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Perspectives on the History of Glass Composition

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The 100th anniversary of The American Ceramic Society corresponds approximately with the 100th anniversary of what might be considered the start of the age of glass science, i.e., the publication, in Germany, in 1886, of the catalog of Schott und Genossen, containing 44 optical glass compositions. The American Ceramic Society centennial seems, accordingly, to be an appropriate occasion to examine the history of glass composition that both preceded and followed the seminal work of Schott and to survey some of the major discoveries and changes in glass composition as well as the reasons that led to them. Although it is certainly of interest to consider a more complete history of the glass industry, we have opted to attempt the more modest task just described. The history of glass structure theories is considered, particularly with regard to the effects of composition on structure, and how these relate to glass properties. The article then continues with a discussion of recent special glasses and concludes with a description of light-guide glasses, the discovery of which has changed the nature of glass science and the glass industry.

I. Introduction

THE 100th anniversary of The American Ceramic Society corresponds approximately with the 100th anniversary of what might be considered the start of the age of glass science—the disclosure, in 1886, of the work of Otto Schott and Ernst Abbe in Germany. This was the publication of the catalog of the ‘‘Glastechnisches Laboratorium, Schott und Genossen’’ (see Fig. 1).[1] Up to this time, very little real glass science had been done, although, with the limited tools at their disposal, earlier workers did quite remarkable things. Most work was done in an attempt to understand what soda–lime–silica glasses were and to improve their quality. Schott[2] conducted detailed studies of the effects of various additions and substitutions to the basic soda–lime glass composition. He and Winkelmann[3,4] were the first to attempt to model glass behavior development by means of a set of factors with which properties could be calculated.

As a result of the coincidental natural occurrence of alkali, alkaline-earth ‘‘impurities,’’ and sand, soda–lime–silica glass became the ‘‘staple’’ glass composition very early in time, and it has continued to be so with only slight changes. Variations in production techniques and specific use requirements have led to the deliberate addition of a variety of other oxides, so that most commercial ‘‘soda–lime’’ glasses now contain six or more constituents. Over the years, the bulk of commercial glasses for most purposes has continued to be based on silica as the primary glass former.

Research (by X-ray technologies, optical spectroscopy, physical property measurements, etc.) during the 20th century has been conducted on simple glass compositions to attempt to understand glasses as materials as well as to attempt to understand their structure and properties well enough to predict properties from composition and to design a glass from a list of requirements. Although glasses with rather remarkable properties ranging from infrared transmission and superionic conductivity to biological activity have been discovered, it is probably not entirely accurate to say that we can design a glass for a given purpose. Available commercial silicate glasses do their job quite admirably, but they are rather *complicated* glasses that fulfill rather *simple* tasks. In 1970, the discovery that a simple (titania–silica)–silica compound glass fiber could conduct light over rather long distances without requiring amplification has resulted in a ‘‘new glass industry’’—the ‘‘light-guide industry.’’ Since then, in somewhat of a turnabout, scientists have discovered that these *simple* glasses display a wide range of unexpected, new, complicated, and often incom-

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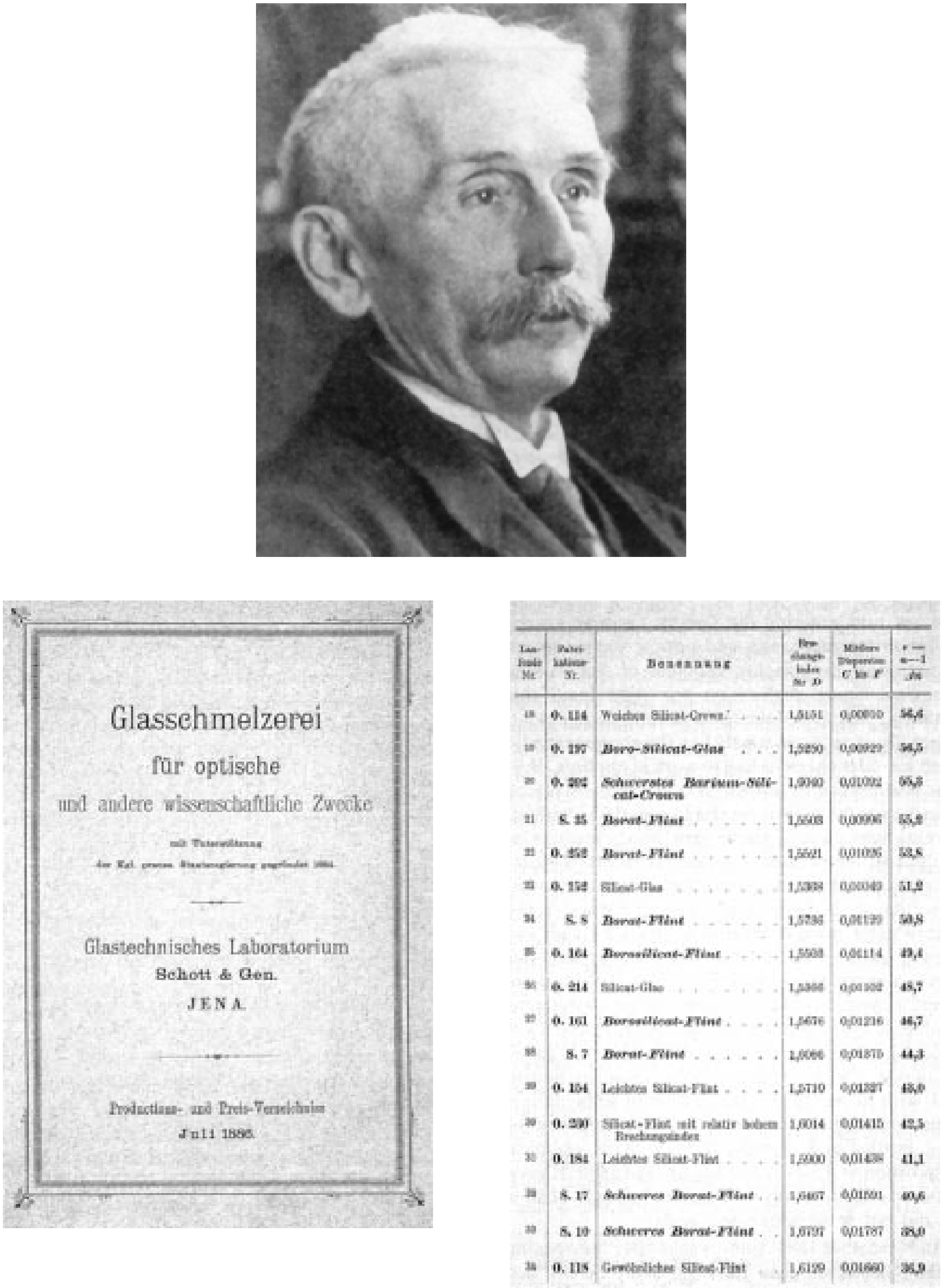
centennial feature



Glasschmelzerei
für optische
und andere wissenschaftliche Zwecke
mit Unterstützung
der Kgl. preuss. Staatsregierung gegründet 1884.

Glastechnisches Laboratorium
Schott & Gen.
JENA.

Productions- und Preis-Verzeichniss
Juli 1886.

Laufende Nr.	Fabrikations-Nr.	Benennung	Brechungsindex für D	Mittlere Dispersion C bis F	ν = (n−1)/Δn
18	O. 114	Weiches Silicat-Crown	1,5151	0,00910	56,6
19	O. 197	*Boro-Silicat-Glas*	1,5250	0,00929	56,5
20	O. 202	*Schwerstes Barium-Silicat-Crown*	1,5660	0,01022	55,5
21	S. 35	*Borat-Flint*	1,5503	0,00996	55,2
22	O. 252	*Borat-Flint*	1,5521	0,01026	53,8
23	O. 152	Silicat-Glas	1,5368	0,01049	51,2
24	S. 8	*Borat-Flint*	1,5736	0,01129	50,8
25	O. 164	*Borosilicat-Flint*	1,5503	0,01114	49,4
26	O. 214	Silicat-Glas	1,5366	0,01102	48,7
27	O. 161	*Borosilicat-Flint*	1,5676	0,01216	46,7
28	S. 7	*Borat-Flint*	1,6086	0,01375	44,3
29	O. 154	Leichtes Silicat-Flint	1,5710	0,01327	43,0
30	O. 250	Silicat-Flint mit relativ hohem Brechungsindex	1,6014	0,01415	42,5
31	O. 184	Leichtes Silicat-Flint	1,5900	0,01436	41,1
32	S. 17	*Schweres Borat-Flint*	1,6467	0,01591	40,6
33	S. 10	*Schweres Borat-Flint*	1,6797	0,01787	38,0
34	O. 118	Gewöhnliches Silicat-Flint	1,6129	0,01660	36,9

Fig. 1. Photograph of Otto Schott and pages from glass catalog.

pletely explained properties. We attempt in this review to illustrate some of the interesting events in this long history.

