

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	iii
ABSTRACT (ENGLISH)	v
ABSTRACT (THAI)	vii
LIST OF TABLES	xii
LIST OF FIGURES	xiv
CHAPTER 1 INTRODUCTION	1
1.1 Introduction	1
1.2 Corundum	2
1.3 Ion implantation modification of corundum	4
1.4 PIXE for corundum analysis	5
1.5 Ionoluminescence (IL) for corundum analysis	8
1.6 Objective of this works	9
CHAPTER 2 BASIC PRINCIPLE	11
2.1 Corundum	11
2.1.1 Corundum and their coloration	11
2.1.2 The corundum deposit	16

2.1.3	Color enhancement of corundum	18
2.2	Ion implantation for gemstone modification	19
2.2.1	Basic knowledge of ion-solid interaction	19
2.2.2	Ion implanter	23
2.3	Ion beam analysis (IBA)	28
2.3.1	Particle-induced X-ray emission (PIXE)	28
2.3.2	Ionoluminescence (IL)	31
2.3.3	Data accumulation, acquisition and analysis of PIXE technique	34
2.3.4	Data accumulation, acquisition of IL technique	35

CHAPTER 3 EXPERIMENTAL PROCEDURES **38**

3.1	Sample preparation	41
3.1.1	Glyptography	41
3.1.2	Elimination of silicate and calcite	42
3.1.3	Elimination of contamination and cleaning	42
3.2	Photo taking	43
3.3	UV-Vis-NIR spectroscopy	44
3.4	Ion beam analysis	46
3.4.1	Particle-induced X-ray emission (PIXE) analysis	46
3.4.2	Ionoluminescence (IL) analysis	49
3.5	Ion beam enhancement	50
3.5.1	Nitrogen and argon ions beam modification	51
3.5.2	Oxygen ion beam modification	52

CHAPTER 4 RESULTS AND DISCUSSIONS	55
4.1 Fingerprint of deposit by PIXE analysis	55
4.2 Fingerprint of deposit by IL analysis	60
4.3 UV-Vis-NIR spectroscopy analysis	62
4.4 Corundum's deposit investigation	64
4.5 Ion beam modification	70
4.5.1 Nitrogen ion implantation	71
4.5.2 Argon ion implantation	79
4.5.3 Oxygen ion implantation	88
CHAPTER 5 CONCLUSIONS	102
5.1 Deposit characterization	102
5.2 Ion beam enhancement	104
5.3 Suggestions for further study	106
REFERENCES	107
APPENDICES	115
APPENDIX A Spectroscopic Notation	116
APPENDIX B Trajectory Simulation in Al ₂ O ₃	117
APPENDIX C Si(Li) X-ray Detector	118
APPENDIX D Converting .SPE File to .PIX File	119
APPENDIX E Fiber Optic Light Guide	121
APPENDIX F Ocean Optics S2000 Spectrometer	122
CURRICULUM VITAE	123

LIST OF TABLES

Table	Page
1.1 Top ten of Thai exports in 2011	3
3.1 Details of natural corundum being investigated by the PIXE technique	39
3.2 Comparison between the measured values and the preferred average values by Pearce <i>et al.</i> (1997) of element concentration in the standard sample (SRM610)	49
4.1 The concentrations of Ti, V, Cr, Fe and Ga in each type of corundum, in parts per million (ppm) by weight as measured by PIXE technique	58
4.2 The color tone of Africa sapphire and the ratio of Fe/Ti concentrations	59
4.3 The Fe/Ti concentration ratios of pre- and post- implantation of Y5	73
4.4 The Fe/Ti concentration ratios of pre- and post- implantation of BG4	75
4.5 The Fe/Ti concentration ratios of pre- and post- implantation of G11	80
4.6 The Fe/Ti concentration ratios of pre- and post- implantation of B5	82
4.7 The Fe/Ti concentration ratios of pre- and post- implantation of BG3	84
4.8 The Fe/Ti and Fe/Cr concentration ratios of pre- and post- implantation of R4	86
4.9 The Fe/Ti concentration ratios of pre- and post- implantation of B8	89
4.10 The Fe/Ti concentration ratios of pre- and post- implantation of DB8	92
4.11 The Fe/Ti concentration ratios of pre- and post- implantation of Y9	95

4.12	The Fe/Ti and Fe/Cr concentration ratios of pre- and post-implantation of R9	97
B	The target depth parameters in Al ₂ O ₃	117
C	The parameters of Si(Li) X-ray detector	118
E	The information of the fiber optic light guide	121
F	The S2000 spectrometer information of Ocean Optics, Inc.	122

