

## LIST OF FIGURES

<i>Figures No.</i>	<i>Page No.</i>
Figure 1.1 : The two general ways of solidifying a melt namely, slow cooling to the crystalline state and the rapid quenching to the amorphous (glassy) state	2
Figure 1.2 : Schematic time-temperature-transformation diagram (TTT-diagram) for the crystallisation of an undercooled melt.	4
Figure 1.3 : Biomaterial historical development and the forecast of the future	10
Figure 1.4 : Hierarchical organization of bone	12
Figure 1.5 : Schematic representation of Hench's Mechanism	20
Figure 1.6 : (a) Crystalline silica (b) Amorphous silica (c) Effect of introduction of network modifier cations in a silica network	22
Figure 1.7 : Composition diagram for bioactivity of melt-derived silicate Glasses (constant 6 wt% P <sub>2</sub> O <sub>5</sub> in the system SiO <sub>2</sub> -Na <sub>2</sub> O-CaO P <sub>2</sub> O <sub>5</sub> )	25
Figure 1.8 : Scheme representing the synthesis conditions and parameters that influence the bioactive process in the sol-gel glasses	28
Figure 1.9 : Bioactive mechanism in simulated body fluid of conventional BG (proposed by Hench in 1970) vs. MBG	31
Figure 2.1 : Chemical Reaction in sol-gel synthesis	46
Figure 2.2 : Schematic representation of EISA process	48
Figure 2.3 : Chemical formula and properties of surfactant P123	49
Figure 2.4 : Type I Isotherm	55
Figure 2.5 : Type II Isotherm	55
Figure 2.6 : Type III Isotherm	55
Figure 2.7 : Type IV Isotherm	56
Figure 2.8 : Type V Isotherm	56
Figure 2.9 : Type VI Isotherm	56
Figure 2.10 : H1 hysteresis loop	57
Figure 2.11 : H2 hysteresis loop	57

<i>Figures No.</i>	<i>Page No.</i>
Figure 2.12 : H3 hysteresis loop	57
Figure 2.13 : H4 hysteresis loop	58
Figure 2.14 : Pore filling stages at different pressures	60
Figure 2.15 : Types of Pores	60
Figure 2.16 : Energy level diagram for representing quanta of the energy $v_0$ hit the molecule, an elastic impact scatters the quantum $v_0$ , inelastic impacts scatter quanta which have energies smaller or larger by the amount of the vibrational energy, $v$	64
Figure 2.17 : The vector at the magic angle (angle $\theta = 54.74^\circ$ between the magnetic field and the rotation axis) as a space diagonal of a cube	70
Figure 2.18 : Illustration of time-dependent voltage (U(t)) and current (I(t)) of a sample subjected to electrical measurements	72
Figure 2.19 : Simultaneous presentation of scaled conductivity master curves for sodium borate glasses. The master curves for three compositions nearly overlap one another after introducing a mobile ion dependent factor $x$ , representing the sodium content, on the scaled frequency axis. Despite considerable similarity it is clear that with decreasing sodium content an increase in curvature results in the region lying between the d.c. plateau and the high frequency response	75
Figure 2.20 : Set-up of the Novocontrol impedance spectrometer with temperature controller	76
Figure 2.21 : Schematic illustration of Novocontrol $\alpha$ -S High Resolution Dielectric analyzer setup	77
Figure 2.22 : Schematic depiction of the in vitro bioactivity test	82
Figure 3.1 : Experimental frequency dependent conductivity spectra of 45S5 glass sample at different temperatures	91
Figure 3.2 : Arrhenius plot of the dc conductivity (multiplied with temperature) of 45S5, 55S4.3, and 60S3.8 normal glasses. The symbols represent experimental data points and the fitted line corresponds to using Arrhenius law	91
Figure 3.3 : Arrhenius plot of the dc conductivity (multiplied with temperature) of 45S5 annealed and unannealed glass	92