In this article we

- Provide a brief review of the early history of glass;
- Review the work of Abbe and Schott, i.e., the start of glass science;
- Review the development of more-modern glass compositions;
- Provide a brief review of the history of glass structure and property relations;
- Bring the history up-to-date by discussing some new special glasses and the new era of optical fibers.

Our purpose here is to provide an overview of the very large field of inorganic glasses for the benefit, perhaps, of a researcher new to glass. We attempt to provide a sense of the present and future of glasses–properties–understanding as well as why and how we arrived at this position. Because of the many glasses that have been studied, we are forced to limit our comments to compositions that illustrate major discoveries or changes; accordingly, some important glass compositions are not discussed.

Besides the apparent limitations imposed by practical considerations and economics, physics appears to impose a real limitation to the variation of properties available in materials that lack a periodic crystalline lattice. Inorganic glasses are generally considered to be isotropic; dielectric; transparent, unless colorants are added; chemically durable and, therefore, chemically inert; and brittle.

These general properties, however, are constrained only in those glasses that are normally thought of when we think of glasses. If we broaden our chemical viewpoint to include chalcogenide, halide, and, especially, metallic glasses, a wide variety of properties becomes available. Although the lack of a crystalline lattice appears to impose a rather severe constraint with regard to some properties at the moment, in most cases, we are not in a position to state unequivocally whether these constraints are absolute. For instance, it had been thought to be impossible to make bulk metallic glasses because their hard sphere structure results in rather simple dense packing, which is, in itself, not conducive to extensive supercooling. However, this recently has been shown to be untrue. Also, it normally is considered that the lack of a crystalline lattice means that plastic flow is not possible because the dislocations that result in plastic flow cannot form. We have yet to determine whether this is completely true, or if it can be sensibly modified.

There were few modern books in English on glass until the publication of George Morey's book, *The Properties of Glass,*[5] in 1938. After World War II, and following the publication of the second edition of Morey in 1954, many other books appeared. Recently, many edited books and edited proceedings have appeared regularly.[6–12] The more general books usually present a short history of glass, a definition and description of glass, and chapters that present properties and compositions of simple glasses, where the chapters are arranged either by property or by glass composition. These books are important and useful, especially as texts on the science and technology of glass. There also have been many excellent review articles and book chapters that present special subjects. Examples are the two excellent series by Doremus and Tomozawa[12] and Uhlmann and Kreidl.[13] In particular, in the Uhlmann and Kreidl series, the Kreidl chapter on glass-forming systems is very useful. It historically, scientifically, and technologically discusses almost every known glass-forming system. Here we attempt, by perhaps rather extreme simplification, to illustrate some of the issues having to do with property–composition development. We present our simplified and personal view of some glass compositions–structures in order to make some simple generalizations. This hopefully leads to a better general understanding of what has been done, in many cases, empirically, and hopefully leads to the possibility of predicting what remains possible. Such predictions were attempted at a meeting to celebrate Kreidl's 80th birthday.[14]

The sections that follow immediately have to do with the early history of glass. The reader is directed to the papers of Cable[15–17] and symposia arranged by Kingery[18,19] for other interesting insights into this history.

II. Early Glasses

(1) Middle Eastern Origins and Roman Growth

The earliest known synthetic glasses were created in Asia Minor several millennia ago. Some isolated examples may be as early as 7000 BC, but it is clear that, by 2500 BC, there were many sources, probably first in Mesopotamia, then in Egypt. The first glassmakers were motivated to create decorative objects, possibly to simulate gems and semiprecious stones, using sintered bodies of silica and desert soda (natron) with appropriate colorants, such as copper, manganese, and iron salts. There was no demonstrated interest in transparency at this time. Beads also were made, and, later, small vessels were constructed by coating sand cores with a glassy skin—the cores were removed after forming.

The earlier and sometimes parallel development of ceramic and metallurgical processes undoubtedly influenced and aided the growth of early glass technology; some furnace improvements and raw materials were applicable to glassmaking. The extensive Egyptian tradition of faience making also must have had an effect, contributing knowledge of raw materials and sintering techniques.

About 2000 years ago, the blowing of glass articles with a pipe was invented, probably in Syria, and this advance in technology was followed by a rapid increase in the use of glassware. Glassblowing spread quickly through the Roman Empire, and soon glass bowls and drinking vessels were in use throughout society, in both ordinary households and among the ruling classes. A desire for clear and transparent vessels came with this remarkable growth of blown glass production. Accordingly, strong efforts were directed toward the elimination of iron and other contaminants, particularly for the higher-quality glassware.[5]

(2) Raw-Material Preparation—The Search for Transparency

Early glasses in the western world were almost all soda–lime–silica compositions that varied depending upon the availability of raw materials, but generally differed little from present-day commercial glasses (Table I). Beach sand and a crude source of alkali were typical ingredients, with both the sand and the alkali containing enough lime or magnesia to give chemical durability adequate for the purposes of the time. In the case of the sand, fragments of shells provided some lime, and plant ash generally brought some magnesia along with the soda and potash.

Two different sources of alkali affected the composition of early glasses. On the Eastern Mediterranean littoral natron (hydrated Na_2CO_3) was usually the favored alkali, because it was available from northern Egypt (see, e.g., glass 2 in Table I).[20] Further east, in Mesopotamia and Persia, the alkali was usually provided by plant ash that contained more K_2O (2%–4%) and MgO (2%–6%) (see, e.g., glass 3 in Table I).[21a] The alkali content of the ash was influenced by the soil in which the plants grew: plants that grew in salty soil or near the sea were high in soda, whereas those that grew inland had higher potash contents.[22] Agricola (1556)[23] refers to the use of salts made from the ashes of salty herbs as well as to natron and ''rock-salt.'' When these were not available, he suggested the ashes of oak could be used, or, as a last resort, the ashes of beech or pine.

The practice of using natron to produce higher-soda glasses continued in the Mediterranean region through early and medieval times. However, there was a surge in the use of potash in glassmaking during the 9th through 13th centuries, before soda again became the predominant alkali.[24]

Much glass made in the Middle Ages was dark green, dark brown, or almost black as a result of the impurities present. This ''waldglas,'' or forest glass, often was used for bottles and drinking vessels, but interest grew in preparing clearer, more-transparent glass. Although little is known about glass technology in the middle ages, we do know that some attention was given to the purification of raw materials. One of the major sources of glass technology information in this period comes from *L'Arte Vetraria,*[25] written by Antonio Neri, an Italian priest and glassworker, in 1612, and translated to English in 1662 by Christopher Merrett, an English physician and one of the founders of the Royal Society. (It also was translated by Johann Kunckel in 1679; both Merrett and Kunckel added valuable personal observations on glassmaking.) Agricola and Neri devoted considerable space to raw-material preparation, discussing the careful selection of crystals (quartz) and clean ''white stones free of black or yellow veins'' to be used in

Table I. Glass Compositions

Glass†	Oxide content (wt%)							
	SiO_2	B_2O_3	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3
(1) Egypt, 1500 BC‡	67.8		16.08	2.08	3.8	2.89	3.22	0.92
(2) Palestine, 4th Century	70.5		15.7	0.8	8.7	0.6	2.7	0.4
(3) Sudan, 3rd century	64.2		15.9	2.65	10.2	2.73	2.06	2.3
(4) Italy, 9th–10th centuries	77.8		6.4	8.7	2.1	0.7	2.2	0.8
(5) Container glass, 1980	73.0		13.7	0.4	10.6	0.3	1.8	
(6) 1:1:6 soda–lime–silica	75.3		13.0		11.7			
(7) Faraday ‘‘heavy glass’’‡	10.6	15.6						
(8) ‘‘Jena Standard Glass’’‡	67.2	2.0	14.0		7.0		2.5	
(9) Schott thermometer glass	72.0	12.0	11.0				5.0	
(10) Schott utensil glass	73.7	6.2	6.6			5.5	3.3	
(11) Schott Welsbach chimney‡	75.8	15.2	4.0					
(12) Nonex‡	73.0	16.5	4.25					
(13) Pyrex	80.5	12.9	3.8	0.4			2.2	
(14) E-glass, typical	54.0	10.0			17.5	4.5	14.0	

†(1) Morey,[5] Table I-1 (10); (2) Brill,[20] Jalame glass, (low potassium, high sodium); (3) Brill,[21a] Sedeinga tomb glass, (high potassium, high magnesium); (4) Brill,[21b] Frattesina glass, (mixed alkali); (5) Ryder and Poole[43]; (6) by calculation; (7) Faraday;[37] (8) Hovestadt,[40] Jena glass 16^{III}, 1884; (9) Hovestadt,[40] p. 246, Jena glass 59^{III}, 1889, ‘‘ideal thermometer glass’’; (10) Steiner,[42] p. 172, Jena glass 202^{III}, 1893, recalculated from batch; (11) Steiner,[42] p. 172, Auer von Welsbach gas light chimney, Jena glass 276^{III}, 1895, recalculated from batch; (12) Corning code 7720; (13) Corning code 7740, Morey;[5] (14) Aubourg and Wolf,[46] typical composition, can vary, depending upon manufacturer and materials. ‡Glass contains other oxides: (1) 0.54% Mn_2O_3, 1.51% CuO, and 1.0% SO_3; (7) 70% PbO; (8) 7.0% ZnO; (11) 4.0% Sb_2O_3 and 0.9% As_2O_3; (12) 6.25% PbO.

place of sand if high clarity was desired. The stones were reduced to fine particles by pounding in a mortar, and the silica powder then often was fritted with the alkali salts. Neri gave considerable attention to alkali preparation, discussing in some detail the washing of various plant ashes to prepare alkali salts for clear crystal glass. The purification process consisted of repeated sieving of the raw salt, dissolving it in boiling water, filtering, and evaporating. Thus the impurities causing color, such as iron compounds, were left behind.

