

Fundamentals of Inorganic Glasses

Arun K. Varshneya

*New York State College of Ceramics
Alfred University
Alfred, New York*



ACADEMIC PRESS, INC.
An Imprint of Elsevier

Boston San Diego New York
London Sydney Tokyo Toronto

Contents

Preface	xv
Acknowledgments	xvii
1. Introduction	1
1.1. Brief History	1
1.2. Glass Families of Interest	2
1.2.1. Vitreous Silica	2
1.2.2. Soda-Lime Glass	4
1.2.3. Borosilicate glass	4
1.2.4. Lead Silicate Glass	4
1.2.5. Aluminosilicate Glass	5
1.2.6. Other Silica-Based Oxide Glasses	5
1.2.7. Other Non-Silica-Based Oxide Glasses	5
1.2.8. Halide Glasses	6
1.2.9. Amorphous Semiconductors	6
1.2.10. Chalcogenide and Chalcohalide Glasses	7
1.2.11. Glassy Metals	8
1.2.12. Oxyhalide, Oxynitride and Oxycarbide Glasses	8
1.3. A Brief Note on Glasses Found in Nature	9
Exercises	11
References	11

2. Fundamentals of the Glassy State	13
2.1. What is Glass?	13
2.2. The $V-T$ Diagram	14
2.3. Pair Correlation Function and Radial Distribution Function	17
2.4. Anomalies in the $V-T$ Diagram	22
Exercises	24
References	25
3. Glass Formation Principles	27
3.1. Structural Theories of Glass Formation	29
3.1.1. Zachariasen's Random Network Theory	29
3.1.2. Sun's Single Bond Strength Criterion	32
3.1.3. Dietzel's Field Strength Criterion	34
3.1.4. Phillips's Topological Constraints Hypothesis	36
3.2. Russian Workers' Criticism of Zachariasen's Hypothesis	39
3.3. The Kinetic Theory of Glass Formation	43
3.3.1. The Nucleation Rate	43
3.3.2. Crystal Growth Rate	48
3.3.3. $T-T-T$ Diagram	54
Exercises	58
References	59
4. Glass Microstructure: Phase Separation and Liquid Immiscibility	61
4.1. Thermodynamics of Mixing	62
4.2. More Formal Analysis of Phase Separation	70
4.3. Electron Microscopy to Observe Phase Separation in Glass	73
4.4. Observations of Phase Separation in Glass	75
4.5. Observations of Controlled Crystallization in Glass (Glass-Ceramics)	80
Exercises	84
References	86
5. Glass Compositions and Structures	87
5.1. Presentation of Glass Formulae	87
5.2. Silica Glass	88
5.3. Boric Oxide Glass	96
5.4. Alkali Silicate Glasses	99

5.5. Alkali-Alkaline Earth-Silicate Glasses	104
5.6. Alkali Borate Glasses	105
5.7. The Boron Anomaly	106
5.8. Alkali Borosilicate Glasses	111
5.9. Alkali Aluminosilicate Glasses	112
5.10. Lead, Bismuth, and Thallium Silicate or Borate Glasses	115
5.11. Phosphate Glasses	116
5.12. Other Oxide Glasses	120
5.13. Amorphous Silicon and Germanium	122
5.14. Glassy Metals	126
5.15. Chalcogenide and Chalcohalide Glasses	131
5.16. Heavy Metal Fluoride Glasses (HMFG)	136
Exercises	139
References	141
6. Composition-Structure-Property Relationship Principles	143
6.1. General Principles	143
6.2. Additivity Relationships	146
References	147
7. Density and Molar Volume	149
7.1. Definitions	149
7.2. Methods of Measurement	150
7.3. Dependence upon Cooling Rate, Temperature, Composition	151
7.4. Densification of Glasses by High Pressure or Irradiation	155
7.5. Calculation of Density	156
Exercises	158
References	159
8. Elastic Properties and Microhardness of Glass	161
8.1. Introduction	161
8.2. Elastic Properties of Glass	162
8.2.1. The Terminology of Elasticity	162
8.2.2. Methods of Measuring Elastic Moduli	164
8.2.3. Elastic Moduli Versus Glass Composition	168
8.2.4. Temperature and Pressure Dependence of Elastic Moduli	171
8.2.5. The Atomistic Approach to Elastic Behavior	174

8.3. Microhardness of Glass	177
8.3.1. Microhardness and Its Measurement	177
8.3.2. Microhardness vs. Glass Composition	179
Exercises	180
References	180
9. The Viscosity of Glass	183
9.1. Introduction	183
9.2. Viscosity—Temperature Dependence	185
9.3. Viscosity Reference Points	189
9.4. Measurement of Viscosity	190
9.5. Viscosity vs. Composition and Temperature Data	194
9.6. Non-Newtonian Viscosity	204
9.7. Volume Viscosity	208
Exercises	209
References	209
10. Thermal Expansion of Glass	211
10.1. Introduction	211
10.2. Definitions	212
10.3. Methods of Thermal Expansion Measurement	212
10.4. Thermal Expansion vs. Composition and Temperature	214
10.5. Concepts of Glass Expansion	219
10.6. Thermal Stresses and the Thermal Shock Resistance	220
Exercises	223
References	224
11. Heat Capacity of Glass	225
11.1. Introduction	225
11.2. Measurement of Heat Capacity	226
11.3. Composition Dependence	226
11.4. Temperature Dependence	227
Exercise	231
References	232
12. Thermal Conductivity and Heat Transfer in Glass	233
12.1. Introduction	233
12.2. Measurement of Thermal Conductivity	235