LIST OF FIGURES

Figure		Page
2.1	The red color appearance of corundum is happened from the substitution of Al^{3+} by Cr^{3+}	13
2.2	Tanabe-Sugano relation for 3d-orbital electrons	13
2.3	The energy level diagram, transition, and color absorption/fluorescence mechanisms in a ruby	14
2.4	The sub-crust activity of the earth	17
2.5	The predominant of basaltic and metamorphic deposits of corundum	17
2.6	The incident ion induces several phenomena in the matter	20
2.7	The different types of ion track in GaN	22
2.8	(a) The photo of Varian Ion Implanter of Chiang Mai University	24
2.8	(b) The schematic diagram of Varian Ion Implanter	24
2.9	The schematic diagram of the focusing, scanning, and deflecting systems of the implanter	25
2.10	The sample holder at the end of beamline	26
2.11	The diagram of the O^- ions irradiation system	28
2.12	The 1.7 MV tandem “Tandatron” accelerator of Chiang Mai University with analysis chamber at the end of the beamline	29

2.13	The diagram of the characteristic X-ray production process	30
2.14	The diagram of the ionoluminescence process	32
2.15	The equipment set up inside the analysis chamber	35
2.16	The diagram of IL accumulation system	37
3.1	The overall process diagram	38
3.2	A photo of corundum used in this study	39
3.3	The ultrasonic bath (a) used for cleaning the particle on the sample surface, and the sample is soaked in the ethyl alcohol (b)	43
3.4	Motic SMZ-168 Series of stereomicroscopes used in this study	44
3.5	Hitachi spectrophotometer U-4100: outside (a) and inside (b)	45
3.6	The holding of sample for UV-Vis-NIR spectroscopic measurement	46
3.7	Control system of the 1.7 MV tandem accelerator (a) and the data accumulation and acquisition system (b)	47
3.8	The PIXE spectrum of a standard sample: NISM SRM610	48
3.9	Data accumulation system of the IL technique	50
3.10	The sample holder used for Ar ⁺ and N ₂ ⁺ ion beam irradiations	51
3.11	The fan-like sample holder for oxygen ion modification	53
3.12	Ion beam fluence estimation	54
4.1	PIXE spectra of all corundum investigated in this study	57
4.2	The five sapphires which were cut at five different color zone of a bigger piece of African sapphire: (a) from dark-blue zone, (b) from yellow green zone, (c) from light-green zone, (d) from green zone, and (e) from green blue zone	60

4.3	IL spectra of corundum in regions 200–600 nm (a) and 600–800 nm (b)	61
4.4	UV-Vis-NIR spectra of blue sapphire from Sri Lanka (light blue curve), ruby from Bo rai (red curve), blue-green sapphire from Bang Kha Cha (green curve), dark-blue sapphire from Pailin (navy blue curve), and yellow sapphire from Montana (yellow curve)	63
4.5	The relation between the ratio of Cr/Ga and Fe/Ti concentrations	65
4.6	The relation between the Cr and Fe concentrations (a) – (b)	65
4.7	The relation between the Ti and Fe concentrations (a) – (b)	67
4.8	The relation between the Ga and Fe concentrations	69
4.9	The relation between the ratio of Ti/V and Fe/Ga concentrations	69
4.10	The changing from yellow to green-blue color of yellow sapphire (Y5) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the Ti and Fe concentrations of the before and after implantation (e)	72
4.11	The brighter green tone of blue-green sapphire (BG4) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e)	75
4.12	The deep blue saturation of blue sapphire (B7) (a) – (b), and UV-Vis-NIR spectrum of the before and after implantation (c)	76
4.13	The clarity enhancement of dull white sapphire (G6) (a) – (b), UV-Vis-NIR spectrum (c), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (d)	78

- 4.14 The clarity enhancement of dull white sapphire (G11) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e) 80
- 4.15 The discoloration of blue sapphire (B5) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e) 82
- 4.16 The discoloration of blue-green sapphire (BG3) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e) 83
- 4.17 The more violet tint of ruby (R4) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e) 86
- 4.18 The less brownish tint of blue sapphire (B8) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation plot between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e) 89
- 4.19 The reduction of green color in blue green sapphire (BG8) (a) – (b) of the before and after implantation 91
- 4.20 The lightener bluish tone of dark-blue sapphire (DB8) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e) 91

4.21	The more vivid of yellowish zone of yellow sapphire (Y9) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e)	94
4.22	The implanted effect for ruby (R9) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e)	97
4.23	The pink sapphire (Moz7) before implantation (a) has more reddish tone after implantation (b)	98
4.24	The pink sapphire (PS12) before implantation (a) has less violet tint after implantation (b)	99
4.25	The dull white sapphire (G13) before implantation (a) has more pale pink tint after implantation (b)	99
4.26	The change in appearance of the faceted ruby after being consecutively irradiated, with 23 keV O ⁻ ions beam, at different period of time in hr:min:sec.	100
d-1	The .SPE spectrum file	119
d-2	The .PIX spectrum file	120