



**Preparation and Characterization of Alumina-Silica
and Alumina-Silica-Magnesia Nano-composites from
Industrial Wastes for Advanced Applications**

Thesis For

Ph.D. Degree in Chemistry

To

**Chemistry Department, Faculty of Science,
Ain Shams University**

By

Moustafa Mohammed Saad Moustafa Sanad

M. Sc. in Chemistry, 2009

2014

**Preparation and Characterization of Alumina-Silica and
Alumina-Silica-Magnesia Nano-composites from
Industrial Wastes for Advanced Applications**

Thesis

**Submitted in the Partial Fulfillment
For
Ph.D. Degree in Chemistry
To
Chemistry Department, Faculty of Science,
Ain Shams University**

By

Moustafa Mohammed Saad Moustafa Sanad

M. Sc. in Chemistry, 2009

Under the Supervision of

Prof. Dr. Mohamed F. El – Shahat

Prof of Analytical and Inorganic Chemistry, Faculty of Science, Ain
Shams University

Prof. Dr. El-Sayed A. Abdel-Aal

Head of Minerals Technology Department, Central Metallurgical
R&D Institute, (CMRDI), Helwan

Prof. Dr. Mohamed M. Rashad

Head of Electronic and Magnetic Materials Division, Central
Metallurgical R&D Institute, (CMRDI), Helwan

**Preparation and Characterization of Alumina-Silica and
Alumina-Silica-Magnesia Nano-composites from
Industrial Wastes for Advanced Applications**

Thesis For

Ph.D. Degree in Chemistry

To

**Chemistry Department, Faculty of Science,
Ain Shams University**

By

Moustafa Mohammed Saad Moustafa Sanad

M. Sc. in Chemistry, 2009

Under the Supervision of

Prof. Dr. Mohamed F. El – Shahat

Professor of Analytical and Inorganic Chemistry, Faculty of Science, Ain
Shams University

Prof. Dr. El-Sayed A. Abdel-Aal

Head of Minerals Technology Department, Central Metallurgical R&D
Institute, (CMRDI), Helwan

Prof. Dr. Mohamed M. Rashad

Head of Electronic and Magnetic Materials Division, Central Metallurgical
R&D Institute, (CMRDI), Helwan

Head of Chemistry Department

Prof. Dr. Hamed Ahmed Derbalah

List of Abbreviations

LIST OF ABBREVIATIONS

Symbol	Definition
SDS	Sodium dodecyl sulfate
CTAB	Cetyl trimethyl ammonium bromide
PVA	Poly vinyl alcohol
PL	Photoluminescence
DTA	Differential thermal analysis
DSC	Differential scanning calorimetry
ICP	Inductively Coupled Plasma Spectrophotometer
XRD	X-ray diffraction analysis
XRF	X-ray fluorescence analysis
SEM	Scanning electron microscope
TEM	Transmission electron microscope
S_{BET}	Specific surface area
rpm	Rotations per minute
x	Ratio of dopant ion
θ	X-Ray diffraction angle
β	Full width at half-maximum of X-ray peak
D	Average crystalline size
λ	X-ray wavelength
E_a	Apparent activation energy
T_p	Crystallization peak temperature
R	Gas constant
Φ	Heating rate per minute

List of Abbreviations

Symbol	Definition
ΔT	Full width at half maximum of the exothermic peak
n	Shape factor (Avrami constant)
ρ	Electrical resistivity
ϵ	Real dielectric permittivity
" ϵ	Imaginary part dielectric permittivity
$\tan\delta$	Dielectric loss factor
HV	Vickers microhardness
DC	Direct current
AC	Alternating current
ICDD	International Center for Diffraction Data
V	Volume of unit cell
a, b, c	Lattice parameters
ppm	Part per million
GPa	Giga Pascal
MHz	Megahertz
GHz	Gigahertz
ALW	Washing liquor of Al etching
ALD	Leaching liquor of Al dross
SR	Leaching liquor of silica wastes
SF	Leaching liquor of silica fume
GB	Leaching liquor of ground bricks of lining furnaces

LIST OF FIGURES

Figure	Page
1. Natural mullite, (a) Thin section micrograph of the lava of the Ben More volcano, (b) SEM of mullite needles grown hydrothermally in small druses of volcanic rocks of the Eifel mountain	2
2. Number of publications dealing primarily with mullite and mullite ceramics which appeared between 2000 and 2013 (date of search 15 th May 2013)	2
3. Technical-grade mullites, (a) Czochralski-grown mullite single crystals of 2/1-composition (b) Microstructures of fully dense polycrystalline mullite ceramics with different bulk Al ₂ O ₃ compositions	5
4. Examples for technical applications of monolithic mullite ceramics (a) Fused-mullite refractory bricks (b) Sinter-mullite-based conveyor belt for continuous charging of annealing furnaces (c) Optically translucent mullite compounds	6
5. Mullite coatings. Examples of technical applications, (a) Panel for a re-entry space vehicle (b) Microstructure of a vacuum plasma mullite-coated C/C–SiC composite	7
6. Mullite matrix composites. Examples of technical applications, (a) Components and structures made of mullite fiber-reinforced mullite matrix composites	8

