STRUCTURAL, LUMINESCENCE AND JUDD-OFELT ANALYSIS OF RARE EARTH DOPED OF MAGNESIUM SULFOBORATE GLASSES AND CRYSTALS

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DEDICATION

Dedicated to

My mother, **Malama Hauwa Muhammad**, whose sacrifice; My father, Malam **Dalhatu Dauda**, whose dream; My **uncle**, Malam Sadiq G. Abubakar whose support and encouragement; And My wife, **Fatima Abdulwahab**, whose patience;

Lead to achieve my doctoral degree

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ABSTRACT

A series of samples of undoped magnesium sulfoborate glasses and crystals with chemical composition of xMgO+(50-x) SO₃+50B₂O₃, with $10 \le x \le 30$ mol% were prepared by melt quenching and solid state reaction method respectively. Then a series of glass and crystal samples doped with rare earth ($RE = Dy_2O_3$, Eu_2O_3 and Sm_2O_3) with the chemical compositions of $10MgO+40SO_3+(50-y)B_2O_3+yRE$, with $0.1 \le y \le 1.0$ mol% were also prepared by melt quenching and solid state reaction method respectively. The amorphous/crystalline phases of the glass and crystal samples were characterized by X-Ray diffraction (XRD), while the structural features of the samples were measured using Fourier transform infrared (FTIR), Raman and nuclear magnetic resonance (NMR) spectroscopy. The optical properties of glass and crystal samples were characterized via UV-Vis-NIR and luminescence spectroscopy. The amorphous phase of the glass samples was confirmed by the diffused broad XRD pattern, while the crystal samples showed two crystalline phases of H₃BO₃ and MgSO₄(H₂O)₆. The infrared spectra show the coexistence of BO₃, BO₄, SO₄²⁻ and S–O–B (sulfoborate group) structural units in both glass and crystal samples. The Raman spectra also reveal the coexistence of BO₄, SO₄²⁻ and S-O-B (sulfoborate group) structural units in both glass and crystal samples. The NMR spectra show the existence BO₄ structural units in both glass and crystalline samples. The luminescence spectra of Dy^{3+} doped glass and doped crystal samples exhibit three emission bands at around 482 nm, 575 nm and 662 nm correspond to the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$, ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{6}H_{11/2}$ transitions respectively. As for Eu³⁺ doped glass samples, the emission spectra show peaks at 592 nm, 616 nm, 658 nm and 697 nm correspond to the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ transitions respectively, while for crystal samples, the emission spectra show six peaks belongs to Eu²⁺ and Eu³⁺ ions. The emission spectra of glass and crystal samples doped with Sm³⁺ ions show dominant peaks at around 565 nm, 601 nm, 646 nm and 706 nm correspond to the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$, ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$, ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ and ${}^{4}G_{5/2} \rightarrow {}^{6}H_{11/2}$ transitions respectively. The refractive index and quantum efficiency were calculated for all the studied samples. The higher value of branching ratios from ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ and ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$ transitions showed that Dy³⁺ and Sm³⁺ doped magnesium sulfoborate glasses and crystals are good candidates for lasing and lighting device applications.

ABSTRAK

Satu siri sampel kaca dan kristal magnesium sulfoborate tak berdop dengan komposisi kimia xMgO+(50-x) SO₃+50B₂O₃, dengan 10 $\leq x \leq$ 30 mol% telah disediakan masing-masing melalui kaedah sepuhlindap leburan dan tindak balas keadaan pepejal. Kemudian satu siri sampel kaca dan kristal berdop dengan nadir bumi (RE Dy_2O_3 , Eu_2O_3 dan Sm₂O₃) dengan komposisi kimia = $10MgO+40SO_3+(50-y)$ B₂O₃+yRE, dengan $0.1 \le y \le 1.0$ mol% juga telah disediakan masing-masing melalui kaedah sepuhlindap leburan dan tindak balas keadaan pepejal. Fasa amorfus/ kristal sampel kaca dan kristal telah dicirikan oleh pembelauan sinar-X (XRD), sementara ciri struktur sampel telah diukur menggunakan spektroskopi inframerah transformasi Fourier (FTIR), Raman dan resonans magnet nuklear (NMR). Sifat optik sampel kaca dan kristal dicirikan melalui spektroskopi UV-Vis-NIR dan luminesens. Fasa amorfus sampel kaca telah disahkan oleh corak belauan XRD yang melebar, sementara sampel kristal menunjukkan dua fasa kristal H₃BO₃ dan MgSO₄(H₂O)₆. Spektrum inframerah menunjukkan ujud sama dan struktur unit bagi BO₃, BO₄, SO₄²⁻ dan S-O-B (kumpulan sulfoborate) dalam kedua-dua sampel kaca dan kristal. Spektrum Raman juga mendedahkan ujud sama struktur unit BO4, SO4²⁻ dan S-O-B (kumpulan sulfoborate) dalam kedua-dua sampel kaca dan kristal. Spektrum NMR menunjukkan kewujudan struktur unit BO4 dalam kedua-dua sampel kaca dan kristal. Spektrum luminesens sampel kaca dan kristal berdop Dy³⁺ mempamerkan tiga jalur pancaran pada sekitar 482 nm, 575 nm dan 662 nm, masing-masing berpadanan dengan peralihan ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$, ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ dan ${}^{4}F_{9/2} \rightarrow {}^{6}H_{11/2}$. Bagi sampel kaca berdop Eu³⁺, spektrum pancaran menunjukkan puncak pada 592 nm, 616 nm, 658 nm dan 697 nm, masing-masing berpadanan dengan peralihan ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ dan ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$, manakala bagi sampel kristal, spektrum pancaran menunjukkan enam puncak kepunyaan ion Eu^{2+} dan Eu^{3+} . Spektrum pancaran bagi sampel kaca dan kristal berdop Sm³⁺ menunjukkan puncak dominan pada sekitar 565 nm, 601 nm, 646 nm dan 706 nm, masing-masing berpadanan dengan peralihan dari ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$, ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$, ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ dan ${}^{4}G_{5/2} \rightarrow {}^{6}H_{11/2}$. Indek biasan dan kecekapan kuantum telah dikira untuk semua sampel yang dikaji. Nilai nisbah cabang yang agak tinggi bagi peralihan ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ dan ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$ menyarankan bahawa sampel kaca dan kristal magnesium sulfoborate berdop ion Dy³⁺ dan Sm³⁺ berpotensi untuk digunakan sebagai bahan laser dan peranti pencahayaan.

