the host lattice absorption and the $4f^7 \leftrightarrow 4f^6 5d^1$ transitions of the Eu^{2+} , respectively (See Figure 2.10-I). In the emission side, the intense band (exhibiting a half bandwidth of 100 nm) centered in the spectrum at 590 nm, originates from the allowed $4f^6 5d \rightarrow 4f^7$ transitions of the divalent europium. In our case, the typical luminescence of Eu^{3+} originating from multiplet structure of trivalent $4d^4 f^6$ configurations, has not been not observed, which appears as sharp lines between 580 and 650 nm, suggesting that the trivalent state of the europium ion in SiAlON [40] (Xie vd., 2004).

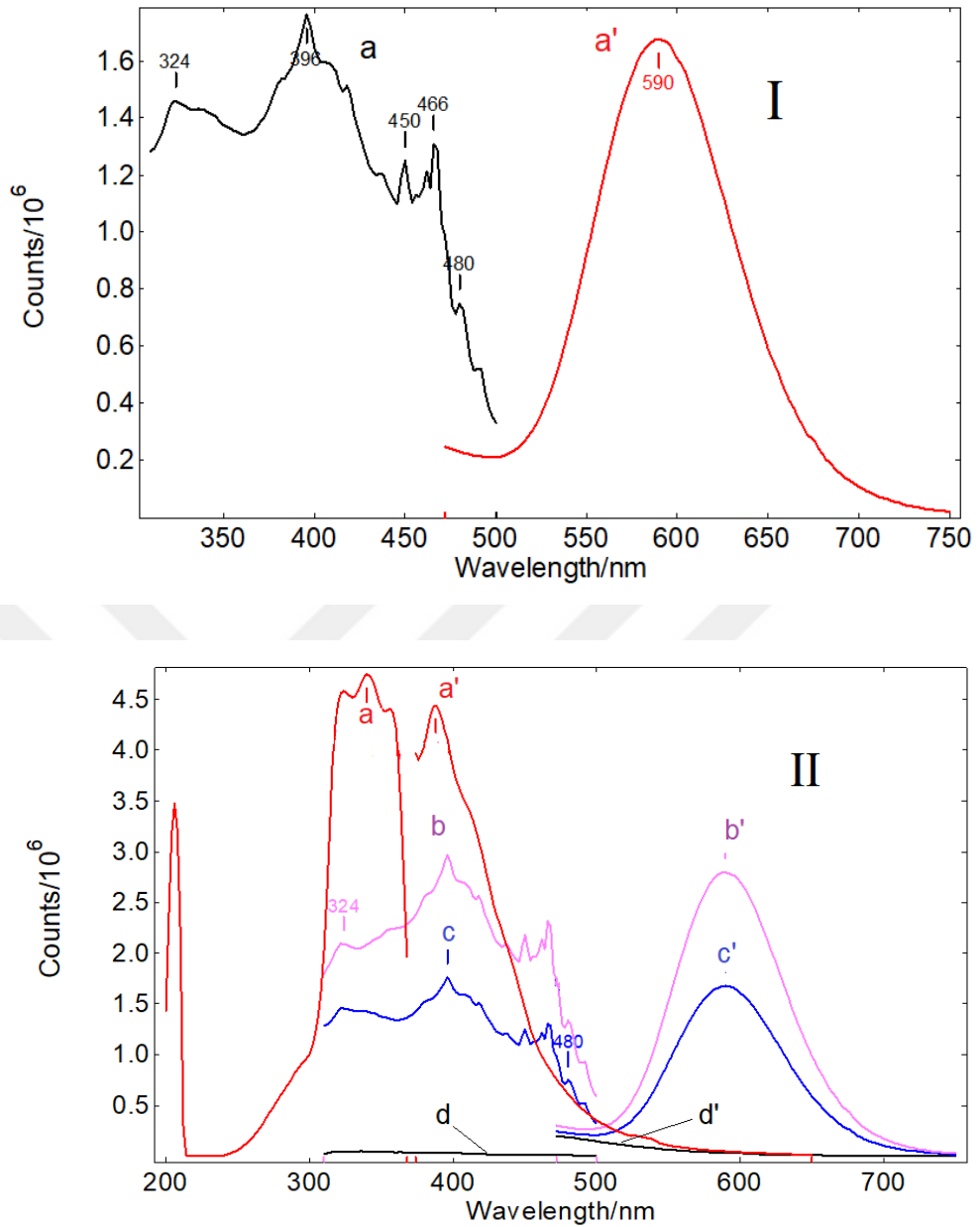


Figure 2.10 I: Excitation-emission spectra of the Ca- α -SiAlON: Eu²⁺ in thin film form in PMMA (λ_{ex} =405 nm, λ_{em} =600 nm) 3-II: Gathered excitation-emission spectra of the different forms in PMMA. A and a': QS (λ_{ex} = 354 nm), b and b': QS-Ca- α -SiAlON: Eu²⁺ blend (λ_{ex} =405 nm), c, c': Ca- α -SiAlON: Eu²⁺ (λ_{ex} = 405 nm), d, d'QS (λ_{ex} = 405 nm)

In the Eu²⁺ activated (oxy) nitride type -SiAlONs, the long-wavelength excitation and emission property arises from the nitrogen-rich microenvironment of the Eu²⁺ in the host which is isostructural to R-silicon nitride, whose single crystal cell contains four units of Si₃N₄. In this form, the higher electronegativity and distinct formal charge

of the oxygen (O^{2-}) compared to the N^{3-} causes to larger ligand related field splitting of the 5d orbitals (Xie et al., 2004).

Figure 2.10-I reveals the 44% enhancement in the emission intensity of the phosphor when embedded along with the QS. The observed increase in the emission intensity of the binary blends can be attributed to the existence of the QS in the microenvironment of each phosphor particle, whose strong Ultraviolet-Visible absorption, and, consequent emission creates intermediate energy levels for the further excitation of phosphorus. Figure 2.11 indicates the normalized partial overlap integral observed in the wavelength range of 410-500 nm between the emission spectrum of the QS and the excitation band of the Ca- α -Sialon: Eu^{2+} . Herein, both, the QS and SiAlON have been excited at 405 nm which results in lower emission intensity for the QS with respect to the SiAlON. However, normalized excitation-emission spectra reveal the potential overlap area briefly. The overlap area, consisting of approximately one-third of the emission band of the QS and the more energetic region of the excitation band of the SiAlON, makes an energy transfer from the QS to the phosphor, possible.

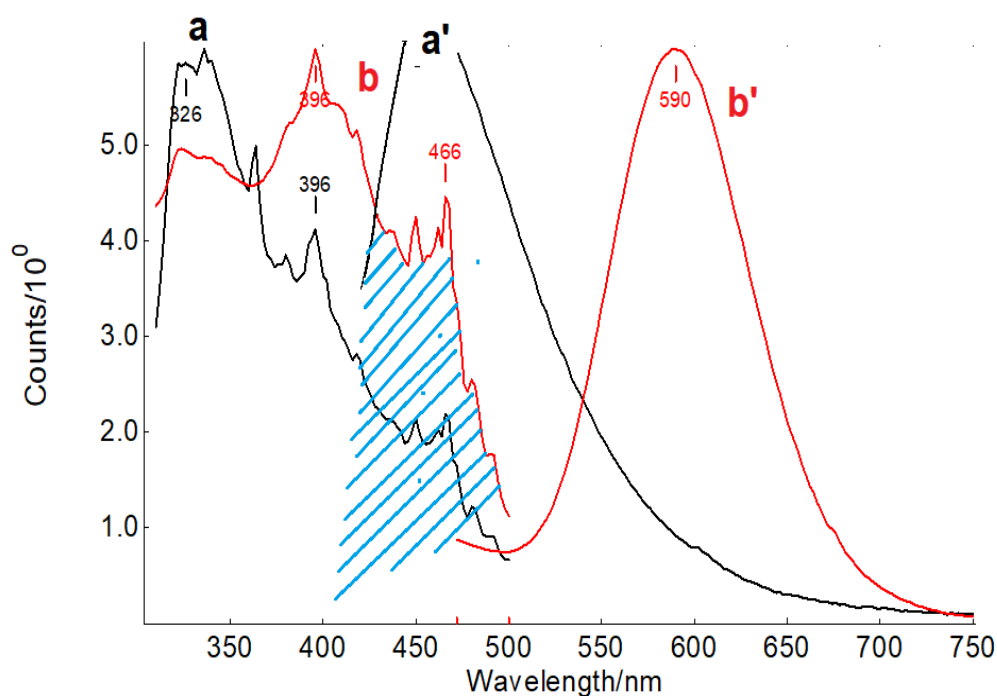


Figure 2.11 Normalized excitation and emission spectrum of the QS (a and a') and the Ca- α -SiAlON: Eu^{2+} (b and b') upon excitation at 405 nm

The observed increase in emission intensity at 600 nm upon excitation at 405 nm can be explained by the re-absorption of blue-band emission the QS by the Ca- α -Sialon: Eu^{2+} , because the phosphor has a strong absorption ability in the blue-green region of the electromagnetic spectrum. It should also be noted that, both of the used luminescent materials (QS and SiAlON) exhibit different radiation lifetimes. The observed spectral enhancement may also be originating from the competing “a few” and “several hundred nanoseconds” time-scale excited state lifetimes of the species under investigation which will be explained in detail the further chapters.

2.3.9 Optical Properties of the LuAG:Ce^{3+} and LuAG:Ce^{3+} / Quinine Sulphate Binary Mixtures

The LuAG exhibited typical excitation and emission behavior in the embedded form in PMMA when excited at 450 nm at room temperature. Figure 2.12-I shows one weak and one strong excitation band maximum; lying between 300-500 nm. The two peaks

recorded at 346 and 450 nm in the excitation spectrum of the lutetium aluminum garnet, correspond to the transitions of the two lowest energy levels of the crystal field components exhibiting D2 symmetry (Figure 2.12-I) (Lakowicz, 2006; Ogiegło, Zych, Jüstel, Meijerink & Ronda, 2013; Setlur & Srivastava, 2007). Corresponding emission spectrum revealed a broad-band emission centered at 512 nm arising from the transitions of the $4f^05d^1$ electrons which undergoes 2D term split ($^2D_{3/2}$ and $^2D_{5/2}$). The 4f electron of the ground $4f_1$ configuration which forms $^2F_{7/2}$ and $^2F_{5/2}$ states via spin-orbit coupling. As a result, the large-band room temperature emission spectrum of the Ce^{3+} -activated LuAG extending from 475 to 675 nm, can be attributed to the sum of the two overlapping sub-bands; originating from the splitting of the 2F state to the $^2F_{5/2}$ and $^2F_{7/2}$ states, respectively. Additionally, Ahn (Ahn & Kim, 2016) and Liu (Liu et al., 2015), in two different works, evidenced existence of radiative recombination of electron-hole pairs on Ce^{3+} ions of defects in LuAG in the vicinity of Ce^{3+} ions which contribute to the observed large band emissions. The Stokes shift of the Ce^{3+} -activated LuAG determined to calculate the energy difference between excitation (450 nm) and emission (514 nm) bands, was found to be 64 nm.

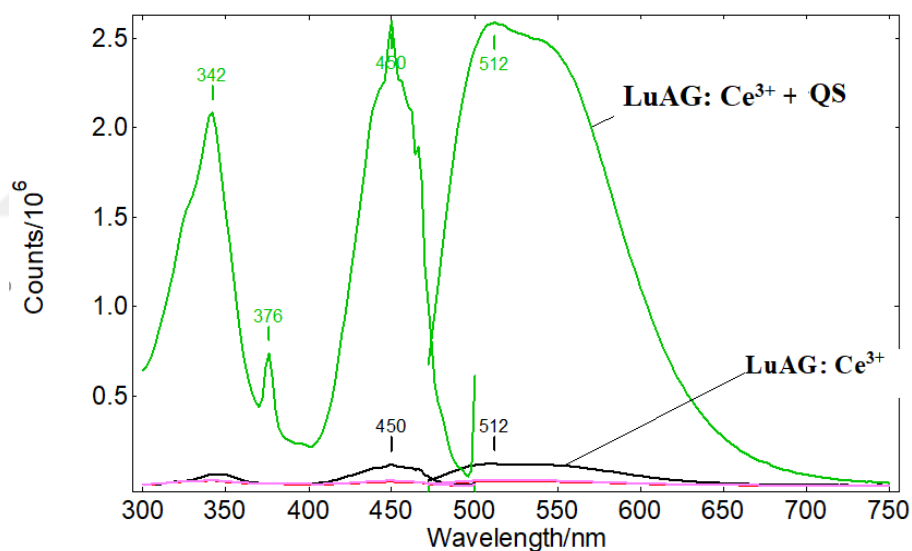
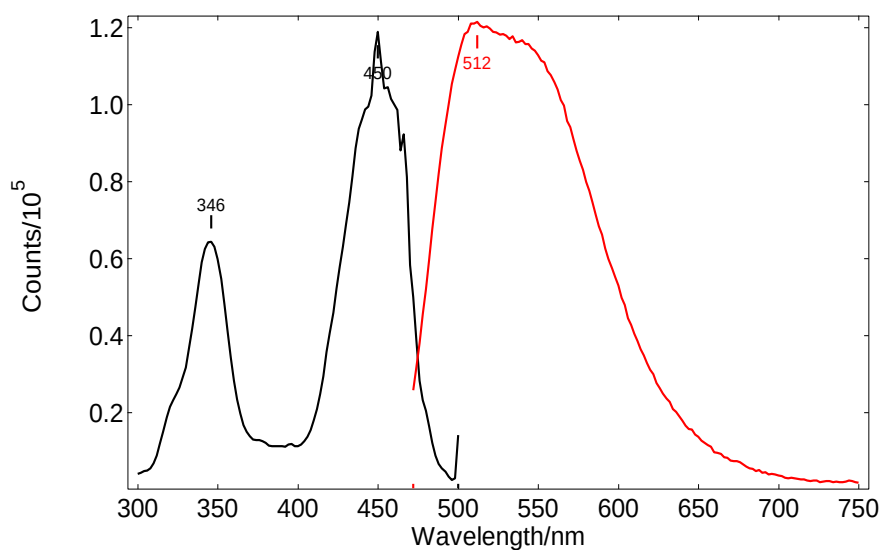


Figure 2.12 I: Excitation-emission spectra of the LuAG:Ce³⁺ in thin film form in PMMA ($\lambda_{ex}=450$ nm, $\lambda_{em}=512$ nm) II: Gathered excitation-emission spectra of the LuAG:Ce³⁺ and LuAG:Ce³⁺/ QS blend in the PMMA

The LuAG / QS comprising composites exhibited an extraordinary brightness in the emission which is 98% higher compared to the individual intensity of the LuAG, without any spectral shift. To better reveal the dramatic enhancement of the emission intensity of the phosphor, we recorded overlay spectra of the LuAG and, LuAG / QS–

based thin films, in embedded form, in the PMMA, respectively. (See Figure 2.12- I and –II)

Individually recorded normalized excitation and emission spectrum of the QS (a and a') and the LuAG: Ce^{3+} - upon excitation at 405 nm was shown in Figure 2.13. The QS exhibited a single and strong excitation band centered at 326 nm. However, the LuAG: Ce^{3+} yielded two absorption bands; one of which completely coinciding with the absorption band of the QS; centered at 326 and 450 nm, respectively (See Figure 2.13). A partial overlap between the emission band of QS and the excitation band of LuAG, is subjective. In spite of the smaller overlap integral between the QS and LuAG, with respect to the SiAlON / QS counterparts (Figure 2.13), herein, the light-induced interactions between the donor and acceptor pairs look like more efficient due to the exact matching of the overlap integral with the excitation wavelength of phosphor, at 450 nm.

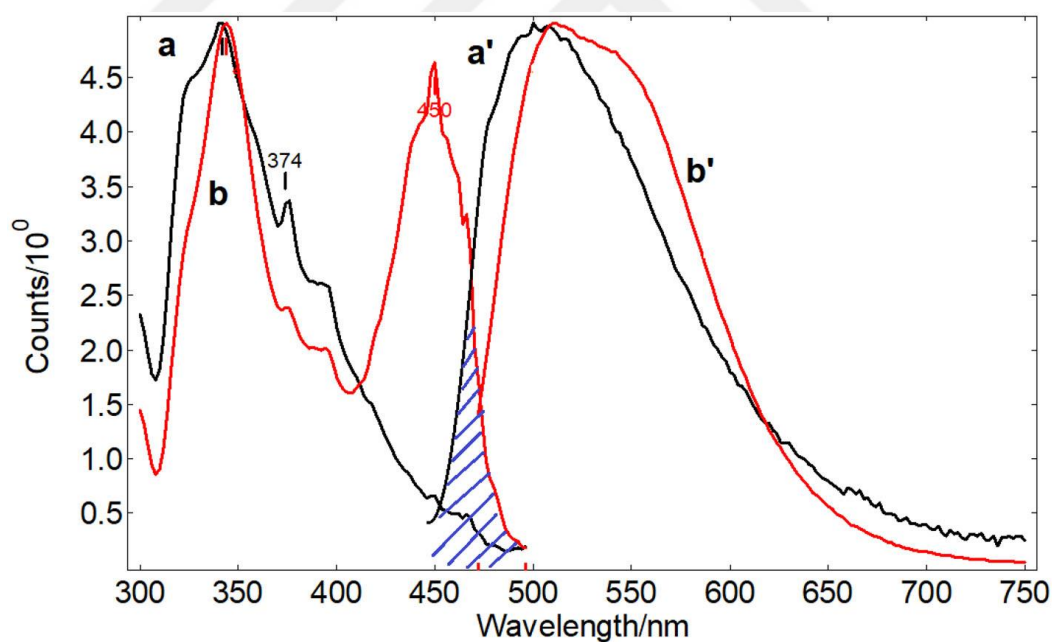


Figure 2.13 Normalized excitation and emission spectrum of the QS (a and a') and the LuAG:Ce³⁺- upon excitation at 405 nm

2.3.9.1 Decay Time Measurements

Excited-state lifetimes of the QS, SiAlON and LuAG individually and, their binary blends were acquired on both, nanosecond and microsecond time scales, for the PMMA embedded forms of the luminescent materials (See Figure 2.14, 2.15, and 2.16).

Nanosecond-scale decay data of the individual QS, SiAlON and LuAG acquired in PMMA were shown in the Figure 2.14, Figure 2.15, and Figure 2.16, respectively.