Unfortunately, much of the alkaline-earth and alumina of the ashes were left behind as well; therefore, many clear glasses prepared from the purified raw materials had relatively poor resistance to attack by moisture. The much-admired clear ‘‘cristallo’’ glass produced in Venice–Murano in the early 1500s suffered from low lime and magnesia content. As a result, many of the elegant examples of the elaborate Venetian glass of that period now in museums have developed surface crizzling (a multitude of fine surface fractures) because of their poor chemical durability; some extreme examples are sticky to the touch and appear to sweat.[26] These cristallo glasses provide an example of an unintended consequence of the desire to optimize one glass property, colorless clarity in this case, causing a deterioration in another property, durability.

(3) Colored Glasses

Although the preceding section described colorless glasses purposely made free of unwanted color, other glasses were colored purposely for decoration since the earliest days of glassmaking. Glassworkers in Egypt, the Middle East, and the Roman Empire knew that small amounts of certain salts could be incorporated in the melt to produce strongly colored glasses, some transparent, some opaque. This addition of colorants was probably the first example of the use of minor ingredients to change glass properties to produce a desired effect.

The earliest and most widely used solution colorants were salts of copper (blue-green from the presence of Cu^{2+}), iron (blue to green from Fe^{2+}, yellow to brown from Fe^{3+}), and manganese (amethyst or purple from Mn^{3+}).[27] The use of small quantities of manganese as a decolorizer to compensate for iron colors, also known in the Middle Ages, was referred to by Agricola and Neri and was used by the Venetians in the production of cristallo. Cobalt was first used in the 14th century BC (deep blue from Co^{2+}). The use of chromium as a solution colorant probably began early in the 19th century.[27]

Copper and gold ruby glasses were prized highly for their beauty and for their scarcity, the latter a result of the difficulty of producing these colloidal colors. Both glasses presented serious challenges to the glassmaker because of their sensitivity to composition, melting conditions, and subsequent thermal history. The ruby color is caused by the selective absorption of light by small gold or copper crystals (~50 nm in diameter) that are formed by the precipitation of the metals in their atomic state. The formation of the metal crystals is enhanced by reheating the glass (‘‘striking’’) and by the presence of reducing agents, e.g., stannous chloride. The red glasses found in old church windows are most likely copper reds, either copper rubies, suspensions of cuprous oxide, or copper stains, because gold rubies do not seem to have been made with any certainty until the 17th century.[25,28]

Opaque glasses colored by suspensions of relatively large crystals (with diameters in the micrometer range), where the crystals behave essentially as color pigments, have been known since antiquity. The pigments are generally insoluble or of limited solubility in the matrix glass. Some of the opaque colors formed in this way are white glasses containing suspensions of tin oxide, arsenic pentoxide, or calcium antimonate, and yellow glasses colored by lead antimonate. Opaque blue glasses colored by copper calcium silicate or cobalt aluminate, green glasses colored by chromic oxide, and brown or red-browns from iron or iron-manganese oxide mixtures also are used.

The most dramatic examples of colored glass are probably the church windows of the Middle Ages, with the greatest created during the 10th through 14th centuries. Most of these windows also contain much stained glass, wherein a colorant is diffused into the glass surface at temperatures well below that of molten glass. Copper reds and silver yellows are perhaps the best-known examples of surface stains.

(4) Lead Glasses

The first major departure from alkali–lime–silica glasses came during the 17th century with the commercial introduction of lead flint glasses. Lead had long been a minor constituent in glazes, mosaics, and artificial gems. It was introduced as calcined lead or lead oxide, primarily for its fluxing effect. Neri discussed lead glasses at some length in *L'Arte Vetraria* and emphasized that great care must be taken to thoroughly calcine the lead to avoid the formation of molten lead because ‘‘the least lead remaining breaks out the bottom of the pots and lets all the metall run into the fire.’’[25]

Shortly after the publication of Merrett's English translation of Neri's work in 1662, George Ravenscroft, an English glass merchant, turned glassmaker to develop a clear glass based on English ingredients.[29,30] This latter requirement was motivated by the difficulty English glassmakers were experiencing in obtaining raw materials at acceptable cost, because a monopoly controlled the import of plant ashes for soda.[31] The glass merchants also were struggling with unresponsive foreign suppliers, much breakage in transit, and oppressive tariffs.[32] After a series of experiments, Ravenscroft introduced a clear potash lead glass that was the ancestor of English lead crystal. The Worshipful Company of Glass Sellers of London, a trade guild, quickly recognized the potential of Ravenscroft's invention and negotiated to buy his entire production. The first glasses suffered from poor chemical durability and crizzling, and it was a few years before a truly moisture-resistant lead crystal was produced. The glass was called ‘‘crystal,’’ and the fact that lead was the key ingredient was kept secret by Ravenscroft and his immediate successors. These glasses also were called flint glasses, because they were based on high-purity silica from the flint nodules found commonly in the Cretaceous chalk deposits of southeast England, plus calcined lead oxide, niter (potassium nitrate), and potash from wood ashes (good quality potash had become more readily available in the latter part of the 17th century). A substantial business grew in the manufacture of lead crystal articles that took advantage of the higher refractive index and the ease of cutting and polishing of the lead flint to create sparkling goblets, bowls, and vases.

The 17th century also was a period of growing interest in science, and glass improvements became driven by scientists seeking better optical instruments, particularly telescopes. Galileo and Kepler made a number of discoveries in optics that made possible considerable improvement in telescopes, using the soda–lime–silica crown glasses of the time. (Crown glass was the name given to window glass of the period that was made by the crown process, wherein a large blown bubble of glass was transferred to a pontil, opened, and spun into a circular disk by centrifugal force.) However, later optical physicists and astronomers found themselves increasingly frustrated by poor glass quality and by the difficulty imposed by chromatic aberration in obtaining a clear, sharp focus. After Newton explained the refraction of light by prisms, he examined many glasses and studied their dispersion (the variation in refractive index with wavelength). Because the glasses were probably all reasonably similar in composition, given the limited variety of glasses available, he concluded, incorrectly, that all glasses had the same dispersion, and, therefore, that chromatic aberration was an uncorrectable fault in lenses. Accordingly, Newton then decided that it was useless to attempt to build a better refracting telescope and switched his energies to reflecting telescopes. Others did the same, and refracting telescopes went into eclipse until well into the 18th century.[33]

During the early 1730s, Chester Moor Hall, an English lawyer with an amateur interest in telescopes, recognized that lead flint glasses had higher dispersion than soda–lime crown glasses. He reasoned that chromatic aberration could be corrected by an objective lens with two elements: a convex crown element and a concave flint element. (‘‘Crown’’ and ‘‘flint’’ became the terms used to describe, respectively, low refractive index (low dispersion) and high refractive index (high dispersion) optical glasses, respectively.) This doublet worked, and some telescopes were built using this first achromatic lens. The invention was not patented or publicized, however, and was rediscovered by John Dollond, who patented it in 1758. Dollond and his son Peter were skillful, well-known opticians, and they were quite successful in marketing the achromats.[34] These doublets were largely successful in bringing the red light and blue light to focus in a common image, although a secondary spectrum remained. This improvement should have encouraged investigations of the effects of composition on the optical properties of glass, but progress was slow because of the problems of making homogeneous glass. Poor-quality optical glass persisted until stirring of the melt was introduced by Pierre Louis Guinand and his successors in the beginning of the 19th century.

Joseph Fraunhofer entered optical physics from the practical side, working for a time in an optical institute where Guinand was employed both as a glassmaker and as an optician grinding and polishing lenses. Fraunhofer made some excellent achromats, which helped revive refracting telescopes. In the process, he experimented with glass compositions and recognized that more choices were needed in refractive index and dispersion

‘‘Deceptively like a Solid’’

Roald Hoffman

The conference is on Glass, in Montreal. Wintry light declines
to penetrate windows, and soon will be lit glass-enclosed glows
so that we may talk, talk into the night (fortified by bottled
mineral waters), of the metric of order trespassing on prevailing
chaos that gives this warder of our warmed up air, clinker,
its viscious, transparent strength.