TABLE OF CONTENTS

СНАР	TER	TITLE	PAGE
	DEC	LARATION	ii
	DED	ICATION	iii
	ACK	NOWLEDGEMENT	iv
	ABS	TRACT	V
	ABS	TRAK	vi
	TAB	LE OF CONTENTS	vii
	LIST	FOF TABLES	xi
	LIST	FOF FIGURES	xvi
	LIST	COF ABBREVIATIONS	xxiii
	LIST	FOF SYMBOLS	XXV
	LIST	SOF APPENDICES	xxvi
1	INTI	RODUCTION	1
	1.1	Background of the Research	1
	1.2	Problem Statement	5
	1.3	Objectives of the Study	5
	1.4	Scope of the Research	6
	1.5	Significance of the study	6
	1.6	Outline of Study	7
2	LITH	ERATURE REVIEW	8
	2.1	Introduction	8

2.2	Glass and Crystal X-Ray Diffraction	8
2.3	Infrared spectra Studies of Borate Glasses and Crystals	10

Infrared spectra Studies of Sulfoborate Glasses and	
Crystals	13
Raman Studies of borate Glasses and Crystals	15
Raman Spectra Studies of Sulfoborate Glasses	
and Crystals	18
Basic Theory of Nuclear Magnetic Resonance	21
Optical properties Analysis	25
2.8.1 Absorption Analysis	25
2.8.2 Judd–Ofelt Theory and Analysis	32
Luminescence Studies	38
2.9.1 Excitation and Emission Spectra Doped	
Dysprosium Ions	38
2.9.2 Excitation and Emission Spectra Doped	
Europium Ions	41
2.9.3 Excitation and Emission Spectra Doped	
Samarium Ions	45
2.9.4 Lifetime Analysis	47
	Infrared spectra Studies of Sulfoborate Glasses and Crystals Raman Studies of borate Glasses and Crystals Raman Spectra Studies of Sulfoborate Glasses and Crystals Basic Theory of Nuclear Magnetic Resonance Optical properties Analysis 2.8.1 Absorption Analysis 2.8.2 Judd–Ofelt Theory and Analysis Luminescence Studies 2.9.1 Excitation and Emission Spectra Doped Dysprosium Ions 2.9.2 Excitation and Emission Spectra Doped Europium Ions 2.9.3 Excitation and Emission Spectra Doped Samarium Ions 2.9.4 Lifetime Analysis

METHODOLOGY

METI	HODOLOGY	52
3.1	Introduction	52
3.2	Samples Preparation	52
3.3	X-ray Diffraction Characterization	54
3.4	Infrared Spectrometer Characterization	55
3.5	Raman Spectrometer Characterization	56
3.6	Nuclear Magnetic Resonance Characterization	57
3.7	Luminescence Spectrophotometer Characterization	58
3.8	UV-Vis-NIR Spectrophotometer Characterization	59
3.9	Judd–Ofelt calculation method	60
3.10	Radiative properties calculation method	64
RESU	LTS AND DISCUSSION FOR GLASSES SYSTEM	67
4.1	Introduction	67
4.2	Structural Features Analysis	67

4.2.1 X-Ray Diffraction Analysis

	4.2.2 Infrared Spectra Analysis	72
	4.2.3 Raman Spectra Analysis	79
	4.2.4 Nuclear Magnetic Resonance Spectra Analysis	87
4.3	Optical Properties Analysis	95
	4.3.1 Absorption Spectra Analysis of Dy ³⁺ , Eu ³⁺	
	and Sm ³⁺ Ions	95
	4.3.2 Energy Band Gap Analysis of Dy ³⁺ , Eu ³⁺	
	and Sm ³⁺ Ions	102
4.4	Judd–Ofelt Analysis	107
	4.4.1 Dysprosium Ions Doped Sulfoborate Glasses	107
	4.4.2 Europium Ions Doped Sulfoborate Glasses	108
	4.4.3 Samarium Ions Doped Sulfoborate Glasses	111
4.5	Luminescence Properties Analysis	114
	4.5.1 Emission Spectra Analysis Dy ³⁺ , Eu ³⁺	
	and Sm ³⁺ ions	114
	4.5.2 Radiative Properties Analysis of Dy ³⁺ , Eu ³⁺	
	and Sm ³⁺ ions	131

5

RESULTS AND DISCUSSION FOR CRYSTALLINE

SYSTEM		135
5.1	Introduction	135
5.2	Structural Features Analysis	135
	5.2.1 Crystalline Phase Analysis	135
	5.2.2 Infrared Spectra Analysis	139
	5.2.3 Raman Spectra Analysis	149
	5.2.4 Nuclear magnetic resonance Spectra Analysis	158
5.3	Optical Properties Analysis	164
	5.3.1 Absorption Spectra Analysis of Dysprosium,	
	Europium and Samarium Ions	164
	5.3.2 Energy Band Gap Analysis of Dysprosium,	
	Europium and Samarium Ions	171
5.4	Judd–Ofelt Analysis	176
	5.4.1 Dysprosium Ions Doped Crystal	176
	5.4.1 Europium Ions Doped Crystal	177

	5.4.2 Samarium Ions Doped Crystal	178
5.5	Luminescence Properties Analysis	182
	5.5.1 Emission Spectra Analysis Dy ³⁺ , Eu ³⁺	
	and Sm ³⁺ ions	182
	5.5.2 Europium Ions Doped Sulfoborate Crystal	187
	5.5.3 Samarium Ions Doped Sulfoborate Crystal	192
	5.5.4 Radiative Properties Analysis of Dy ³⁺ , Eu ³⁺	
	and Sm ³⁺ ions	197
CON	CLUSION AND RECOMMENDATION	201
6.1	Conclusion	201

6.2	Recommendation	204

REFERENCES	206
Appendices A – D	216 - 226

6

LIST OF TABLES

TABLE NO.