12.3. Composition and Temperature Dependence	236
Exercises	239
References	239
13. Glass Transition Range Behavior	241
13.1. Introduction	241
13.2. Viscoelastic Properties of Glass	243
13.2.1. About Relaxation	244
13.2.2. The Maxwell Element	249
13.2.3. The Voigt–Kelvin Element	251
13.2.4. Delayed Elasticity	252
13.3. Structural Relaxation due to Temperature Change	254
13.4. Viscosity–Free Volume Theories of Glass Transition	256
13.5. Thermodynamics of the Glass Transition	260
13.6. Kinetics of the Glass Transition	277
13.6.1. “Watching” the Relaxation (Concept of the Deborah Number)	277
13.6.2. Tool’s Fictive Temperature Theory	278
13.6.3. About the DTA and DSC of the Glass Transition	280
13.6.4. Difficulties with Tool’s Single T_f Concept	282
13.6.5. Narayanaswamy’s Model of Structural Relaxation	287
13.6.6. Description of the Crossover Experiment in Terms of Narayanaswamy’s Model for Relaxation	289
13.7. Properties Data in the T_g Range	291
13.8. Development of Permanent Stresses in Glass by Cooling through the Glass Transition Range	297
13.9. Concepts of Annealing and Tempering	302
13.10. Summary of Glass Transition Range Behavior	309
Exercises	311
References	312
14. Permeation, Diffusion, and Ionic Conduction in Glass	315
14.1. Introduction	315
14.2. More on the Atomic Theory of Diffusion and Electrical Conduction	320
14.2.1. Mechanisms of Diffusion	320
14.2.2. Correlation Effects	320
14.2.3. Haven Ratio	322
14.2.4. Isotope Effect	323
14.2.5. Temperature Dependence of Diffusion and Electrical Conduction	323

14.3. Measurement of Gas Permeability	325
14.4. Measurement of Diffusion Coefficients	325
14.4.1. Self-Diffusion Coefficients	325
14.4.2. Measurement of Chemical Diffusion Coefficients	327
14.5. Measurement of Electrical Conductivity	328
14.6. Data on Permeability and Molecular Diffusion of Gases in Glass	331
14.7. Data on Ionic Diffusion and Electrical Conduction in Glass	333
14.8. Some Aspects of Diffusion and Conduction Phenomena	339
14.8.1. Ion Exchange	339
14.8.2. Multicomponent Diffusion	344
14.8.3. Fast Ion Conduction	346
14.8.4. Anionic Conduction	348
Exercises	349
References	350
15. Dielectric Properties	353
15.1. Introduction	353
15.2. Measurement of Dielectric Properties	363
15.3. Data on Dielectric Properties	364
References	365
16. Electronic Conduction	367
16.1. Introduction	367
16.2. Concepts of Electronic Conduction in Amorphous Solids	368
16.3. Defects in Amorphous Solids and Their Management	381
16.4. Photoconductivity, Photoluminescence, and Xerography	385
16.5. Photovoltaics and Solar Cells	389
16.6. Switching and Computer Memory Devices	391
References	394
17. Chemical Durability	397
17.1. Introduction	397
17.2. Mechanisms of Durability and Weatherability	398
17.3. Measurement of Chemical Durability	399
17.4. Data on Chemical Durability	400
17.5. Methods of Improving Chemical Durability	407
Exercise	408
References	408

18. Strength and Toughness	409
18.1. Introduction	409
18.2. Theoretical Strength of a Flawless Brittle Solid	411
18.3. Strength of a Flawed Brittle Solid: Griffith's Analysis	412
18.4. Elementary Fracture Mechanics Concepts	414
18.5. Glass Fatigue	416
18.6. Mechanism of Strength Based upon Slow Crack Growth	424
18.7. Elementary Fractographic Analysis	425
18.8. Fracture Statistics	432
18.9. Life Prediction	436
18.10. Experimental Measurement of Glass Strength and Fracture Toughness	438
18.11. Data on Strength and Fatigue Parameters	442
18.12. Strengthening and Toughening	444
Exercises	450
References	451
19. Optical Properties	455
19.1. Introduction	455
19.2. Some Theoretical Concepts	457
19.2.1. Dispersion	457
19.2.2. Scattering	461
19.2.3. Absorption in the Visible Region (Colors in Glass)	463
19.2.4. Absorption in the UV	473
19.2.5. Absorption in the IR	476
19.2.6. Photoelastic Properties	478
19.2.7. Anomalous Birefringence	482
19.3. Measurement of Optical Properties	483
19.4. Data on Optical Properties	484
19.5. Special Applications	491
19.5.1. Photosensitive Glasses	491
19.5.2. Nonlinear Optics	491
19.5.3. Glass as a Laser Host	495
19.5.4. Fiber Optics	497
19.5.5. Coatings on Glass to Improve Optical Quality	503
Exercises	505
References	505
20. Fundamentals of Inorganic Glassmaking	507
20.1. Laboratory Melting of Oxide Glasses	507

20.2. Continuous Melting of Glass	513
20.3. Non-Fusion-Based Techniques of Glassmaking	519
20.3.1. Glassmaking Directly from the Solid State	519
20.3.2. Glassmaking Directly from the Gaseous State	520
20.3.3. Glassmaking via the Sol-Gel Process	521
20.4. The Forming of Glass Products	530
20.4.1. Glass Containers	530
20.4.2. Flat Glass	534
20.4.3. Glass Tubes and Rods	541
20.4.4. Glass Fibers	543
Exercise	549
References	549
Appendix I. Elements of Linear Elasticity	551
Appendix II. Units and General Data Conversions	561
Index	565