Inorganic Glasses for Photonics
Wiley Series in Materials for Electronic and Optoelectronic Applications
www.wiley.com/go/meoa

Series Editors
Professor Arthur Willoughby, University of Southampton, Southampton, UK
Dr Peter Capper, formerly of SELEX Galileo Infrared Ltd, Southampton, UK
Professor Safa Kasap, University of Saskatchewan, Saskatoon, Canada

Published Titles
Bulk Crystal Growth of Electronic, Optical and Optoelectronic Materials, Edited by P. Capper
Charge Transport in Disordered Solids with Applications in Electronics, Edited by S. Baranovski
Optical Properties of Condensed Matter and Applications, Edited by J. Singh
Thin Film Solar Cells: Fabrication, Characterization, and Applications, Edited by J. Poortmans and V. Arkhipov
Dielectric Films for Advanced Microelectronics, Edited by M. R. Baklanov, M. Green, and K. Maex
Liquid Phase Epitaxy of Electronic, Optical and Optoelectronic Materials, Edited by P. Capper and M. Mauk
Molecular Electronics: From Principles to Practice, M. Petty
CVD Diamond for Electronic Devices and Sensors, Edited by R. S. Sussmann
Mercury Cadmium Telluride, Edited by P. Capper and J. Garland
Zinc Oxide Materials for Electronic and Optoelectronic Device Applications, Edited by C. Litton, D. C. Reynolds, and T. C. Collins
Lead-Free Solders: Materials Reliability for Electronics, Edited by K. N. Subramanian
Silicon Photonics: Fundamentals and Devices, M. Jamal Deen and P. K. Basu
Nanostructured and Subwavelength Waveguides: Fundamentals and Applications, M. Skorobogaty
Photovoltaic Materials: From Crystalline Silicon to Third-Generation Approaches, G. Conibeer and A. Willoughby
Glancing Angle Deposition of Thin Films: Engineering the Nanoscale, Matthew M. Hawkeye, Michael T. Taschuk, and Michael J. Brett
Spintronics for Next Generation Innovative Devices, Edited by Katsuaki Sato and Eiji Saitoh
Physical Properties of High-Temperature Superconductors, Rainer Wesche
Inorganic Glasses for Photonics Fundamentals, Engineering and Applications

ANIMESH JHA
Institute for Materials Research, University of Leeds, UK

WILEY
To my beloved parents for enthusing me to pursue science and engineering!

My parents’ family for supporting the journey to fulfil my ambitions in my early career pursued in engineering in India!

To my friends and peers for supporting me in my academic career!

To my work place at the University of Leeds where I exchange knowledge!

To my wife, Aparna and children, Prashant and Govind, for building a home in Leeds and inspiration for life!
## Contents

*Series Preface*  
 Preface  

**1. Introduction**  
1.1 Definition of Glassy States  
1.2 The Glassy State and Glass Transition Temperature ($T_g$)  
1.3 Kauzmann Paradox and Negative Change in Entropy  
1.4 Glass-Forming Characteristics and Thermodynamic Properties  
1.5 Glass Formation and Co-ordination Number of Cations  
1.6 Ionicity of Bonds of Oxide Constituents in Glass-Forming Systems  
1.7 Definitions of Glass Network Formers, Intermediates and Modifiers and Glass-Forming Systems  
1.7.1 Constituents of Inorganic Glass-Forming Systems  
1.7.2 Strongly Covalent Inorganic Glass-Forming Networks  
1.7.3 Conditional Glass Formers Based on Heavy-Metal Oxide Glasses  
1.7.4 Fluoride and Halide Network Forming and Conditional Glass-Forming Systems  
1.7.5 Silicon Oxynitride Conditional Glass-Forming Systems  
1.7.6 Chalcogenide Glass-Forming Systems  
1.7.7 Chalcohalide Glasses  
1.8 Conclusions  

Selected Biography  
References  

**2. Glass Structure, Properties and Characterization**  
2.1 Introduction  
2.1.1 Kinetic Theory of Glass Formation and Prediction of Critical Cooling Rates  
2.1.2 Classical Nucleation Theory  
2.1.3 Non-Steady State Nucleation  
2.1.4 Heterogeneous Nucleation  
2.1.5 Nucleation Studies in Fluoride Glasses  
2.1.6 Growth Rate  
2.1.7 Combined Growth and Nucleation Rates, Phase Transformation and Critical Cooling Rate
2.2 Thermal Characterization using Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) Techniques
   2.2.1 General Features of a Thermal Characterization
   2.2.2 Methods of Characterization
   2.2.3 Determining the Characteristic Temperatures
   2.2.4 Determination of Apparent Activation Energy of Devitrification

2.3 Coefficients of Thermal Expansion of Inorganic Glasses

2.4 Viscosity Behaviour in the near-$T_g$, above $T_g$ and in the Liquidus Temperature Ranges

2.5 Density of Inorganic Glasses

2.6 Specific Heat and its Temperature Dependence in the Glassy State

2.7 Conclusion

References

3. Bulk Glass Fabrication and Properties
   3.1 Introduction
   3.2 Fabrication Steps for Bulk Glasses
      3.2.1 Chemical Vapour Technique for Oxide Glasses
      3.2.2 Batch Preparation for Melting Glasses
      3.2.3 Chemical Treatment Before and During Melting
   3.3 Chemical Purification Methods for Heavier Oxide (GeO$_2$ and TeO$_2$) Glasses
   3.4 Drying, Fusion and Melting Techniques for Fluoride Glasses
      3.4.1 Raw Materials
      3.4.2 Control of Hydroxyl Ions during Drying and Melting of Fluorides
   3.5 Chemistry of Purification and Melting Reactions for Chalcogenide Materials
   3.6 Need for Annealing Glass after Casting
   3.7 Fabrication of Transparent Glass Ceramics
   3.8 Sol–Gel Technique for Glass Formation
      3.8.1 Background Theory
      3.8.2 Examples of Materials Chemistry and Sol–Gel Forming Techniques
   3.9 Conclusions
   References

