Contents

1. Overview 1
Klaus Bange, Wilfried Heimerl, Dieter Krause
1.1 The "Object": Amorphous Material, Glass, and Glass Ceramics 2
1.2 Qualitative Relations of Properties with Composition and Structure 8
1.3 The Importance of the Chemical Composition 11
1.3.1 Methods and Strategies 12
1.3.2 Indirect Analysis 13
1.3.3 Direct Analysis 13
1.3.4 New Developments and Future Trends 15
1.4 Methods for Structure Determination 17
1.5 Analysis of Glass Defects 20
References 26

2. The Chemical Analysis of Glasses, Glass Ceramics, and Related Materials 29
2.1 Sampling and Sample Preparation 29
2.1.1 Mechanical Pretreatment Before Digestion *Lothar Meckel* 29
2.1.2 Methods of Decomposing Glasses and Glass Ceramics for Analysis *Lothar Meckel* 32
2.1.3 Methods of Preparing Samples for Analysis in the Solid State *Hartmut Müller, Bernd Valentin* 39
2.2 Methods for Digested (Wet) Samples *Lothar Meckel* 42
2.2.1 Gravimetric Methods 42
2.2.2 Volumetric Methods 43
2.2.3 Molecular Absorption Spectroscopy (MAS) 44
2.2.4 Atomic Absorption Spectroscopy (AAS) 45
2.2.5 Atomic Emission Spectroscopy (AES) 47
2.2.6 Infrared (IR) Detection and Measurement of the Thermal Conductivity 48
2.2.7 Mass Spectrometry 49

2.3 Methods for Direct Instrumental Analysis of Solid Samples 50
2.3.1 Inductively Coupled Mass Spectrometry with Laser Ablation System *Christine Strubel* 50
2.3.2 Electron Probe Microanalysis (EPMA) *Hartmut Müller* 52
2.3.3 X-Ray Fluorescence (XRF) Analysis *Bernd Valentin* 58
2.3.4 Special Applications of XRF in the Glass Industry *Bernd Valentin* 62
2.3.5 Laser-Induced Breakdown Spectroscopy (LIBS) *Lothar Meckel* 65
2.3.6 Gas-Analysis and Extraction Methods *Matthias Jäger* 66
2.4 Specific Examples and Results for Glass and Glass Ceramics 73
2.4.1 Qualitative and Quantitative Analysis of Major Components *Lothar Meckel, Hartmut Müller, Bernd Valentin* 73
2.4.2 Species Analysis *Ruth Effenberger* 94
2.4.3 Quantitative Analysis of Trace-Element Concentrations *Friedrich G.K. Baucke, Frank Dauth, Brigitte Leibecke, Lothar Meckel* 96
2.4.4 Quantitative Analysis of Water Content *Fritz W. Krämer, Rainer Haspel* 120
2.4.5 Quantitative Analysis of Gas Content *Fritz W. Krämer* 124
2.5 Analysis of Cullet, Dust, Sludge, and Waste Water *Lothar Meckel* 128
References 131

3. The Quasi-Static Structure of Oxide Glasses 141
3.1 How to Describe the Topological Structure of Glasses *Christian Schultz-Münzenberg* 141
3.1.1 The Concept of Atom-Specific Structure Elements (ASEs) for Oxide Glasses 143
3.1.2 Distribution of ASEs in Binary Silicate Glasses 149
3.2 Some Selected Methods of Determining ASEs *Christian Schultz-Münzenberg* 153
3.2.1 Mössbauer Spectroscopy 153
3.2.2 Photoelectron Spectroscopy (XPS) 159
3.2.3 X-Ray Absorption Spectroscopy (XAS) 163
3.2.4 Raman Spectroscopy 168

3.3 Quantitative Results for ASEs
Christian Schultz-Münzenberg 171
3.3.1 Binary Silicate Glasses 171
3.3.2 Sodium Aluminosilicate Glasses (NAS Glasses) 180
3.3.3 Sn and Sb in Sodium Silicate Glasses 188
3.4 NMR Investigation of the Structure of Glasses: Conventional MAS NMR Experiments *Christian Jäger* 199
3.4.1 Advantages and Limitations of NMR 199
3.4.2 Results of Structural Studies of Glasses 200
3.5 Two-Dimensional NMR Investigation of the Structure of Glasses: Novel Approaches *Christian Jäger* 208
3.5.1 Measurements of $Q^{[n]}$ Group Connectivities and of Borate Units in Glasses 212
3.5.2 Measurement of Heterogroup Connectivities (Structural Units with Different Central Atoms 217
3.5.3 Characterization of Oxygen Bonds in Glasses with ^{17}O DAS and MQMAS NMR 222
3.5.4 Order Phenomena in Extruded Calcium Phosphate Glasses 230
3.5.5 Summary and Outlook 232
3.6 Thermochemistry and Structure of Oxide Glasses
Reinhard Conradt 234
3.6.1 Thermodynamic Features of the Glassy State 235
3.6.2 Structural Aspects in the Thermodynamic Treatment of Mixed Phases 238
3.6.3 Glasses as Medium Range Order (MRO) Mixtures 244
3.6.4 Quantitative Thermochemical Treatment of Glasses and Glass Melts 253
3.7 How Can Computer Simulations Contribute to the Understanding of the Static Structure of Glasses?
Kurt Binder, Walter Kob 257
3.7.1 The Molecular Dynamics Method 257
3.7.2 Basic Features of a Molecular Dynamics Program: An Introduction for the Novice 258
3.7.3 A Case Study: Cooling-Rate Dependence of the Structure of Amorphous SiO_2 262
3.7.4 Concluding Remarks 267
3.8 Flow-Induced Anisotropies in Glasses and Glass Melts
Rolf Brückner 269
3.8.1 Birefringence and Internal Stresses 270
3.8.2 Birefringence by External Elastic Stresses or Strains . . 271
3.8.3 Birefringence by Flow Stresses or Deformation Rates (Flow Birefringence) 272