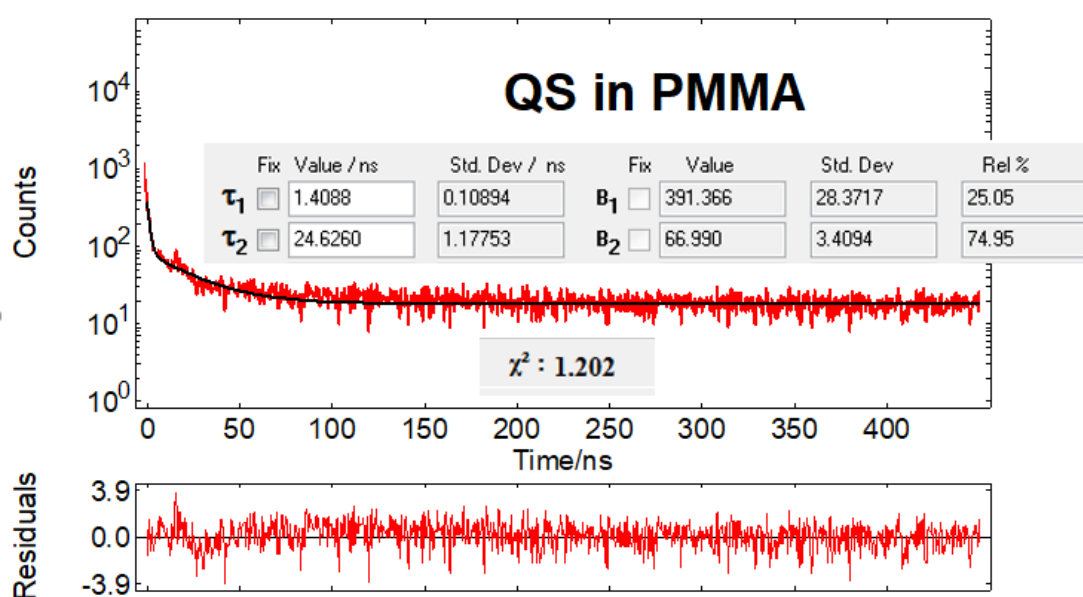


Figure 2.14 Decay curve of the QS acquired in the PMMA matrix

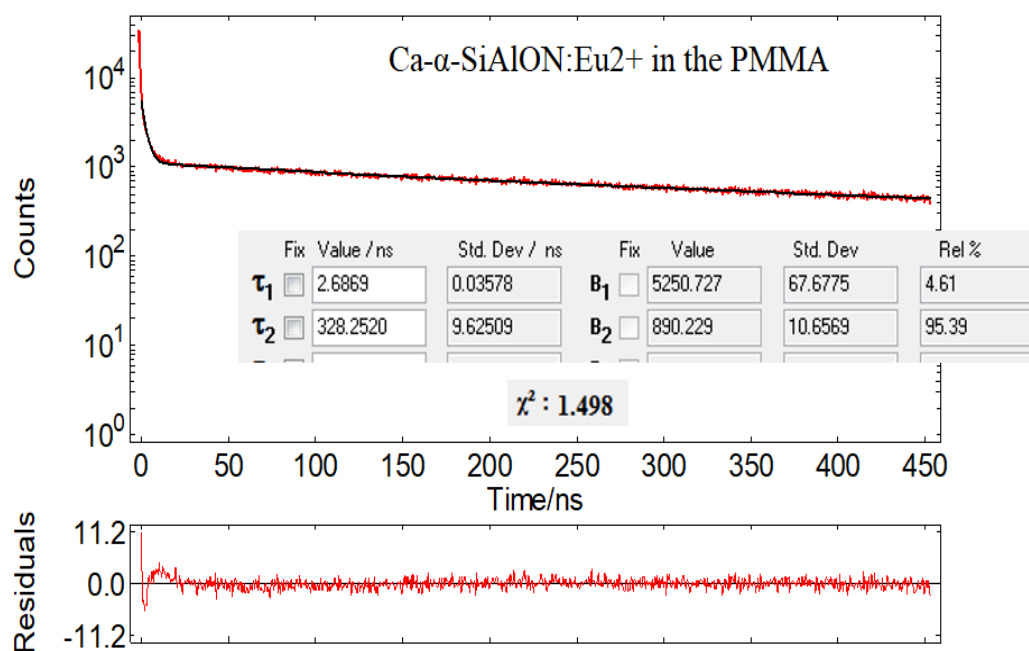


Figure 2.15 Decay curve of the Ca- α -Sialon:Eu²⁺ acquired in the PMMA matrix

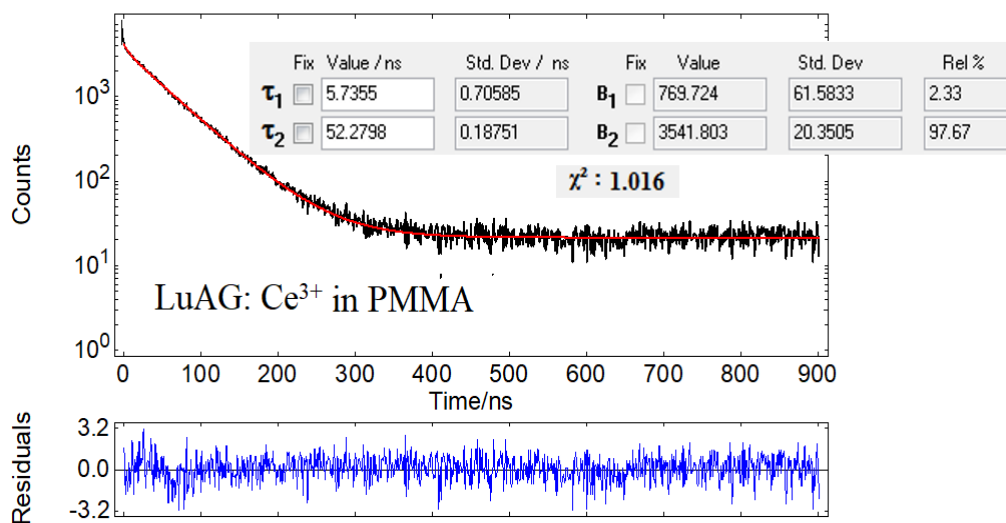


Figure 2.16 Decay curve of the LuAG:Ce³⁺ acquired in the PMMA matrix

The microsecond flash lamp excitation was performed to investigate whether longer decay dynamics exist. However, for both forms, we could not detect significant decay performance for the microsecond time-scale. The nanosecond time-scale data were acquired for different excitation wavelengths by using picoseconds-pulsed diode lasers at two different energies (λ_{ex} =367 nm and 467.8 nm), whose pulse width was

dramatically shorter than the expected nanosecond-scale decay times of the samples. The data were recorded by using a high speed detector system that allows the acquisition of the decays for both timescales with a high accuracy. However, since no decay at the level of microsecond time-scale was detected in the measurements, further work on all samples was performed in nanosecond time scale. Further details of the decay times including the abundance of the short and long lifetime components, and, standard deviation information were shown in Table 2.2.



Table 2.2 Decay times of the composites prepared by donor; Quinine Sulphate and their blends including varying amounts of the acceptor counterparts; α -SiAlON:Eu²⁺ and LuAG:Ce³⁺

Sample	Donor	Acceptor	$\lambda_{\max}^{\text{em}}$ (nm)	χ^2		Decay Time (ns)	Std.Dev. (ns)	Rel. (%)
Quinine Sulphate	-	-	384	1.202	τ_1	1.4088	0.10894	25.05
					τ_2	24.6260	1.17753	74.94
					τ_{avr}		18.81009	
α -SiAlON:Eu ²⁺	-	-	590	1.498	τ_1	2.6869	0.03578	4.61
					τ_2	328.2520	9.62509	95.39
					τ_{avr}		313.243	
Quinine Sulphate – α -SiAlON:Eu ²⁺	Quinine Sulphate (5 mg)	α -SiAlON:Eu ²⁺ (1.25 mg)	586	1.354	τ_1	3.0044	0.0581	7.16
					τ_2	266.1719	9.70946	92.84
					τ_{avr}		247.329	
Quinine Sulphate – α -SiAlON:Eu ²⁺	Quinine Sulphate (5 mg)	α -SiAlON:Eu ²⁺ (2.5 mg)	588	1.447	τ_1	2.847	0.039	4.85
					τ_2	321.46	9.739	95.15
					τ_{avr}		306	
Quinine Sulphate – α -SiAlON:Eu ²⁺	Quinine Sulphate (5 mg)	α -SiAlON:Eu ²⁺ (5 mg)	590	1.224	τ_1	2.716	0.0538	1.41
					τ_2	416.465	11.318	98.59
					τ_{avr}		410.63	
LuAG: Ce ³⁺	-	-	510	1.272	τ_1	5.7711	0.24471	3.59
					τ_2	51.6672	0.09076	96.41
					τ_{avr}		50.0195	
Quinine Sulphate- LuAG: Ce ³⁺	Quinine Sulphate (5 mg)	LuAG: Ce ³⁺ (1.25 mg)	512	1.099	τ_1	3.7442	0.06549	21.51
					τ_2	50.0563	0.27535	78.49
					τ_{avr}		40.0946	
Quinine Sulphate- LuAG: Ce ³⁺	Quinine Sulphate (5 mg)	LuAG: Ce ³⁺ (2.5 mg)	510	1.152	τ_1	3.4212	0.08198	14.65
					τ_2	50.3161	0.25903	85.35
					τ_{avr}		43.446	
Quinine Sulphate- LuAG: Ce ³⁺	Quinine Sulphate (5 mg)	LuAG: Ce ³⁺ (5 mg)	512	1.022	τ_1	9.6034	0.56588	3.99
					τ_2	52.0276	0.12624	96.01
					τ_{avr}		50.3349	

2.3.9.2 *Decay Characteristics of the QS in the PMMA*

Similar to the steady-state mode studies, the decay time data of the QS have also been acquired in PMMA based thin films when it was alone, and, in form of the composites. The QS yielded bi-exponential decay components of 1.41 (25%) and 24.60 (75%) ns, corresponding to an average decay time of 18.8 ns (See Figure 2.13). Reported decay characteristics in this work, differs from most of the previous studies in terms of the long lifetime component. Up to now, the decay time of the QS has been reported many times. Most of these works have been performed in the solution phase and exhibited differences in being mono-exponential or bi-exponential (Joshi & Pant, 2014; Joshi & Pant, 2012; O'Connor, Meech & Phillips, 1982). In contrast to the findings of the most of the previous works, in a recent study, Kristoffersen and colleagues stated single-exponential decay times for three different diluted sulphuric acid solutions of the QS (Kristoffersen, Erga, Hamre & Frette, 2018). Studies carried out on photo-physics and photochemistry of the QS in restricted environments including different protic and aprotic polymers and gels indicate that the QS molecule is very sensitive for the interactions taking place in its microenvironment (Meneses-Nava, Barbosa-García, Díaz-Torres, Chávez-Cerda & King, 1999; Pant, Tripathi & Pant, 1992; Rocha, Gehlen, Silva & Donate, 1999; Shiu et al., 1997).

Yadav et al. studied excited-state dynamics of the QS, and its di-cation form, doped in polyvinyl alcohol along with nanostructured silver islands. By this work, they revealed excited state dynamics of the QS in the restricted microenvironments measuring 2.39 ± 0.79 (3%), 8.28 ± 0.57 (39%), and 17.68 ± 0.58 (58%) ns of tri-exponential decay times, for the di-cation form of the QS, respectively. They attributed the long-lifetime decay component of 17.68 ns, and accompanying two short-lifetime decay components, to two major relaxation processes; a charge-transfer process and a solvent re-orientation process, which occurs in the polymer moiety (Yadav, Rawat, Pokharia, Jit & Mishra, 2019).

Therefore, in this work the recorded short and long lifetime components (1.41 (25%) and 24.60 (75%) ns) of the QS can be attributed to the intramolecular charge

transfer taking place within the molecule, and, dipole-dipole interactions, respectively, that occur during rotational movements by the orientation of polar side groups of the QS within the PMMA chains (Shima, Sato, Atsumi & Hatada, 1994).

2.3.9.3 *Decay Characteristics of the QS/Ca- α -Sialon: Eu²⁺ Binary Blends*

The PMMA embedded SiAlON exhibited bi-exponential decays of 2.7 (5%) and 328 (95%) ns; corresponding to an average decay time of 313 ns, when it is alone (See Figure 2.14). However, when blended with the QS, exhibited non-regular variations depending on the concentration of the composite. Herein, we followed a different strategy when measuring the decay times of the phosphorus-QS-blends. Firstly, we focused on the classical donor-acceptor approach where if both; donor and acceptor are the emitting species, energy transfer manifests itself through a reduction in the donor lifetime and a quenching of fluorescence intensity. In this case, an increase accompanies to the acceptor emission. If we consider the QS as the donor, the decay time of the QS should exhibit a decrease, for the increasing amounts of the SiAlON. Therefore, decay dynamics of the SiAlON /QS blends were investigated on basis of the QS. In the beginning, mass % of the QS in composites was kept high and constant (100%). It was continued with increasing amounts of the SiAlON in the composite. When 5 mg of the QS was mixed with 1.25, 2.5, and 5 mg of the SiAlON respectively, the composites exhibited average decay times of 247, 306, and 410 ns. The observed excited state lifetimes for the composites were closer to the decay times of the phosphors, rather than the QS. The variations observed in the decay times of the QS based composites for the increasing concentrations of the phosphor were not regular, and therefore, the results were not in accordance with the theory.

In further work, we focused on investigation of the formulation, exhibiting the highest emission efficiency; consisting of an equal mass of the QS and the phosphor (5 mg QS – 5 mg SiAlON w/w, /Kg/polymer). The composite exhibited the highest variation in the average decay time when compared to the pure SiAlON, from 313, to 410 ns; which can be attributed to the interactions between the fast decays of the QS, and, their interaction with the transitions taking place between multi closely spaced $4f_6$

5d states of the Eu^{2+} lying in the Ca- α -Sialon host. This interaction is probably in direction of re-absorption of the emission of QS by the phosphor on the SiAlON/QS interface and should not be misunderstood as a degradation or a loss process. Variation of the long lifetime component from 328 to 416 ns for the QS-free phosphor and the SiAlON / QS blend, respectively supports this idea. In a recent work, Diab and co-workers revealed the effect of re-absorption phenomenon arising from photon recycling and light trapping on the optical characteristics of organic and inorganic lead-based perovskites indicating a long rise time and a lengthening of the decay. According to the authors, in such structures, the fast decay time is related to the energies close to the absorption edge and indicates the effect of re-absorption of the high-energy photons as well as the diffusion of excess carriers out of the initial excitation region. However, a longer decay occurs at energy levels where photons are weakly reabsorbed (Diab et al., 2017). Table 2.2 shows further details of the reported decay times for the composites. As mentioned earlier, non-radiative fluorescence resonance energy transfer is well-defined for the solution phase. However, herein, we could not observe a regular increase in the decay time of the donor counterpart for the increasing concentrations of the acceptor. In solid state, the exact mechanism remains unclear, although the possibility of the energy transfer from donor species to acceptor sites still exists. Probably, for the phosphors, the mechanism promotes in a different way from the solution phase due to the existence of traps and energy depths, and, the competing contributions of the charge carriers, excitons, and defects to the luminescence.

2.3.9.4 Decay Characteristics of the LuAG: Ce^{3+} / QS Blends

Similar to the SiAlON based experiments, the excitation studies of the phosphor and QS/LuAG based binary blends were performed by using different light sources, emitting at 376 and 470 nm. The 376 nm excitation of the phosphor, resulted in an average decay time of 5.68 ns. The long and short lifetime components of this fast decay were found to be 0.72 (61.41%) and 2.52 (38.59%) ns, respectively where many free electrons and holes of the host and, cerium ions take place. When excited at 470 nm, the polymer-free LuAG exhibited its typical average decay time of 52 ns; arising

from the $5d \rightarrow 4f$ transitions of the trivalent Ce ions where the energy of the excitation light is lower than that of the bandgap energy of the related host. As reported in our previous work, the short and long lifetime components of the phosphor powders were found to be 26 (11%) and 55 (89%) ns, respectively (Yildirim et al., 2021). When encapsulated in the PMMA matrix, the phosphor yielded 51.67 (96.41%) and 0.24ns (3.59%) of bi-exponential decays exhibiting a distinct decrease in short lifetime component, both in duration and relative abundance with respect to its PMMA-free form. When blended with the QS, average decay times of 40.09, 43.45, and 50.33 ns were recorded, for the increasing concentrations of the phosphor, in the composite, respectively. If we look at from the perspective of the lifetime of the LuAG:Ce^{3+} , it can be said that, the lifetimes of the blends are shortened with respect to the excited state lifetime of the QS-free phosphorus (See Table 2.2). On the other hand, if, we consider the QS as the donor ($\tau_{\text{avr}}=18.81\text{ns}$) and the LuAG as the acceptor ($\tau_{\text{avr}}=50.02$ ns), the recorded lifetimes of the phosphor blends were found to be longer than that of the decay time of the QS ($\tau_{\text{avr}}=40.09, 43.45$ and 50.33 ns). Similar to the results observed for the SiAlON / QS binary blends, the most significant variation in the excited state lifetime was observed when the LuAG and QS were blended in equal mass, in the composite. Although there have been studies examining donor acceptor interactions in the solid phase, most of them discusses the energy transfer in the context of dopant-co-dopant, mainly embedded in the same host or lattice network. As expected, a decrease in the decay time of the donor species is observed versus increasing amounts of the of the acceptor, which promotes through the dopant and co-dopant taking place in the same crystal cell (Huang, Zhang, Wang & Zhang, 2021; Marasanov, Mironov, Sgibnev, Kolesnikov & Nikonorov, 2020; Wu et al., 2021; Wu, Du, Zheng, Pei, Ren & Hai, 2021).

In this study, the attained results can be associated with and energy transfer, and this was supported by excitation-emission spectra. However, decay time measurements do not fully support an energy transfer. It should be noted that, the phosphor particles are not in a co-dopant position. This is a blended material, and, when the QS was mixed with increasing amounts of the LuAG exhibited a regular enhancement in the brightness up to the equal mass ratio. Utilization of excess

concentrations of the phosphor resulted in self-quenching or another deactivation process. When mixed at critical concentration, however, the LuAG / QS blend exhibited 98% enhancement in the intensity with respect to the QS-free phosphors. There is a possible energy transfer between QS and phosphorus particles, although this does not fully support by the decay time measurements that give more accurate results for the solution phase. Therefore, in blended forms, perhaps a different perspective should be brought for such kinds of interactions.

2.4 Conclusion

In this part of the thesis, photoluminescence of the two commercially available phosphors, Eu^{2+} doped Ca- α -Sialon (Ca- α -SiAlON: Eu^{2+}) and Ce^{3+} doped lutetium aluminum garnet (LuAG: Ce^{3+}) and their blends with QS were investigated by steady-state and decay time measurements. The phosphors and their blends with the QS, have been excited by the 405 and 450 nm, commonly used in LED or display applications. When the phosphors are embedded along with the QS; which can absorb and emit the light in a large spectrum; they displayed an unexpected enhancement in the emission intensities. The Ca- α -SiAlON: Eu^{2+} exhibited 44% increase in the intensity when blended together with the QS. Similarly, the QS-LuAG: Ce^{3+} -blend exhibited 98% enhancement in the intensity in compare to the QS-free phosphors. Decay characteristics of the phosphors were also investigated in nanosecond and microsecond time scales. Spectral data presented some evidence for the donor-acceptor relationship of the QS/ Ca- α -SiAlON: Eu^{2+} and QS/LuAG: Ce^{3+} counterparts where the QS was the donor. The offered phosphor blends, exhibited 44 and 98% enhancement in the brightness without any spectral shift. The proposed materials may be a promising solution for the phosphors in terms of the brightness towards efficient and warmer colors.

CHAPTER THREE

CO₂ SENSING STUDIES

In this chapter we investigated spectral properties and CO₂ sensitivity of the 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium-salt (HPTS) dye in an EC matrix together with the sol-gel based 13-93 bioactive glass powders. The bioactive glasses were equipped with the single Er³⁺, Tb³⁺ and Er³⁺ and Tb³⁺. The glassy structures have been used as substrate due to their porous structure optical transparency and intrinsic fluorescence arising from Er³⁺ and Tb³⁺. When the dye was used along with the bioactive glasses, exhibited enhanced fluorescence emission due to the energy transfer interactions. On the other hand, the Ethyl Cellulose (EC) encapsulated HPTS dye is known as high sensitivity towards the CO₂ and has been tested many times on the Mylar sheets in form of thin films. However, for the first time we used the dye along with the bioactive glasses and ionic liquid which enhanced its both intensity and stability. We recorded the excitation and emission spectra of the bioactive glasses and their HPTS blends, respectively. Their decay time related data were also recorded in nanoseconds time scale. After spectral characterization steps we exposed the composites towards varying concentrations of gaseous CO₂ and recorded the response both in steady-state and kinetic mode. We also determined the decay times in the absence and presence of the CO₂.

3.1 Bioactive Glasses

Bioactive glasses have been find a large application area due to its temperature resistance, low thermal expansion coefficient, inert characteristics towards corrosive chemicals and biocompatibility (Howes et al., 2011). Among them, rare earth-doped hydroxyapatite and bioactive glasses showing luminescent properties have attracted attention due to their potential applications in tissue engineering, drug release and biological imaging (Grabmaier, 1994; Neacsu, Stoica, Vasile & Andronescu, 2019).

Bioactive glasses are functional materials in the form of particle, microsphere, fiber and scaffolds due to their role in tissue repair and regeneration (Gerhard & Boccaccini, 2010; Hench, Splinter, Allen & Greenlee, 1971; Hench, Wilson, 1984; Rahaman et al., 2011). While silicate-based bioactive glass composition encoded as 45S5, another bioactive glass 1393 has higher SiO₂ concentration and some additional elements in form of K₂O and MgO in its composition (Brink, Turunen, Happonen & Yli-Urpo, 1997). Additionally, bioactive glasses encoded as 1393 have better processing features which permits the sintering of the glass scaffolds with lower crystallization (Brink, Turunen, Happonen & Yli-Urpo, 1997; Rahaman et al., 2011). The fabrication efforts on luminescent bioactive glasses doped with the rare earths have been reported previously. Fan et al. (Fan Y et al. 2009) investigated the drug delivery abilities of luminescent Eu³⁺-doped bioactive glasses. While, the drug-loaded glasses exhibiting red luminescence under UV light excitation, the emission peaks of Eu³⁺ in the glass changed as a function of drug release (Fan Y et al., 2009). Similarly, Li et al. (Li et al., 2014) studied with Eu³⁺ doped photoluminescent silicate-based glass-ceramics for tissue engineering applications which gained a red color radiation under UV light, and a decrease in the emission intensities in cell-culture experiments (Li et al., 2014). Saarinen et al. (Saarinen et al. 2018) studied on the borosilicate and the phosphate glasses in the presence of persistent luminescent phosphor SrAl₂O₄:Eu²⁺, Dy³⁺ which allows long term monitoring of the bioactive glass scaffolds implanted into body (Saarinen et al. 2018).