4. Optical Fibre Design, Engineering, Fabrication and Characterization
   4.1 Introduction to Geometrical Optics of Fibres: Geometrical Optics of Fibres and Waveguides (Propagation, Critical and Acceptance Angles, Numerical Aperture)
   4.2 Solutions for Dielectric Waveguides using Maxwell’s Equation
      4.2.1 Analysis of Mode Field Diameter in Single Mode Fibres
   4.3 Materials Properties Affecting Degradation of Signal in Optical Waveguides
      4.3.1 Total Intrinsic Loss
4.3.2 Electronic Absorption 118
4.3.3 Experimental Aspects of Determining the Short Wavelength Absorption 121
4.3.4 Scattering 121
4.3.5 Infrared Absorption 124
4.3.6 Characterization of Vibrational Structures using Raman and IR Spectroscopy 126
4.3.7 Experimental Aspects of Raman Spectroscopic Technique 127
4.3.8 Fourier Transform Infrared (FTIR) spectroscopy 128
4.3.9 Examples of the Analysis of Raman and IR spectra 130
4.4 Fabrication of Core–Clad Structures of Glass Preforms and Fibres and their Properties 141
4.4.1 Comparison of Fabrication Techniques for Silica Optical Fibres with Non-silica Optical Fibres 143
4.4.2 Fibre Fabrication using Non-silica Glass Core–Clad Structures 151
4.4.3 Loss Characterization of Fibres 153
4.5 Refractive Indices and Dispersion Characteristics of Inorganic Glasses 158
4.5.1 Experimental Procedure for Measuring Refractive Index of a Glass or Thin Film 163
4.5.2 Dependence of Density on Temperature and Relationship with Refractive Index 166
4.5.3 Effect of Residual Stress on Refractive Index of a Medium and its Effect 169
4.6 Conclusion 170
References 170

5. Thin-film Fabrication and Characterization 178
5.1 Introduction 178
5.2 Physical Techniques for Thick and Thin Film Deposition 179
5.3 Evaporation 179
5.3.1 General Description 179
5.3.2 Technique, Materials and Process Control 179
5.4 Sputtering 181
5.4.1 Principle of Sputtering 181
5.5 Pulsed Laser Deposition 183
5.5.1 Introduction and Principle 183
5.5.2 Process 184
5.5.3 Key Features of PLD process 186
5.5.4 Controlling Parameters and Materials Investigated 187
5.5.5 Fabrication of Thin Film Structures using PLD and Molecular Beam Epitaxy 188
5.6 Ion Implantation 192
5.6.1 Introduction 192
5.6.2 Technique and Structural Changes 192
5.6.3 Governing Parameters for Ion Implantation 193
5.6.4 Materials Systems Investigated 194
5.7 Chemical Techniques
  5.7.1 Characteristics of Chemical Vapour Deposition Processes 195
  5.7.2 Materials System Studied and Applications 196
  5.7.3 Molecular Beam Epitaxy (MBE) 196
5.8 Ion-Exchange Technique 197
5.9 Chemical Solution or Sol–Gel Deposition (CSD) 200
  5.9.1 Introduction 200
  5.9.2 CSD Technique and Materials Deposited 202
5.10 Conclusion 203
References 203

6. Spectroscopic Properties of Lanthaneide (Ln\(^{3+}\)) and Transition Metal (M\(^{3+}\))-Ion Doped Glasses 209
6.1 Introduction 209
6.2 Theory of Radiative Transition 209
6.3 Classical Model for Dipoles and Decay Process 212
6.4 Factors Influencing the Line Shape Broadening of Optical Transitions 214
6.5 Characteristics of Dipole and Multi-Poles and Selection Rules for Optical Transitions:
  6.5.1 Analysis of Dipole Transitions Based on Fermi’s Golden Rule 218
  6.5.2 Electronic Structure and Some Important Properties of Lanthanides 219
  6.5.3 Laporte Selection Rules for Rare-Earth and Transition Metal Ions 221
6.6 Comparison of Oscillator Strength Parameters, Optical Transition Probabilities and Overall Lifetimes of Excited States 224
  6.6.1 Radiative and Non-Radiative Rate Equation 227
  6.6.2 Energy Transfer and Related Non-Radiative Processes 231
  6.6.3 Upconversion Process 233
6.7 Selected Examples of Spectroscopic Processes in Rare-Earth Ion Doped Glasses 238
  6.7.1 Spectroscopic Properties of Trivalent Lanthaneide (Ln\(^{3+}\))-Doped Inorganic Glasses 239
  6.7.2 Brief Comparison of Spectroscopic Properties of Er\(^{3+}\)-Doped Glasses 241
  6.7.3 Spectroscopic Properties of Tm\(^{3+}\)-Doped Inorganic Glasses 247
6.8 Conclusions 257
References 257

7. Applications of Inorganic Photonic Glasses 261
7.1 Introduction 261
7.2 Dispersion in Optical Fibres and its Control and Management 261
  7.2.1 Intramodal Dispersion 262
  7.2.2 Intermodal Distortion 265
  7.2.3 Polarization Mode Dispersion (PMD) 266
  7.2.4 Methods of Controlling and Managing Dispersion in Fibres 267
### 7.3 Unconventional Fibre Structures

- **7.3.1 Fibres with Periodic Defects and Bandgap**
- **7.3.2 TIR and Endlessly Single Mode Propagation in PCF with Positive Core–Cladding Difference**
- **7.3.3 Negative Core–Cladding Refractive Index Difference**
- **7.3.4 Control of Group Velocity Dispersion (GVD)**
- **7.3.5 Birefringence in Microstructured Optical Fibres**

### 7.4 Optical Nonlinearity in Glasses, Glass-Ceramics and Optical Fibres

- **7.4.1 Theory of Harmonic Generation**
- **7.4.2 Nonlinear Materials for Harmonic Generations and Parametric Processes**
- **7.4.3 Fibre Based Kerr Media and its Application**
- **7.4.4 Resonant Nonlinearity in Doped Glassy Hosts**
- **7.4.5 Second Harmonic Generation in Inorganic Glasses**
- **7.4.6 Electric-Field Poling and Poled Glass**
- **7.4.7 Raman Gain Medium**
- **7.4.8 Photo-induced Bragg and Long-Period Gratings in Fibres**

### 7.5 Applications of Selected Rare-earth ion and Bi-ion Doped Amplifying Devices

- **7.5.1 Introduction**
- **7.5.2 Examples of Three-Level or Pseudo-Three-Level Transitions**
- **7.5.3 Examples of Four-Level Laser Systems**

### 7.6 Emerging Opportunities for the Future

### 7.7 Conclusions

**Supplementary References** 311

**Symbols and Notations Used** 315

**Index** 317
Series Preface

Wiley Series in Materials for Electronic and Optoelectronic Applications

This book series is devoted to the rapidly developing class of materials used for electronic and optoelectronic applications. It is designed to provide much-needed information on the fundamental scientific principles of these materials, together with how these are employed in technological applications. The books are aimed at (postgraduate) students, researchers, and technologists, engaged in research, development, and the study of materials in electronics and photonics, and industrial scientists developing new materials, devices, and circuits for the electronic, optoelectronic, and communications industries.