<i>Figures No.</i>	<i>Page No.</i>
Figure 3.4 : Scaled Isotherms of the real part of the conductivity, $\sigma'(v)$ , of the 45S5 glass	93
Figure 3.5 : Room temperature Raman spectra of 45S5, 55S4.3, and 60S3.8 glasses	94
Figure 3.6 : Temperature-dependent Raman Spectra for 45S5 normal glass sample	95
Figure 3.7 : Temperature-dependent Raman Spectra for 55S4.3 normal glass sample	95
Figure 3.8 : Various phosphate and silicate $Q^n$ species present in glass system under investigation.	96
Figure 3.9 : Deconvoluted Raman spectra of 45S5 glass sample measured at 298K and 873K (open symbols) and a representative fitting (lines) with five Gaussian bands to resolve the fine structure.	97
Figure 3.10 : Distribution of various structural units ( $Q^n$ ) and their relative abundance as a function of temperature in 45S5, 55S4.3 and 60S3.8 normal glass samples	98
Figure 3.11 : Distribution of various structural units ( $Q^n$ ) and their relative abundance as a function of temperature in 45S5 and 55S4.3 annealed glass samples	100
Figure 4.1 : Experimental frequency-dependent conductivity spectra of 73S10C glass sample at different temperatures	109
Figure 4.2 : Arrhenius plot of the dc conductivity (multiplied by the temperature) of 73S10C, 63S20C, and 53S30C glasses. The symbols represent the experimental data points and the fitted line corresponds to using the Arrhenius law	109
Figure 4.3 : Scaled Isotherms of the real part of the conductivity, $\sigma'(v)$ , of the 73S10C glass	111
Figure 4.4 : Scaled Isotherms of the real part of the conductivity, $\sigma'(v)$ , of the 63S20C glass	111
Figure 4.5 : Scaled Isotherm of the real part of the conductivity, $\sigma'(v)$ , of the 63S20C glass, with the additional scaling factor $T^\alpha$ with $\alpha=2.5$ . The reference temperature $T_0$ is 300K	112
Figure 4.6 : Room temperature Raman spectra of 73S10C, 63S20C and 53S30C glass sample	113

<i>Figures No.</i>	<i>Page No.</i>
Figure 4.7 : Deconvoluted Raman spectra of glass sample measured at Room temperature (open symbols) and the representative fitting (lines)	114
Figure 4.8 : Room temperature <sup>29</sup> Si MAS-NMR spectra for 73S10C, 60S20C, 53S30C glass samples.	116
Figure 4.9 : Deconvoluted <sup>29</sup> Si spectra of 73S10C, 63S20C, and 53S30C glass sample measured at Room temperature (open symbols) and the representative fitting (lines)	118
Figure 4.10 : Room temperature <sup>31</sup> P MAS-NMR spectra for 73S10C, 60S20C, and 53S30C	118
Figure 4.11 : Deconvoluted <sup>31</sup> P spectra of 73S10C, 63S20C, and 53S30C glass sample measured at Room temperature (open symbols) and the representative fitting (lines)	119
Figure 5.1 : WAXRD and SAXRD (inset) patterns of calcined MSSG-10	131
Figure 5.2 : FTIR spectra of calcined MSSGs as a function of alkali oxide content	132
Figure 5.3 : (a) HRTEM image of acid treated-calcined MSSG-10 and the corresponding electron diffraction pattern (inset) (b) HRTEM image of MSSG-10 before acid treatment (c) EDAX Pattern of calcined MSSG-10	134
Figure 5.4 : DSC-TGA Thermograms of MSG-10 and the inset shows the DSC thermogram of NaAc (sodium acetate)	134
Figure 5.5 : Nitrogen adsorption-desorption isotherm and pore size distribution (inset) of MSSG-30 and MSSG-10	135
Figure 5.6 : The variation of the BET surface area and pore size of xNa <sub>2</sub> O ·(100-x)SiO <sub>2</sub> MSSGs with (5 ≤ x ≤ 30).	137
Figure 5.7 : The variation of pH values of the SBF with soaking time of MSSG-10 and MSSG-30	138
Figure 5.8 : XRD patterns of (a) MSSG-10 and (b) MSSG-30 after soaking in SBF for 1, 3 and 7 days (represented as 1D, 3D and 7D) compared with that of HAp (JCPDS 24-0033)	139
Figure 5.9 : FTIR spectra for MSSG-10 and MSSG-30 glasses as a function of soaking time (1D-1day, 3D-3days, 7D-7-days). Shown are the bands of phosphate (○) and bands of carbonate (Δ)	140