TITLE

PAGE

2.1	FTIR absorption peaks position (cm ⁻¹) for some	
	borate and sulfoborate glass and crystal system	16
2.2	The Raman band assignment (cm ⁻¹) for some borate	
	and sulfoborate glasses and crystals series	20
3.1	The undoped chemical composition (mol %) of	
	$xMgO+(50-x)$ SO ₃ +50B ₂ O ₃ with $10 \le x \le 30mol \%$	
	glass and crystal samples	53
3.2	The doped chemical composition (mol %) of	
	$10MgO+40SO_3+(50-y) B_2O_3+yDy_2O_3$ with $0.1 \le y \le 1.0$	
	mol % glass and crystal samples	54
3.3	The doped chemical composition (mol %) of	
	10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃ with	
	$0.1 \le y \le 1.0 \text{ mol } \%$ glass and crystal samples	54
3.4	The doped chemical composition (mol %) of	
	10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃ with	
	$0.1 \le y \le 1.0 \text{ mol } \%$ glass and crystal samples	54
4.1	Infrared band assignments and the reported values for	
	xMgO+(50-x) SO ₃ +50B ₂ O ₃ with ($10 \le x \le 30 \text{ mol }\%$) glasses	74
4.2	Infrared band assignments and the reported values for	
	10MgO+40SO ₃ +(50–y) B ₂ O ₃ +yRE, (RE= Dy ₂ O ₃ , Eu ₂ O ₃	
	and Sm ₂ O ₃ glasses series	78
4.3	Raman band assignments and the reported values for	
	xMgO+(50-x) SO ₃ +50B ₂ O ₃ glasses series	81

4.4	Raman band assignments and the reported values for	
	$10MgO+40SO_3+(50-y) B_2O_3+yRE$, (RE = Dy ₂ O ₃ ,	
	Eu ₂ O ₃ and Sm ₂ O ₃) glass series	86
4.5	Resonance position of BO ₄ for 10MgO+40SO ₃ +(50-y)	
	B ₂ O ₃ +yRE (RE = Dy ³⁺ , Eu ³⁺ , Sm ³⁺) glass series	94
4.6	Observed band positions (cm ⁻¹) and bonding parameter	
	(β and δ) of the 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	glasses series	97
4.7	Observed band positions (cm ⁻¹) and bonding parameter	
	(β and δ) 10MgO+40SO ₃ +(50–y) B ₂ O ₃ +yEu ₂ O ₃ glasses series	100
4.8	Observed band positions (cm ⁻¹) and bonding parameters	
	(β and δ) of the 10MgO+40SO ₃ +(50–y) B ₂ O ₃ +ySm ₂ O ₃	
	glasses series	102
4.9	Indirect band gap energy Eg, (eV) and refractive index for	
	10MgO+40 SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃ glasses series	103
4.10	Indirect band gap energy and refractive index (n) for	
	10MgO+40 SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃ glasses series	105
4.11	Indirect band gap energy and Refractive index (n) for	
	10MgO+40 SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃ glasses series	106
4.12	The Judd–Ofelt intensity parameters Ω_2 , Ω_4 and Ω_6 of	
	the 10MgO+40 SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃ glasses series	
	and previous reported	108
4.13	Experimental and calculated oscillator field strength (x 10^{-6}) and	root
	mean square deviation (δrms) for 10MgO+40SO ₃ +(50–y)	
	$B_2O_3+yDy_2O_3$ with ($0.1 \le y \le 1.0 \text{ mol \%}$) glasses series	110
4.14	The Judd–Ofelt intensity parameters Ω_2 and Ω_4 of the	
	10MgO+40 SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃ glasses and	
	previous reported	111
4.15	The Judd–Ofelt intensity parameters Ω_2 , Ω_4 and Ω_6 of the	
	10MgO+40 SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃ glasses and	
	previous reported	112

4.16	Experimental and calculated oscillator field strength	
	(x 10 ⁻⁶) and root mean square deviation (δ_{rms}) for	
	10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃ with	
	$(0.1 \le y \le 1.0 \text{ mol } \%)$ glasses	113
4.17	Experimental lifetime, calculated lifetimes and quantum	
	efficiency (η %) for 10MgO+40SO ₃ +(50–y) B ₂ O ₃ +yDy ₂ O ₃	
	glass series	119
4.18	Experimental lifetime, calculated lifetimes and quantum	
	efficiency (η %) for 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃	
	glass series	125
4.19	Experimental lifetime, calculated lifetimes and quantum	
	efficiency (η %) for 10MgO+40SO ₃ +(50–y) B ₂ O ₃ +ySm ₂ O ₃	
	glass series	131
4.20	Emission band position (λ_p , nm), radiative transition	
	probability (A_{rad} , s^{-1}), total radiative transition probability (A_T),	
	fluorescence branching ratio (β_r), calculated and experimental	
	lifetime for 10MgO+40 SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃ glasses series	132
4.21	Emission band position (λ_p , nm), radiative transition	
	probability (A _{rad} , s^{-1}), total radiative transition probability	
	(A _T), fluorescence branching ratio (β r) and calculated lifetime for	
	10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃ glasses series	133
4.22	Emission band position (λ_p , nm), radiative transition	
	probability (A _{rad} , s^{-1}), total radiative transition probability (A _T),	
	fluorescence branching ratio (β r), calculated and experimental	
	lifetime for 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃ glasses series	134
5.1	Infrared band assignments and the reported values for	
	xMgO+(50-x) SO ₃ +50B ₂ O ₃ crystals series	142
5.2	FTIR band assignments and the reported values	
	10MgO+40SO ₃ +(50–y) B ₂ O ₃ +yRE (RE = Dy ₂ O ₃ , Eu ₂ O ₃	
	and Sm ₂ O ₃) crystal samples.	148
5.3	Raman band assignments and the reported values for	
	xMgO+(50-x) SO ₃ +50B ₂ O ₃ crystal series	151