The development of new electronic and optoelectronic materials depends not only on materials engineering at a practical level, but also on a clear understanding of the properties of materials, and the fundamental science behind these properties. It is the properties of a material that eventually determine its usefulness in an application. The series therefore also includes such titles as electrical conduction in solids, optical properties, thermal properties, and so on, all with applications and examples of materials in electronics and optoelectronics.

The characterization of materials is also covered within the series in as much as it is impossible to develop new materials without the proper characterization of their structure and properties. Structure–property relationships have always been fundamentally and intrinsically important to materials science and engineering.

Materials science is well known for being one of the most interdisciplinary sciences. It is the interdisciplinary aspect of materials science that has led to many exciting discoveries, new materials, and new applications. It is not unusual to find scientists with a chemical engineering background working on materials projects with applications in electronics. In selecting titles for the series, we have tried to maintain the interdisciplinary aspect of the field, and hence its excitement to researchers in this field.

Arthur Willoughby
Peter Capper
Safa Kasap
Preface

The pleasure of scientific and philosophical expression or communication prompts deeper thinking, which, as human beings, we share for promoting knowledge. Sharing and dissemination of knowledge is the second greatest charity, after saving and protecting life and the environment – that is what my parents taught me! Without this beacon of knowledge in human beings, civilization will remain trapped in the labyrinth of darkness. Can we imagine human civilization without any epic of knowledge – where we would be today as a civilization? These are very powerful statements and as an academic I sincerely believe in the true pursuit of knowledge and, for me, this pursuance became a reality when I completed this book.

Several years ago some of my distinguished colleagues asked me whether I would be willing to write a book on “Inorganic Glasses for Photonics”, to fill a gap in this important area of physical and materials science. Perhaps it is appropriate to state at this point the importance of the subject area without emphasizing it too much. No engineering discipline can grow without materials science and vice versa. We chose the title Inorganic Glasses for Photonics because it bears two key aspects of materials science, the structure of the glassy state and its suitability for functionalizing properties for photonic applications. The study of structure–property relationships is an intrinsic part of understanding materials science, and in this book I have attempted to bring out this feature in every chapter in a concise and contextual manner, and wherever possible with examples.

During the course of writing this book, as expected, I faced many challenges and, in most cases, I turned these challenges into opportunities for learning new experiences, which helped me in forming my thoughts to adopt a different style of expression. This may become apparent to those who seek to understand the structure–property relationship of materials. Before writing a complex section, I often felt that my thoughts were in a whirlwind of thermal and configurational entropy, and that the energy requirement for achieving a coherence of thoughts, as in the manner of a laser cavity, was too high. Consequently the “slope efficiency” for writing each chapter was not the same. Exemplifying the structure–property relationship was not easy, which becomes apparent in some sections of the book, and I am sure this feature will continue to evolve in future. For this, if the readers feel there are omissions I apologize in advance. However, I have purposely kept away from incorporating chapters and sections that are well covered in other established text books in the related subject areas.

Not realizing at the outset of writing this textbook that the year 2015 would be declared by the United Nations as the Year of Light, in which year I would be able to finish this textbook, the conclusion of this project brought a personal sense of achievement. One hundred years ago in 1915, Albert Einstein rose to world fame by explaining new properties of light in the
context of general relativity. Einstein also discovered two other important aspects of light and matter – the discovery of Brownian motion helped in confirming the value of Avogadro’s number independently. Einstein’s Nobel Prize winning work on the photoelectric effect is at the genesis of quantum theory. A chance to celebrate the great achievements of Einstein in the form of a book on “Inorganic Glasses for Photonics” is an infinitesimal contribution to the world community of scientists and engineers.

In this book there are seven chapters, which in future may grow into much fuller shape by incorporating emerging aspects of nonlinear optics, nano-photonics and plasmonics using inorganic glass as a medium for controlling and manipulating light. Although I have written a significant section on nonlinear optics in Chapter 7, the aspects of nano-photonics and plasmonics are not discussed because I feel these two areas have not yet reached maturity in terms of using glass as a medium for wider device applications. I hope that you would agree!

In Chapter 1, the main focus is on the glass science and structures of inorganic glasses that are commonly used for photonic devices. A range of inorganic glasses are discussed in this chapter, with examples of oxide, fluoride, chalcogenide and mixed anion glasses. I have also attempted to explain the thermodynamics of glass-forming liquids in the vicinity of deep eutectic liquid, which is often the composition range for stable glass formation. The theory of co-ordination number is also discussed in the context of phonon structure.

For photonic device applications, a chosen glass composition must be engineered using the thermal, physical and viscosity properties of a glass. These properties are discussed in Chapter 2 by emphasizing the roles of nucleation and crystal growth, e.g. for fibre drawing.

Having discussed the important thermal, viscosity and physical properties of glasses in Chapter 2, in Chapter 3 the fabrication of bulk inorganic glasses using melting and casting is discussed for a majority of known inorganic glasses. In this chapter the fabrication principles of glass-ceramic materials are also discussed. The theory of sol–gel formation and sol–gel based glass fabrication are also discussed briefly in this chapter.

In Chapter 4, I have introduced the standard geometrical optics for fibre optics and briefly discussed the Maxwell’s equation for modal analysis and its importance in fibre and waveguide optics. In this chapter I have also brought together the signal degradation mechanism in waveguides and discussed them in some detail, by making comparisons. In this approach I have also attempted to bring together the properties of various glasses for fibre and waveguide fabrication. This chapter concludes with a detailed discussion on refractive index and its dependence on compositions, density, temperature and stress. The relationship of these properties in controlling bulk optical properties is especially emphasized.

In Chapter 5, the main emphasis is on the methods of thin-film fabrication using physical and chemical vapour deposition and pulsed laser deposition including ion implantation techniques. The pros and cons of each technique are discussed with some examples.