<i>Figures No.</i>	<i>Page No.</i>
Figure 5.10 : SEM micrographs of MSSG-10 (a) before soaking in SBF (b) after soaking in SBF for 7 days and MSSG-30 (c) before soaking in SBF (d) after soaking in SBF for 7 days	141
Figure 5.11 : Cross-Sectional SEM micrographs for MSSG-30 and MSSG-10 after soakin for 1D, 3D and 7D in SBF	143
Figure 5.12 : Nitrogen adsorption-desorption isotherm and pore size distribution (inset) with the time variation on the apatite layer formation of MSSG-30.	144
Figure 5.13 : Nitrogen adsorption-desorption isotherm and pore size distribution (inset) with the time variation on the apatite layer formation of MSSG-10.	145
Figure 6.1 : FTIR Spectra of MBG-67SQ, MBG-62SQ, MBG-57SQ, MBG-52SQ MBG-75SNP, MBG-70SNP, MBG-75SNC, and MBG-70SNC glasses before soaking in SBF	156
Figure 6.2 : Nitrogen adsorption-desorption isotherm and pore size distribution (inset) of (A) MBG- 67SQ (B) MBG-57SQ glasses	159
Figure 6.3 : Nitrogen adsorption-desorption isotherm and pore size distribution (inset) of (A) MBG-75SNP (B) MBG-70SNP glasses	159
Figure 6.4 : Nitrogen adsorption-desorption isotherm and pore size distribution (inset) of (A) MBG-75SNC (B) MBG-70SNC glasses	160
Figure 6.5 : The variation of pH values of the SBF with soaking time on different MBG's	161
Figure 6.6 : XRD pattern of (A) MBG-67SQ glass after soaking in SBF for 12h, 1D and 3D (B) MBG-62SQ, MBG-57SQ, and MBG-52SQ glass after soaking in SBF for 3D	162
Figure 6.7 : XRD pattern of (A) MBG-75SNP (B) MBG-70SNP (C) MBG-75SNC (D) MBG-70SNC after soaking in SBF for 12h, 1D and 3D	163
Figure 6.8 : FTIR Spectra of (A) MBG-67SQ (B) MBG-62SQ (C) MBG-70SNP (D) MBG-70SNC glasses as a function of soaking time in SBF for 12h, 1D and 3D	165
Figure 6.9 : SEM micrographs of (A) MBG-67SQ (B) MBG-62SQ glasses before and after soaking in SBF for 12h, 1D and 3D	167