The beginning was, is silica, this peon stuff
of the earth, in quartz, cristobalite, coesite,
stishovite. Pristine marching bands of atoms
(surpassing the names we give them)
build crystalline lattices from chains, rings, of Si
alternating with oxygen, each silicon tetrhedrally
coordinated by O's, each oxygen
ion, so different from the life-giving, inflaming
diatomic gas, joining two silicons; on to rings
in diamondoid perfection in cristobalite;
helical O-Si-O chains in quartz, handed in
coiling, mirror images of each other, hard, ionic SiO_2.

There must be reasons for such perfection—
time lent to the earth: then lava flowed, the air
blew thicker, still no compound or simple eye to
fret defect into the unliquid from which silica
crystallized. But in time we did come, handy,
set to garner sand, limestone, soda ash, to break
the still witness of silica. Heat disrupts. Not the
warmth of Alabama midsummer evenings, not
your hand but formless wonder of prolonged fire,
the blast of air drawn in, controlled fire storms.
Sand, which is silica, melts. To a liquid, where
order is local but not long-range. Atoms wander
from their places, bonds break, tetrahedra in a
tizzy, juxtapose, chains tilt, bump and stretch—
Jaggerwalky.

The restive structures in microscopic turmoil
meld to gross flow, bubbling eddies of the melt.

Peace in crystal meshes, peace
in hot yellow flux. But the gloved
men who hold the ladies get nervy volcanoes
on their minds. So—tilt, pour . . . douse,
so quench, freeze in that micro lurch.
Glass forms, and who would have thought it clear?

We posit that the chanced, in its innards so upset,
ought not be transparent. Light scattered from
entangled polymer blocks, adventitious dirt,
owes it to us— oh, we see it so clearly—to
lose its way, come awash in black or at least
in the muddy browns of spring run-off, another flux.

But light's submicroscopic tap dance is done in place.
The crossed fields shimmer, resonant, they plink
electron orbits of O and Si.
Atoms matter, their neighbors less, the tangle of the locked-in
liquid irrelevant in the birthing of color, or lack of it.

Optical fibers   Crystal Palace
The Worshipful Company of Glass Sellers
recycled   Millefiori
prone to shattering   Prince Rupert's drops
Chartres, Rouen, Amiens   float
Pyrex   Vycor   glass wool
network modifiers   the Palomar mirror
smoked for viewing eclipses   thermos
lead glass   microcrack
etched with hydrofluoric acid   spun
frustration   bull's eyes   annealed
borosilicate   softening point

High winds on Etna or Kilauea
spin off the surface of a lava lake thin fibers.
Pele's hair. The Goddesses' hair, here black.

From *The Metamict State*; pp. 44–48.
University of Central Florida Press, Orlando, FL, 1987.

> ''Glass . . . is much more gentile, graceful, and noble than any Metall, . . . it is more delightful, polite, and sightly than any other material at this day known to the world,''
>
> Antonio Neri, 1612

beyond those of ordinary crown and flint glasses if better lenses were to be made that corrected the secondary spectrum. Fraunhofer also wrote about the chemical durability of glasses and was probably the discoverer of the mixed-alkali effect, noting that glasses with mixed alkalis had superior durability. (The mixed-alkali effect is the distinctly nonlinear behavior observed in some properties when one alkali ion is gradually substituted for another alkali ion. This phenomenon is observed in properties affected by transport mechanisms, such as electrical conductivity, dielectric loss, internal friction, and self-diffusion.) Later, Fraunhofer's spectral studies enabled him to make observations on dispersion for the principal glass components of the day.[17,22,25,35,36]

Impressed by Fraunhofer's results, the Royal Society established, in 1824, a commission consisting of Michael Faraday, John Herschel (the astronomer), and George Dollond (another of the famed clan of opticians), to study the possibility of making superior glasses for telescope objectives. Faraday became interested in glassmelting and made some prolonged investigations during 1825–1830 that demonstrated the benefits of melting glasses in platinum containers and the importance of stirring melts to improve homogeneity. His experiments, unfortunately, did not contribute much to the knowledge of glass composition, although he did demonstrate that boron could be used in glassmaking to make a passable lead borosilicate flint glass. Faraday later (1845) conducted some experiments of significance with his ''heavy glass'' (see glass 7 in Table I), in which he demonstrated the Faraday effect (rotation of the plane of polarization of light in a magnetic field).[15,33,35,37,38]

It may seem surprising today that eminent scientists and intellectuals of the time were deeply interested in finding solutions to glass composition problems. For example, Vogel states, ''Goethe, then Prime Minister of a German duchy . . . in 1829 wrote to his friend, the noted chemist Döbreiner at the University of Jena, 'it would be most important to determine the relation of refraction and dispersion in your [barium and strontium] glasses . . . I should be pleased to contribute the modest funding . . .'.''[36,‡]

The first, however, to make an extensive study of the effects of a wide range of elements on the properties of glass was the Rev. William Vernon Harcourt, an English clergyman. The late 18th century and the early 19th century was a period of highly significant advances in the discovery and isolation of new elements, and, in the 1830s, Harcourt began investigations of the effects of many of these new elements on the optical properties of glass. Among the elements he first used in glass were beryllium, cadmium, fluorine, lithium, magnesium, molybdenum, nickel, tungsten, uranium, and vanadium. He also studied the effects of other elements, including antimony, arsenic, barium, boron, phosphorus, tin, and zinc, first introduced into glass by others. Harcourt did not confine his studies to silicate glasses, but also melted some phosphates, borates, and titanates, in part because he found it difficult to fuse the silicates to a homogeneous glass. He did not widely publicize his findings, but Sir George Stokes, the noted mathematician and physicist, learned of his work, collaborated with him, and helped to bring the results to the attention of the scientific community in 1871, the year of Harcourt's death. In 1874, Stokes made a small, three-component lens that was largely free of the secondary spectrum from some of Harcourt's glasses. Therefore, even though Harcourt's glasses were not completely homogeneous, his work demonstrated that different glassmaking ingredients did bring changes in dispersion and refractive index that could yield glasses that began to solve the optical problems of the time.[16,31,39]

Although the work of Harcourt should have encouraged the British glass industry to investigate further the effects of different glass constituents, it did little beyond the production of some standard optical crowns and flints by Chance Brothers in Birmingham. Experimentation to develop new glass compositions was severely constrained at that time in England by exorbitant taxes on all glassmelting. Therefore, Chance Brothers concentrated instead on improving the quality of the standard glasses by stirring the melt. Accordingly, the initiative in glass composition research passed to German glassmakers, who built on the work of Fraunhofer and Harcourt.[31]

As is evident from the foregoing, until the late 19th century, the development of new glasses was largely a matter of an occasional fortuitous discovery. These early investigations, although often motivated by a need, were not pursued systematically, had difficulty in yielding a homogeneous product, and, with the exception of Harcourt's work, usually used the same few ingredients. Hovestadt wrote, in 1900, ''. . . the development of the art of glassmaking in response to optical requirements kept, for a long time, to one narrow groove, and no new fluxes broke the monotony of a uniform series of crowns and flints.''[40]

III. Abbe and Schott

Ernst Abbe, professor of physics at Jena University, became interested in optical glasses through his work with Carl Zeiss, a microscope maker at the university. Similar to the telescope makers, Abbe soon realized that a wider variation in dispersion for a given refractive index was needed to remove completely the secondary spectrum from optical images. He wrote on the subject in the late 1870s, and his remarks attracted the interest of Otto Schott, a young German chemist who had been exploring glassmelting phenomena in connection with his family's glassworks in Westphalia. Schott contacted Abbe and sent him some lithium glasses he had prepared with the thought the samples might aid Abbe in his research for glasses with different optical properties. By 1881 Abbe and Schott were collaborating and thus was born one of the greatest and most productive associations in the history of glass composition.[31,40]

Schott moved to Jena in 1882 to be closer to Abbe and Zeiss. Abbe (the scientist), Schott (the glassmaker), and Zeiss (the instrument builder) worked together in a synergistic manner that bore dramatic results. Abbe and Schott would discuss the composition changes to be made, Schott would then prepare homogeneous glass melts, and Abbe would measure the results. If the properties appeared to be an improvement, Zeiss would grind and polish lenses and observe the performance of the

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[‡] The poem on the previous page was authored by Roald Hoffman, the Nobel Laureate in chemistry in 1981 with Kenichi Fukui for ''His application of molecular orbital theory to chemical reactions.'' Also, the 1977 Nobel Prize in physics was awarded to P. W. Anderson, Sir N. F. Mott, and J. H. van Vleck for ''Their fundamental theoretical investigations of the electronic structure of magnetic and disordered systems.'' The eminent scientists continue to find glassy systems of interest.