I have adopted a different style of presentation in Chapter 6, starting with an introduction to classical radiative transition theory based on dipole models, and have then explained the concept of dipoles and electron–phonon coupling in the text. By emphasizing various quantum mechanical rules, I have then attempted to discuss the radiative, non-radiative, energy transfer and upconversion processes. In view of a wealth of information on rare-earth doped glass based lasers and amplifiers, my focus has been on exemplifying the significance of a set of optical transitions for specific rare-earth ions in selected glass based devices for explaining the structure–property relationships.
The final chapter 7 is on the photonic device applications of inorganic glasses, fibres and waveguides. In this context I have discussed the importance of dispersion and dispersion control in optical fibres, unconventional fibres, namely, microstructured fibres, optical nonlinearity and finally concluding with examples of three- and four-level lasers and their applications. The book concludes with a short discussion on the emerging opportunities for inorganic glasses.

To help readers, there is an extensive list of references and supplementary references for further reading and in-depth comprehension of topical areas.

Earlier this year, in January 2015, Dr Charles Townes, who discovered masers, passed away 6 months before reaching his 100th birthday, and in this context the Optical Society of America’s OPN monthly journal (May 2015 issue, pp. 44–51) published a feature article on the late Dr Townes. In the inset of this article the “Family Matters” of the Townes–Schawlow were also printed. Here is an excerpt that is quite a profound metaphor, and it goes like this: “Tiny rabbit and beaver were looking up at the Hoover Dam. The beaver is saying to the rabbit, ‘No I didn’t build it, but it was based on an idea of mine’”. Since the discovery of masers in 1953 and then of lasers in 1960, today we are in the era of ultrafast femto- and atto-second lasers. The beavers have long gone, but the Hoover Dam continues to pour out knowledge. For me, it will be truly sensational to produce the most coherent and the purest form of light. Today, glass-based fibre lasers have been commoditized for manufacturing and materials processing. I hope that this book might help burgeoning minds to discover new sources of light, perhaps using novel glasses that are not yet discovered. Such engineered materials might make a significant impact in future.

Animesh Jha
July 2015, University of Leeds, Leeds (UK)
1

Introduction

1.1 Definition of Glassy States

A “glassy or vitreous” state is classified as a state of condensed matter in which there is a clear absence of a three-dimensional periodic structure. The periodicity is defined by the repetition of point groups (e.g. atoms or ions) occupying sites in the structure, following a crystallographic symmetry, namely, the mirror, inversion and rotation. A glass is a condensed matter exhibiting elasticity below a phase transition temperature, known as the glass transition temperature, which is designated in this text as \( T_g \). By comparison, an “amorphous” state, as in the “vitreous” state, has an all-pervasive lack of three-dimensional periodicity; it is more comparable with a liquid rather than a solid. An amorphous structure lacks elasticity and has a propensity to flow under its own weight more readily than a solid-like vitreous state does below \( T_g \).

An amorphous inorganic film also has a glass transition temperature and elastic behaviour, which varies with that of the corresponding vitreous state of the same material. The recognition of apparent differences in the properties of “vitreous” and “amorphous” structures, will be discussed in subsequent chapters on fabrication and processing and such comparative characterizations are essential in developing a deeper understanding of a structure–optical and spectroscopic properties of transparent “inorganic glasses as photonic materials” for guiding photons and their interactions with the medium. Such differences in structural and thermal properties between a glassy or amorphous and a crystalline state explain why the disordered materials demonstrate unique physical, thermo-mechanical, optical and spectroscopic properties, facilitating light confinement and propagation for long-haul distances better than any other condensed matter.

1.2 The Glassy State and Glass Transition Temperature \( (T_g) \)

The liquid-to-solid phase transition at the melting point \( (T_l) \) of a solid, for example, is characterized as a thermodynamically reversible or an equilibrium transition point, at which both the liquid and solid phases co-exist. Since at the melting point both phases are in equilibrium, the resulting Gibbs energy change \( (\Delta G^f) \), as shown in Equation 1.1, of the phase

---

transition is zero, which then helps in defining the net entropy change associated with the phase change at $T_f$:

$$\Delta G^f = \Delta H^f - T_f \Delta S^f = 0$$  \hspace{1cm} (1.1)

In Equation 1.1, $\Delta H^f$ and $\Delta S^f$ are the enthalpy and entropy changes at the melting point. Since $\Delta G^f$ equates to a zero value at $T_f$, from Equation 1.1, the entropy change at $T_f$ consequently is equal to:

$$\Delta S^f = \frac{\Delta H^f}{T_f}$$  \hspace{1cm} (1.2a)

From Equation 1.2a, for pure solids the magnitude of entropic disorder can thus be determined at the melting point by measuring the enthalpy of fusion. This characteristic of a solid–liquid transition will become quite relevant in the examination of glass-formation in multicomponent systems. In Figure 1.1, the liquid-to-crystal and liquid-to-glass transitions are shown by identifying the $T_f$ and a range of transition temperatures, $T_1^g$, $T_2^g$ and $T_3^g$, respectively. These glass transition temperatures are dependent on the quenching paths AA$_1$E, AA$_2$F and AA$_3$G, which differ from the equilibrium route ABCD for liquid-crystal transition at $T_f$.

In Figure 1.1, the glass experiencing the fastest quenching rate ($Q_3$) has the corresponding transition temperature at $T_3^g$, whereas the quenching rates $Q_2$ and $Q_1$ yield glasses having transition temperature at $T_2^g$ and $T_1^g$, respectively. The end entropic points thus relate to the thermal history of each glass. The slowest cooling rate yields the lowest temperature, as the supercooled liquid state below $T_f$ attains a metastable thermodynamic state, which is

---

**Figure 1.1** Plot of the entropy change ($\Delta S^f$ in J mol$^{-1}$ K$^{-1}$) in a solid–liquid and liquid-glassy state transitions, shown schematically to illustrate the respective apparent change in the value of entropy end point, as a result of various quench rates applied, which are designated by the paths AA$_1$E, AA$_2$F, and AA$_3$G.
still higher in Gibbs energy than the equilibrium crystalline state designated by line CD in Figure 1.1. When the fastest quenching rate path, AA₃G, is followed the liquid has little time to achieve the thermodynamic equilibrium, as reflected by the transition temperature $T_{g}^{3}$ which is closest to the melting point.