3.8.4 Double-Phase Glasses and Glass Melts ($\eta > 10^7$ Pa s) . . . 287
3.8.5 Optically "Anomalous" Anisotropic Glasses and Melts 292
References . . . 296

4. Dynamics of the Glass Structure . . . 315
4.1 Applying the Dynamics of the Structure to Tailor the Glass Properties *Ulrich Fotheringham* . . . 315
4.1.1 The Original Tool Model, Derived with a Double-Well-Potential Consideration . . . 315
4.1.2 Monitoring the Structural Dynamics via a Dynamic Measurement of the Specific Heat . . . 319
4.1.3 The Tool–Narayanaswamy Model . . . 329
4.1.4 Tailoring Two Exemplary Glass Properties . . . 339
4.2 How Can Computer Simulations Contribute to the Understanding of the Dynamics of Glasses and Glass Melts? *Walter Kob, Kurt Binder* . . . 346
4.2.1 Model and Details of the Simulation . . . 347
4.2.2 Results . . . 348
4.2.3 Conclusions . . . 358
4.3 How Can Inelastic Neutron Scattering Contribute to the Understanding of the Dynamics of Glasses? *Ulrich Buchenau, Andreas Wischnewski* . . . 359
4.3.1 Neutron Measurements . . . 363
4.3.2 Data Analysis . . . 365
4.3.3 Implications for Sound Wave Scattering . . . 367
4.4 Titania-Activated Nucleation in Lithium–Aluminosilicate Glass Ceramics Investigated by Raman Spectroscopy *Rüdiger Sprengard* . . . 368
4.4.1 Titanium Coordination in $SiO_2 \cdot n LiAlO_2$ Glass . . . 369
4.4.2 Titanium Segregation from the Glass Network . . . 373
4.4.3 Conclusion . . . 380
4.5 Nucleation at Silicate Glass Surfaces *Stefan Reinsch, Ralf Müller* . . . 381
4.5.1 Experimental Procedure . . . 381
4.5.2 Surface Nucleation Kinetics . . . 382
4.5.3 Surface Nucleation Sites . . . 383
4.5.4 Benefit of a Tuneable Surface Nucleation Density . . . 390
References . . . 394

5. Chemical Resistance and Corrosion, and Ion Release 401
5.1 Requirements for Different Glass Products *Wilfried Heimerl* 401
5.2 Determination Methods and Standards, and Specific Examples *Wilfried Heimerl* 402
5.3 Ionic Processes between Glasses and Solutions *Friedrich G.K. Baucke* 407
5.3.1 The Electrochemically Structured Interface Glass/Solution: Interfacial Equilibria 409
5.3.2 Interfacial Equilibria Under the Influence of Subsurface Concentration Gradients 412
5.3.3 Specific Reactions Between Glasses and Solutions: An Example 421
5.4 Development of Glasses with Improved Corrosion Resistance *Peter Brix* 424
5.4.1 Requirements Profile and Design 424
5.4.2 Chemical Stability 430
5.4.3 Coincidence, Trial and Error 435
5.5 Thermodynamics of Glass Corrosion *Reinhard Conradt* 438
5.5.1 Physical Boundary Conditions in Different Corrosion Scenarios 438
5.5.2 Discussion of Individual Corrosion Models 439
5.5.3 The Gibbs Free Energy of Hydration of Multi-Component Glasses 442
5.5.4 Surface and Subsurface Effects 446
5.5.5 Application of a Corrosion Model 447
References 449

6. Analysis and Diagnosis of Local Defects 453
6.1 Bubbles *Rudolf Feile, Adolf Götz, Fritz W. Krämer* 453
6.1.1 Analysis of Gaseous Inclusions 453
6.1.2 Bubble Defect Diagnosis 467
6.2 Knots, Striae, and Stones *Hartmut Müller* 470
6.3 Glass Interaction with AZS *Hartmut Müller* 474
6.4 Microphase Separation in Glasses *Werner Vogel* 479
6.4.1 Two-Phase Glasses and Functional Change of Microphases 480
6.4.2 Multiple Phase Separation 482

6.4.3 Droplet Agglomeration after Secondary Phase Separation . . . 485
6.4.4 Shell Formation Around Microphases . . . 487
6.4.5 Other Practical Significances of Phase Separation Processes in Glasses . . . 489
6.4.6 Control of Phase Separation . . . 492
6.4.7 General Conclusions on Immiscibility Behaviour and Microstructure . . . 493
6.5 Metal Inclusions: Platinum *Joseph S. Hayden, Alexander J. Marker III* . . . 493
6.5.1 Sources of Platinum . . . 494
6.5.2 Phosphate Laser Glass Melting Experiments . . . 494
6.5.3 Summary and Conclusions . . . 496
6.6 Platinum Particle Detection in Phosphate Laser Glasses *John H. Campbell, James F. Kimmons, Sheldon Schwartz* . . . 498
6.6.1 Basis for Platinum Particle Detection: Laser-Induced Damage . . . 500
6.6.2 Description of the Pt-Inclusion Inspection System . . . 507
6.6.3 Inclusion Test Specification and Procedures . . . 510
6.6.4 Past System Operational Experience and Current Status . . . 512
References . . . 513

List of Contributing Authors . . . 520

Sources of Figures and Tables . . . 521

Index . . . 525