Schott und Genossen

As stated by Douglas and Frank,[31] ''The success of the firm [Schott und Genossen] was spectacular. Its first price list of 1886 contained forty-four optical glasses of which nineteen were essentially new compositions. The first supplement of 1888 added twenty-four glasses, including eight new barium light flints which were remarkable for their small dispersion compared with refractive index. They contained so little lead oxide that the usual light absorption shown by flint glasses was greatly reduced. New glasses were added to the list every few years, and the effect on the manufacture of optical systems was so great that Germany, which had previously imported ninety percent of its optical systems from England and France, started to export to these countries. Thus, an industrial development which was accomplished in less than ten years virtually eliminated existing manufacturers and, for about 30 years, until the outbreak of the World War I, Jena held an effective world monopoly in the manufacture of optical glass.''

finished pieces, then feed his observations back to Abbe and Schott. In this manner they started with silica, soda, potash, lime, and lead oxide and eventually added 28 other elements in quantities of at least 10% to produce glasses of refractive indexes and dispersions substantially different from those made previously.

The techniques used by Abbe and Schott in their studies were based on careful observation and measurement, although almost totally empirical, because no reasonable theories existed to guide their work. Additions of new minor ingredients were made to correct or offset faults in the original compositions. For example, Schott found that, in borate and phosphate glasses, alkalis had to be used very sparingly, if at all; otherwise surface staining resulted on exposure to air. However, when alumina, zinc oxide, and barium oxide were added, the surface durability could be improved enough to make the glasses serviceable. Schott soon learned that the addition of some elements would have no effect on optical properties but would have a favorable effect on other properties.

In an effort to at least make their results usable, Schott, and Winkelmann developed what probably was the first composition–property model.[4] They produced a series of oxide factors that allowed them to calculate the value of a property knowing the composition. Today, many such models are available because of computers (see Cable[41]).

Early useful results were obtained with boron, barium, and fluorine, leading to families of borosilicate crowns, barium flints, and fluor crowns. (The demarcation between crowns and flints is arbitrarily defined by their dispersion and is shown in Fig. 2.) The government was quite impressed by the progress and made some large grants to support the work of the laboratory that became, in 1884, the Jena firm of Schott und Genossen.

The discoveries of Abbe and Schott were not confined to optical glasses. In the 1890s, the group at Jena analyzed the problem of the secular rise of the zero in the aging of glass thermometers. It was noted in one of the early observations of the mixed alkali effect that the zero rise was particularly pronounced (more than one celsius degree) in glasses with approximately equal quantities of soda and potash. Glasses made with either only soda or only potash as the alkali suffered only one tenth or less the secular rise as the mixed alkali glasses. The most stable glass was found to be a borosilicate (see glass 9 in Table I).[40]

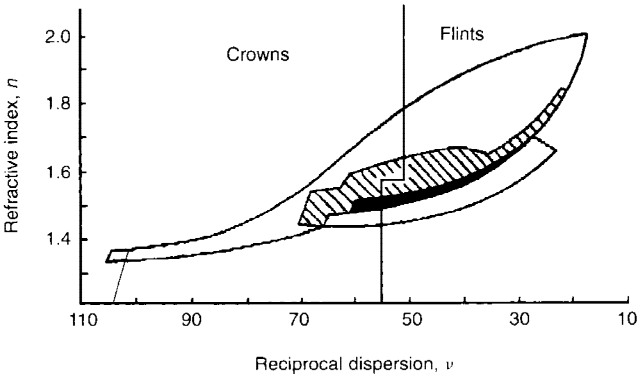

Fig. 2. Refractive index, n, versus reciprocal dispersion, ν, showing historical development of optical glasses.[34] (White area within curve represents modern glasses (Morey *et al.*); hatched area represents earlier glasses, i.e., 1880–1934 (Schott *et al.*); and black area represents glasses before 1880.)

Improved laboratory glassware also resulted from Schott's further pursuit of boron in glass with the discovery that borosilicate glasses had exceptional resistance to attack by boiling water. Accordingly, these glasses also made excellent boiler gauge glasses. It also was noted that boric oxide was the most effective addition to silicate glasses in reducing the coefficient of thermal expansion, and this discovery led to laboratory glassware with improved resistance to thermal shock.[40]

In the remarkably short period from 1879 to 1886, Otto Schott, with the assistance of Abbe and Zeiss, created and offered commercially a surprising array of optical glasses. Besides using a systematic approach to glass composition research, Schott had mastered the small-scale melt-stirring process so as to be able to make a homogeneous product. The glasses also had been carefully characterized, so they were sold with exact measured values of refractive index and dispersion. This work was a watershed in the history of glass composition in that it demonstrated for the first time the ability to tailor the properties of a glass by judicious adjustments in composition based on a composition–property model.[42]

IV. Modern Glasses

(1) Soda–Lime–Silica Glasses

Although sand and alkali were known from the earliest days of glass to be necessary ingredients, the role of lime was not apparent until much later times. Lime was not recognized as an important glass constituent by early glassmakers, because adequate amounts of lime were generally added unknowingly as an impurity in the sand and alkali. Lime appears to have been added consciously to glass batches in Roman times, but Neri mentioned lime only casually in suggesting that small quantities could be added ''. . . to make a very fair and beautiful Crystall.''[12] Only in the 17th, 18th, and 19th centuries did the increase in chemical durability brought about by the addition of lime to alkali silicate glasses become understood. Bohemian glassmakers added lime to their fine crystal in the 17th century, and, during the late 1700s, P. D. Deslandes added up to 6% lime to increase the resistance of Saint-Gobain's plate glass to attack by moisture.[31] Guinand and Fraunhofer observed that it was necessary to add lime to increase glass durability, and, in 1830, J. B. Dumas, a French glass technologist, noted that the chemical durability of glass was improved by adding one part of lime to one part of soda and six parts of silica. The addition of lime to the batch became essential in practical glassmaking

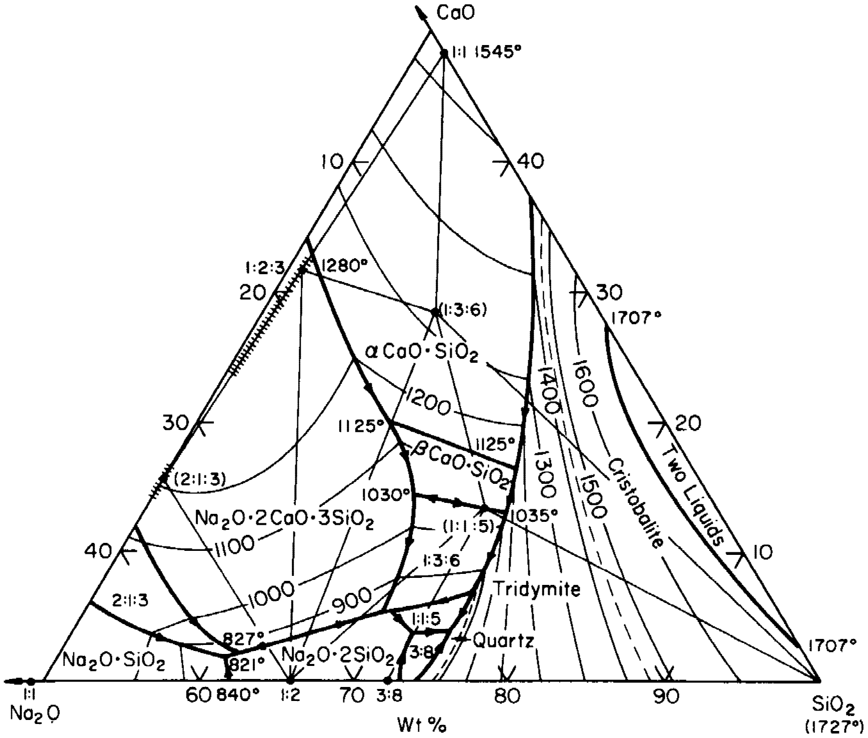

Fig. 3. Soda–lime–silica phase diagram (R. S. Roth, T. Negas, and L. P. Cook; Fig. 5321 in *Phase Diagrams for Ceramists,* Vol. IV. Edited by G. Smith. American Ceramic Society, Columbus, OH, 1981).

to preserve durability as the use of synthetic soda ash (pure Na_2CO_3, with no $CaCO_3$) became wide-spread. This practice began early in the 19th century, because soda ash from the Leblanc process became available and its use was common practice after the 1860s when the Solvay process became the principal source of soda.