The annealing of the fastest quenched glass in Figure 1.1, having a transition temperature at $T_{g}^{3}$, provides the driving force for structural relaxation to lower energy states progressively. With a prolonged isothermal annealing, the end point entropy state might eventually reach much closer to the equilibrium crystalline state (line CD in Figure 1.1). As the annealing allows the quenched glass to dissipate most of the energy in a metastable quenched state, the end point entropy never approaches the line CD, which is consistent with the theory proposed by Boltzmann in the context of the second law of thermodynamics. This condition mathematically limits the value of viscosity approaching infinity, an impossible value. Considering the thermodynamic state properties, e.g. the molar volume ($V$) and entropy ($S$), and their dependence on pressure ($P$) and temperature ($T$), any change in the entropy of a state corresponds to a proportional change in the molar volume, which follows from the differentials in Equations 1.2b–d, shown below. It is for this reason that in Figure 1.1 the discontinuity in fractional change in molar free volume ($v_{f}$), which is dependent on $V$, is shown along with the entropy change:

$$dG = -SdT + VdP$$

$$\left[ \frac{\partial G}{\partial T} \right]_{P} = -S$$

$$\left[ \frac{\partial G}{\partial P} \right]_{T} = +V$$

The implication of thermodynamic state analysis in Equations 1.2b–d is that the discontinuities in glassy states are also observed when their state properties, such as the enthalpy ($H$), specific heats at constant pressure ($C_{p}$) and volume ($C_{v}$), thermal expansion coefficient ($\alpha_{V}$) and isothermal compressibility ($\beta_{T}$), are plotted against temperature. Discontinuities in the thermodynamic state properties for several glass-forming liquids are compared and discussed by Paul [1] and Wong and Angell [2] in publications that readers may find helpful.

From Figure 1.1, the glass transition temperature is represented by the presence of a discontinuity, which is dependent on the quenching rate ($Q$), and the points representing $T_{g}$ are not sharp or abrupt, as shown in the liquid-to-crystal transition. The range of $T_{g}$ in Figure 1.1 is characterized as the “fictive glass temperature” and their position is dependent on the quenching history. Several textbooks designate the fictive temperature as $T_{f}$, and readers should cautiously interpret this temperature along with the quench rate and associated thermal history, because unlike $T_{f}$, the $T_{g}$ are not fixed phase transition points. A major discrepancy in the property characterization might arise if experiments are not carefully designed to study the sub-$T_{g}$ and above-$T_{g}$ structural relaxation phenomena, which are discussed in great detail by Varsheney [3a] in his textbook. Elliott [4] explains the exponential relationship between quenching rate and $T_{g}$ in Equation 1.3, showing that the corresponding relaxation time (which is the inverse of the quenching rate) is likely to be imperceptibly long, since a glass is annealed to achieve a new metastable equilibrium.
state above a crystalline phase, corresponding to line CD in Figure 1.1:

\[ Q_i = Q_o \exp \left( -B \left( \frac{1}{T_g} - \frac{1}{T_f} \right) \right) \]  

(1.3)

In Equation 1.3, the value of \( Q_o \) for different glasses differs, as observed by Owen [5], and was found to be of the order of \( 10^{23} \) and \( 10^9 \) K s\(^{-1} \) between Se and As\(_2\)S\(_3\) glasses. The constant \( B \) was found to be of the order of \( 3 \times 10^{-5} \) K. An analysis of quenching rates and glass transition temperature implies that near \( T_g \), there is an Arrhenius type activation energy barrier, which is path dependent and can be reached in numerous ways by following different thermal histories, which is discussed extensively by Varsheney [3b]. Based on path dependence analysis and the associated changes in the first order thermodynamic properties, namely the enthalpy of glass transition, the phase transition is a “first-order” transition and, unlike the Curie temperature in a magnetic metallic glass, the glass transition is not a second-order transition. The Curie temperature is a fixed point, dependent upon the electronic-spin relaxation, the time-scale for which is of the order of \( 10^{15} \) (femto to sub-femto) seconds, which is six orders of magnitude faster than the molecular relaxation characterized by an Arrhenius type of energy barrier. From reaction rate theory, the pre-exponential in the rate equation is equal to \( k_B T/h \), where \( k_B \) and \( h \) are the Boltzmann constant and Planck’s constant, respectively and \( T \) is the absolute temperature. Applying the reaction rate theory for quenching of a glass, the minimum and maximum values therefore may vary between \( 10^{-7} \) and \( 10^{-9} \) s, which leads to an interesting discussion on the interaction of ultrafast lasers (pico- and femtosecond) with a glass and consequent structural changes. It is therefore not unreasonable to expect a dramatic change in the relaxation properties of glassy thin films formed in a femtosecond quenching regime when compared with the same composition glass produced via splat (\( 10^6 \) K s\(^{-1} \)) and air quenching (\( 10^2 \) K s\(^{-1} \)) techniques. Such a large difference in the magnitude of quenching glass is likely to yield structural variations (molar volume, expansion coefficients, refractive index, electronic edge), which may then be manifested in the corresponding relaxation rate, in accordance with Equation 1.3

1.3 Kauzmann Paradox and Negative Change in Entropy

There has been continued debate on the Kauzmann paradox in the glass literature, in relation to the path dependence of quenching of glass-forming liquids and the attainment of an overall entropy state that is lower than that of the crystalline state (line CD in Figure 1.1), which implies that the glass attains a negative entropic state. Based on the entropy change in supercooled glycerol, reported earlier by Jäckle [6] in Figure 1.2, Kauzmann’s data [7] were critically analysed by Varsheney [3b], who explained that the laws of thermodynamics are not exempt within the concept of the “Kauzmann paradox”.