5.4	Raman band assignments and the reported values for		
	10MgO+40SO ₃ +(50–y) B ₂ O ₃ +yRE, (RE = Dy ₂ O ₃ , Eu ₂ O ₃		
	and Sm ₂ O ₃) crystal series	157	
5.5	Observed band positions (cm ⁻¹) and bonding parameters		
	(β and δ) of the 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃		
	crystals series	166	
5.6	Observed band positions (cm ⁻¹) and bonding parameters		
	(β and δ) of the 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃		
	crystals series	169	
5.7	Observed band positions (cm ⁻¹) and bonding parameters		
	(β and δ) of the 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃		
	crystals series	171	
5.8	Indirect band gap energy Eg, (eV) and refractive index for		
	10MgO+40 SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃ crystals series	172	
5.9	Indirect band gap energy and refractive index for		
	10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃ crystals series	174	
5.10	Indirect band gap energy and Refractive index (n) for		
	10MgO+40 SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃ crystals series	175	
5.11	The Judd–Ofelt intensity parameters Ω_2 , Ω_4 and Ω_6 of the		
	10MgO+40 SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃ crystals series		
	along with the previous reported.	177	
5.12	Experimental and calculated oscillator field strength		
	(x 10 ⁻⁶) and root mean square deviation (δ_{rms}) for		
	10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃ crystal series	178	
5.13	The Judd–Ofelt intensity parameters Ω_2 and Ω_4 of the		
	10MgO+40 SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃ crystals series		
	along with the previous reported	179	
5.14	The Judd–Ofelt intensity parameters Ω_2 , Ω_4 and Ω_6 of the		
	10MgO+40 SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃ crystals series along		
	with previous reports	180	
5.15	Experimental and calculated oscillator field strength (x 10 ⁻⁶)		
	and root mean square deviation (δ_{rms}) for 10MgO+40SO ₃ +(50–y)		
	$B_2O_3+ySm_2O_3$ with $(0.1 \le y \le 1.0)$ crystal	181	

5.16	Experimental lifetime, calculated lifetime and quantum			
	efficiency (η%) of 10MgO+40SO ₃ +(50–y) B ₂ O ₃ +yDy ₂ O ₃			
	crystals series	187		
5.17	Experimental lifetime, calculated lifetime and quantum			
	efficiency (η%) of 10MgO+40SO ₃ +(50–y) B ₂ O ₃ +yEu ₂ O ₃			
	crystals series	192		
5.18	Experimental lifetime, calculated lifetime and quantum			
	efficiency (n%) of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃			
	crystals series	197		
5.19	Emission band position (λ_p , nm), radiative transition probability			
	(A^{rad}, s^{-1}) , total radiative transition probability (A_T) ,			
	fluorescence branching ratio (β_r), calculated and experimental			
	lifetime for 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃ crystals series	198		
5.20	Emission band position (λ_p , nm), radiative transition probability			
	(A_{rad}, s^{-1}) , total radiative transition probability (A_T) ,			
	fluorescence branching ratio (β_r), calculated and experimental			
	lifetime for 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃ crystals series	199		
5.21	Emission band position (λ_p , nm), radiative transition probability			
	(Arad, s^{-1}), total radiative transition probability (A _T),			
	fluorescence branching ratio (β r), calculated and experimental			
	lifetime for 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃ crystals series	200		

LIST OF FIGURES

FIGURE NO.

TITLE

PAGE

2.1	XRD pattern of 20Li ₂ O–10MgO–(70–x)B ₂ O ₃ –xSm ₂ O ₃		
	(Reduan et al., 2014)	9	
2.2	XRD pattern of $Sr_3Y_2(BO_3)_4$ doped Dy^{3+} crystal (Li et al., 2008)	9	
2.3	Structural groups in borate network		
	(Meera and Ramakrishna, 1993)	11	
2.4	IR spectra of MgO-Li ₂ O-B ₂ O ₃ glasses doped with Nd ₂ O ₃		
	(Mhareb et al., 2014a)	13	
2.5	Infrared spectra of (1) 0.2MgSO4.0.6Na2B4O7.0.2KHSO4 and		
	(2) 0.2Mg SO ₄ .0.6Na ₂ B ₄ O ₇ .0.2K ₂ SO ₄ glasses		
	(Vyatchina et al., 2005)	15	
2.6	Raman spectra experimental and calculated of Mg ₂ B ₂ O ₅		
	micron-crystal rod (Li et al., 2012)	18	
2.7	Raman spectra of (1) 0.2MgSO4+0.6Na2B4O7+0.2KHSO4 and		
	(2) 0.2 MgSO ₄ +0.6Na ₂ B ₄ O ₇ +0.2K ₂ SO ₄ glasses		
	(Vyatchina et al., 2005)	19	
2.8	Graphical method for finding N ₄ in a ¹¹ B NMR spectrum		
	at the bottom (Bray, 1999)	24	
2.9	¹¹ B MAS NMR spectra of Li ₂ SO ₄ –Li ₂ O–B ₂ O ₃ glasses at		
	constant value of B ₂ O ₃ (Ganguli and Rao, 1999)	25	
2.10	Optical absorption spectrum of 0.4 mol% of dysprosium		
	ions doped lithium magnesium borate glasses in Vis- NIR region		
	(Alajerami et al., 2012)	26	
2.11	Optical absorption spectrum of 0.2 mol% of europium ions		
	doped borate glass in UV-Vis and NIR region		
	(Venkateswarlu and Rudramadevi, 2015)	27	