Most of the current commercial glasses are soda–lime–silica glasses. It is significant that the compositions of these glasses, used typically for containers and flat glass, has changed little over the centuries, ranging from 65% to 75% silica, with alkali ranging from 10% to 20%, and lime as the balance. Although most older soda–lime–silica glasses contained a few percent alumina from raw-material impurities and from refractories, a similar amount has been added customarily since Schott, based on his observations of Thuringian glasses, demonstrated, in the late 1880s, that it benefited durability and resistance to devitrification. Glasses with these compositions are relatively easy to melt and form, do not devitrify easily, and generally have reasonable resistance to attack by moisture. They can be made quite color-free and nontoxic with pure raw materials that are available worldwide at acceptable cost.[5,40]

Improvements in melting technology—e.g., more-resistant refractories and higher temperatures—have increased chemical durability through lower alkali and higher lime contents. This trend also has been encouraged by the comparative costs of soda and lime, and, currently, economic factors are the principal determinant for soda–lime–silica compositions. Enough is now known about the effects of composition on properties to permit major glass constituents to be adjusted several percentage points to compensate for differences in raw-material prices to reach the lowest-cost composition.[43]

(2) Borosilicate Glasses

The first new major glass system to be explored beyond the soda–lime–silica glasses utilized the other great glass-former, boric oxide, important for its many commercial applications. Although borax was known and used in the Middle Ages as an exotic flux, its use in practical glassmaking became a realistic possibility with the discovery of extensive deposits in Turkey, Chile, and, in particular, California, in the latter part of the 19th century.[42]

As noted in an earlier section, Abbe and Schott, during the 1880s, were the first to use boron compounds in glass in significant amounts, first in optical glasses, then in glasses for laboratory apparatus. Both Faraday and Harcourt had made some use of boron in glass, but Abbe and Schott clearly established that borosilicate glasses had superior resistance than soda–lime–silica glasses to chemical attack and had better thermal shock resistance because of their lower coefficient of thermal expansion. The introduction of the Auer von Welsbach mantle in gas lamps in 1887 created a need for a lamp cylinder or chimney with improved resistance to thermal shock. Schott met this need with a glass containing 15% boric oxide (see glass 11 in Table I) having a very low coefficient of expansion.[36,40,42]

At about this time in the United States, cracking and breakage of the globes of railroad brakemen's lanterns was a problem when rain showers struck the hot glass. Why Schott heat-resistant glasses were not used to solve this problem is not known; perhaps it was due to the poor international technical communications of the times. Corning Glass Works, the leading U.S. manufacturer of lamp chimneys and bulbs for electric lamps, was asked to investigate the matter, and it became the first assignment of the newly formed research laboratory in 1908. In 1909, Corning introduced a borosilicate glass that solved the lantern globe thermal shock problem, but had poor chemical durability. Corning's first research director, Eugene C. Sullivan, a chemist hired from the U.S. Geological Survey, and William C. Taylor, a young chemist colleague recently from Massachusetts Institute of Technology, worked further on the problem.[44] By 1912, they had perfected a chemically durable, shock-resistant, lead borosilicate glass marketed under the name Nonex® (for nonexpanding) that reduced lantern globe breakage by 60% (see glass 12 in Table I). Nonex also proved to double the life of the battery jars used by the railroads in their new electrically powered signal systems.

Corning continued to explore borosilicate glass compositions and their applications. In 1913, Corning physicist Jesse T. Littleton suggested that Nonex glass vessels might be used for baking pans, and a cake baked by his wife in the bottom of a battery jar demonstrated that the idea was sound. However, Nonex contained too much lead for food preparation. Therefore, a lead-free borosilicate composition was developed by Sullivan and Taylor which was named Pyrex® (see glass 13 in Table I). A pressed Pyrex ovenware line was introduced in 1915, and it became an immediate sales success. At about this time, the supply of glassware to U.S. laboratories from Schott and other European suppliers was interrupted by World War I, and it soon became apparent that blown Pyrex borosilicate glass was an extremely good glass for laboratory apparatus because of its low expansion and its chemical durability. According to Morey,[5] ''. . . [this] glass has the lowest liquidus temperature of any known mixture having so high a silica content and in this fact doubtless is to be found a clue to its exceptional ability to withstand devitrification.''

Other variations of borosilicate glass were explored by Corning for special applications that would benefit from low expansion and corrosion-resistant glasses. One noteworthy example was the development of a glass with an expansion 25% lower than that of Pyrex ovenware that was used for casting the 200 in. mirror for Mt. Palomar's Hale telescope in 1934. The astronomers had sought the lowest possible expansion in their quest for a mirror that would show the least distortion with temperature changes. This glass also had the low liquidus temperature necessary to survive the extremely slow cooling rate of the cast blank without devitrification or phase separation.[22,45]

Glass chemists Harrison P. Hood and Martin E. Nordberg observed during experimentation with borosilicates at Corning in the 1930s that very large changes in properties would occasionally result when some compositions were heat-treated. Further investigation revealed that these glasses were separating into two intermingled glassy phases, one of which was silica-rich. A composition was developed that separated upon heat treatment into a very-high-silica phase and a very-alkali-rich phase, with the latter being easily dissolved and leached out by hot nitric acid. The remaining porous, silica-rich skeleton could then be consolidated into a solid, pore-free form by heating. This glass, given the name Vycor®, in 1939, could be melted and formed easily before the leaching and consolidation steps. The 96% silica composition of the finished glass meant that it had physical and chemical properties closely approaching those of pure-silica glass, yet it could be fashioned before heat treatment into shapes that were impossible to form with fused silica because of the extremely high viscosity of silica glass at even very high temperatures.[45] This is an example of a new glass composition being created by carefully exploiting the observation of a new phenomenon.

Another important step in borosilicate glass composition development also occurred in the 1930s with the introduction of E-glass fibers. A fiberglass material was needed for electrical insulation applications, and standard soda–lime–silica compositions were not suitable, because their conductivity was too high. Soda–lime glasses also proved generally unsuitable for fiberglass, because the great surface area to volume ratio made them particularly vulnerable to attack and dissolution by water. Accordingly, Urban Bowes, R. A. Schoenlaub, and others at Owens–Corning Fiberglas reduced and ultimately removed the alkalis and added boric oxide and alumina and increased the lime.[46] The boric oxide and lime reduced viscosity and increased durability, and the alumina also helped durability and lowered the liquidus. The resulting lime–alumina–borosilicate glass (see glass 14 in Table I) had excellent electrical resistivity, superior resistance to attack by moisture, and good mechanical properties. Therefore, it is not surprising that glasses of this general composition make up 90% of the continuous glass fiber currently produced.[46] (Historical note: In this same publication, Dumbaugh and Danielson[47] reference a 1925 patent issued to F. M. and F. J. Locke[48] for a series of aluminosilicates that is broad enough to include these alkaline-earth aluminoborosilicates.) Also, most commercial fiberglass compositions are based on ternary or quaternary eutectics, thus taking advantage of the well-known fact that the most stable glasses are often close to eutectic compositions.

(3) Photosensitive Glasses and Glass-Ceramics

No account of the history of glass compositions would be complete without some reference to the discovery of glass-ceramics. Accordingly, a brief description of the early work on glass-ceramics is presented here.

The natural tendency of glasses to devitrify must have led glassmakers occasionally over the ages to consider pursuing the phenomenon to its logical conclusion—a completely crystalline product. The French chemist Réaumur is known to have attempted to produce crystalline vessels by holding glass bottles packed in gypsum at a red heat for several days. Although these did devitrify to a crystalline form, he was unable to control the process, and the bottles were deformed and of low strength.[49] Others experimented with the limited precipitation of crystals from glass to create ruby or opal glasses, but the development of a process to control the massive crystallization of bulk glass did not occur until the middle of the 20th century.

There was a series of glass composition inventions during the 1940s and 1950s based upon nucleation and controlled growth of crystals experiments conducted at Corning Glass Works. The work was led by S. Donald Stookey, but ultimately involved several others, including Armistead, Beall, MacDowell, Araujo, Rittler, and Grossman.

Stookey had been investigating nucleation and precipitation of crystals in ruby and opal glasses and found, in 1942, that copper, gold, and silver could be deposited as tiny particles of metal through photo-induced heterogeneous nucleation. The process was aided by the presence of a ''sensitizer,'' such as cerium or tin. Taking this a step further in 1951, he learned he could photo-induce a sodium fluoride opal in a silicate glass nucleated with silver (Fotalite®).[50]

Stookey made an unanticipated discovery, in 1954, of the controlled crystallization of glass ceramics. He had invented, in the late 1940s, a process for preparing lithium silicate crystal images in glass with a photosensitive technique (Fotoform®). Very small quantities of silver (~0.06 mol%) were introduced in the lithium silicate glass as a nucleating agent, and, after selective exposure to ultraviolet radiation, a heat treatment at ~600°C caused lithium metasilicate crystals to form that then could be leached out of the unexposed glass.