List of Figures

(b) Segmented combustor tiles made of WHIPOX for the use as thermal protection systems in combustors of stationary and aircraft gas turbine engines	8
7. Examples of cordierite kiln furniture for temperature below 1200°C, mullite-cordierite composite kiln furniture for temperature below 1350°C and mullite-corundum composite kiln furniture for temperature below 1400°C	11
8. Different shapes and sizes of oil refining cordierite ceramic honeycomb filter plate	12
9. Number of publications dealing primarily with cordierite and cordierite ceramics which appeared between 2000 and 2013 (date of search 15 th May 2013)	13
10. Phase diagram for the alumina-silica system	14
11. MgO-Al ₂ O ₃ -SiO ₂ Ternary phase diagram	16
12. XRD pattern of aluminum dross sample	65
13. Effect of annealing temperature on Al extraction	66
14. Effect of mole ratio Na ₂ O: (Al ₂ O ₃ ,SiO ₂) on Al extraction	66
15. Effect of annealing time on Al extraction	67
16. XRD pattern of silica fume sample	70
17. Effect of NaOH:SiO ₂ mole ratio on Si extraction at 4 h and 100°C	71
18. Effect of reaction temperature on Si extraction at 4 h and stoichiometry 3	71

List of Figures

19. Effect of reaction time on Si extraction at 100°C and stoichiometry 3	72
20. XRD pattern of acidic silica effluents sample	74
21. Effect of annealing temperature on Al and Si extraction	75
22. Effect of stoichiometric ratio $\text{Na}_2\text{O}:(\text{Al}_2\text{O}_3, \text{SiO}_2)$ on Al and Si extraction	75
23. Effect of annealing time on Al and Si extraction	76
24. XRD patterns of mullite precursors prepared at different pH values annealed at 1200 °C for 3 h	79
25. XRD patterns of mullite precursor annealed at various temperatures (900-1400°C) for 3 h	80
26. XRD patterns of mullite precursors annealed at 1000°C for various annealing times	81
27. XRD patterns of mullite precursors annealed at 1000°C for 1 h in presence and absence of surfactants	82
28. DTA Thermograms of prepared mullite precursors measured at various heating rates	83
29. Kissinger plot for the activation energy determination of mullite crystallization	84
30. SEM micrographs of synthesized mullite nanoparticles at (a) 1000°C, (b) 1200°C; (c) 1400°C [Magnification X10,000] for 3 h	85

List of Figures

31. TEM micrographs of synthesized mullite nanoparticles at (a) 1000°C, (b) 1200°C, (c) 1400° for 3 h	86
32. SEM micrographs of synthesized mullite nanoparticles at 1000°C for 3 h (a) in absence of surfactant, (b) in presence of 1000 ppm CETAB [Magnification X15,000]	87
33. TEM micrographs of synthesized mullite nanoparticles in presence of 1000 ppm (a) CTAB and (b) SDS and (c) in absence of surfactant	88
34. Dependence of dielectric permittivity (ϵ) of mullite samples on heating rate sintered at (a) 1300°C (b) 1400°C (c) 1500°C (d) 1600°C	92
35. Effect of frequency region on dielectric properties of sintered mullite ceramics at various heating rates (a) 5°min ⁻¹ (b) 30°min ⁻¹	93
36. Dependence of dielectric loss tangent ($\tan\delta$) of mullite samples on heating rate and sintering temperature at 1.5 GHz	93
37. Effect of heating rate on linear shrinkage of sintered mullite samples	94
38. Effect of heating rate on sintering properties of mullite samples sintered at various temperatures for 5 h	95
39. XRD patterns of mullite precursors prepared from	97

List of Figures

different raw materials	
40. XRD patterns of un-doped and doped mullite nanoparticles annealed at 1300 °C for 2 h	101
41. DTA curves of metal ion doped mullite precursors	103
42. TEM micrographs of nanocrystalline o-mullite (a) undoped, (b) 0.5% Y^{3+} ion doped mullite, (c) 0.5% Gd^{3+} ion doped mullite, (d) 0.5% La^{3+} ion doped mullite	104
43. FT-IR spectra of the produced undoped and doped mullite nanoparticles annealed at 1300 °C for 2 h	105
44. Photoluminescence emission spectra of produced undoped and doped mullite nanoparticles at ($\lambda_{ex}=254$ nm)	107
45. Variation of the dielectric permittivity with the type of dopant ion in o-mullite ceramics. Inset change in dielectric loss with the type of dopant ion	109
46. XRD patterns of cordierite precursor annealed at various temperatures (1000-1300°C) for 3 h	111
47. XRD patterns of cordierite precursors annealed at 1200°C for various annealing times	112
48. XRD patterns of cordierite precursors annealed at 1300°C for 3 h in presence and absence of surfactants	113
49. DTA Thermograms of prepared cordierite precursors measured at various heating rates	114
50. Kissinger plot for the activation energy determination	115