2.12	Optical absorption spectrum of 1.0 mol% of samarium	
	ions doped borate glass (Agarwal et al., 2009)	28
2.13	Tauc plots of indirect optical band gap energy for	
	Li ₂ O-K ₂ O-B ₂ O ₃ -Sm ₂ O ₃ glasses (Azizan et al., 2014)	30
2.14	The Tauc's plot for 54B ₂ O ₃ +25Li ₂ O+15MO+5LiF+1Eu ₂ O ₃	
	(Arunkumar and Marimuthu, 2013)	31
2.15	Tauc plots of direct optical band gap energy for	
	20Li ₂ O–10NaCO ₃ –(70–x) B ₂ O ₃ –xSm ₂ O ₃ glasses	
	(Dawaud et al., 2014)	32
2.16	Excitation spectra of 0.04 mol% of dysprosium ions	
	doped borate phosphor (Liu et al., 2011)	39
2.17	Excitation spectra of 1.0 mol% of dysprosium ions doped	
	strontium lithium bismuth borate glasses (Rajesh et al., 2012b)	40
2.18	Emission spectra of calcium fluoroborate doped Dy ³⁺ glasses	
	(Kumar et al., 2010)	42
2.19	Emission spectra of LiSr ₃ .98(BO ₃) ₃ :0.02Dy ³⁺ phosphors at	
	different synthesis temperatures (Zhang et al., 2013)	43
2.20	Excitation spectra for 0.2 mol% of europium ions doped	
	borate glasses (Venkateswarlu and Rudramadevi, 2015)	44
2.21	Emission spectra for 0.2 mol% of europium ions doped	
	borate glass (Venkateswarlu and Rudramadevi, 2015)	44
2.22	Excitation spectra for different concentration of samarium	
	ions doped borate glasses (Swapna et al., 2014)	46
2.23	Emission spectra for different concentration of Sm ³⁺ ions	
	in borate glasses (Swapna et al., 2014)	47
2.24	The decay profile for Dy^{3+} ions in lead borate glasses	
	(Pisarska, 2009)	49
2.25	Luminescence decay profile for Eu ³⁺ ions doped SrB ₄ O ₇ :	
	Eu glass and polycrystals (Padlyak et al., 2010)	50
2.26	decay curves of the cadmium bismuth borate glasses doped	
	Sm ³⁺ ions (Sailaja et al., 2013)	51
3.1	Photograph of the XRD facility XRD-6000 Shimadzu model	55
3.2	Fourier Transform Infrared Spectrometer	56
3.3	Raman Xplora plus spectrometer	57

3.4	Nuclear Magnetic Resonance (NMR)	58
3.5	JASCO FP-8500 Series Fluorescence spectrometer	59
3.6	Ultraviolet Visible Near Infrared Spectrophotometer	60
4.1	XRD pattern of undoped xMgO+(50-x) SO ₃ +50B ₂ O ₃	
	glass series	68
4.2	XRD pattern of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	glass series	69
4.3	XRD pattern of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃	
	glass series	70
4.4	XRD pattern of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃	
	glass series	71
4.5	FTIR spectra of xMgO+(50-x) SO ₃ +50B ₂ O ₃ glasses series	73
4.6	FTIR spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	glass series	75
4.7	FTIR spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃	
	glass series	76
4.8	FTIR spectra of 10MgO+40SO ₃ +(50–y) B ₂ O ₃ +ySm ₂ O ₃	
	glass series	77
4.9	Raman spectra of xMgO+(50-x) SO ₃ +50B ₂ O ₃ glasses series	80
4.10	Raman spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	glass series	83
4.11	Raman spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃	
	glass series	84
4.12	Raman spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃	
	glass series	85
4.13	Static ¹¹ B MAS NMR spectra from H ₃ BO ₃ (solid) showing the	
	positions of the central peaks	88
4.14	¹¹ B MAS NMR spectra from xMgO+(50-x) SO ₃ +50B ₂ O ₃ Glasses	
	series. Spinning side bands are labelled with asterisks (*)	89
4.15	¹¹ B MAS NMR spectra from 10MgO+40SO ₃ +(50–y)	
	B ₂ O ₃ +yDy ₂ O ₃ glasses series. Spinning side bands are	
	labelled with asterisks (*)	91

4.16	¹¹ B MAS NMR spectra from 10MgO+40SO ₃ +(50-y)	
	B2O3+yEu2O3 glasses series. Spinning side bands are	
	labelled with asterisks (*)	92
4.17	¹¹ B MAS NMR spectra from10MgO+40SO ₃ +(50-y)	
	B2O3+ySm2O3 glasses series. Spinning side bands are	
	labelled with asterisks (*)	93
4.18	BO3 and BO4 borate units in magnesium sulfoborate glasses	94
4.19	Sketch of the expected bonding scheme of BO3 and BO4	
	borate units in the magnesium sulfoborate glasses network	95
4.20	Absorption spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	glasses series	96
4.21	(a) Absorption spectra of 10MgO+40SO ₃ +(50–y) B ₂ O ₃ +yEu ₂ O ₃	
	glasses series in UV-Visible regions	98
4.22	(b) Absorption spectra of 10MgO+40SO ₃ +(50–y) B ₂ O ₃ +yEu ₂ O ₃	
	glasses series in IR regions	99
4.23	Absorption spectra of 10MgO+40SO ₃ +(50–y) B ₂ O ₃ +ySm ₂ O ₃	
	glasses series	101
4.24	Graph of $(\alpha hv)^{1/2}$ against photon energy hv for indirect allowed	
	transitions of the 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	glasses series	104
4.25	Graph of $(\alpha hv)^{1/2}$ against photon energy hv for indirect allowed	
	transitions of the 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃	
	glasses series	104
4.26	Graph of $(\alpha hv)^{1/2}$ against photon energy hv for indirect allowed	
	transitions of the 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃	
	glasses series	106
4.27	Excitation spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	glass series	115
4.28	Emission spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	glass series	116
4.29	Energy level diagram of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	glass series	117