One day, Stookey placed a plate of preexposed lithium silicate glass in a laboratory oven to perform the 600°C heat treatment. The temperature controller stuck in the ''on'' position and the glass was heated to 900°C, where it normally would be quite soft and fluid. Stookey was alarmed by the overheating, and he was certain that he had ruined the oven. He knew that this glass melted and flowed below 700°C, and he believed that it would flow on to the floor of the oven. However, in his own words, ''Imagine my astonishment on opening the door to see an undeformed, opaque solid plate! Snatching a pair of tongs, I immediately pulled the plate out of the hot furnace, but it slipped from the tongs and fell to the tile-covered concrete floor, clanging like a piece of steel but remaining unbroken! It took no great imagination to realize that this piece of Fotoform was not glass, but something new and different. It must have crystallized so completely that it could not flow, even though the temperature was more than 200°C above the softening temperature of the glass. And obviously it was much stronger than ordinary glass.''[50] An examination of the fine-grained glass-ceramic that had been formed revealed that it was composed of lithium disilicate and quartz crystals, and was much harder and higher in electrical resistivity than regular glass. This episode demonstrates the power of the prepared mind in recognizing a seminal event: Stookey quickly realized that, theoretically, all glasses can be converted to crystalline bodies having new properties that depend on the nature of the particular crystals formed.[51] A vigorous research and development program was then followed by Stookey, Beall, and others at Corning that continues to this day and has produced many very useful glass-ceramics.

Stookey later (1959) made another discovery based on photosensitive precipitation work with the invention of photochromic glasses, i.e., glasses that darken when exposed to sunlight and regain their clarity when the ultraviolet radiation is removed. Stookey, acting on a suggestion from Armistead, introduced silver halides (chlorides and bromides) in small quantities (~0.5 wt%) to glasses that had been doped with a copper sensitizer. The glasses were heat-treated at 600°C to precipitate supersaturated microcrystals of silver halide. When photons strike the microcrystals, some of the silver is reduced to the metallic Ag^0 state, with the electron being borrowed from a chloride ion. The metallic silver particles color the glass gray, or darken it. When the ultraviolet source is removed, the metallic silver is oxidized back to Ag^+, and the glass clears.[52]

V. Structure and Properties

As stated earlier, the early soda–lime–silica glass compositions were very close to the standard soda–lime–silica glasses that are currently in use. The fact that they were first discovered by accident, and yet are fortuitously close to the ideal commercial composition, remains somewhat of a surprise. However, the raw materials were relatively available, and compositions that were very different would probably either crystallize, dissolve, or be unmeltable, and, therefore, in a sense, this may be considered a Darwinian result. Shortly after the start of the glass science era, i.e., the early 1920s, after Schott's work, the opening of the Corning Research Laboratory in 1908, and the formation of the Department of Glass Technology (initially named Department of Glass Manufacture) in 1915 under the direction of Professor W. E. S. Turner in Sheffield, England, the new tool of X-ray diffractometry was first applied to the study of silicate crystals, and then to silicate glasses.[53] This led to an overall attack by the scientific community on the problem of the understanding of this unusual material.

(1) History of Glass Structure Studies

Although it was very early realized by Tammann[54] that glass formation was a kinetic phenomenon, it also was clear that the kinetic processes involved were controlled by the details of the structure of the materials involved. Although, in 1926, Goldschmidt[55] indicated that SiO_2, GeO_2, B_2O_3, P_2O_5, As_2O_3, As_2S_3, Sb_2O_3, as well as the (silica) model, BeF_2, were all able to form glasses by themselves (i.e., they were glass-formers), the history of the discovery of the existence of these simple inorganic glass-formers was not clear. Even in the case of silica, the first recorded instance of the recognition of its ability to form a glass on its own is not clear. Sosman[56] points out that, in 1813, Marcel formed glassy silica by heating small quartz crystals in an oxygen-injected alcohol lamp. Again, a check of the literature shows that, according to Rawson,[57] in 1834, Berzelius melted glasses in several tellurite systems, while, in 1868, Roscoe investigated a series of $BaO–V_2O_5$ glasses. As indicated earlier, in the mid-1800s, Harcourt[39] melted mainly phosphate glasses, because he found that silicate glasses were ''pasty.'

The first detailed descriptions of the expected ''crystal'' structures and the reasons that such structures formed glasses were proposed by Hägg,[58] Goldschmidt,[55] and Zachariasen.[59,60] They were crystallographers/chemists who, since the discovery of X-rays had studied crystal structures with this tool and, therefore, quite understandably approached the problem of glass formation and structure from the results of those studies. Arguably, Zachariasen's rules constitute the most famous work in glass science to date. These rules describe what he considered to be the necessary conditions for glass formation:

- An oxygen is linked to not more than two central atoms;
- The number of oxygen atoms surrounding a central atom must be small;
- Oxygen polyhedra share corners—not edges or faces—with each other;
- At least three corners in each oxygen polyhedra must be shared.

Over the years, the validity of these rules has been debated. Recently, many workers have argued for,[61] against,[62] and about these rules and the ''continuous random network'' to which they imply. The rules have been discussed and updated by Cooper.[61,63] They also have been modernized in the sense that the topological basis of these rules has been extended (Gupta and Cooper[64] and others[65]).

That such structures (as proposed by Zachariasen) were indeed found in simple glasses was first demonstrated by Warren and co-workers (Fig. 4(a))[66,67] using X-ray diffractometry. The

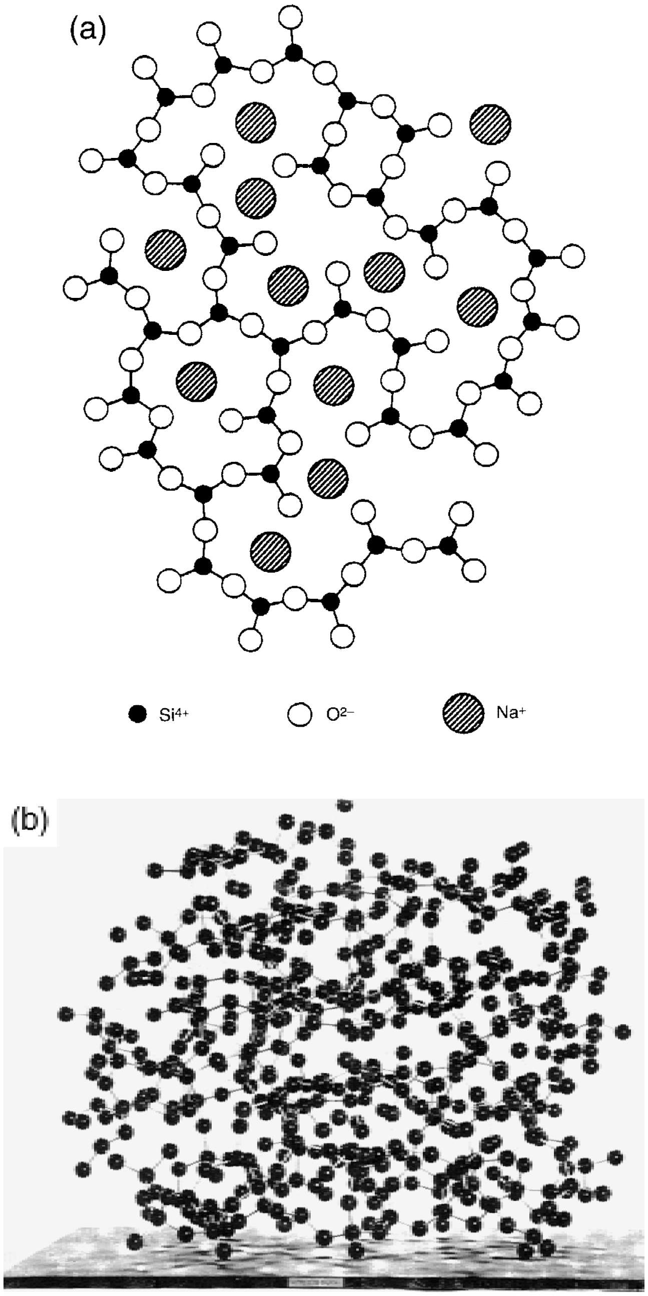

Fig. 4. (a) Two-dimensional representation of a disordered sodium silicate network.[66] (b) Continuous random network model of vitreous silica.[74]

details of these experiments and the controversy over the details of the continuous random network (CRN) model proposed by Warren continues. Indeed, in 1921, prior to the work of Hägg, Goldschmidt, and Zachariasen, Lebedev[68] had proposed a microcrystallite model that was apparently completely at odds with the CRN model. The initial, basic controversy had to do with the amount of medium- and long-range order that exists in normal glassy (e.g., silicate) solids. The controversy appeared to have started as a result of the X-ray studies of Warren (1932) in the United States on the one hand and Lebedev and his co-workers in Russia (1922) on the other hand. However, Nemilov[69] has recently suggested that Frankenheim was perhaps the first to propose a model for the structure of glasses early in the 19th century. Frankenheim[70] states in his 1835 book, *The Teaching of Cohesion,* ''It seems possible that glasses, which are seemingly quite noncrystalline, are, nevertheless, aggregates of finely disperse crystals, which are partly sintered with each other, and partly combined like a mortar.'' Since that time, the popularity of a given model for glass structure has been found to be cyclic. Indeed, at almost the same time as Frankenheim's book appeared, Faraday characterized glass ''. . . rather as [a] solution of different substances one in another rather than as a strong chemical compound.''[37]

Therefore, we see that various models for the structure of glass have been proposed over the years, and, as illustrated by one of the present authors,[72] these proposals seem to show a cyclic character. One of the early proponents of the microcrystallite model (Porai-Koshits[73]) commented, ''. . . investigators who, like Bell and Dean[74] (Fig. 4(b)), construct and utilize the random network models, come to the same conclusion about the validity of Zachariasen's hypothesis. But those investigators who use the quasi-crystalline models, find crystallinity or crystal-like regions in glasses.''