Both erbium (III) and terbium (III) are luminescent rare earths (Ganjali, Gupta, Faridbod & Norouzi, 2016) where Er³⁺ shows fluorescent properties upon excitation by daylight (Patnaik, 2002). It has been utilized in a variety of applications including laser surgery and dental studies (Ganjali, Gupta, Faridbod & Norouzi, 2016). Alshemary et al. (Alshemary et. Al, 2015) reported the effects of Er³⁺ doping on the in vitro bioactivity and the photoluminescence features of hydroxyapatite (HA) and revealed high bioactivity and green and red light emissions. Similarly, Pham et al. (Pham, Van, Tam & Ha, 2016) studied Er³⁺-doped hydroxyapatite powders having high bioactivity and photoluminescence properties. Mondal and co-workers (Mondal et al., 2020) synthesized similar Er³⁺-containing hydroxyapatite nanocrystals for

biomedical applications. Figure 3.1 indicates basic tetrahedral silica unit, its crystalline form and amorphous structures, respectively.

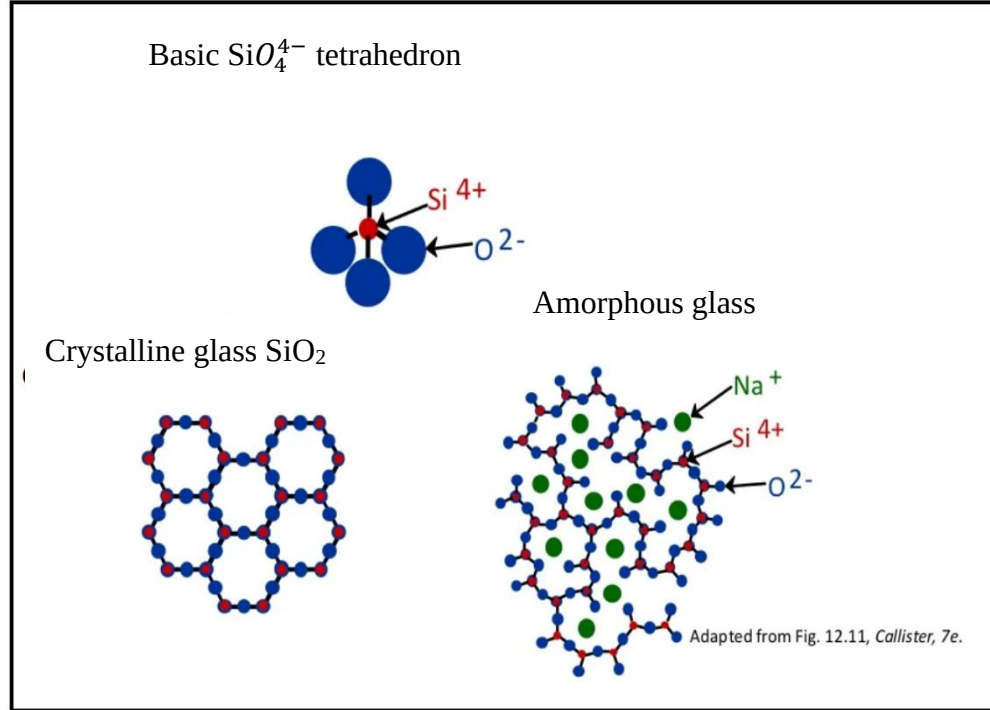


Figure 3.1 Basic SiO_4 tetrahedron, crystalline form and amorphous glass structures (was taken from: <https://www.slideshare.net/hzharraz/silica-sand-and-glass-industry> and re-arranged).

Deliormanlı et al. synthesized, sol–gel-based erbium (Er^{3+}), terbium (Tb^{3+}) and Er^{3+} : Tb^{3+} co-doped 1393 bioactive glass powders and studied their structural and morphological characteristics as well as the photoluminescence properties (Deliormanlı, Rahman, Oguzlar & Ertekin, 2021). In this work, the particle size and average diameter of the offered materials were found to be in the range of 1.5-3.5 μm . In addition to the structural characterization, excitation and emission spectra and decay kinetics of the newly synthesized materials were investigated. All the samples prepared in the study exhibited bright green emission upon excitation at 374 nm and it was concluded that Er^{3+} and Tb^{3+} -containing 1393 bioactive glasses have had a potential to be used in tissue engineering and bio-imaging applications (Deliormanlı, Rahman, Oguzlar & Ertekin, 2021).

On the other hand, monitoring of concentrations of the CO₂ is quite important in environmental analysis, automotive industry, and climate studies. Apart from these studies, analysis of the CO₂ levels in the blood, living cells, tissue or in incubators is also very important. Biotechnological research including in-vivo and in-vitro investigations requires biocompatible materials. From this point of view, we intended to use the biocompatible bioactive glasses in the design of a CO₂ sensor along with the HPTS dye. Up to now, the HPTS dye has been used many times as a CO₂ sensing agent in a number of applications in a lot of different matrices including EC capillary arrays (Wang, Wen, Yang & Yang, 2017), EC/PMMA nanofibers (Aydogdu, Ertekin, Suslu, Ozdemir, Celik & Cocen, 2011), LDPE thin films (Mills & Yusufu, 2016), layered double hydroxide composites (Li, Su, Bai, Xu & Pei, 2016), Sol-gel (Dansby-Sparks et. al., 2010) Octyl tri-EOS/TEOS (Chu & Lo, 2009) EMIMBF₄-doped EC films (Oter, Ertekin & Derinkuyu, 2008) ORMOSILs/hybrid xerogels (Chu & Lo, 2008), 1-methyl-3-butyl imidazolium tetrafluoroborate (RTIL-I) 1-methyl-3-butyl imidazolium bromide (RTIL-II) (Oter, Ertekin, Topkaya & Alp, 2006), and in form of ZnO NPs incorporated HPTS or ZnO@Ag NPs incorporated HPTS in EC (Ongun, 2020).

The Polymer-encapsulated HPTS dye has been studied repeatedly on the Mylar sheet substrates in form of polymeric thin films. However, for the first time we blended the ion pair of the dye with the bioactive glasses in the presence of ionic liquid which enhanced both its intensity and stability. We recorded the excitation and emission spectra of the bioactive glasses and their HPTS coated forms, respectively. Their decay time related data were also recorded. The HPTS exhibited higher emission intensity when blended with the bioactive glasses with respect to the its individual form. This behavior provided better relative signal intensity when exposed to the CO₂.

3.2 Experimental

3.2.1 Chemicals

Bioactive glasses (sol-gel-based erbium (Er³⁺), terbium (Tb³⁺) and Er³⁺: Tb³⁺ co-doped 1393 bioactive glass powders) were provided by Prof. Dr. M. Aylin

Deliormanlı. Trisodium salt of 8-hydroxypyrene 1, 3, 6-trisulfonic acid (HPTS) and NaHCO_3 were purchased from Sigma Aldrich and used in the ion-pair form. The ion pair was prepared by using stoichiometric amount of the tetraoctyl ammonium bromide (TOABr) (Sigma- Aldrich) . Ethyl cellulose (EC), was from Acros. The ionic liquid, 1-ethyl- 3-methylimidazolium tetrafluoroborate (EMIMBF_4) and tetraoctyl ammonium hydroxide (TOAOH) were from Fluka. The TOAOH was in the form of 20 % solution in methanol. Dioctyl phthalate (DOP) was from Aldrich. Deionized water was prepared by Millipore instrument, with an electrical resistivity of 18 M Ω . Cylinders of carbon dioxide and nitrogen gas of 99,99% purity were obtained from Linde Gas, Izmir, Turkey.

3.2.2 Instruments

Concentrations of the carbon dioxide samples were tuned by mixing the carbon dioxide and nitrogen gases with a programmable Sonimix-gas blender which works on principle of mass flow controllers. The carbon dioxide was bubbled through a tube filled with deionized water at room temperature to humidify the gas which was maintained at 80%. The relative fluorescence intensity measurements were recorded at a pressure of 101,3 kPa at room temperature using a spectrofluorometer (Edinburgh Instruments, FLS920) working at steady state mode. Kinetic measurements were performed on the same instrument in Kinetic mode. Decay time data were acquired on time correlated single photon counting mode (TCSP) of the same device equipped with 367.8 or 467 nm pulsed laser sources with a pulse width of 118,2 ps.

3.2.3 Gas Blender

Carbon dioxide (99.99%) and nitrogen (99.999%) gases were blended in the concentration range of 0.1–100.0 % in a programmable gas blender (Sonimix 7000A) equipped with mass flow controllers. The total pressure was maintained at atmospheric pressure; 760 Torr which corresponds to 1333.22 HPa. The output flow rate of the blended gas was maintained at 550 mL.min⁻¹. Gas mixtures were introduced onto the sensing agent in the cuvette of the instrument via 2.0 m of Teflon tubing's with in inner

diameter of 5.0 mm, by a diffuser needle after humidification at room temperature. The experimental setup was shown in Figure 3.2. The humidification of the CO₂ blends was performed by bubbling the gas through a thermostated washing bottle containing deionized water at 25°C. The tip of the needle was fixed in the disposable cuvette to avoid the movement of the tubing's. The upper side of the cuvette was covered with a parafilm having tiny holes at the top.

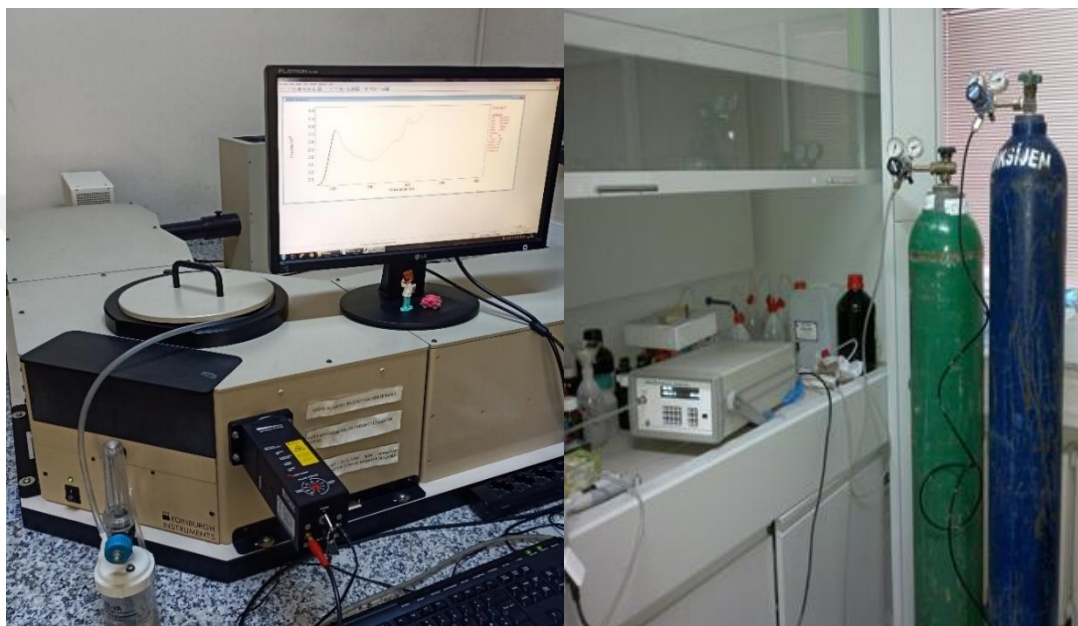


Figure 3.2 Gas humidification and gas blender systems used in the research lab

3.3 Results and Discussions

3.3.1 *Characterization of the Used Bioactive Glasses*

SEM photographs of the dopant-free, Er³⁺, Tb³⁺ and/or Tb³⁺-Er³⁺ co-doped 1393 bioactive glasses powder were shown in Figure 3.3. Bioactive glass particles revealed bi-modal size distribution exhibiting larger particles in the range of 1,45-3,57 μm in diameter and fine particles having a diameter of approximately 50 nm, respectively.

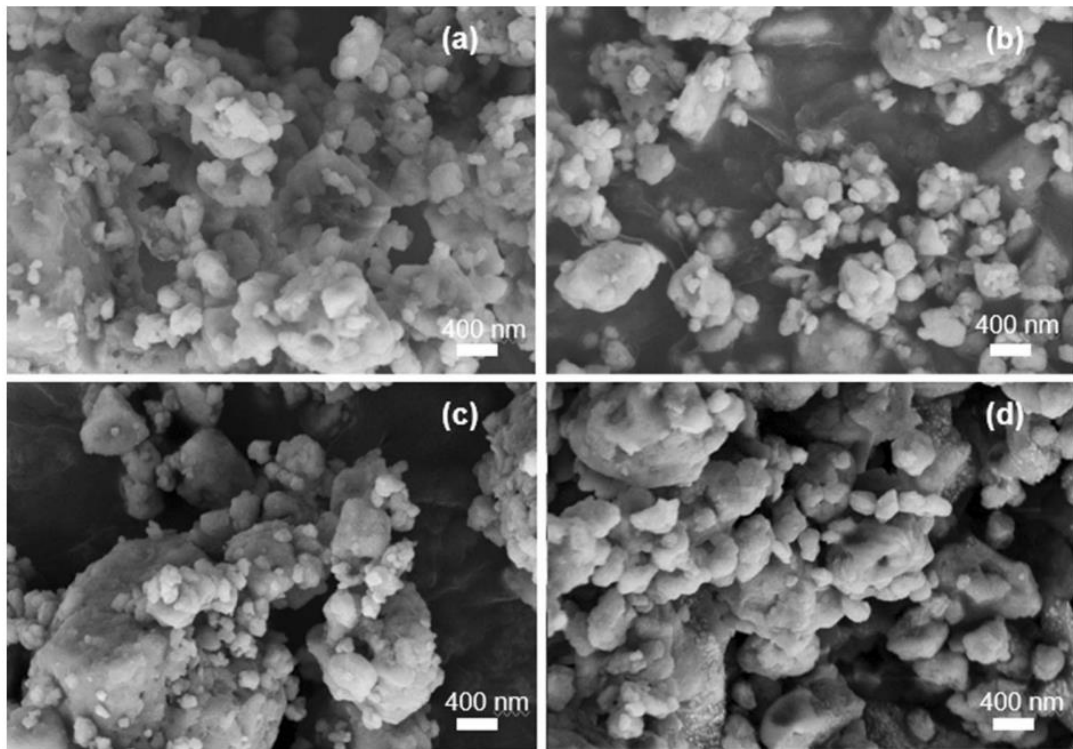


Figure 3.3 SEM micrographs of the bioactive glass powders synthesized in the study a) dopant-free bioactive glass 1393, b) 5% Er doped-1393, c) 5% Tb doped-1393, d) 5 % Er:Tb doped-1393 (Deliormanlı, Rahman, Oguzlar & Ertekin, 2021)

The XRD and XPS characterization and particle size distribution results of the used sol-gel-derived dopant-free bioactive glass 1393, 5% Er doped-1393, 5% Tb doped-1393 and 5% Er:Tb doped-1393 particles were shown in the literature (Deliormanlı, Rahman, Oguzlar & Ertekin, 2021).

3.3.2 *Synthesis of Ion Pair of HPTS*

The ion pair of the HPTS and tetra-octylammonium bromide has been prepared following the given procedure. The trisodium salt of HPTS (200 mg) and corresponding amount of tetra-octylammonium bromide (TOABr) were dissolved in appropriate amount of alkaline water and dicloro methane (DCM), respectively. The two components were shaken in a separatory funnel. After certain resting time, the ion pair was extracted from the alkaline aqueous phase into the dicloro methane. The DCM phase was washed with 0.05 M of NaOH at least three times and then separated. After

the evaporation of organic solvent under vacuum evaporator, the ion pair was obtained. Schematic chemical structure of the ion pair of the HPTS with tetraoctylammonium counter ion is shown in Figure 3.4.

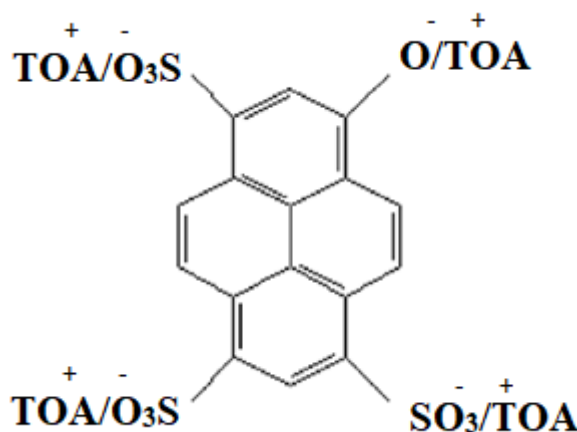


Figure 3.4 Schematic chemical structure of the ion pair of the HPTS with tetraoctylammonium counter ion

Therefore, we enhanced the solubility of the HPTS in the EC matrix (Ertekin, Klimant, Neurauder & Wolfbeis, 2003).

3.3.3 Preparation and Chemistry of the Indicator Composite

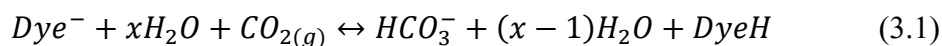
The 30 mg of Ion pair form of the HPTS was treated by the tetraoctylammonium hydroxide (TOAOH) in 2 mL of THF to make the indicator dye alkaline as well as its humidification. 120 mg of EC, 96 mg of DOP, 24 mg of Ionic liquid and 2 mL of THF were mixed in a 25 mL of glass vial until a homogenous mixture was obtained. Then 120 μ L of the alkaline HPTS and 5 mg of Bioactive glass were added into the content of the glass vial and mixed under magnetic steering for further 2 hours. Composition of the utilized test material was shown in Table 3.1.

Table 3.1 Composition of the utilized test materials

Indicator Dye (in form of ion pair with TBAOH, alkaline form, 30 mg)	Matrix (120 mg)	Solvent (THF mL)	Additive (DOP mg)	IL (mg)
HPTS	EC	2	96	24
HPTS	EC+1393 BO	2	96	24
HPTS	EC+%1 ErBO	2	96	24
HPTS	EC+% 5 Tb BO	2	96	24
HPTS	EC+% 3 Er- TbBO	2	96	24
HPTS	EC+1393 BO	2	96	-
HPTS	EC+%1 Er BO	2	96	-
HPTS	EC+% 5 Tb BO	2	96	-
HPTS	% 3 Er-TbBO	2	96	-

The composite was spread on to the quartz glass (cm) as a thin film. The coated quartz was diagonally placed into sample cuvette of the spectrofluorometer and covered with the parafilm. The CO₂ gas from the output of the gas blender at a 240 cm³min⁻¹ rate was introduced into the cuvette via a needle and kept constant through the work.

Presence of the TBAOH in the sensing moiety is critically important for the sensitivity of the indicator dye. The excess amount of the TBAOH is neutralized by the atmospheric carbon dioxide or the acidic vapors in the ambient air of the laboratory forming a hydrogen carbonate buffer which also enables trapping of trace amounts of water molecules. This is necessary for the working of the HPTS dye as an indicator for the CO₂ according to the following equilibrium where the dye refers to the anionic form of the HPTS.



On the other hand, presence of the ionic liquid (IL) in the matrix enhances the working of the above mentioned equilibrium as well as the stability of the dye providing an increased solubility for the CO_2 in the sensing moiety. 10 to 20 times higher solubilities were reported for the CO_2 in water-miscible ionic liquids than that of the measured solubilities in solvents, polymers or water. The pronounced high solubility of the CO_2 in room temperature ionic liquids (RTILs) has been attributed to the formation of weak Lewis acid–base complexes between gas (the electron-pair acceptor) and the anionic site of the RTIL which also acts as an additional sink buffer in the sensing moiety (Anthony, Maginn & Brennecke, 2002; Bates, Mayton, Ntai & Davis, 2002).

In most of the CO_2 sensors the ion pair form of the HPTS and the counter ion “quaternary ammonium base; TOAOH; is encapsulated in an ethyl cellulose matrix for stabilizing the anionic (deprotonated) form of the HPTS. However, in further designs, in the presence of the RTIL; the anion exchange equilibrium takes place between the TOAOH and the IL.

Consequent interaction of the resulting product of this ion-exchange equilibrium with the H_2CO_3 enhances the formation of the HCO_3^- within the matrix which results in a slower but more stable response towards the CO_2 (Oter, Ertekin & Derinkuyu, 2008).