4.30	Decay curves of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	glass series	119
4.31	Excitation spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃	
	glass series	121
4.32	Emission spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃	
	glass series	122
4.33	Energy level diagram of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃	
	with glass series	123
4.34	Decay curves of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃	
	glass series	125
4.35	Excitation spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃	
	glasses series	127
4.36	Emission spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃	
	glasses series	128
4.37	Energy level diagram of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃	
	glasses series	129
4.38	Decay curves of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃ glasses	
	series	130
5.1	XRD pattern of un-doped xMgO+(50-x) SO ₃ +50B ₂ O ₃	
	crystals series	136
5.2	XRD pattern of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	crystals series	137
5.3	XRD pattern of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃	
	crystals series	138
5.4	XRD pattern of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃	
	crystals series	139
5.5	FTIR spectra of xMgO+(50-x) SO ₃ +50B ₂ O ₃ crystals series	141
5.6	FTIR spectra of 10MgO+40SO ₃ +(50–y) B ₂ O ₃ +yDy ₂ O ₃	
	crystals series	145
5.7	FTIR spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃	
	crystals series	146
5.8	FTIR spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃	
	crystals series	147

5.9	Raman spectra of xMgO+(50-x) SO ₃ +50B ₂ O ₃	
	crystals series	150
5.10	Raman spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	crystals series	154
5.11	Raman spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃	
	crystals series	155
5.12:	Raman spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃	
	crystals series	156
5.13	¹¹ B MAS NMR spectra of xMgO+(50–x) SO ₃ +50B ₂ O ₃	
	crystals series. Spinning side bands are labelled with	
	asterisks (*)	159
5.14	¹¹ B MAS NMR spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	crystals series. Spinning side bands are labelled with asterisks (*)	160
5.15	¹¹ B MAS NMR spectra of $10MgO+40SO_3+(50-y) B_2O_3+yEu_2O_3$	
	crystals series. Spinning side bands are labelled with asterisks (*)	161
5.16	¹¹ B MAS NMR spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃	
	crystals series. Spinning side bands are labelled with asterisks (*)	162
5.17	BO3 and BO4 borate units in magnesium sulfoborate crystal	163
5.18	Sketch of the expected bonding scheme of BO3 and BO4	
	borate units in the magnesium sulfoborate crystal network	163
5.19	Absorption spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	crystals series	165
5.20	(a)Absorption spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃	
	crystals series in UV–Visible regions	167
5.21	(b)Absorption spectra of 10MgO+40SO ₃ +(50–y) B ₂ O ₃ +yEu ₂ O ₃	
	crystals series in IR regions.	168
5.22	Absorption spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃	
	crystals series	170
5.23	Graph of $(\alpha hv)^{1/2}$ against photon energy (hv) for indirect	
	allowed transitions of the 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃	
	crystals series	172
5.24	Graph of $(\alpha hv)^{1/2}$ against photon energy (hv) for indirect	
	allowed transitions of the 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃	
	crystals series	173

5.25	Graph of $(\alpha hv)^{1/2}$ against photon energy (hv) for indirect		
	allowed transitions of the 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃		
	crystals series	175	
5.26	Excitation spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃		
	crystals series	183	
5.27	Emission spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃		
	crystals series	184	
5.28	Energy level diagram of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yDy ₂ O ₃		
	crystals series	185	
5.29	Decay curves of 10MgO+40SO ₃ +(50–y) B ₂ O ₃ +yDy ₂ O ₃		
	crystals series	186	
5.30	Excitation spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃		
	crystals series	188	
5.31	Emission spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃		
	crystals series	189	
5.32	Energy level diagram of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +yEu ₂ O ₃		
	crystals series	190	
5.33	Decay curves of 10MgO+40SO ₃ +(50–y) B ₂ O ₃ +yEu ₂ O ₃		
	crystals series	191	
5.34	Excitation spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃		
	crystals series	193	
5.35	Emission spectra of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃		
	crystals series	194	
5.36	Energy level diagram of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃		
	crystals series	195	
5.37	Decay curves of 10MgO+40SO ₃ +(50-y) B ₂ O ₃ +ySm ₂ O ₃		
	crystals series	196	

LIST OF ABBREVIATIONS

B_2O_3	-	Borate
В	_	Boron
H ₂ SO ₄	_	Sulfuric Acid
MgO	_	Magnesium Oxide
Dy ₂ O ₃	_	Dysprosium Oxide
Eu ₂ O ₃	_	Europium Oxide
Sm ₂ O ₃	_	Samarium Oxide
Dy^{3+}	—	Dysprosium Ion
Eu ³⁺	_	Europium Ion
Sm ³⁺	_	Samarium Ion
CTB	_	Charge transfer band
fexp	_	Experimental oscillator strengths
f_{cal}	_	Calculated oscillator strengths
IR	_	Infrared
Sed	_	Electric dipole line strength
S _{md}	—	Magnetic dipole line strength
Arad	—	Radiative transition probability
$ au_{ m rad}$	_	Radiative lifetime
β_r	_	Branching ratio
NMR	_	Nuclear Magnetic Resonance
λ_P	_	Emission band position
FTIR	_	Fourier Transform Infrared
KBr	_	Potassium bromide
XRD	_	X-Ray Diffraction
UV	_	Ultraviolet

RE	-	Rare Earth
PL	_	Photoluminescence
IR	_	Infrared
LED	_	Lead Emitting Diode

LIST OF SYMBOLS

τ	_	Decay time
h	_	Planck's constant
⁰ C	_	Degree Celsius
ν	_	Frequency
c	_	Speed of light
t	_	time
$\alpha(v)$	_	Absorption coefficient
β	_	Nepheleuxetic ratios
Ω_2	_	Judd–Ofelt parameter
Ω_4	_	Judd–Ofelt parameter
Ω_6	_	Judd–Ofelt parameter
It	_	Actual luminescence intensity
J	_	Total angular momentum
θ	_	Diffracted angle of the X-Ray beam
λ	_	Wavelength
n	_	Refractive Index

LIST OF APPENDICES

APPENDIX

TITLE

PAGE

А	Batch calculation for undoped glass sample	216
В	Judd–Ofelt calculation for glass doped Dy ³⁺ ion	218
С	Radiative properties calculation for glass doped	
	Eu ³⁺ ion	223
D	Publications	226

CHAPTER 1

INTRODUCTION

1.1 Background of the Research

A Glass is solid that has an amorphous structure, short range order of atomic arrangement, lack of uniformity, and have no long range periodically which yielded fairly random structure unlike crystal with a well–defined structure and atoms arranged in three dimensional periodic and long range order. Therefore, instead of crystalline sharp peaks, a glass has broad hump is seen in the X–ray diffraction pattern of a glass. A glass has significance role both scientifically and technologically due to its good transparency, chemical durability, electrical and thermal features (Alajerami et al., 2012). Hence, glass has wide range of application, such as television screen, containers, chemical laboratory equipment, fiber optics, lasers (Mhareb et al., 2014a). Therefore, the difference between glass and crystal are the presence of long range arrangement, symmetric and uniformity in the crystal structure (Sahar, 1998). Crystal is playing significant role, due to their potential applications in various field, such as phosphor for plasma display panels, nonlinear optical (NLO), luminescent materials and optical communication components (Pavani et al., 2011).