List of Figures

of μ -cordierite crystallization	
51. SEM micrographs of synthesized cordierite nanoparticles at (a) 1100°C, (b) 1200°C; (c) 1300°C [Magnification X 5000] for 3 h	116
52. SEM micrographs of synthesized cordierite nanoparticles at 1300°C for 3 h (a) in absence of surfactant, (b) in presence of 1000 ppm CETAB, (c) in presence of 1000 ppm SDS [Magnification X 3500]	117
53. SEM micrographs of cordierite ceramics sintered at (a) 1200°C, (b) 1250°C, (c) 1300°C, (d) 1350°C	118
54. Variation of dielectric permittivity (ϵ') of cordierite samples versus frequency at different annealing temperatures	120
55. The dielectric permittivity and dielectric loss of cordierite samples at different sintering temperatures at 1 GHz	121
56. Effect of sintering temperature on shrinkage of sintered cordierite samples	122
57. Effect of sintering temperature on sintering properties of cordierite samples	123
58. XRD patterns of cordierite precursors prepared from different raw materials annealed at 1300 °C for 3 h	125

List of Figures

59. XRD patterns of un-doped and doped cordierite nanoparticles annealed at 1300 °C for 2 h	128
60. DTA curves of metal ion doped cordierite precursors of additives	130
61. SEM micrographs of cordierite ceramics sintered at 1300 for 3 h (a) undoped sample, (b) Mo ⁶⁺ ion doped sample, (c) Sr ²⁺ ion doped sample, (d) Zr ⁴⁺ ion doped sample	131
62. FT-IR spectra of the produced undoped and doped cordierite nanoparticles annealed at 1300 °C for 2 h	133
63. Variation of the dielectric permittivity with the type of dopant ion in cordierite ceramics	136

LIST OF TABLES

Table	Page
1. Thermo-mechanical properties of mullite ceramics and other advanced oxide ceramics	4
2. Main physical properties of cordierite	9
3. Chemical analysis of the spent washing liquor of Al etching	63
4. Chemical analysis of original aluminum dross	64
5. Optimum conditions for processing of aluminum dross	68
6. Chemical analysis of original fumed silica	69
7. Optimum conditions for processing of silica fume	72
8. Chemical analysis of washed sample of the acidic silica effluents	73
9. Optimum conditions for processing of acidic silica effluents	77
10. Kinetics parameters for crystallization of mullite precursors annealed at 1200°C with different heating rates	84
11. Textural and optical properties of mullite precursors annealed at various temperatures for 3 h	89
12. Textural and optical properties of mullite precursors in presence and absence of surfactants	89

List of Tables

13. Effect of heating rate on DC electrical resistivity of mullite samples	90
14. Effect of heating rate on microhardness of sintered mullite samples	96
15. Effect of precursor's raw materials on crystallite size of mullite nanoparticles synthesized at 1200°C for 3 h	98
16. Effect of precursor's raw materials on DC and AC electrical properties of mullite ceramics sintered at 1300°C for 5h	99
17. Effect of precursor's raw materials on microhardness of sintered mullite ceramics at 1300°C for 5h	99
18. Lattice parameters of undoped and doped mullite samples annealed at 1300 °C for 2 h	102
19. FT-IR frequency assignments of undoped and doped mullite samples	106
20. Effect of dopant ion type on DC and AC electrical properties of mullite ceramics sintered at 1300°C for 5h	108
21. Kinetics parameters for crystallization of cordierite precursors annealed at 1200°C with different heating rates	115

List of Tables

22. Effect of annealing temperature on DC electrical resistivity of cordierite samples	119
23. Effect of annealing temperature on microhardness of cordierite samples	124
24. Effect of precursor's raw materials on crystallite size of cordierite nanoparticles synthesized at 1300°C for 3 h	125
25. Effect of precursor's raw materials on DC and AC electrical properties of cordierite ceramics sintered at 1300°C for 2h	126
26. Effect of precursor's raw materials on microhardness of sintered cordierite ceramics at 1300°C for 2h	127
27. Effect of doping ion (M^{n+}) type and place on crystallite size of cordierite samples annealed at 1300 °C for 3 h	129
28. FT-IR frequency assignments of undoped and doped cordierite samples	133
29. Ionic radii, valence state and electronic configuration of the cations replaced in the cordierite	134
30. Effect of doping ion (M^{n+}) type and place on sintering and mechanical properties of cordierite ceramics sintered at 1300 °C for 2 h	135