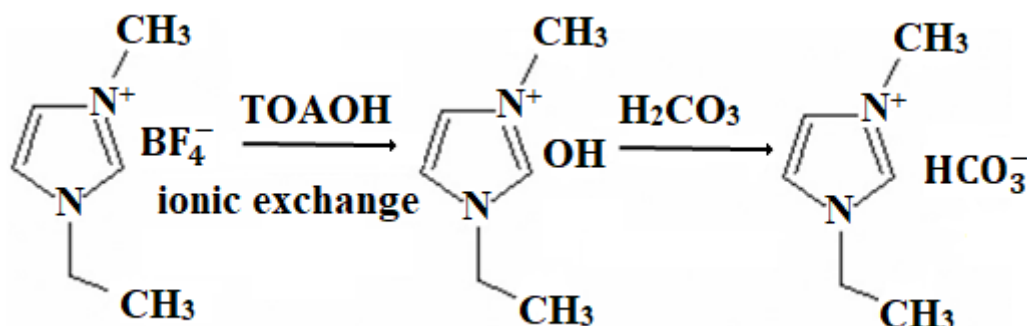


Figure 3.5 The anion exchange scheme between TOAOH and EMIMBF₄ and consequent interaction with H_2CO_3 (was taken from: Oter, Ertekin & Derinkuyu, 2008) (Oter, Ertekin & Derinkuyu, 2008)

3.3.4 Spectral Characterization of the Bioactive Glasses and HPTS

Spectral Characterization of all of the Bioactive Glasses and HPTS was performed when the bioactive glasses were in polymer free form and along with the HPTS in the EC matrix respectively. Figure 3.6 indicates gathered excitation and emission spectra of the dopant free, 1.0, 3.0 and 5.0 % Er^{3+} - containing bioactive glass particles. The 1.0% Er^{3+} doped particles were chosen for further studies due to the high excitation and emission response. Diameter of the studied particles were found to be between 1.45 to 3.57 micrometer. Upon excitation by 374 nm, 1.0% Er^{3+} doped particles exhibited narrow emission bands corresponding to the blue (436 nm) and green (506) wavelengths. The intense band observed at 506 nm can be attributed to $^4\text{F}_{7/2} \rightarrow ^4\text{I}_{15/2}$ transition of the Er^{3+} . The less intense band appeared at 566 nm is related to the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions from the excited state of the Er^{3+} to the ground state (Deliormanlı, Rahman, Oguzlar & Ertekin, 2021).

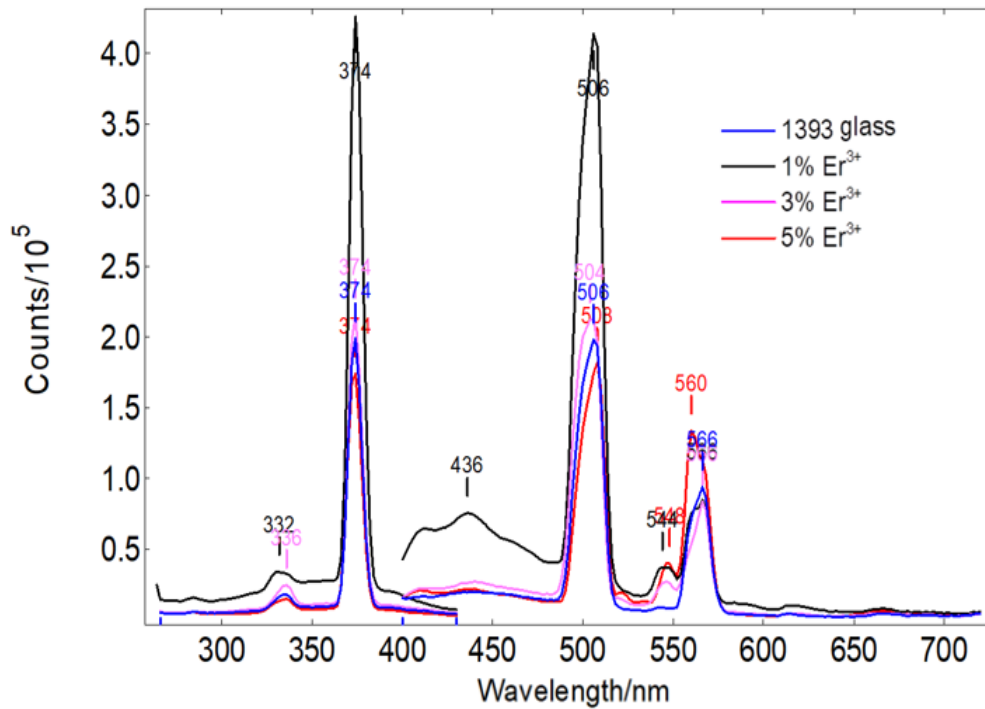


Figure 3.6 Gathered excitation and emission spectra of the different concentrations of Er^{3+} - containing bioactive glass particles (was taken from: Deliormanlı, Rahman, Oguzlar & Ertekin, 2021)

Gathered excitation and emission spectra of the different concentrations of Tb^{3+} -containing bioactive glasses were shown in Figure 3.7. When excited at 374 nm the Tb^{3+} particles yielded to distinct emission peaks at 488 and 544 nm, respectively. Emission maxima observed at 488 and 544 and further emissions appeared at 584 and 622 nm are related to the $^5D_4 \rightarrow ^7F_6$, $^7F_5$, $^7F_4$ and $^7F_3$ electronic transitions of the Tb^{3+} , respectively (Deliormanlı, Rahman, Oguzlar & Ertekin, 2021). The 5% Tb doped glass exhibited highest emission performance and used in further studies as the substrate for the HPTS.

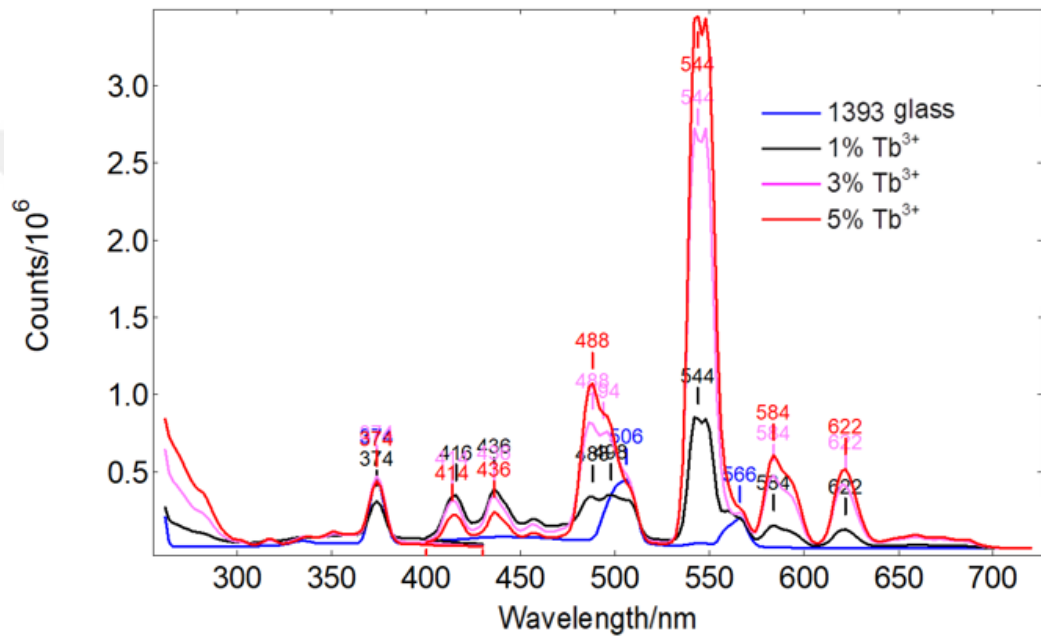


Figure 3.7 Gathered excitation and emission spectra of the different concentrations of Tb^{3+} -containing bioactive glass particles (was taken from: Deliormanlı, Rahman, Oguzlar & Ertekin, 2021)

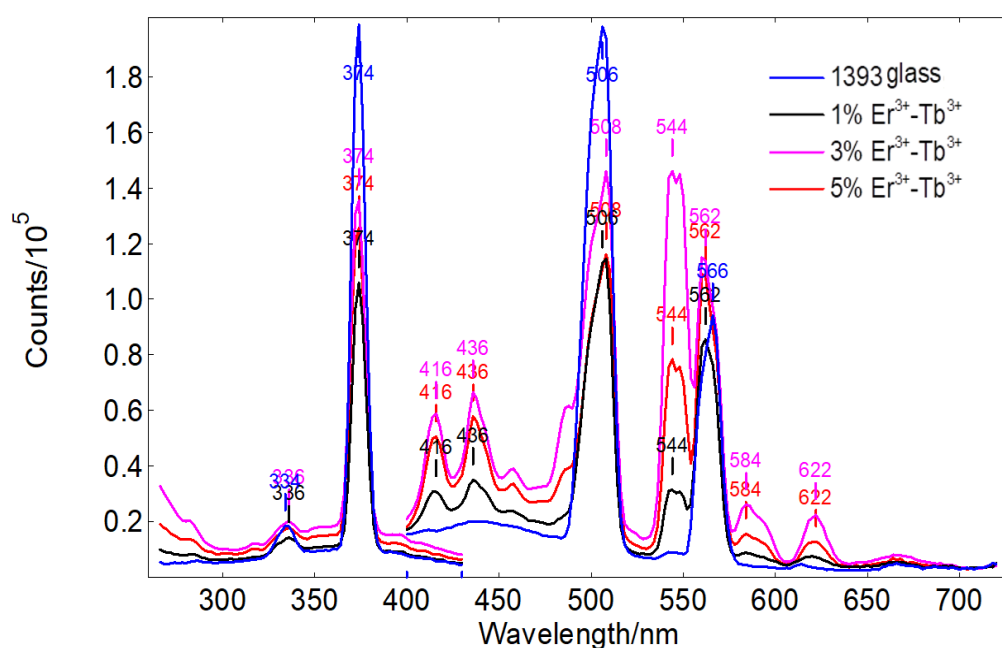


Figure 3.8 Gathered excitation and emission spectra of the different concentrations of Er^{3+} - Tb^{3+} co-doped bioactive glass particles (was taken from: Deliormanlı, Rahman, Oguzlar & Ertekin, 2021)

Gathered photoluminescence spectra of the bare and 1% Er^{3+} - Tb^{3+} , 3% Er^{3+} - Tb^{3+} and 5% Er^{3+} - Tb^{3+} co-doped bioactive glasses were shown in Figure 3.8. Among them the 3% Er^{3+} - Tb^{3+} co-doped glass exhibited higher emission intensity at 544 nm band due to the energy transfers between the Er^{3+} and Tb^{3+} where the Er^{3+} is the donor and the Tb is the acceptor counter parts. Therefore, for further studies we used the 3% Er - Tb co-doped Bioactive glasses as the substrate of the CO_2 sensing composites (Deliormanlı, Rahman, Oguzlar & Ertekin, 2021).

3.3.5 Combination of the HPTS Dye and Bioactive Glass Particles

In order to understand potential interactions between the HPTS and bioactive glasses we recorded the excitation and emission spectra of the related species individually and in gathered form in the EC matrix, both in the absence and presence of the IL. Figure 3.9 shows the overlay spectra of the EC doped HPTS, bare bioactive glass and their combination in form of thin film, respectively.

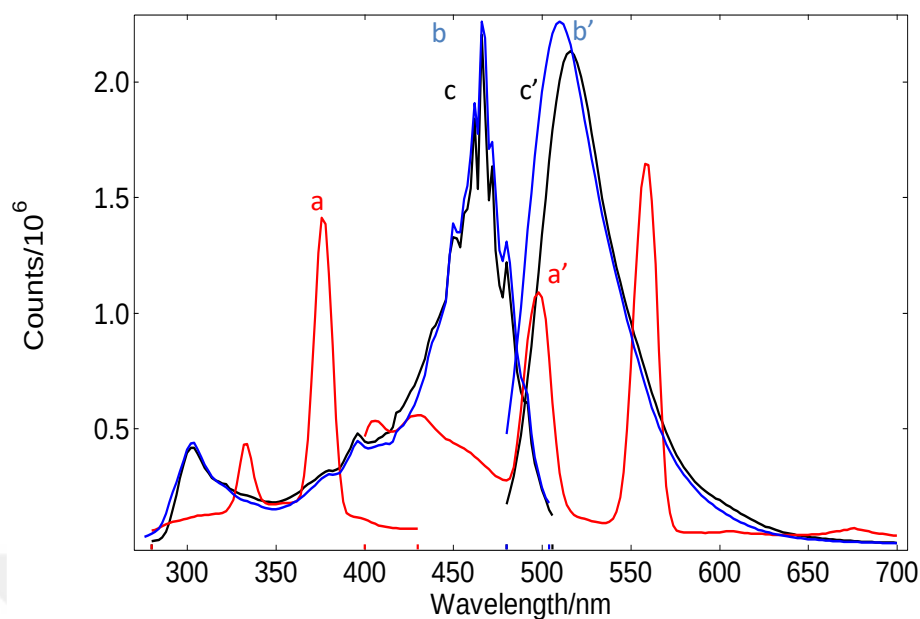


Figure 3.9 Overlay spectra of the IL-free EC doped HPTS, bare bioactive glass and their combination in form of thin film. (a, a': bare bioactive glass, b, b': HPTS only, c, c', HPTS and bioactive glass)

As can be concluded from the Figure 3.9 no significant enhancement was observed in the photoluminescence of the HPTS when combined with the bare bioactive glasses. The emission maximum of the EC doped HPTS shifted from 510 to 515 nm exhibiting 5 nm of red shift. In further studies we tested performance of the HPTS along with the Er^{3+} , Tb^{3+} and $\text{Tb}^{3+}\text{-Er}^{3+}$ co-doped 1393 bioactive glasses powders in the EC matrix.

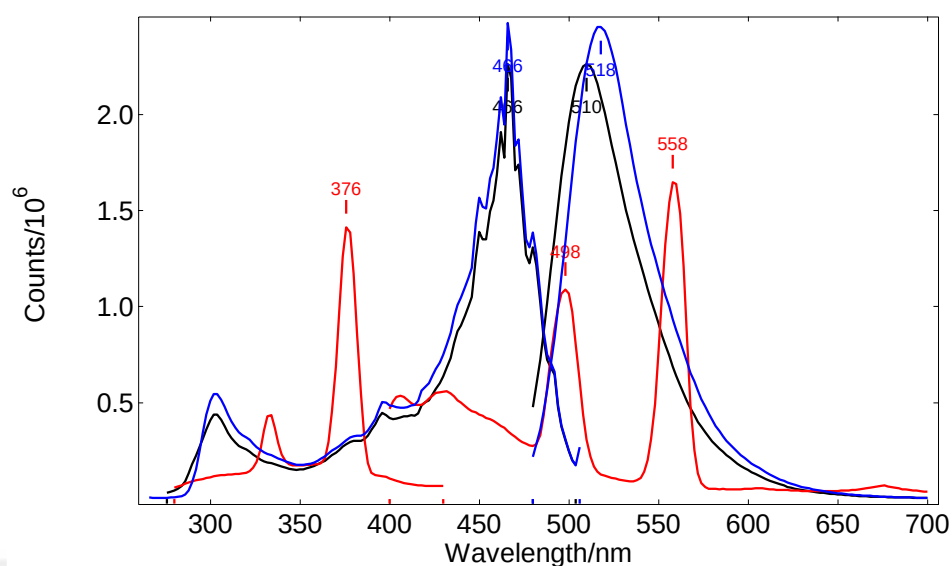


Figure 3.10 Overlay spectra of the IL-doped HPTS, bare bioactive glass and their combination in form of thin film. (red: bare bioactive glass, black: HPTS only, blue: HPTS and bioactive glass)

When blended with the IL, the composite exhibited 8 nm of red shift and approximately 7.0 % enhancement in the emission intensity.

3.3.6 Photoluminescence Spectra of the HPTS and 1% Er Doped Bioactive Glass Containing Composites

Similarly, excitation emission spectra of the HPTS and 1% Er³⁺ doped bioactive glass containing composites were recorded in the absence and presence of the IL in gathered manner. When the HPTS dye blended with the 1% Er³⁺ containing glass, exhibited 1.54-fold (35.3%) enhancement both in the excitation and emission intensity in the absence of the IL. The emission maximum of the EC doped HPTS shifted from 510 to 516 nm exhibiting 6 nm of red shift (See Figure 3.11). The enhancement observed in the emission performance can be explained by the Fluorescence Resonance Energy Transfer (FRET). According to the theory, there should be an overlap between the emission spectrum of the donor and excitation spectrum of the acceptor to satisfy the requirement of the energy transfer. As can be concluded from the Figure 3.11, there is an overlap integral between the emission band of the bioactive glass and the excitation band of the HPTS which makes an energy transfer from the

glass to the HPTS dye, possible. In order to clarify, the overlap area we also recorded the normalized excitation-emission spectra of the donor and acceptor counterparts, respectively.

Existence of the overlap integral is an evidence for the ET. However, it should be supported by the decay time measurements.

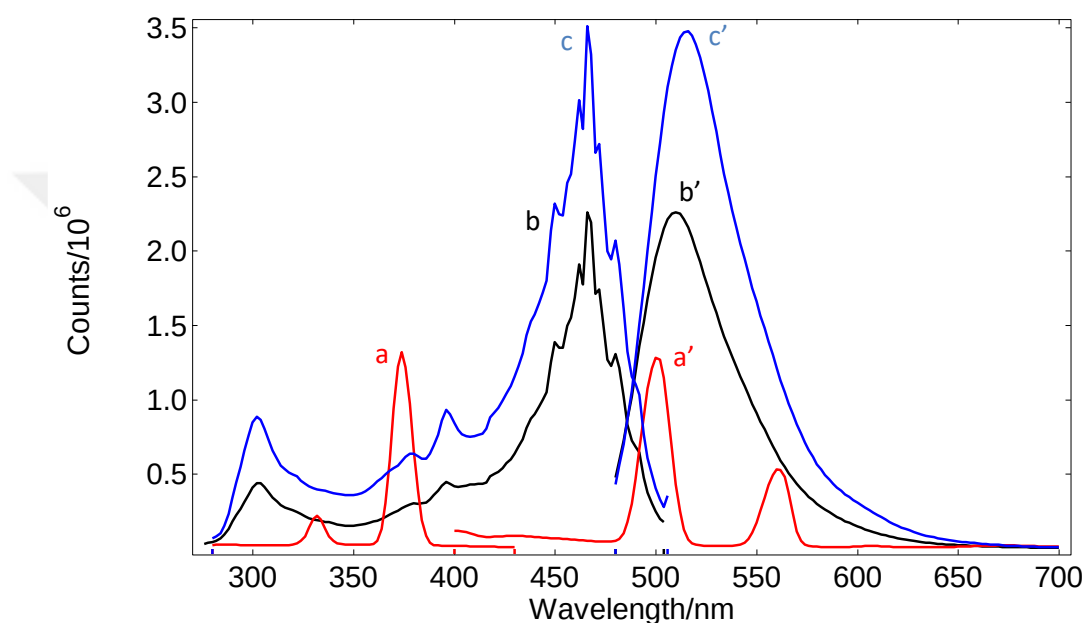


Figure 3.11 Overlay spectra of the IL-Free HPTS, 1% Er^{3+} doped bioactive glass and their combination in form of thin film in EC. (a, a': 1% Er^{3+} doped bioactive glass, b, b': HPTS only, c, c', HPTS and 1% Er^{3+} bioactive glass)

When blended with the BMIMBF₄, the composite exhibited 4 nm of red shift and approximately 1.18-fold (15.7 %) enhancement in the emission intensity (See Figure 3.12).

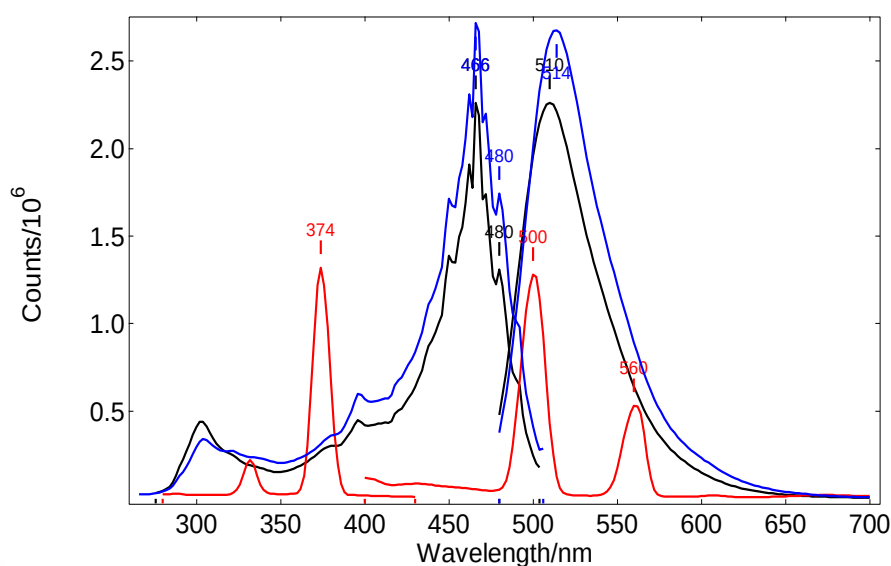


Figure 3.12 Overlay spectra of the IL-doped HPTS, 1% Er^{3+} doped bioactive glass and their combination in form of thin film. (red: 1% Er^{3+} doped bioactive glass, black: HPTS only, blue: HPTS and bioactive glass)

We recorded excitation and emission spectra of the HPTS and 1% Er^{3+} doped bioactive glass, individually and then gathered them in form of the normalized overlay spectra. Therefore, we observed donor-acceptor pairs for a potential fluorescence resonance energy transfer (FRET) where the emission spectra of the bioactive glass make a small overlap with the excitation spectra of the HPTS. The 15.7% enhancement in the emission intensity relies on an energy transfer from the Er^{3+} containing bioactive glasses towards the HPTS dye. In further studies, we also recorded the decay times of the potential donor-acceptor pairs to find out evidence for the energy transfer. Figure 3.13 indicates normalized overlay spectra of the HPTS and 1% Er^{3+} doped bioactive glass along with the IL in form of thin film.