The glass composition is very significant for the formation of glass. The basic condition for glass formation is the existence of strongly bonded large networks or long chains of atoms in the liquid, and showed that a good glass must contain many bonds or linkages of the types that have high bond strengths such as B–O–B, Si–O,

Ge–O and P–O as glass formers. However, some oxides are defined as glass formers such as borate (B₂O₃), Phosphate (P₂O₅), silicate (SiO₂) and Germinate (GeO₂), because they have glass–forming ability under normal quenching conditions by themselves, but act like glass formers when combined with others such as ZnO, PbO, MgO CaO, BaO (Gautam *et al.*, 2012).

For the formation of crystal, generally, the glass compositions are decided for crystal. The formation of Bi₃B₅O₁₂ and Bi₄B₂O₉ crystalline phase by heat treatment from the composition of glass $3Bi_2O_3-5B_2O_3$ (Bajaj et al., 2009; Burianek et al., 2006; Muehlberg et al., 2002). Bi₃B₅O₁₂ and Bi₄B₂O₉ crystals also could be formed in the glasses with composition of xBi₂O₃-(100-x)B₂O₃ (x = 20 to 66 mol%) (Bajaj et al., 2009). According to Lin et al., 2007 the composition La₂O₃-3B₂O₃-0.06Eu₂O₃ formed both.

Currently, much more attention has been paid to borate glass and crystal due their applications in technological such as solid state lasers, nonlinear optics and solar (Alajerami et al., 2012). Borate glass are known to have important properties which include low melting point, good thermal stability, good solubility of rare–earth ions (Guana et al., 2013). Borate acts as the glass former, because of its high bond strength, lower cation size and smaller heat of fusion and is incorporated into various glass systems as a flux material to attain materials of high technological application (Sumalatha et al., 2011). Borate constitute an interesting system, which the network building unit can be either borate triangles (BO₃) with non–bridging atoms or borate tetrahedral (BO₄) with all bridging oxygen atoms. Borate glass can easily be melted, owning smaller mass compare to other glass network former, thermal stable and chemical durable. In addition, they are high transparency and acted as a good host for transition metal ions and rare earth ions making them suitable for optical materials. Therefore, hydroscopic properties and the high phonon energy of B₂O₃ are considered as a drawback to the glass industry (Vijayakumar et al., 2015).

The use of sulfate as a intermediate in to the borate network influence the structure of the borate units and the boron in the system retain of four coordinate from interaction between sulfate and borate units, as observed from Raman, IR and NMR spectroscopy (Ganguli and Rao, 1999). The sulfate have lower operating

temperature of 700–1000 oC (Pitha et al., 1947). Sulfate have studied because of good properties such as good transparency and low melting temperature which are material for good UV and IR transmission. However, sulfate is an attractive compound and important for a range of many applications (Gedam et al., 2006). Unfortunately, poor chemical durability and hygroscopic nature of sulfate discourage their limit practical applications. Therefore, addition of alkali earth metals has proven to enhance their chemical stability (Vyatchina et al., 2005).

However, to overcome the individual limitations of borate and sulfate, the two are combined to form a new material called "Sulfoborate" which offers greater advantage as they show different properties (Vyatchina et al., 2005). The presence of SO₃ in the borate glass can enhance the glass quality when modified with alkali earth metals (Vyatchina et al., 2009). Vyatchina et al. (2005) reported that sulfoborate glass have acceptable chemical durability compared to pure borate and has drawn attention of researchers because of their good stability.

Meanwhile, according to Mansour, (2012) addition of network modifier (magnesium oxide) into borate glass could create the conversion of the triangular BO₃ structural units to BO₄ tetrahedral, and also alter the structure and improve the glass and crystal properties (Reduan et al., 2014). Alkali or alkaline oxides were frequently applied as modifiers; Therefore, this modifier shift up the boroxyl rings, and the active groups in the mixture, to form tri–and tetra–bond on the host (Alajerami et al., 2012). The alkaline earth ions based borates have been used in various applications such as vacuum ultraviolet (VUV) optics, radiation dosimetry and solar energy converters (Lim et al., 2014a). Addition of magnesium as modifier into sulfoborate can enhance the release of electrons and to reduce the hygroscopic nature of sulfoborate (Mhareb et al., 2014a).

Furthermore, glass and crystal activated with activator. Such activator is either rare earth or transition metals ion which have been identified as a good luminescence host material which convert an incident energy input into emission of electromagnetic waves in the ultraviolet (UV), visible (Vis), or infrared (IR) regions of the spectrum (You et al., 2011). Rare earth (RE) doped glasses and crystal materials have potential application in the fields such as laser material, fiber, information display, optoelectronic (Rajesh et al., 2012a). Rare earth (RE) doped materials correspond to the 4f–4f and 4f–5d electronic transitions which is due to the shielding effect from the outer orbital (5s and 5p) on the 4f electrons. The rare earth doped materials have potential applications for instance in lasers, security, decoration, semiconductor and medication. Some of the products for example fluorescence lamp, escape routes, television monitor, warning signs, light emitting diodes, laser detection, luminous paints and so on. The sulfoborate glass host doped with rare earth ion are known to have important properties such as lower melting point, good solubility of rare earth ion and good thermal stability (Lim et al., 2014).