In supercooled liquids the structural arrangements are so rapid that the resultant changes cannot be depicted on the time-scale of measurements. There is, though, a further argument that continues to support the nature of thermodynamic laws that the entropy change in a “system” may be negative. However, the “total or universe” entropic change is a sum of the entropies of a “system” and its “surrounding”. Two examples are characterized herein to make an important point on the negative nature of entropy. The solidification point of quartz is
Introduction

2273 K, and the entropy of fusion ($\Delta S^f_{\text{System}}$), from Equation 1.2a, is $-4.52 \text{ J mol}^{-1} \text{ K}^{-1}$, yielding an enthalpy ($\Delta H^f$) of solidification that is equal to $-10278 \text{ J mol}^{-1}$. Since there is only a small difference in the entropies of crystalline quartz, liquid silica and the glassy states, with a comparable value of around $4.52 \text{ J mol}^{-1} \text{ K}^{-1}$, during quenching as the liquid is solidifying to a lower volume state the sign of entropy “changes to a negative” value below the melting point, indicating more structural order than in the liquid state above its melting point, which is consistent with Equation 1.1. The enthalpy released into the surrounding at 300 K, which is absorbing the heat ($\delta Q$), is $+10278 \text{ J mol}^{-1}$ and therefore the corresponding entropy change in the surrounding ($\Delta S_{\text{Surrounding}}$), from the second law of thermodynamics, is equal to:

$$\frac{\delta Q}{T_{\text{Surrounding}}} = \frac{+10278}{300} = +34.26 \text{ J mol}^{-1} \text{ K}^{-1}$$

which yields a net change in entropy of the universe that is equal to $+29.74 \text{ J mol}^{-1} \text{ K}^{-1}$. The formation of a layer of amorphous alumina via the reaction:

$$2\text{Al(solid)} + \frac{3}{2}\text{O}_2(gas) = \text{Al}_2\text{O}_3(\text{solid})$$

over the surface of aluminium follows an identical argument because of the exothermic nature of the enthalpy of formation of alumina, which is $-1.8046 \times 10^6 \text{ J mol}^{-1}$ of alumina and the corresponding negative value of entropy change is nearly $-132 \text{ J mol}^{-1} \text{ K}^{-1}$. For an endothermic reaction, the signs will reverse and the argument still holds, implying that the “exemption from the universal thermodynamic laws” is “impossible” in a physical phenomenon. The irreversible and path-dependent nature of metastable glassy states beautifully follows the laws of thermodynamics, irrespective of the route by which a glass or an amorphous state is achieved, namely via the quenching, sol–gel, pulsed laser deposition and mechanical grinding techniques.

### 1.4 Glass-Forming Characteristics and Thermodynamic Properties

In Table 1.1 we compare the enthalpy, entropy, melting and glass transition points for several glass-forming unary compounds. This comparative exercise of melting, glass-transition and thermodynamic properties at $T_f$ will help us in identifying an important structural feature,
Table 1.1 Comparison of the thermodynamic state properties, enthalpy ($\Delta H_f$, J mol$^{-1}$), lattice energy ($\Delta H_{lat}$, kJ mol$^{-1}$) and entropy ($\Delta S_f$, in eu), and melting points ($T_f$, K) of glass-forming compounds and their glass transition temperatures ($T_g$, K) [4,8,9].

<table>
<thead>
<tr>
<th>Unary compound</th>
<th>$T_f$ (K)</th>
<th>$\Delta H_f$ (J mol$^{-1}$)</th>
<th>$\Delta S_f$ (eu)</th>
<th>$T_g$ (K)</th>
<th>Ratio $T_g/T_f$</th>
<th>$\Delta H_{lat}$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (SiO$_2$)</td>
<td>1996</td>
<td>7700–10 880</td>
<td>1.08–1.30</td>
<td>1453</td>
<td>0.73</td>
<td>−911</td>
</tr>
<tr>
<td>Beryllium fluoride (BeF$_2$)</td>
<td>825</td>
<td>4750</td>
<td>1.37</td>
<td>598</td>
<td>0.73</td>
<td>−1028</td>
</tr>
<tr>
<td>Germanium oxide (GeO$_2$)</td>
<td>1388</td>
<td>8140</td>
<td>1.4</td>
<td>853</td>
<td>0.61</td>
<td>−580</td>
</tr>
<tr>
<td>Boric oxide (B$_2$O$_3$)</td>
<td>723</td>
<td>22 180–24 060</td>
<td>7.33–7.95</td>
<td>530</td>
<td>0.73</td>
<td>−1272</td>
</tr>
<tr>
<td>Zinc chloride (ZnCl$_2$)</td>
<td>591</td>
<td>10250</td>
<td>4.14</td>
<td>380</td>
<td>0.64</td>
<td>−415</td>
</tr>
<tr>
<td>Sulfur (S)</td>
<td>388</td>
<td>1720</td>
<td>4.14</td>
<td>246</td>
<td>0.63</td>
<td>—</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>494</td>
<td>5860</td>
<td>2.83</td>
<td>318</td>
<td>0.64</td>
<td>—</td>
</tr>
<tr>
<td>Arsenic trisulfide (As$_2$S$_3$)</td>
<td>585</td>
<td>28675</td>
<td>11.71</td>
<td>478</td>
<td>0.82</td>
<td>−168</td>
</tr>
<tr>
<td>Arsenic triselenide (As$_2$Se$_3$)</td>
<td>633</td>
<td>40815</td>
<td>15.0</td>
<td>468</td>
<td>0.74</td>
<td>−102</td>
</tr>
<tr>
<td>Arsenic tritelluride (As$_2$Te$_3$)</td>
<td>633</td>
<td>46883</td>
<td>17.28</td>
<td>379</td>
<td>0.60</td>
<td>−38</td>
</tr>
<tr>
<td>Germanium disulfide (GeS$_2$)</td>
<td>1113</td>
<td></td>
<td></td>
<td>765</td>
<td>0.69</td>
<td>−157</td>
</tr>
<tr>
<td>Germanium selenide (GeSe$_2$)</td>
<td>1013</td>
<td></td>
<td></td>
<td>695</td>
<td>0.69</td>
<td>−113</td>
</tr>
<tr>
<td>Si</td>
<td>1685</td>
<td>50570</td>
<td>7.17</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>ZrF$_4$</td>
<td>1205</td>
<td>Sublimes at 1177 K</td>
<td></td>
<td>—</td>
<td>—</td>
<td>−1909</td>
</tr>
<tr>
<td>BaF$_2$</td>
<td>1563</td>
<td>28.5</td>
<td>4.35</td>
<td>—</td>
<td>—</td>
<td>−1210</td>
</tr>
<tr>
<td>NaF</td>
<td>1269</td>
<td>33.5</td>
<td>6.30</td>
<td>—</td>
<td>—</td>
<td>−374</td>
</tr>
<tr>
<td>ZrF$_4$–BaF$_2$ equimolar glass</td>
<td>823</td>
<td></td>
<td></td>
<td>543</td>
<td>—</td>
<td>−392</td>
</tr>
<tr>
<td>CdCl$_2$</td>
<td>842</td>
<td>30.1</td>
<td>8.55</td>
<td>—</td>
<td>—</td>
<td>−858</td>
</tr>
<tr>
<td>BaCl$_2$</td>
<td>1195</td>
<td>17.2</td>
<td>2.06</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CdCl$_2$–BaCl$_2$ equimolar glass</td>
<td>583</td>
<td></td>
<td></td>
<td>425</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
which will aid our understanding of the structure–property relationship. In this process of a comparative analysis of thermodynamic properties, we represent the entropy of melting in Equation 1.2a, which is divided by a factor 4.187, the conversion factor for 1 calorie unit into a joule unit. The ratio in Equation 1.2a, therefore, is redefined in terms of an “entropy unit (eu)” in Equation 1.4 as a measure of disorder:

\[
\Delta S_f = \frac{\Delta H^f}{4.187T_f} \text{(eu)}
\]  

(1.4).