<i>Figures No.</i>	<i>Page No.</i>
Figure 6.10 : SEM micrographs of (A) MBG-70SNP (B) MBG-70SNC glasses before and after soaking in SBF for 12h, 1D and 3D	168
Figure 6.11 : Nitrogen adsorption-desorption isotherm and pore size distribution (inset) of (A) MBG-67SQ (B) MBG-57SQ (C) MBG -70SNP (D) MBG-70SNC glasses after soaking in SBF for 3 days	170
Figure 7.1 : WAXRD patterns of 73S10C, 63S20C, and 53S30C before soaking in SBF	181
Figure 7.2 : FTIR Spectra of 73S10C, 63S20C, and 53S30C before soaking in SBF	182
Figure 7.3 : Nitrogen sorption isotherms and pore size distribution (inset) of 73S10C, 63S20C, and 53S30C before soaking in SBF	183
Figure 7.4 : <sup>29</sup> Si MAS-NMR spectra of representative pristine sol-gel glasses and glass-ceramic	184
Figure 7.5 : <sup>29</sup> Si Spectra for pristine glasses and glass ceramic after deconvolution into various Q-species for silica. (Open circle represents the obtained spectra and solid line represents deconvoluted spectra)	186
Figure 7.6 : <sup>31</sup> P MAS-NMR spectra of representative pristine sol-gel glasses and glass-ceramic. (DCPA: Dicalcium phosphate anhydrous or dehydrate and DCPD: Dicalcium phosphate Dihydrate)	187
Figure 7.7 : <sup>31</sup> P Spectra for pristine glasses and glass ceramic after deconvolution into various Q-species for phosphate. (Open circle represents the obtained spectra and solid line represents deconvoluted spectra)	188
Figure 7.8 : Ca, P, Si and Na concentrations in SBF as a function of soaking time for 73S10C, and 53S30C	191
Figure 7.9 : Total consumption of Ca and P for 73S10C and 53S30C.	192
Figure 7.10 : WAXRD pattern of 53S30C after soaking in SBF for 12h, 1D and 3D	192
Figure 7.11 : WAXRD pattern of 73S10C(A) and 63S20C(B) mesoporous glass samples after soaking in SBF for 12h, 1D and 3D	193
Figure 7.12 : FTIR spectra for 73S10C, 63S20C, and 53S30C after soaking in SBF for 3D	194

<i>Figures No.</i>	<i>Page No.</i>
Figure 7.13 : SEM micrographs of (A) 73S10C (B) 63S20C (C) 53S30C after soaking in SBF for 12h and 3D	195
Figure 7.14 : TEM micrographs and corresponding SAED pattern of (A) 73S10C (B) 63S20C and (C) 53S30C after soaking in SBF for 3D	196
Figure 7.15 : Nitrogen sorption isotherms and Pore size distribution (inset) of 73S10C, 63S20C, and 53S30C after soaking in SBF	197

## LIST OF TABLES

<i>Tables No.</i>	<i>Page No.</i>
Table 1.1 : The types of bioceramics and their tissue attachments	14
Table 1.2 : Composition of common bioactive glasses	17
Table 2.1 : Molar Composition of melt-derived bulk glasses	46
Table 2.2 : Molar Composition of sol-gel derived mesoporous glasses	57
Table 2.3 : Concentration (mM) and pH of simulated body fluid (SBF) and human plasma	81
Table 3.1 : Q <sup>n</sup> distribution of 45S5 Normal glass sample at 298K and 573K Obtained by Deconvolution procedure	97
Table 4.1 : DC conductivity ( $\sigma_{dc}$ ), activation energy ( $E_a$ ), density ( $\rho$ ) and number density (N) ( $Na^+$ ions) for 73S10C, 63S20C, and 53S30C glass samples.	110
Table 4.2 : Q <sup>n</sup> distribution of 73S10C, 63S20C and 53S30C glass samples at room temperature obtained by deconvolution of Raman spectra	115
Table 4.3 : Chemical shifts, relative peak areas, and Q <sup>n</sup> species obtained after deconvolution of <sup>29</sup> Si and <sup>31</sup> P NMR spectra	116
Table 5.1 : Textural Parameters Obtained by N <sub>2</sub> Adsorption Porosimetry for Mesoporous xNa <sub>2</sub> O · (1-x)SiO <sub>2</sub> Glasses	136
Table 5.2 : Textural Parameters Obtained by N <sub>2</sub> adsorption porosimetry on the nucleated growth of the apatite layer of MSSG-10 and MSSG-30	144
Table 6.1 : Chemical composition and textural parameters	158
Table 6.2 : Textural parameters of samples after soaking in SBF for 3 days	171
Table 7.1 : Chemical composition and textural parameters	183
Table 7.2 : Relative populations (expressed as percentages) of Q <sup>n</sup> <sub>Si</sub> species obtained after deconvolution of the obtained spectra.	185
Table 7.3 : Relative populations (expressed as percentages) of Q <sup>n</sup> <sub>P</sub> species obtained after deconvolution of the obtained spectra.	188
Table 7.4 : Textural parameters of samples after soaking in SBF for 3 days	198