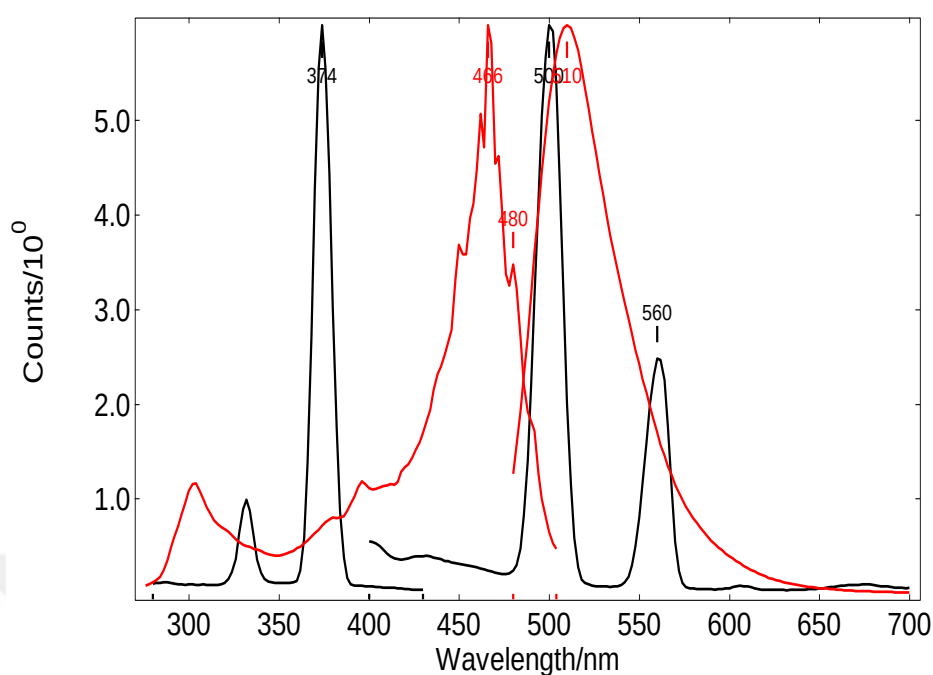


Figure 3.13 Normalized overlay spectra of the HPTS and 1% Er^{3+} doped bioactive glass in form of thin film. (black: 1% Er^{3+} doped bioactive glass, red: HPTS only) (λ_{exc} for the HPTS: 466 nm., λ_{exc} for the bioactive glass: 374 nm)

3.3.7 Photoluminescence Spectra of the HPTS and 5% Tb^{3+} Doped Bioactive Glass Containing Composites

Similar to the Er^{3+} doped samples, presence of the 5% Tb^{3+} doped Bioactive glasses resulted in 1.51 fold (32.8%) enhancement in the emission intensity of the HPTS in IL-free samples. The emission maximum was shifted from 514 to 520 nm. A distinct band broadening was observed both in the excitation and emission bands of the HPTS. Figure 3.14 indicates overlay spectra of the EC doped HPTS, 5% Tb^{3+} doped bioactive glass and their combination in form of thin film, in the absence of the ionic liquid.

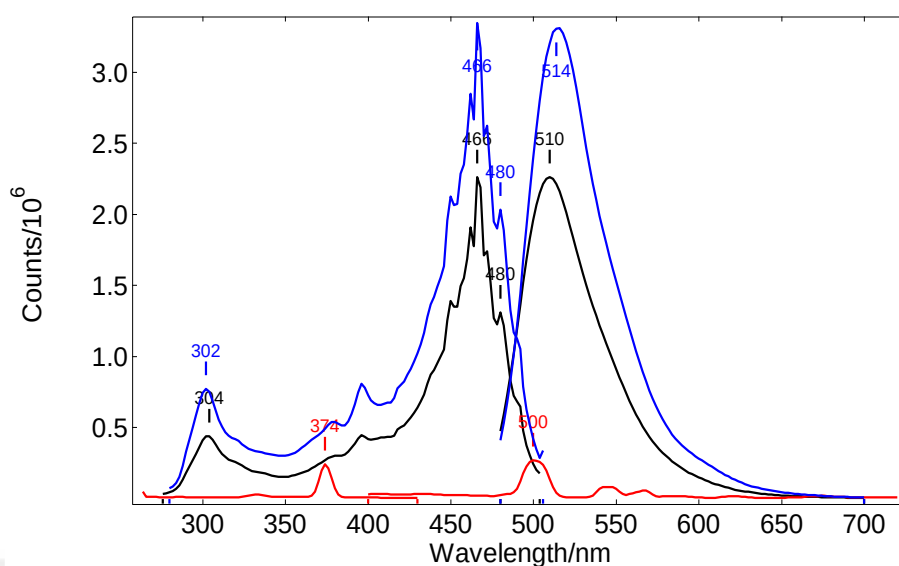


Figure 3.14 Overlay spectra of the IL-free HPTS, 5% Tb³⁺ doped bioactive glass and their combination in form of thin film in EC. (red: 5% Tb³⁺ doped bioactive glass, black: HPTS only, blue: HPTS and 5% Tb³⁺ bioactive glass)

Emission maximum of the HPTS was shifted from 510 to 514 nm when blended with the 5% Tb³⁺ doped bioactive glass. Additionally, 1.47 fold (31.8%) increase was observed in the emission intensity of the HPTS (See Figure 3.14).

In case of IL doped composites the emission maximum was shifted from 510 to 518 nm exhibiting 8 nm of red shift. 2.04 fold (51%) increase in the emission intensity was accompanied to the red shift.

Figure 3.15 indicates excitation and emission records of the composite in the presence of the IL.

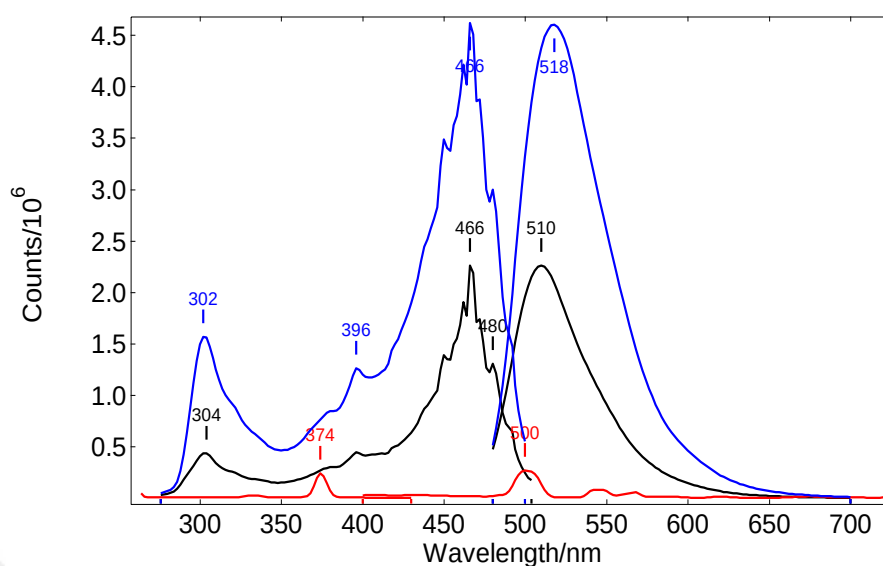


Figure 3.15 Overlay spectra of the IL-doped HPTS, 5% Tb³⁺ doped bioactive glass and their combination in form of thin film. (red: 5% Tb³⁺ doped bioactive glass, black: HPTS only, blue: HPTS and bioactive glass)

The 51% increase in the emission intensity can be explained by the FRET.

The normalized excitation and emission data of the potential donor-acceptor counterparts reveals the overlap integral of the Tb-doped glass and the HPTS species, respectively (See Figure 3.16).

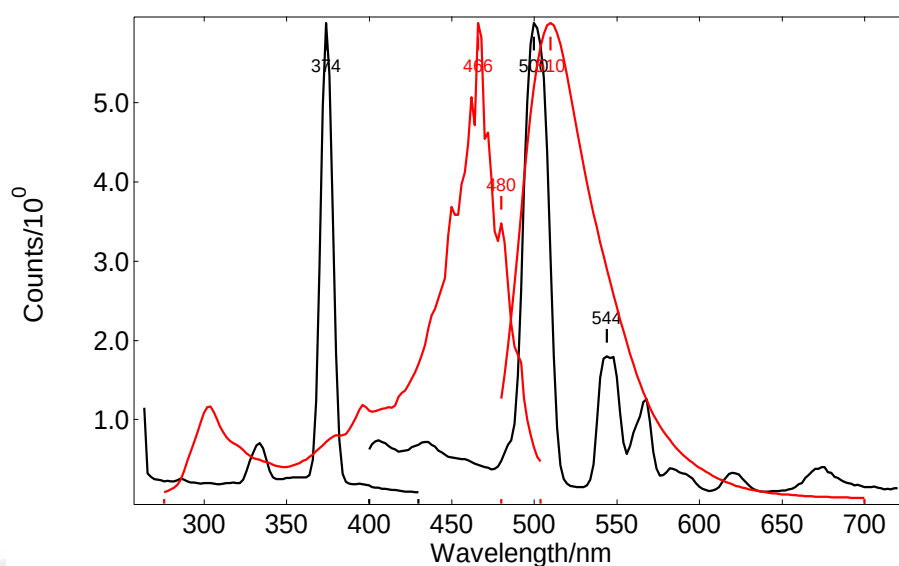


Figure 3.16 Normalized overlay spectra of the HPTS and 5% Tb³⁺ doped bioactive glass in form of thin film. (black: 5% Tb³⁺ doped bioactive glass, red: HPTS only) (λ_{ex} for the HPTS: 466 nm., λ_{ex} for the bioactive glass: 374 nm)

3.3.8 Photoluminescence Spectra of the HPTS and 3% Er³⁺-Tb³⁺ Doped Bioactive Glass Containing Composites

Combination of the 3% Er³⁺-Tb³⁺ glass and HPTS in the EC matrix in the absence of the IL resulted in 1.42 fold (29.6.0 %) increase in emission intensity and an accompanying red shift of 6 nm, respectively (See Figure 3.17).

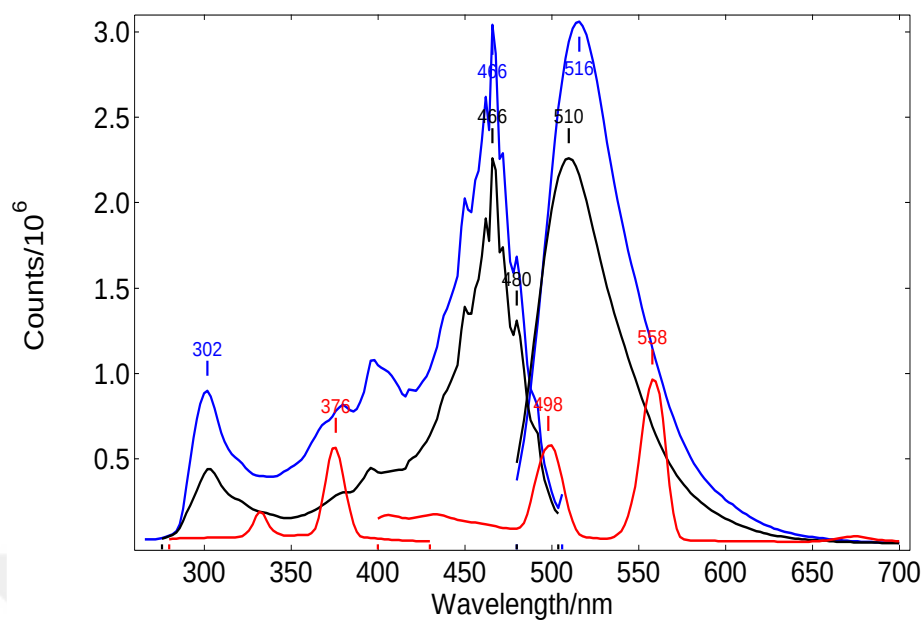


Figure 3.17 Overlay spectra of the IL-free HPTS, 3% Er³⁺-Tb³⁺ doped bioactive glass and their combination in form of thin film. (red: 3% Er³⁺-Tb³⁺ doped bioactive glass, black: HPTS only, blue: HPTS and 3% Er³⁺-Tb³⁺ bioactive glass.)

In case of IL-doped forms, we observed 2.04 fold (50.9%) increase in emission intensity and an accompanying red shift of 6 nm, respectively (See Figure 3.18).

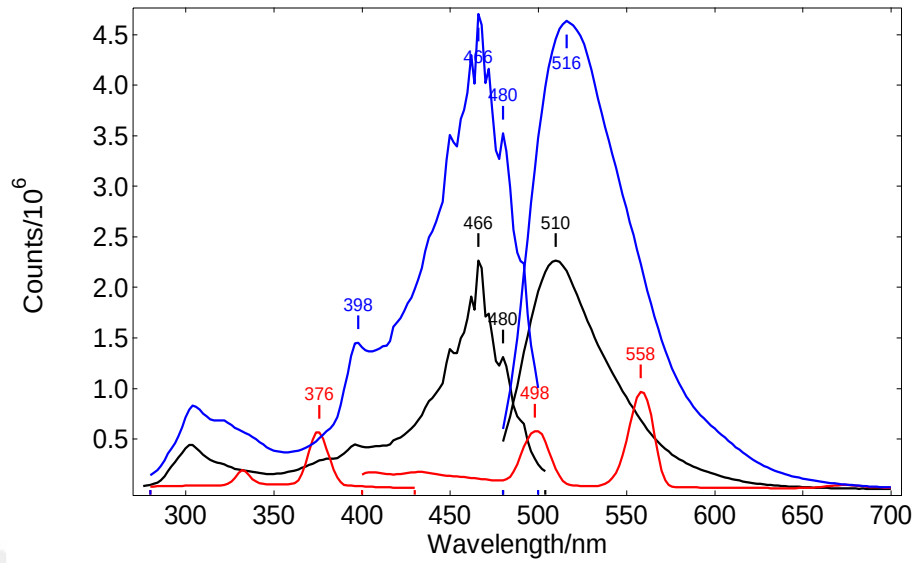


Figure 3.18 Overlay spectra of the IL-doped HPTS, 3% Er^{3+} - Tb^{3+} doped bioactive glass and their combination in form of thin film. (red: 3% Er^{3+} - Tb^{3+} doped bioactive glass, black: HPTS only, blue: HPTS and 3% Er^{3+} - Tb^{3+} bioactive glass.)

Similar to the previous work, in order to understand the donor-acceptor interactions we recorded the normalized overlay spectra of the **HPTS** and 3% Er^{3+} - Tb^{3+} doped bioactive glass, respectively. As expected the spectral data shown in Figure 3.19 revealed the existence of an overlap integral between the excitation spectrum of the **HPTS** and emission band of the 3% Er^{3+} - Tb^{3+} doped bioactive glass.

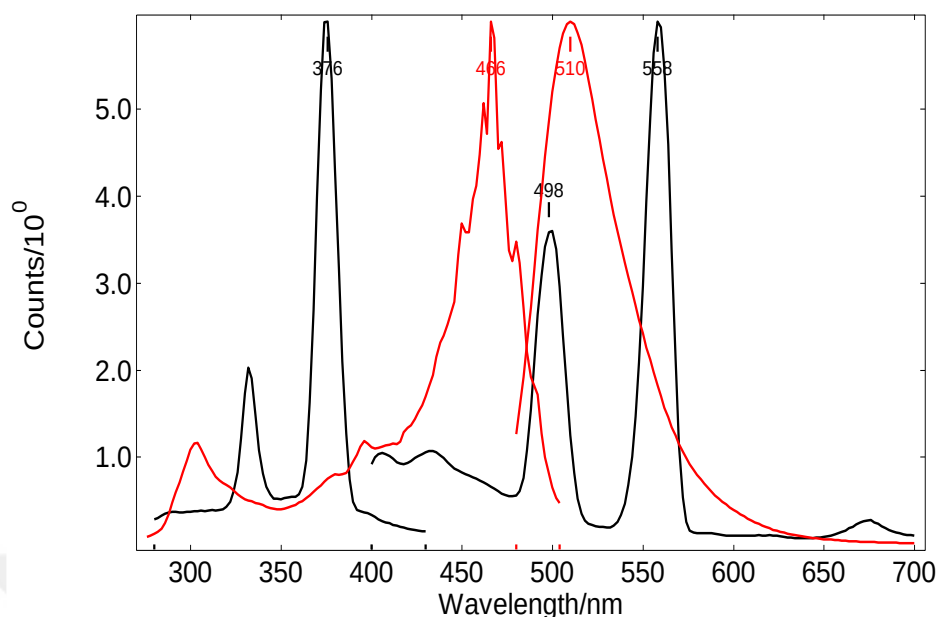


Figure 3.19 Normalized overlay spectra of the HPTS and 3% Er^{3+} - Tb^{3+} co-doped bioactive glass in form of thin film. (black: 3% Er^{3+} - Tb^{3+} co-doped bioactive glass, red: HPTS only) (λ_{ex} for the HPTS: 466 nm., λ_{ex} for the bioactive glass: 376 nm)

In all of the blended forms, the normalized overlay spectra supported existence of a potential energy transfer from the glass particles to the HPTS where the glass and HPTS are the donor and acceptor species, respectively.

3.3.9 CO_2 Induced Response of the Composites

CO_2 induced response of the bioactive containing composites were investigated in the absence and presence of the ionic liquid, spectroscopically. The response was evaluated in terms of I_0/I_{100} parameter as well as calibration plots. The I_0/I_{100} ratio is a convenient way to explain the sensitivity of the studied material and the I_0 and I_{100} refers the emission intensity in the absence (0.0%) and presence of the CO_2 (100%) concentration, respectively. In all cases, the composite exhibited significant response towards the CO_2 for the concentration range of 0.0-20.0% CO_2 . The I_0/I_{100} ratio was recorded as 109 and 50 for the IL-free and IL-doped forms respectively. In the absence of the IL, the CO_2 induced response was in direction of decrease in the emission

intensity and non-linear, however presence of the IL resulted in more linear calibration plots.

3.3.10 CO₂ Induced Response of Er³⁺ Doped Bioactive Glass and HPTS

Figure 3.20 indicates CO₂ induced excitation and emission spectra of the 1% Er³⁺ doped Bioactive glass and HPTS based composite for different concentrations of the CO₂.

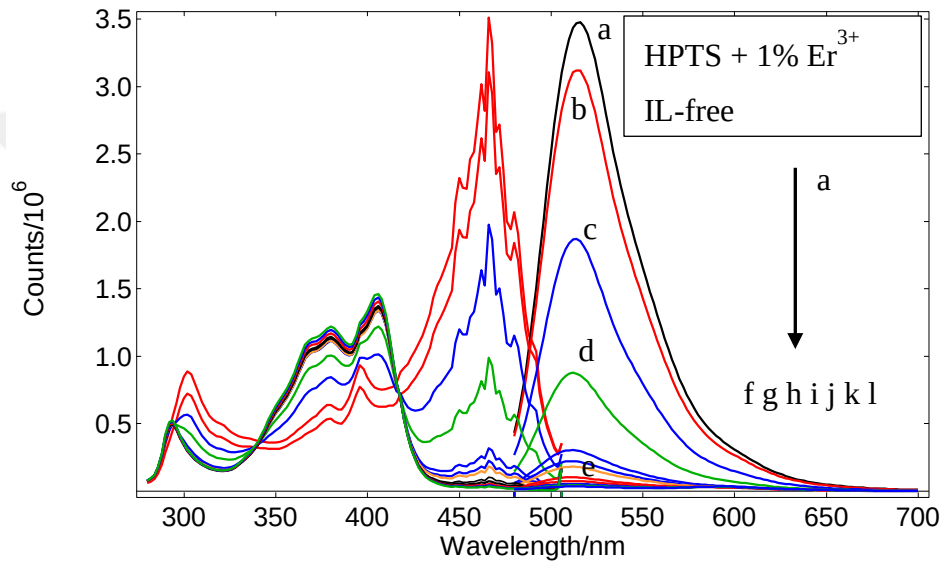


Figure 3.20 CO₂ induced excitation and emission spectra of the 1% Er³⁺ doped Bioactive glass and HPTS based composite for different concentrations of the CO₂. a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g:20.0, h: 30.0, i: 40.0, j: 60.0, k:80.0, l:100.0% [CO₂]

Similarly, CO₂ based response of the IL-doped composite was shown in Figure 3.21.