From this expression, an eu is a measure of disorder at the melting point, which shifts the entropy of a corresponding liquid at \( T_f \) along the line BC in Figure 1.1. In Table 1.1, the last but one column gives the ratio \( T_g \) over \( T_r \), which is often used to define the glass-forming tendency of a liquid, and is known to vary between 0.60 and 0.80 for most glass formers. We also point out to the reader that the literature frequently uses terminologies such as “glass-forming ability” and “glass-forming tendency” which carry analogous meaning. However, neither of these two terminologies should be confused with the “metastable stability” of a glassy state, which can only be quantified by the kinetics of glass formation. Several glass-stability parameters have also been used in the literature, some of which are explained in the context of the kinetics of glass formation and the classical theory of crystal nucleation and growth.

A comparison of the values of eu for various unary glass formers in Table 1.1 demonstrates that there are unary compounds, namely SiO\(_2\), BeF\(_2\) and GeO\(_2\), which have a relatively lower value of eu (~1.1 to 1.4) on melting, suggesting that the extent of structural disorder as a result of melting at \( T_r \) is comparatively much smaller than any other groups of compounds in this table. The values of eu for arsenic based chalcogenides (As\(_2\)S\(_3\), As\(_2\)Se\(_3\) and As\(_2\)Te\(_3\)) are naturally the largest, due to their high vapour pressures at the melting points. Unfortunately, a similar comparison for germanium based chalcogenides cannot be carried out, due to the lack of relevant thermodynamic data in the literature. In Table 1.1 we also find that the values of the ratio of \( T_g \) to \( T_r \) for glass-formers such as SiO\(_2\), GeO\(_2\), BeF\(_2\), ZnCl\(_2\), S and Se are predominantly in the range 0.65–0.72, which falls in a “critical undercooling range” of roughly \( \frac{1}{2} \) of the corresponding melting point of the unary glass-forming compound. Table 1.1 thus shows two important features: (i) there is an entropic disorder associated with the glass formation in unary compounds and (ii) each glass-former requires undercooling, with respect to melting point. Discussion of the aspects of undercooling and entropic changes associated with glass formation will be resumed later in this chapter and in Chapter 2, to help in explaining the thermal properties and viscosity of various types of glasses.

In Table 1.1 we also compare the lattice energies of commonly known glass-forming compounds and constituent components of multi-constituent glassy phases. The importance of the lattice energies of constituents is explained below in the context of eutectic compositions, at which a vast majority of liquids, when quenched, transform into a glassy phase. The lattice energy of various compounds are best quantified by their heats of formation, which yield the resulting bonds, e.g. in SiO\(_2\) the Si–O bond, as explained by the Born–Haber cycle. In Table 1.1, the values of lattice energies (or the heats of formation) of pure glass-forming elements, namely Si, Se and S, are zero [8]. To estimate the differences in lattice energies of multi-constituent glasses, say, for example, the equimolar compositions for AgI-CsI, the lattice energy difference can be estimated by simply subtracting the value of CsI from that of AgI and dividing it by 2.
A vast majority of practical inorganic glasses used for engineering applications are constituted of more than one component. This means that the thermodynamic properties of liquid mixtures are relevant in the discussion of glass-forming liquids, which may be characterized using the concepts of classical thermodynamics. Comprehensive essays on the properties of liquid mixtures with examples of metallic and inorganic oxides are cited in a number of text books on this subject by the pioneers of applied thermodynamics, Darken and Gurry [10], Swalin [11], Richardson [12], Lupis [13], Turkdogan [9b], and also in classical ceramic and halide salt references [14,15]. The properties of liquid mixtures and the use of phase diagrams for the determination of partial molar quantities of component end members in a binary mixture are especially discussed in References 9b–13. In a binary liquid, for example, in which more than one component is required for glass formation, the overall change in the entropy of a mixture differs significantly. Thermodynamically a binary mixture, for example with \( X_A \) and \( X_B \) fractions of constituents A and B, respectively, is more stable than the pure constituents, A and B. This becomes apparent when we consider the depression in the melting point of a pure constituent, with respect to a liquidus temperature \( (T^l)_i \) at a given mole fraction, \( X_i \), which is analogous to Equation 1.2a:

\[
(T^l)_i = \frac{\Delta H^f + \Delta S_i}{\Delta S^f + \Delta S_i}
\]

where \( \Delta H^i \) and \( \Delta S_i \) are the partial molar enthalpy and entropy of mixing of a binary mixture. The value of \( \Delta H^i \) can be assumed to be zero for ideal mixtures. For non-ideal mixtures with negative enthalpy of mixing, the partial enthalpies are also negative in the numerator of Equation 1.5. The denominator, however, has a partial entropy of mixing \( \Delta S_i \) term, which is always positive, and for a simple ideal mixture it is equal to \(-R \ln X_i\). Substituting \(-R \ln X_i\) in Equation 1.5 yields Equation 1.6, in which the liquidus temperature, \( (T^l)_i \) can be expressed in terms of composition \( (X_i) \) and the melting point and entropy of an end member in a binary mixture. Here \( R \) is the universal gas constant, with a value 8.314 J mol\(^{-1}\) K\(^{-1}\) in SI units:

\[
(T^l)_i = \frac{\Delta H^f}{\Delta S^f - R \ln X_i} = \frac{T_f}{1 - \frac{R}{\Delta S^f} (\ln X_i)}
\]