In addition, intensity trivalent rare earth ions, some host media were describing and estimated quantitatively via Judd–Ofelt theory (Agarwal et al., 2009). In the Judd–Ofelt theory the transition probability between any pair of stark sublevels of the rare earth (RE) ion activator in 4f^N configuration can be written in terms of three phenomenological parameters called Ω_{λ} ($\lambda = 2, 4, 6$), which are called Judd–Ofelt parameters. These parameters are determined experimentally by means of an adjustment intensities of the lines with corresponding theoretical and experimental lines registered in the absorption spectrum. Most of the study have conducted to describe the behaviour of these parameters, for instance, according to Kindrat et al., (2015b) the intensity parameter Ω_2 shows the dependence on the covalence between rare earth ions (RE) and ligands an ions, since the parameter Ω_2 reflects the asymmetry of the local environment at the rare earth ion (RE) site, and therefore Ω_2 is very small for ionic materials, and quite large for covalent materials, while the parameters $\Omega 4$ and Ω_6 are related to the rigidity of the matrix. These parameters are used to evaluate the radiative properties such as radiative transition probability (Arad, s^{-1}), radiative lifetime (τ_{rad} , sec) and an important parameter called fluorescence branching ratio (β_r) that characterizes the lasing power transition (Agarwal et al., 2009).

Over the past few decades, much attention has been focused towards dysprosium, europium and samarium ions doped glass or crystal materials for the development of optical devices such as lighting devices and solid state laser (Li et al., 2010). To date, these material become an interesting topic in the field of material science and hence need to be further investigate.

1.2 Problem Statement

Currently, a great deal of research has been focused on rare earth doped magnesium borate glasses due to their potential applications (Reduan et al., 2014b; Alajerami et al., 2012). But, the investigation on the luminescence properties of rare earth doped sulfoborate glass and crystal is not many. However, there was limited structural information regarding effect in the sulfo–borate as the host that can be reasoned to find a good luminescence material. Meanwhile, the study on the luminescence properties of rare earth doped sulfo–borate glass and crystal are not fully understood. In addition, the Judd–Ofelt analysis on the Dy³⁺, Eu³⁺ and Sm³⁺ ions doped in sulfoborate glass and crystal is very less reported. Therefore, in this study, magnesium sulfoborate doped Dy³⁺, Eu³⁺ and Sm³⁺ ions present to synthesis the glass and crystal materials by using melt quenching and solid state reaction method respectively. The investigation of structural features was important in order to study the structures changes in the doped and un–doped samples. Also, to investigate the influence of vary concentration of Dy³⁺, Eu³⁺ and Sm³⁺ ions on the optical properties.

1.3 Objectives of the Study

The following are the objectives of this study

- i. To determine the influence of doped and undoped magnesium sulfoborate glasses in terms of structure features and to compare with the similar composition of the crystalline.
- To determine the impact of concentration and types of dopants such as Dy³⁺, Eu³⁺ and Sm³⁺ ions in terms of enhancement of luminescence characteristic between glass and crystal.
- iii. To analyse and compare the absorption and emission data of sulfoborate glass and crystal doped Dy³⁺, Eu³⁺ and Sm³⁺ ions in terms of radiative properties by using Judd–Ofelt analysis.

1.4 Scope of the Research

In this study, the samples undoped magnesium sulfoborate glasses and crystals with chemical composition xMgO+(50-x) SO₃+50B₂O₃ with $10 \le x \le 30$ mol % were prepared by conventional melt quenching and solid state reaction method respectively. The series of glass and crystal samples doped with rare earth Dy_2O_3 , Eu_2O_3 and Sm_2O_3) with the chemical compositions of (RE = $10MgO+40SO_3+(50-y)$ B₂O₃+yRE with $0.1 \le y \le 1.0$ mol% were also been prepared by conventional melt quenching and solid state reaction method respectively. Sulpur oxide was incorporate into borate as intermediate to enhance the host network whereas magnesium oxide was used as modifier to reduce the hygroscopic properties. Dy^{3+} , Eu^{3+} and Sm^{3+} ions were chosen to be dopant ions in order to investigate the impact of the dopant on the structural, luminescence properties and Judd-Ofelt analysis. Different types of measurements were used. The phase of the prepared samples was determined by the X-Ray Diffraction measurement. The structural features for doped and un-doped samples were determined by Infrared, Raman and Nuclear magnetic resonance spectrometer. As for luminescence properties was determined by photoluminescence spectrometer. The optical properties in the glass and crystal samples was determined using UV-Visible-NIR spectrometer, meanwhile, band gap, refractive index, Judd-Ofelt parameters was calculated from UV-Visible-NIR spectra and radiative properties was calculated from emission spectra.

1.5 Significance of the study

This study has been done to understand more on the structural features, luminescence properties and Judd–Ofelt analysis of glass and crystal. However, doping the samples with Dy³⁺, Eu³⁺ and Sm³⁺ may develop new luminescence materials. In addition, the study on optical and luminescence properties in this work is important in providing a baseline data that can be used for further research and development of luminescence host material for solid state lighting devices.

1.6 Outline of Study

There are six chapters in this study. The background, problem statement, objectives, Scope, Significance and outline of study are described related to magnesium sulfoborate glass and crystal, and magnesium sulfoborate doped with Dy³⁺, Eu³⁺ and Sm³⁺ ions are presented in chapter 1. Chapter 2 covered the general review on magnesium sulfoborate glass and crystal with more emphasis on its structural features, luminescence properties and Judd–Ofelt analysis. Chapter 3 presents the experimental procedures which including their method of preparation, types of spectroscopy being used and the principles of X–Ray Diffraction (XRD), FTIR, Raman and NMR spectroscopy, luminescence and UV–Visible–NIR spectrometer. The results and discussion of glass along with the Tables and figures are stated in chapter 4. Chapter 5 covered the crystal results and discussion together with tables and figures. Lastly, chapter 6 presents conclusion, and recommendation for future work.

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