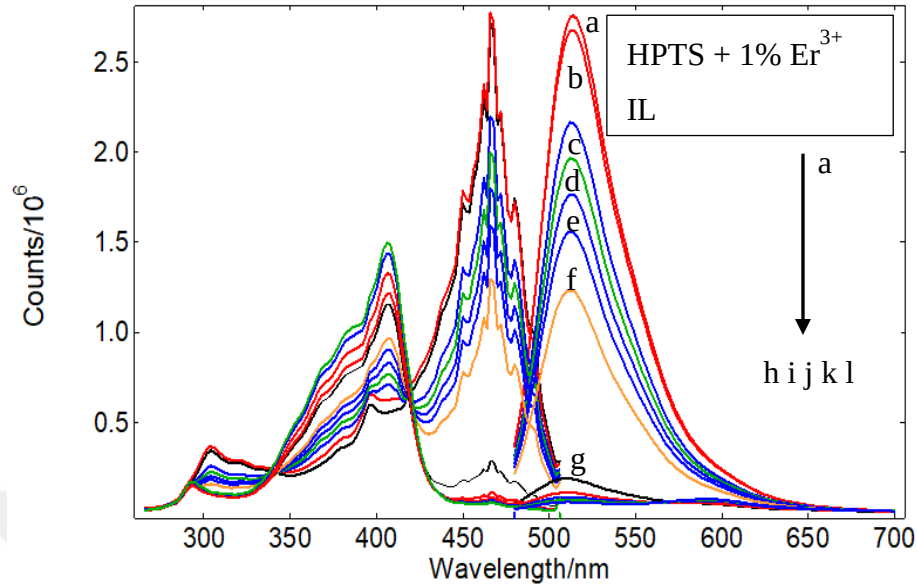


Figure 3.21 CO₂ induced excitation and emission spectra of the 1% Er³⁺ doped Bioactive glass and HPTS based composite for different concentrations of the CO₂ in the presence of IL. a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g:20.0, h: 30.0, i: 40.0, j: : 60.0, k:80.0, l:100.0% [CO₂]

Calibration plots of the studied materials were drawn for different concentrations of the CO₂ versus emission intensity. Figure 3.22 and 3.23 indicate the related calibration plots for the 1% Er³⁺ doped Bioactive glass and HPTS including composites, for the IL-free and IL-doped sensing agents, respectively.

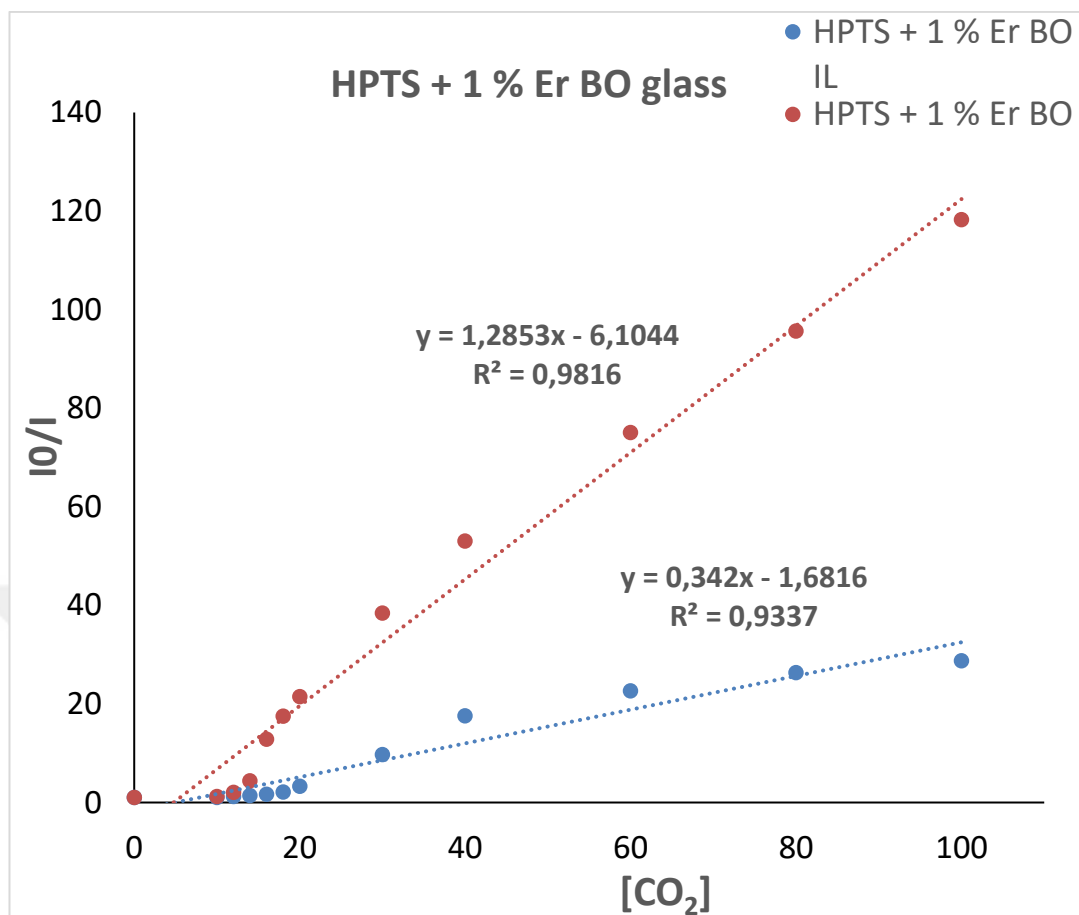


Figure 3.22 Calibration plots of the composites for different concentrations the CO_2 : a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g: 20.0, h: 30.0, i: 40.0, j: 60.0, k: 80.0, l: 100.0% $[CO_2]$

We enforced the linear fit for the whole concentration range of 0.0-100.0% CO_2 . While the calibration plot of the IL-free composite exhibiting higher slope (1.28), the IL containing form yielded almost $\frac{1}{4}$ of the slope of the IL doped form (0.34). The R^2 values of 0.9816 and 0.9337 were recorded for the IL-free and IL doped forms, respectively. However, the calibration sensitivity should also be evaluated for the concentration range of 0.0-20.0% CO_2 . Figure 3.22 indicates the CO_2 induced response for the narrowed range of the CO_2 .

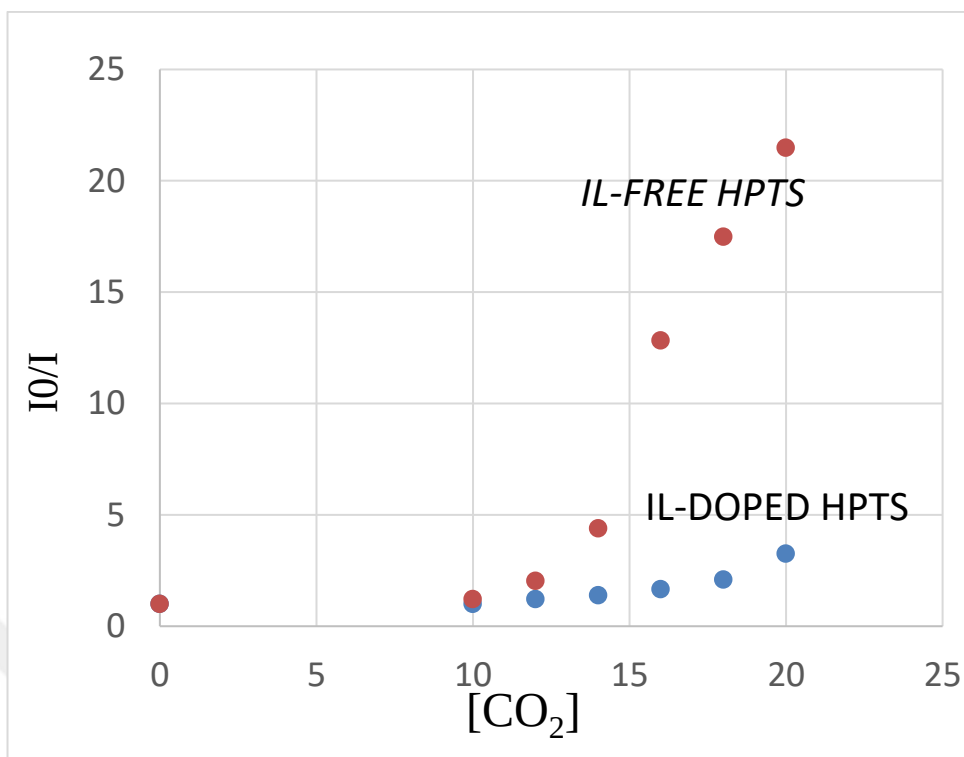


Figure 3.23 CO₂ induced response of the 1% Er³⁺ doped Bioactive glass and HPTS based composite for 0.0-20.0% [CO₂]

From Figure 3.23 it can be concluded that the CO₂ induced calibration response could not be linearized for the concentration range of 0.0-20.0% [CO₂] due to the hyper sensitivity of the composite towards the gasses carbon dioxide.

3.3.11 CO₂ Induced Response of Tb³⁺ Doped Bioactive Glass and HPTS

Similar to the previous work, CO₂ based response of the Tb³⁺ doped bioactive glass containing composites were spectroscopically investigated in the absence and presence of the ionic liquid. We recorded excitation emission based response of the composite towards the varying concentrations of the CO₂. Figure 3.24 and 3.25 reveal CO₂ induced excitation and emission spectra of the 5% Tb³⁺ doped Bioactive glass and HPTS based composite for different concentrations of the CO₂ between 0.0-100.0% [CO₂].

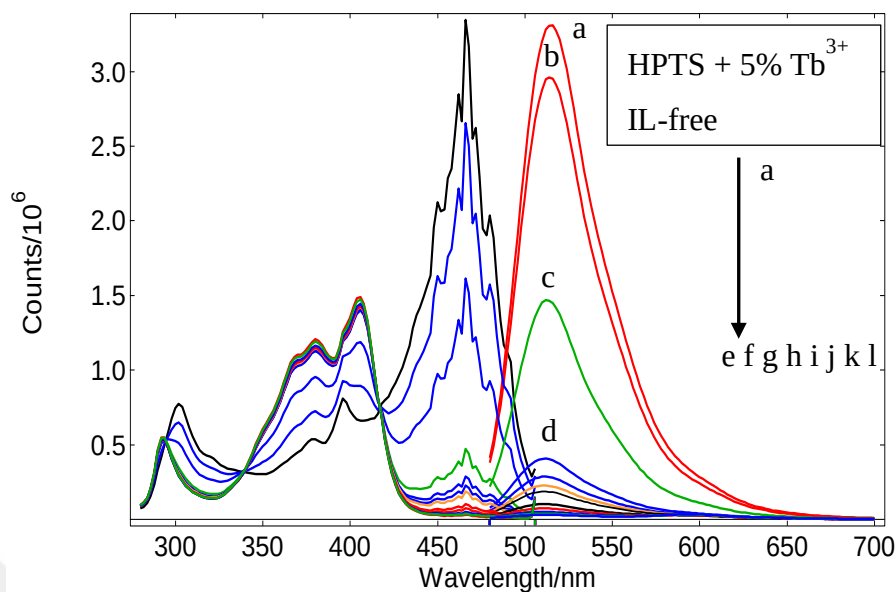


Figure 3.24 CO₂ induced excitation and emission spectra of the 5% Tb³⁺ doped Bioactive glass and HPTS based composite for different concentrations of the CO₂. a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g:20.0, h: 30.0, i: 40.0, j: 60.0, k:80.0, l:100.0% [CO₂]

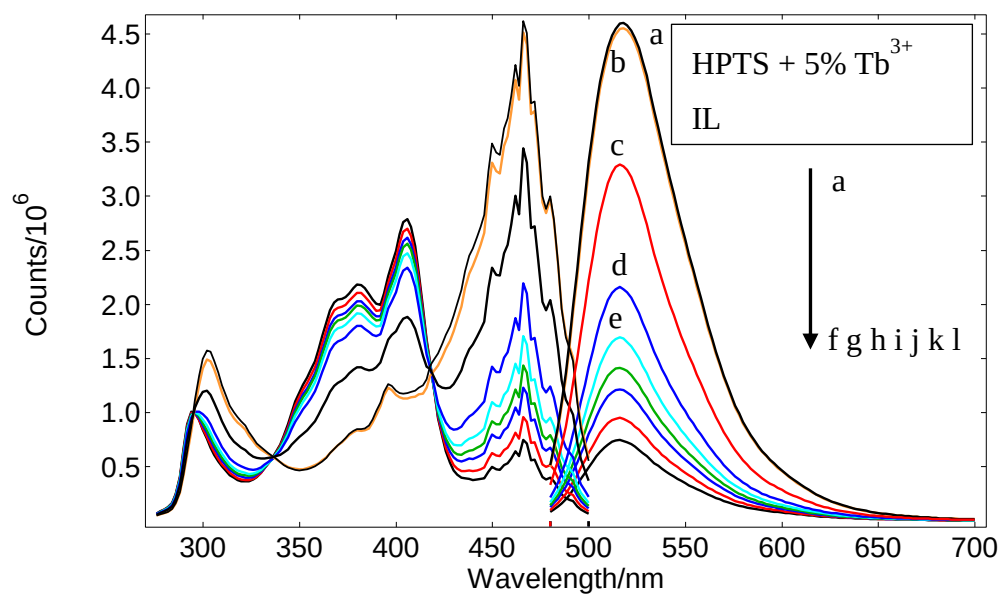


Figure 3.25 CO₂ induced excitation and emission spectra of the 5% Tb³⁺ doped Bioactive glass and HPTS based composite for different concentrations of the CO₂ in the presence of IL. a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g:20.0, h: 30.0, i: 40.0, j: 60.0, k:80.0, l:100.0% [CO₂]

The IL-free composite exhibited more sensitive response yielding calibration equation of; $y = 1,256x - 6,7563$ and regression coefficient of $R^2 = 0,9902$ which was better than that of the response of IL containing one in terms of the slop and regression coefficient ($y = 0,0526x + 0,9418$ and $R^2 = 0,9799$) (See Figure 3.26)

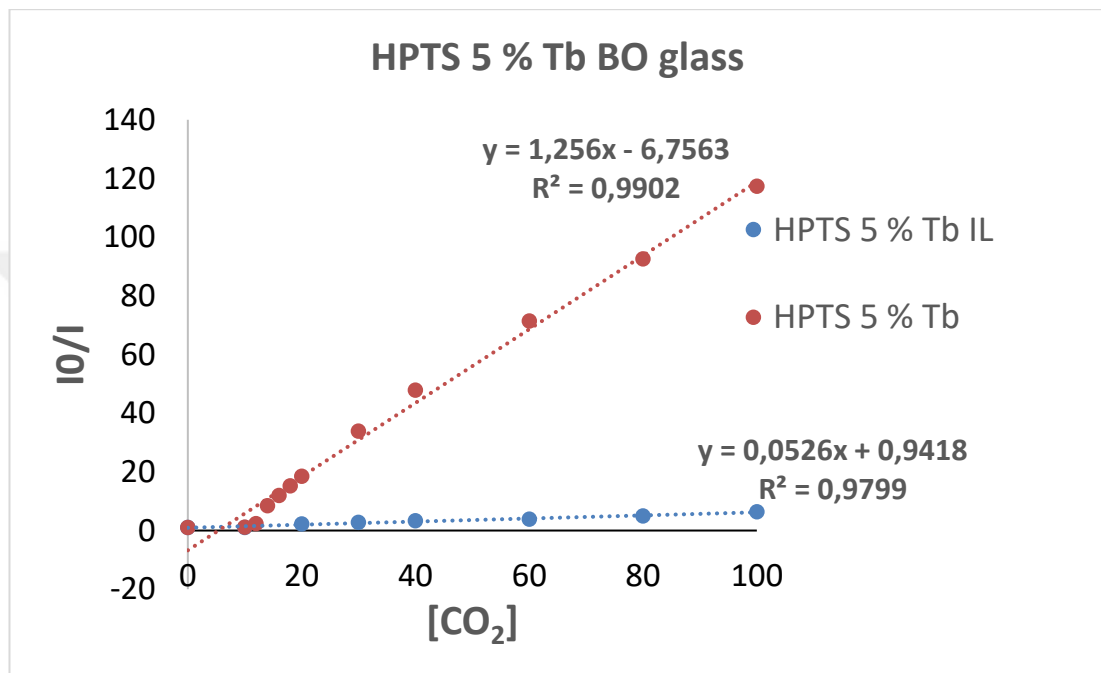


Figure 3.26 Calibration plots of the IL-free and IL containing composites for different concentrations the CO₂: a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g: 20.0, h: 30.0, i: 40.0, j: 60.0, k: 80.0, l: 100.0% [CO₂]

3.3.12 CO₂ Based Response of the Er³⁺-Tb³⁺ Doped Bioactive Glass and HPTS

Spectroscopic response of the Er³⁺-Tb³⁺ co-doped Bioactive glass and HPTS towards CO₂ has been investigated. The composite exhibited hyper sensitive response for the concentration range of 0.0-12.0% CO₂ for the IL-free blends. This was almost 80% of the intensity based response (See Figure 3.27 and 3.28).

The IL-equipped composite yielded approximately 50% of the response for the concentration range of 0.0-14.0% CO₂. Figure 3.28 indicates CO₂ induced excitation

and emission spectra of the 3% Er^{3+} - Tb^{3+} doped Bioactive glass and HPTS based composite for different concentrations of the CO_2 in the presence of IL.

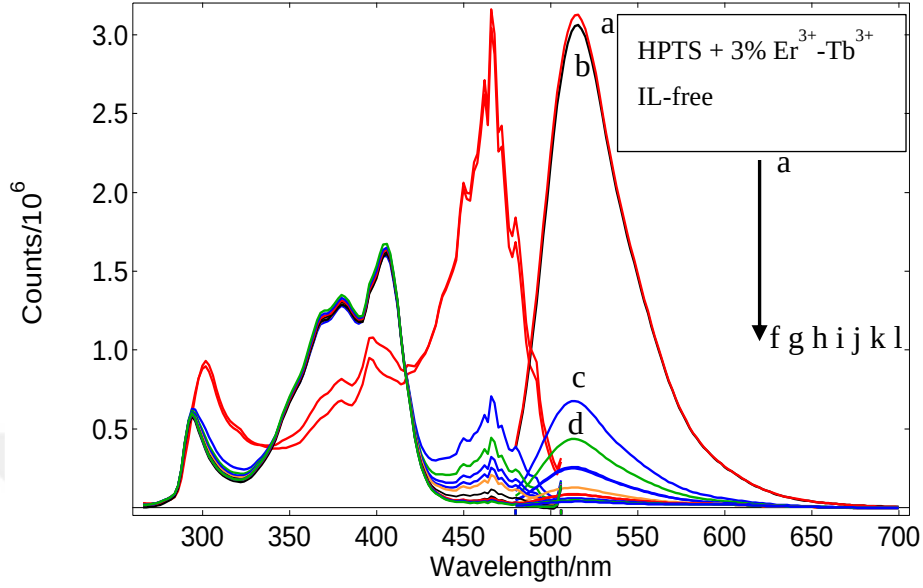


Figure 3.27 CO_2 induced excitation and emission spectra of the 3% Er^{3+} - Tb^{3+} doped Bioactive glass and HPTS based composite for different concentrations of the CO_2 . a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g:20.0, h: 30.0, i: 40.0, j: 60.0, k:80.0, l: 100.0% [CO_2]

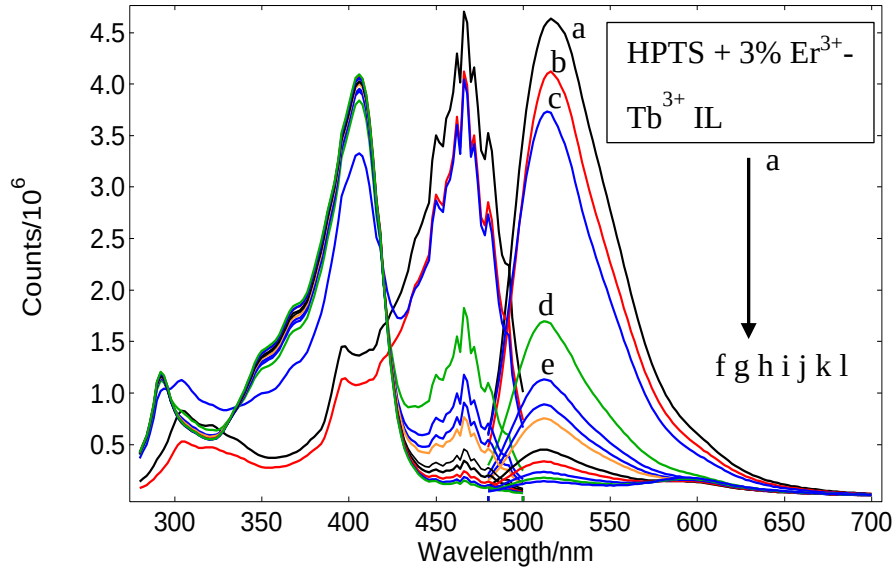


Figure 3.28 CO_2 induced excitation and emission spectra of the 3% Er^{3+} - Tb^{3+} doped Bioactive glass and HPTS based composite for different concentrations of the CO_2 in the presence of IL. a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g:20.0, h: 30.0, i: 40, j: 60.0, k:80.0, l:100.0% [CO_2]

The IL-free composite yielded exponential response towards CO₂ between 0.0-16.0% for the [CO₂]. The IL doped form exhibited similar response for the concentration range of 0.0-14.0% [CO₂]. Therefore, the CO₂ induced response cannot be linearized for the subjective concentration ranges for both of the composites.