From this simple equation we find that for a given value of \( X_i \) in a binary or multicomponent liquid the drop in the liquidus temperatures, \( (T^l)_i \) is large when the value of \( \Delta S^f \) is small. In addition, if we consider a non-ideal glass-forming liquid in which the value of \( \Delta H^i \) is negative, the corresponding reduction in the value of predicted \( (T^l)_i \) is expected to be much larger than when a liquid mixture behaves as an ideal mixture. We can, thereby, critically examine examples of glass formation in inorganic glass-forming liquids. Based on such comparisons, the corresponding drop in the liquidus leading to formation of eutectic mixtures is discussed in the context of the partial molar properties of the two binary mixtures. The first glass-forming system is a monovalent mixture of AgI-CsI, followed by the CdF\(_2\)-BaCl\(_2\) system, and finally a series of tetravalent–monovalent and tetravalent–divalent fluoride liquid mixtures, especially in the ZrF\(_4\)-NaF and ZrF\(_4\)-BaF\(_2\) systems. These liquids are classed as predominantly “ionic liquids”, in which the diffusion of cations and anions is at least 2–3 orders of magnitude larger than in covalent liquids of, say, meta silicates, phosphates and borates. The importance of such a discussion on glass-formation in ionic liquids will become
apparent when the tendency for polymerization and evolution of glass-forming networks is discussed by emphasizing the predominance of complex ordering of structures in liquids, as often seen in the properties of silicate, phosphate, germanate, and borate glasses. The nature of such ordering is then manifested through the shape and slopes of liquidus curves in the resulting phase diagrams.

Glass-formation in chloride, bromide and iodide systems, e.g. in the AgI-CsI binary, were first reported by Ding and co-workers [14]. The diffusion coefficient of Ag$^+$ ions in the AgI-CsI liquids is of the order of $10^{-1}$ to $10^{-2}$ cm$^2$ s$^{-1}$ below 100$^\circ$C [15]. Hulme and co-workers [16] analysed the phase constitution in AgI-CsI, including the shape of liquidus curve, leading to the formation of eutectic points. The calculated liquidus lines using Equation 1.6 and the empirically determined phase equilibrium boundaries are compared in Figure 1.3, in which it is apparent that the ideal solution model, based on Raoult’s law, predicts a eutectic temperature that is $\sim$180 K higher than the actual temperature in the vicinity of 470 K in the binary AgI-CsI system [16]. Evidently, in the AgI-CsI mixture there is a significant departure from ideal behaviour, which can be measured with respect to the value of partial molar enthalpy, $\Delta H_i$, in Equation 1.5. A detailed analysis of the partial enthalpy of mixing in the binary halide system may be made using the Hildebrand’s Regular solution and Guggenheim models both of which are well cited in the literature.

At the eutectic points the liquid solution freezes and yield solids, as shown in Figure 1.3, two of which are based on silver iodide polyanionic complexes $[\text{Ag}_2\text{I}_3]$ and $[\text{AgI}_3]^2\text{−}$, as shown in Figure 1.4, and form AgCs$_2$I$_3$ and Ag$_2$CsI$_3$ crystals, respectively. As explained by Brink and
co-workers [17], the $[\text{M}_2\text{X}_3]^{-}$ and $[\text{MX}_3]^2-$ forma via edge-sharing and corner-sharing, which has been further explained by Wells [18] in his treatise on structural chemistry. The cationic radii of Ag$^+$ and Cs$^+$ are 0.127 and 0.168 nm, respectively, and the corresponding values of electronegativity are 1.9 and 0.7, which imply that in the $[\text{M}_2\text{X}_3]^{-}$ and $[\text{MX}_3]^2-$ complexes the Ag$^+$ cations, due to their smaller size and larger electronegativity than the Cs$^+$ ions, are responsible for the formation of $[\text{M}_2\text{X}_3]^{-}$ and $[\text{MX}_3]^2-$ polyanionic species (Figure 1.4).

The second example of polymerization in ionic liquids is illustrated by the examples of glass formation in CdF$_2$-BaCl$_2$, which was reported by Poulain and Matecki [19]. An essential aspect of structural analysis in the divalent mixture is the Gibbs energy of mixing, which is a means of identifying how far a glass-forming solution departs from an ideal Raoult’s law, as explained above in Equations 1.5 and 1.6. The determination of non-ideality in CdF$_2$-BaCl$_2$ can be explained by introducing a thermodynamic term, which will help later on in establishing the relationship between the viscosity and glass structure, IR absorption and spectroscopic properties.

The departure from non-ideal Raoult behaviour of a reciprocal salt mixture, CdF$_2$-BaCl$_2$, can be defined by calculating the entropy of mixture. When a solid mixture of CdF$_2$-BaCl$_2$ is heated above the melting points of its constituents, the following ionic exchange reaction occurs:

$$\text{CdF}_2(\ell) + \text{BaCl}_2(\ell) = \text{CdCl}_2(\ell) + \text{BaF}_2(\ell)$$  \hspace{1cm} (1.7a)

$$\Delta G_{1.7a} = -38650 - 18.37 \text{ J mol}^{-1}$$  \hspace{1cm} (1.7b)

In Equation 1.7a we observe that as a result of ionic exchange CdCl$_2$ and BaF$_2$ are produced. However, if the solution were an ideal one, the difference in the entropies of unmixed solid states before melting ($S_{\text{unmix}}$) and after melting ($S_{\text{mix}}$), $\Delta S_{\text{mixture}}$, is equal to zero. This means that there is no preferential structural association by forming a polyanionic complex in liquids. In reality such ideal behaviour is much rarer than the non-ideal, and as a result of mixing in CdF$_2$ and BaCl$_2$, the large difference in their lattice energies (enthalpy of compound formation), the heat or enthalpy of mixing is not zero (see Equation 1.6). This means that in Equation 1.5 the partial thermodynamic quantities in the numerator and denominator become non-zero, and consequently the preferential structural association for complex formation is likely to increase. Thus the “ideal configurational entropy”, which can be

---

**Figure 1.4** Structures of polyanionic $[\text{MX}_3]^2-$ and $[\text{M}_2\text{X}_3]^{-}$ are shown in (b) and (c), respectively, where (a) large grey and small grey circles represent iodine and silver ions, respectively. (b) Corner shared AgI chains are prevalent in the AgCs$_2$I$_3$ complex, (c) whereas double edge-shared AgI chains dominate the Ag$_2$CsI$_3$ structures. The dotted pyramids in (c) represent the backplane of the paper, which is why along a shared edge four-iodine ions are shown, (see arrow) and is not required in the building of this structure. At other shared edges in (c) this is not apparent [16–18]. Source: Hulme 1989. Reproduced with permission from The Society of Glass Technology, Sheffield.