Figure 3.29 reveals Calibration behavior of the both IL-free and IL-doped composites for different concentrations the CO₂: between 0.0-100.0% [CO₂] which can be defined by the equations of $y = 0,8466x - 0,2698$ $R^2 = 0,9576$ and $y = 0,3616x - 1,101$ $R^2 = 0,9889$, respectively.

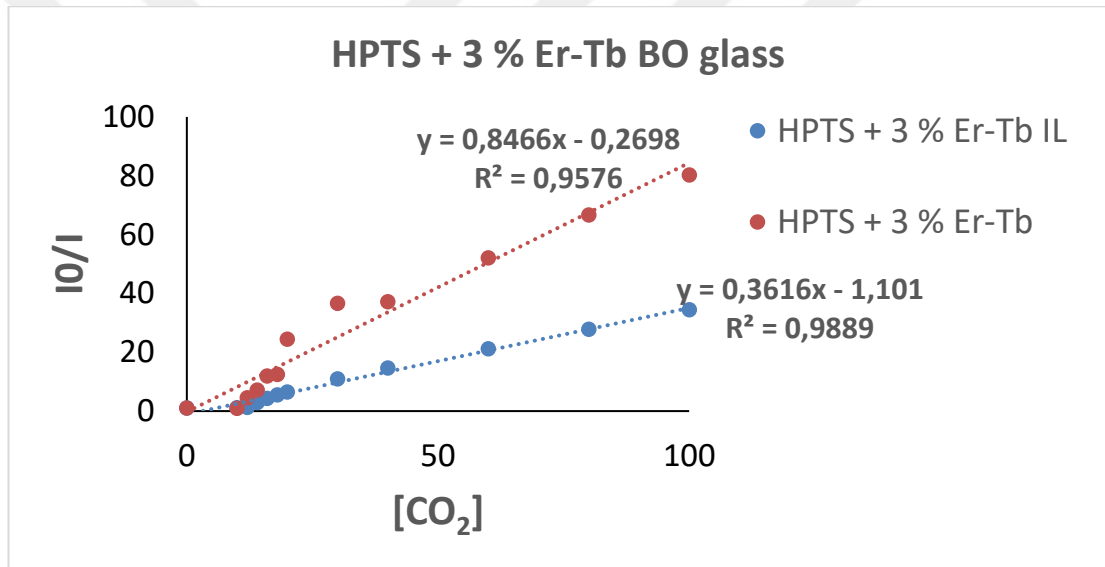


Figure 3.29 Calibration plots of the composites for different concentrations the CO₂: a: 0.0, b: 10.0, c: 12.0, d: 14.0, e: 16.0, f: 18.0, g: 20.0, h: 30.0, i: 40.0, j: 60.0, k: 80.0, l: 100.0% [CO₂]

For the whole concentration range (0.0-100.0 pCO₂), response of the IL-free composite can be defined by the equation of $y=0.8466x-0.2698$ and $R^2=0.9576$. The IL-doped material exhibited a more linear response which can be defined by the equation of $y=0.3616x-1.101$ and $R^2=0.9889$ for the same concentration range.

The I₀/I₁₀₀ parameter is another indicator of the sensitivity of the material under investigation. Therefore, we extracted the I₀/I₁₀₀ parameters of the utilized composites where I₀ and I₁₀₀ are the emission intensities for the 0.0 and 100.0% pCO₂ (See Table

3.2). In all cases, presence of the IL in the matrix resulted in lower slopes in the calibration plots which means worsened sensitivity. However, the ionic liquid provided better linearity in most of the studied matrices.

Table 3.2 I_0/I_{100} parameters of the utilized composites (I_0 =emission intensity at the 0.0% pCO₂ I_{100} =emission intensity at the 100.0% pCO₂)

Sample	IL Doped	IL-free
	I_0/I_{100}	I_0/I_{100}
HPTS	31	47
HPTS + 1393 BO	39	87
HPTS + 1% Er BO	50	109
HPTS + 5% Tb BO	45	115
HPTS + 3% Er-Tb BO	34	81

The 5% Tb doped IL-free BO glass yielded the I_0/I_{100} value of 115 when exposed to the CO₂. This was the highest response for the gas obtained by the HPTS equipped bioactive glasses. The 1.0% Er-doped glass followed this material exhibiting I_0/I_{100} value of 109. Among the IL doped composites the HPTS equipped-1% Er doped bioactive glass yielded the highest I_0/I_{100} value (50) for the CO₂. The IL is known as a stabilizer for the HPTS and has been used many times in polymeric matrices to enhance its long term photostability (Aydogdu, Ertekin, Suslu, Ozdemir, Celik & Cocen, 2011; Oter, Ertekin & Derinkuyu, 2008). Presence of the IL in the composites decreased the I_0/I_{100} parameter in all cases.

3.3.13 Decay Time Measurements of HPTS Equipped Bioactive Glasses

Decay curves of all of the test materials were recorded in the absence and presence of the CO₂ where absence and presence refer 0.0 and 100.0% partial pressure of the gaseous CO₂. Figure 3.30-3.38 represent the subjective decay curves together with the composition information. Additional tables for the interpretation of the experimental data were also given. All of the test materials exhibited bi-exponential decay in nanosecond time scale. Table 3.3 and 3.4 indicate the bi-exponential decays and related statistics of the IL-free and IL-doped composites respectively.

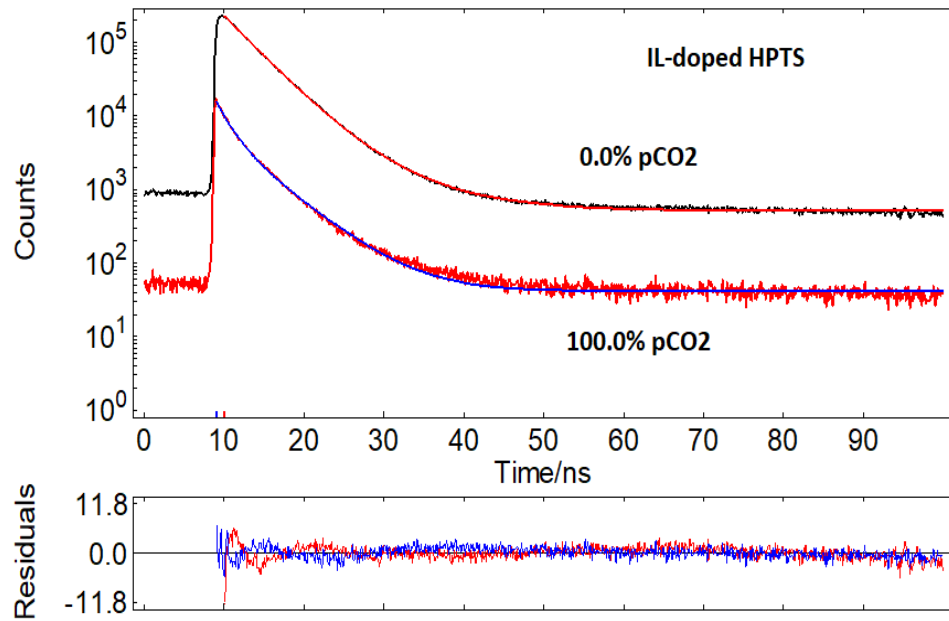


Figure 3.30 Decay curves of the IL-doped HPTS in the absence (0.0% pCO₂) and presence (100.0% pCO₂) of the CO₂

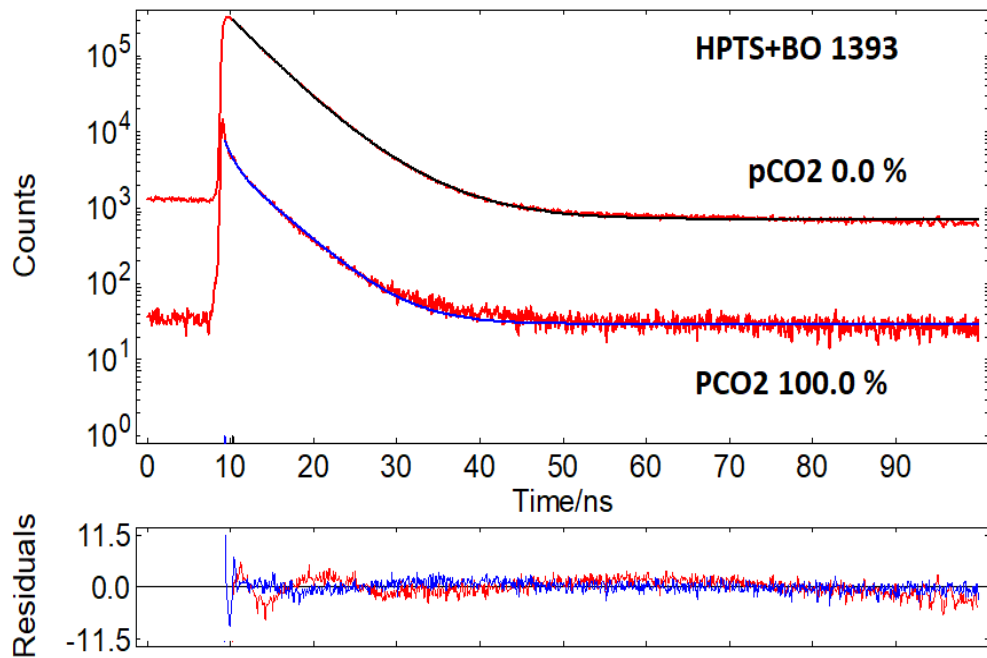


Figure 3.31 Decay curves of the HPTS and 1393 BO containing composites in the absence (0.0% pCO₂) and presence (100.0% pCO₂) of the CO₂

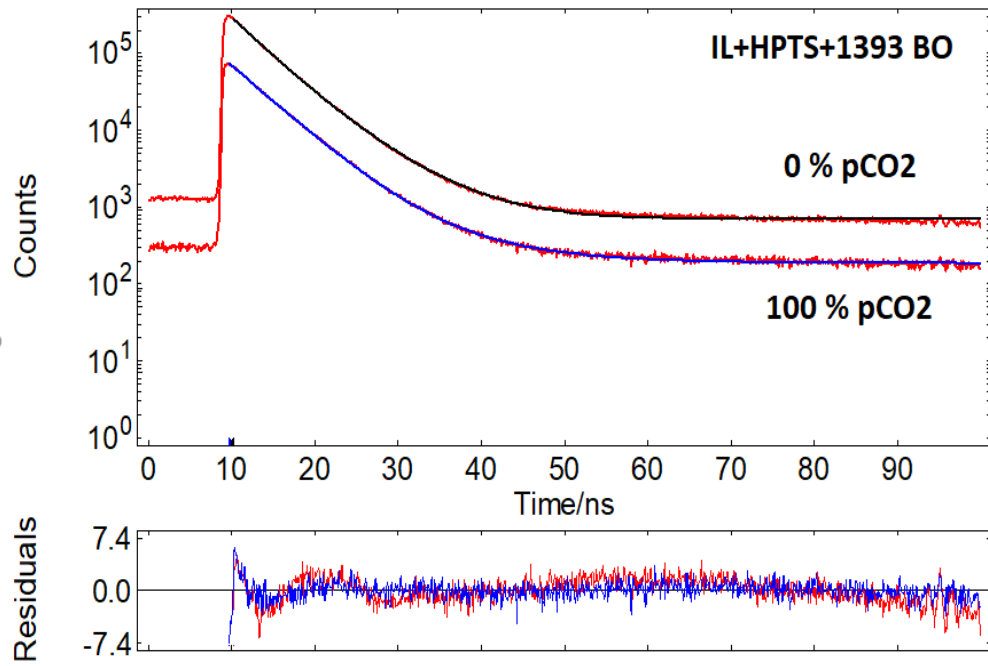


Figure 3.32 Decay curves of the IL, HPTS and 1393 BO containing composites in the absence (0.0% pCO₂) and presence (100.0% pCO₂) of the CO₂

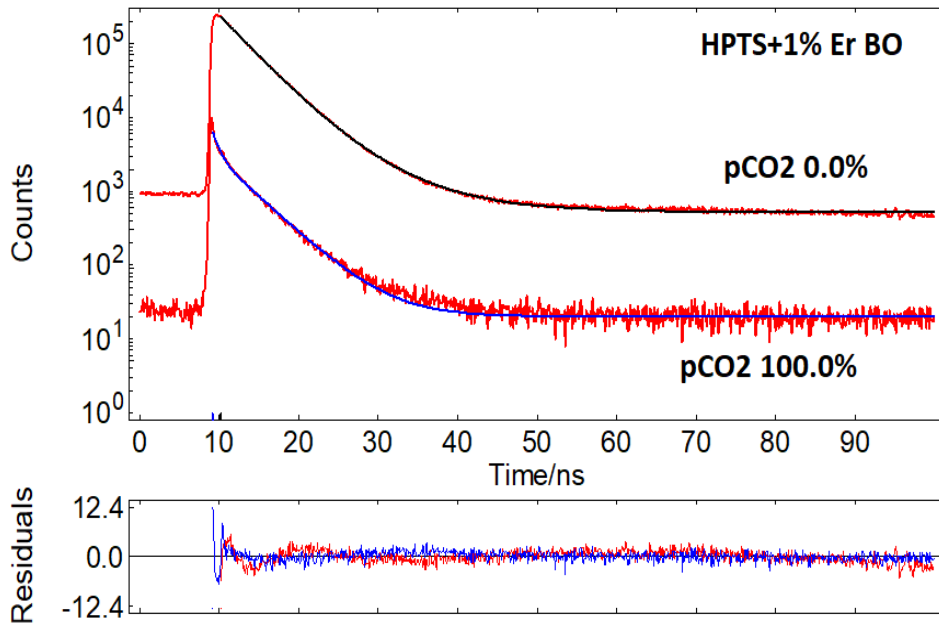


Figure 3.33 Decay curves of the IL-free, HPTS and 1% Er doped BO containing composites in the absence (0.0% pCO₂) and presence (100.0% pCO₂) of the CO₂

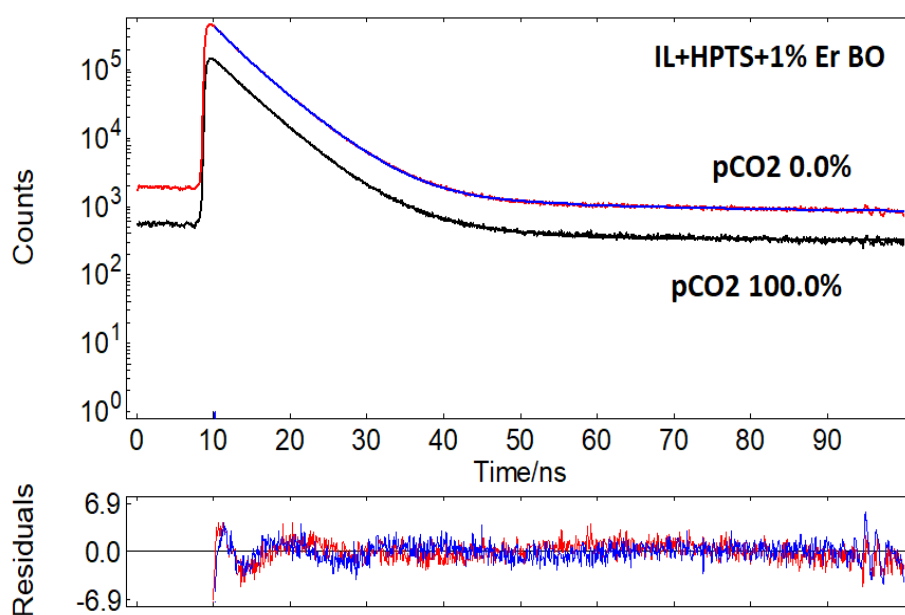


Figure 3.34 Decay curves of the IL, HPTS and 1% Er doped BO containing composites in the absence (0.0% pCO₂) and presence (100.0% pCO₂) of the CO₂

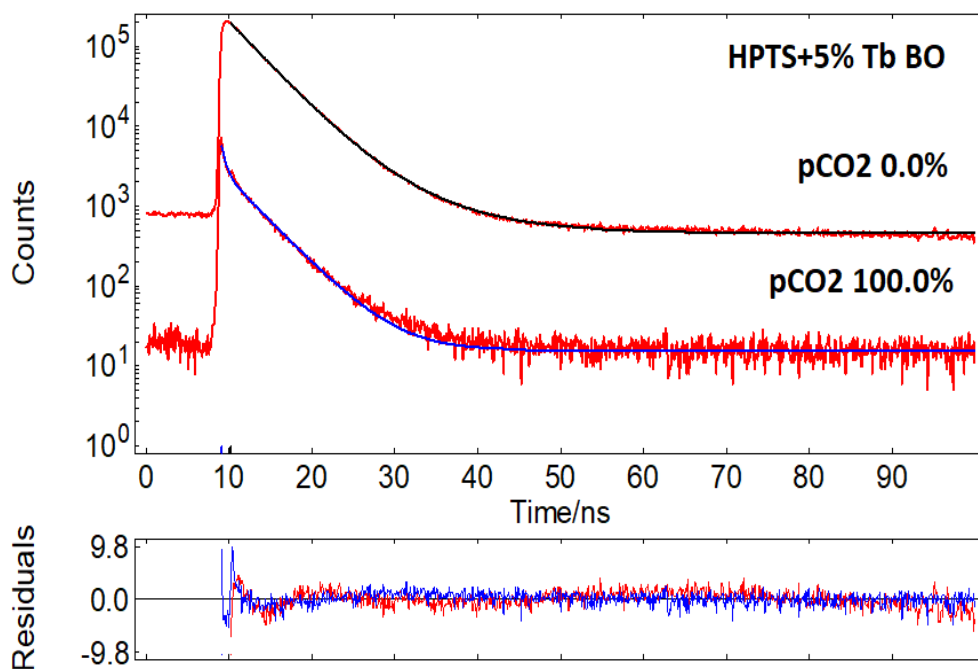


Figure 3.35 Decay curves of the HPTS and 5% Tb doped BO containing composites in the absence (0.0% pCO₂) and presence (100.0% pCO₂) of the CO₂

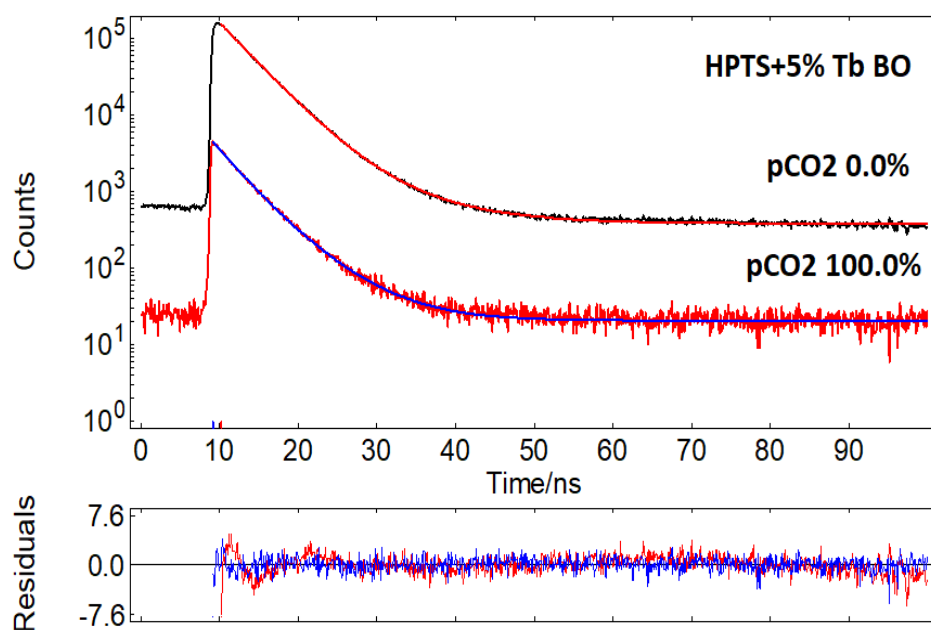


Figure 3.36 Decay curves of the IL, HPTS and 5% Tb doped BO containing composites in the absence (0.0% pCO₂) and presence (100.0% pCO₂) of the CO₂

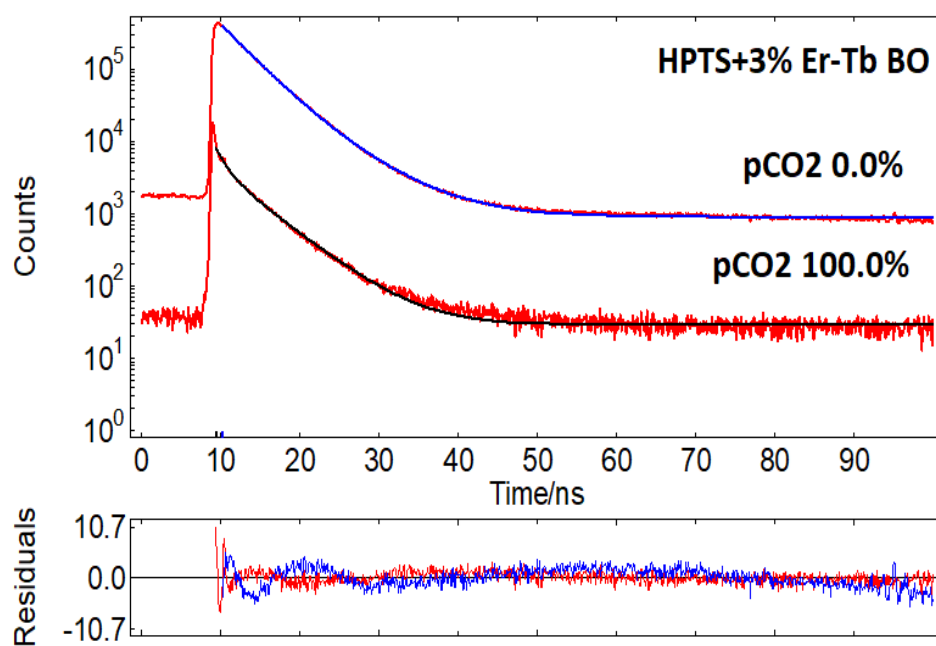


Figure 3.37 Decay curves of the HPTS and 3% Er-Tb co-doped BO containing composites in the absence (0.0% pCO₂) and presence (100.0% pCO₂) of the CO₂

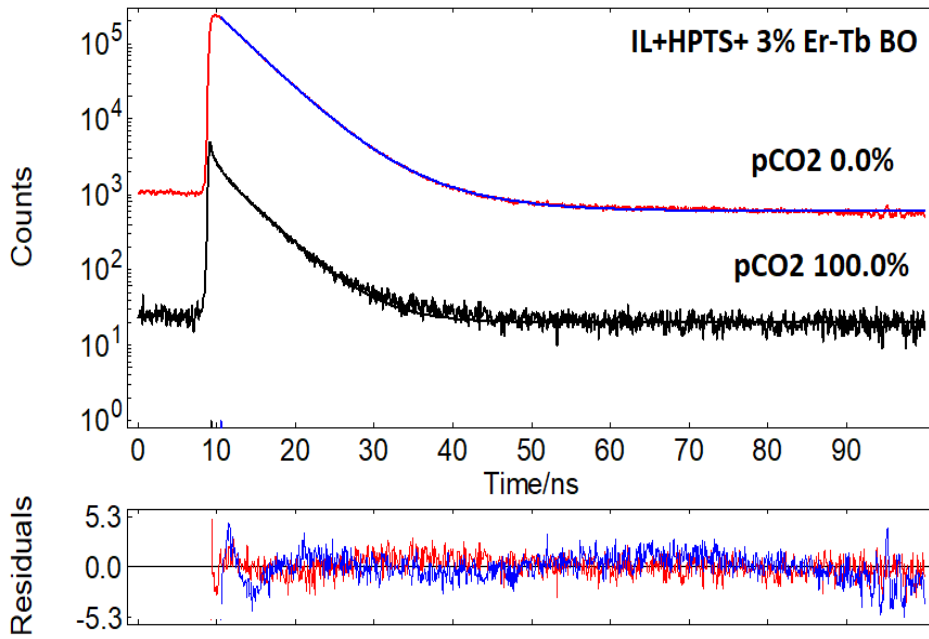


Figure 3.38 Decay curves of the IL, HPTS and 3% Er-Tb co-doped BO containing composites in the absence (0.0% pCO₂) and presence (100.0% pCO₂) of the CO₂

Upon excitation by 467 nm pulsed laser the HPTS-equipped bioactive glasses of HPTS-1393 BO, HPTS-1% Er BO, HPTS-5% Tb BO and HPTS-3% Er-Tb BO, exhibited average decay times of 4.46, 4.32, 4.38 and 4.40 respectively. All of the decay times were bi-exponential. Decay times of the bioactive containing composites did not exhibit a significant variation in comparison to the decay time of the bare HPTS in the absence of the CO₂. When exposed to the 100% of the CO₂, the decay times of 3.85, 3.79, 3.59 and 4.33 were recorded for the same composites respectively. The observed slight decreases in the decay times upon exposure to CO₂ which does not provide a strong signal variation to calibrate the proposed composites as decay time based sensor materials.

Table 3.3 Bi-exponential decays and related statistics (decay time, standard deviation and abundance %) of the IL-free composites

IL-free		0% CO ₂ (Em: 510 nm Ex: 467 nm)			100% CO ₂ (Em: 510 nm Ex: 467 nm)			
Composite	τ_0	Decay Time	Std.	Rel. (%)	τ_0	Decay Time (ns)	Std. Dev.	Rel.
	(0% CO ₂)	(ns)	Dev. (ns)		(100% CO ₂)		(ns)	(%)
HPTS + 1393 BO	τ_1	3.7096	0.00926	76.98	τ_1	0.9528	0.02324	18.44
	τ_2	6.9943	0.05011	23.02	τ_2	4.5071	0.02308	81.56
	τ_{avr}	4.46			τ_{avr}	3.85		
HPTS + 1% Er BO	τ_1	3.7194	0.00732	85.33	τ_1	0.7547	0.02076	16.11
	τ_2	7.7892	0.07501	14.67	τ_2	4.3749	0.02166	83.89
	τ_{avr}	4.32			τ_{avr}	3.79		
HPTS + 5% Tb BO	τ_1	3.8404	0.00726	88.18	τ_1	0.4980	0.01399	13.74
	τ_2	8.3906	0.09977	11.82	τ_2	4.0871	0.01976	86.26
	τ_{avr}	4.38			τ_{avr}	3.59		
HPTS + 3% Er-Tb BO	τ_1	3.5701	0.00854	72.92	τ_1	1.2630	0.02947	19.54
	τ_2	6.6468	0.03663	27.08	τ_2	5.0769	0.02644	80.46
	τ_{avr}	4.40			τ_{avr}	4.33		

Similarly, when excited by the same source the IL-doped HPTS equipped bioactive glasses of HPTS-1393 BO, HPTS-1% Er BO, HPTS – 5% Tb BO and HPTS-3% Er-Tb BO, exhibited average decay times of 4.34, 5.03, 5.14, 4.44 and 4.72 ns, respectively. Presence of the IL in the matrix resulted in slightly increased decay times with respect to the IL-free formulations. All of the decay times were bi-exponential except that of decay time of HPTS-1 % Er BO which exhibited a three exponential decay. Decay times of the bioactive containing composites exhibited a slight enhancement in comparison to the decay time of the bare HPTS in the absence of the CO₂. When exposed to the CO₂ decay times of the gas sensitive bioactive based composites exhibited signal drops of 5.0, 11.0, 4.0 and 14.6%, respectively, which is not appropriate for calibration for a decay time based instrument.

Table 3.4 Bi-exponential decay times, standard deviation and abundance % of the IL-doped composites

IL-doped		0% CO ₂ (Em: 510 nm Ex: 467 nm)			100% CO ₂ (Em: 510 nm Ex: 466 nm)			
Composite	τ_0	Decay Time	Std.	Rel. (%)	τ_0	Decay Time	Std. Dev.	Rel.
	(0% CO ₂)	(ns)	Dev.	(ns)	(100% CO ₂)	(ns)	(ns)	(%)
HPTS	τ_1	3.7959	0.00663	88.04	τ_1	1.6254	0.01942	37.21
	τ_2	8.3179	0.08961	11.96	τ_2	5.0733	0.03095	62.79
	τ_{avr}	4.34			τ_{avr}	3.79		
HPTS + 1393 BO	τ_1	4.5470	0.01106	92.20	τ_1	3.8445	0.01377	67.37
	τ_2	10.7908	0.27629	7.80	τ_2	6.7217	0.04368	32.63
	τ_{avr}	5.03			τ_{avr}	4.78		
HPTS + 1% Er BO	τ_1	2.6173	0.02640	24.15	τ_1	4.0403	0.00864	88.96
	τ_2	4.9509	0.02085	73.67	τ_2	8.8227	0.12933	11.04
	τ_3	39.5246	3.68913	2.18				
	τ_{avr}	5.14			τ_{avr}	4.57		
HPTS + 5% Tb BO	τ_1	3.9388	0.00737	90.33	τ_1	3.3198	0.09297	66.61
	τ_2	9.1180	0.13580	9.67	τ_2	6.1990	0.31062	33.39
	τ_{avr}	4.44			τ_{avr}	4.28		
HPTS + 3% Er-Tb BO	τ_1	4.1860	0.00746	89.15	τ_1	0.8463	0.03999	11.68
	τ_2	9.0680	0.11566	10.85	τ_2	4.4552	0.02748	88.32
	τ_{avr}	4.72			τ_{avr}	4.03		

3.3.14 Kinetic Measurements: Response Time and Recovery Characteristics

The kinetic mode measurements were performed under fully CO₂ and nitrogenated conditions, respectively. The response time τ_{90} (the time to achieve 90% of the overall signal change) of the studied composites were determined by the kinetic mode measurements. All of the test materials exhibited similar response in kinetic mode measurements. The response times (τ_{90}) of the test materials were found to be in the range of 8–14 seconds on exposure to 100% CO₂ (see Fig. 3.39-3.42). The reported response times of the employed composites include the dead volume of long gas tubing's rather than the true response times. Lower tubing volumes or utilization of a micro-volume flow cell may provide shorter response times for the same composites. The initial signal intensities for the sensing composites could be completely recovered and no significant drift was observed even after the 6th or further cycles. Between the 1st and 6th cycles the level of reproducibility of upper signal levels was found to be

$4.60 \times 10^6 \pm 0.22 \times 10^6$ (n=5) For the HPTS equipped bioactive glass (HPTS+1393 BO). The regeneration time was found to be 179 s. These parameters were found to be $3.84 \times 10^6 \pm 0.37 \times 10^6$ (n=5), $4.11 \times 10^6 \pm 0.02 \times 10^6$ (n=5), $3.86 \times 10^6 \pm 0.21 \times 10^6$ (n=6) for the IL-Free HPTS- 1 % Er-1393 BO, HPTS- 5% Tb-1393 BO and HPTS- 3 % Er-Tb 1393 BO based materials, respectively. The last two samples; HPTS-5 % Tb-1393 BO and HPTS-3 % Er-Tb 1393 BO yielded more dynamic response in terms of standard deviation, reproducibility, response and recovery times as well as drift losses.

The reported response and recovery times were longer than that of the previously published ones which can be attributed to the long tubing's utilized through the experiments (Oter, Ertekin & Derinkuyu, 2008).

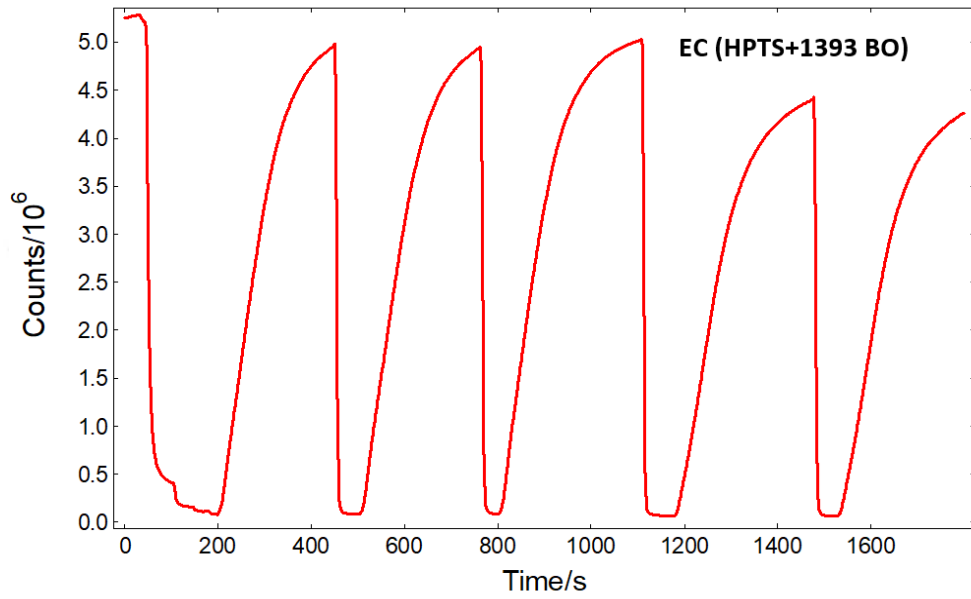


Figure 3.39 Kinetic response of the sensing composite prepared from the IL-Free HPTS- 1393 BO

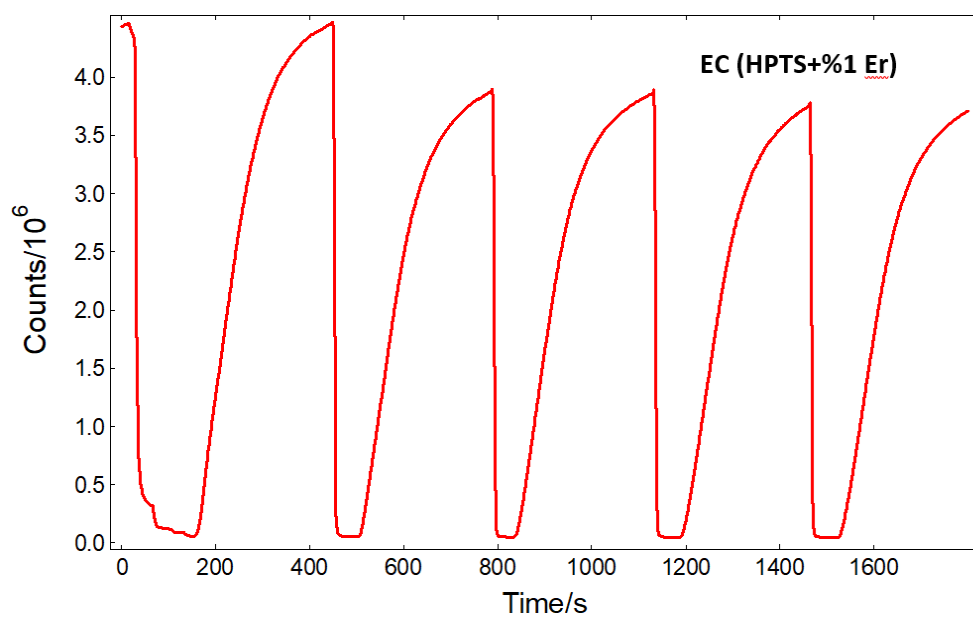


Figure 3.40 Kinetic response of the sensing composite prepared from the IL-Free HPTS- 1% Er-1393 BO

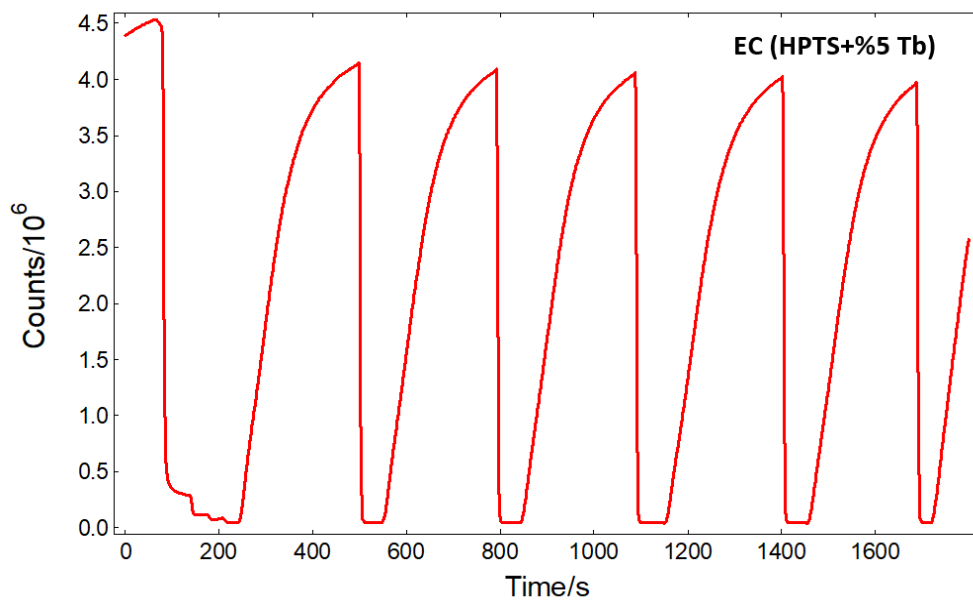


Figure 3.41 Kinetic response of the sensing composite prepared from the IL-Free HPTS- 5% Tb-1393 BO

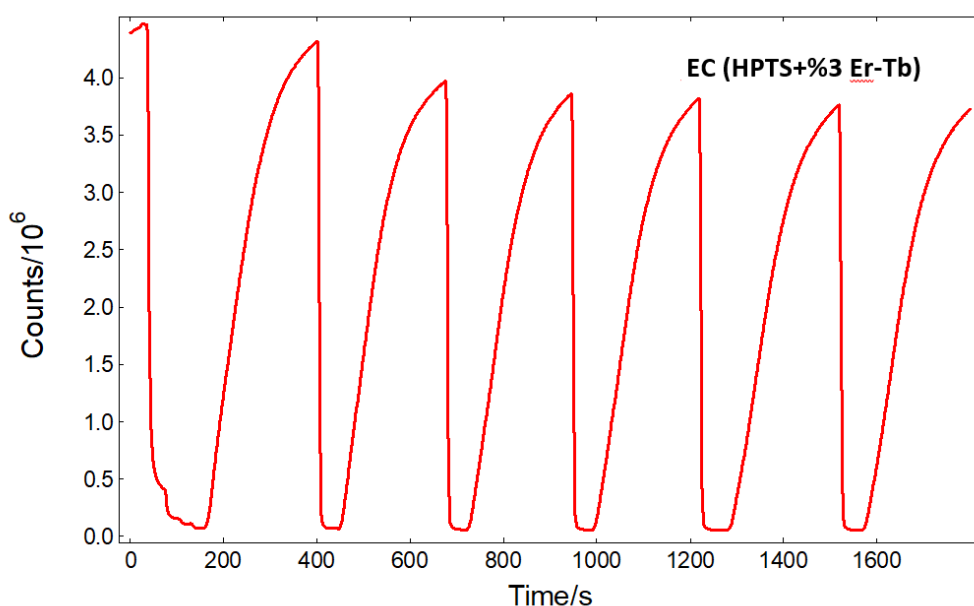


Figure 3.42 Kinetic response of the sensing composite prepared from the IL-Free HPTS- 3%Er- Tb- 1393 BO

3.4 Conclusion

The Ethyl Cellulose (EC) encapsulated HPTS dye is known as high sensitivity towards the CO₂ and has been tested many times on the Mylar sheets in form of thin films. However, for the first time we used the dye along with the bioactive glasses and ionic liquid which enhanced its both intensity and stability. Herein, we investigated excitation-emission behavior and CO₂ sensitivity of the 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium-salt (HPTS) dye in an EC matrix on 13-93 bioactive glass powders. The sol-gel synthesized bioactive glasses were equipped with the rare earths of Er³⁺, Tb³⁺ and Er³⁺ and Tb³⁺, respectively. The glassy structures have been used as substrate due to their porous structure optical transparency and intrinsic fluorescence arising from Er³⁺ and Tb³⁺. When the ion pair form of the HPTS dye was used along with the bioactive glasses, exhibited enhanced fluorescence emission due to the energy transfer interactions. We recorded the excitation and emission spectra of the bioactive glasses and their HPTS coated forms for characterization, respectively. Their decay time related data were recorded in nanoseconds time scale. After spectral characterization steps we exposed the composites towards varying concentrations of

gaseous CO₂ and recorded the response both in steady-state and kinetic mode. We also determined the decay times in the absence and presence of the CO₂.



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