Over the years there have been discussions between different investigators, often because of the advent of a new or improved experimental technique, of the reinforced validity of one or another of the old models, or indeed, new evidence that supports still another new model. In particular, with some new experimental tools (especially magic angle sample spinning (MASS) nuclear magnetic resonance (NMR) and other NMR techniques[75]) that allow, for instance, the determination of the numbers of n-coordinated silicons (Q^n) and computational techniques, additional structural information, even in terms of the illusive medium range order, are now becoming more available.

In this regard, Gaskell[76] recently has reviewed structural analysis techniques and results. He concludes ''. . . all our accessible information may be inadequate to solve the structure in any real sense since the set of possible structures that adequately fits all experimental data within statistical errors may still be so broad that subjective arguments alone distinguish the final choice.'' Wright[77] has stated ''. . . the modern crystallite and random network theories both involve continuous networks and differ mainly in respect of the magnitude of the fluctuations in the degree of intermediate-range order which must occur in any such network and the spatial distribution of defects. Certainly the appearance of new experimental and theoretical techniques holds the promise of eventual breakthroughs in the measurement of the position of each of the atoms in a glass structure. Even so, the question of how such information is to be conveyed may remain. Perhaps we may have to be satisfied with a collection of distribution functions.[78] In addition, while the details are of scientific, and also probably of practical interest and importance, the overall view is probably clear enough to be stated without too much fear of disagreement.'' Indeed, many different ways of looking at, analyzing, and describing these structures have been suggested over the years, with the general picture remaining about the same. As indicated above, at the level of our discussion here, it is not possible, nor is it necessary, to resolve this issue.

Although a more complete understanding of the fundamental structure of any glass is desirable both scientifically and technologically, as Cooper[79] pointed out ''. . . a subjective view of the history of glass composition development has led to the conclusion that, up to the present, the influence of structure on composition development has been meager. Yet, we may expect that, in the future, a greater benefit will accrue from a structural approach.'' As indicated earlier, Cable[41] has reviewed the efforts that have been made to model the composition–property behavior of glasses since the first attempts of Winkelmann and Schott. In this regard, the application of computers and statistical techniques may prove more useful in the future.[78]

> ''To understand science, it is necessary to know its history,''
> Auguste Compte, 1831

(2) Anomalous and Normal Glasses—Silica versus Silicates

Both historically and commercially, silica-based glasses make up almost all of the glasses in current use. The present value of glass products produced today is 42.5% container, 35% flat, 11% fiber, and 11.5% special (i.e., 43% TV, 29% other, 11.5% chemical/pharmaceutical, and 7% optical).[80] Therefore, most of our brief discussion of structure relates to silicate glasses.

The early Egyptians discovered that fluxes were required for (silicate) glasses to melt readily. They were necessary because the production of silica by ordinary melting techniques requires temperatures >2000°C. The naturally occurring additions that were made—sodium, potassium, calcium, etc.—bonded ionically to the oxygen ions by breaking Si—O—Si bonds in some way, thus breaking down the continuously corner-connected three-dimensional silica network. This was very useful, because it resulted in lower melting and processing temperatures (Fig. 5). On the other hand, if too much alkali and/or not

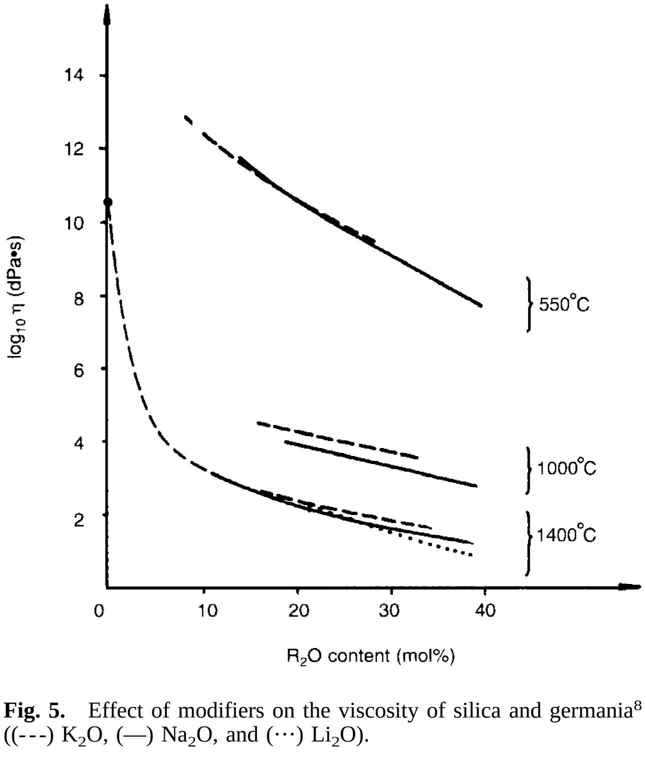

Fig. 5. Effect of modifiers on the viscosity of silica and germania[8] ((- - -) K_2O, (—) Na_2O, and (···) Li_2O).

Cable on Neri/Merrett

In an interesting early proposal of a structural model, Cable[71] recently has suggested that Neri/Merrett[25] was a proto-Zachariasen: ‘‘So far as structural models are concerned, there is a really intriguing comment in Merret that shows him thinking that forming a glass was a matter of the geometry (the ‘‘Figure’’) of the separate oxides and how they could fit together: ‘Besides diaphaneity is a property not communicated to any thing malleable, and who would call that Glass, that were not transparent which are inconsistent with the nature of Glass. For the materials of Glass, Sand, and salts, have such figures as seem incapable of such adhaesion in every part one to another. For all salts have their determinate Figure which they keep too, in their greatest solutions and actions of the fire upon them, unless a total destruction be wrought upon them, as many instances might evince, and that Figure is various according to the salts. Salt-peter, and all Alcalizate-salts are pointed, and by their pungency, and caustickness seem to be made up of infinite sharp pointed needles, And as for Sand the Figure thereof is various, nay, infinite it appears in Microscopes . . . . Now how can any man imagine that such variety of Figures in Sand can so comply with the determinate Figures of salt as to touch one another in minimis which is necessary to make it malleable? Whereas to make it Glass ’tis enough that those two touch one another at certain points onely, whereby such an union it formed, which is necessary to denominate Glass but wholly incompatible with malleability. And this union is that which makes in Glass Pores, from whence comes it’s diaphaneity as you have heard from Lucret. Besides something said before, declares that they both remain the same in the compound [as] they were before. I shall conclude this argument and say, that I conceive that nothing but the Elixir will perform this effect, and that both of them will come into the world together.’ ’’[25]

Cable thus argues that Neri/Merrett suggested that the differences between the opaque and plastic nature of, say, metallic solids on the one hand and transparent brittle glassy solids on the other hand is due to their microstructure, or ‘‘Figures’’ and that, in glasses, the microstructure is perhaps open as a result of bonding only at points, i.e., corners, whereas, in metals, the very compact, close-packing, is responsible for their behavior.

enough alkaline-earth were inadvertently used, the product would not be satisfactory.

Although there currently are disagreements about the details of the randomness of alkali and alkaline-earth silicate glasses, especially at intermediate ranges (~20–200 nm), there is no disagreement over the fact that these additions to silica result in a glass with strikingly different behavior. Clearly, the critical temperatures (liquidus, processing, glass, etc.) are all quantitatively different, but, in addition, most of the properties are qualitatively different as well. In some respects, it is not unlike any pure material with no or few defects: changes in the frequency of these defects or dopants may have a pronounced effect. As indicated above, silica is completely coordinated in three dimensions. Although attempts have been made to model the flow in such a structure, no satisfactory detailed model exists. Although there is three-dimensional coordination with the addition of network modifiers (sodium and calcium), the uniformity and continuity are not retained. The ionic bonding to the modifiers provides weak points for flow, in the liquid and in the solid.

As discussed above, in pure silica, such weak points are not available. Thus, qualitatively, the flow processes are different. This means that comparing either the viscous behavior at 1400°C or the hardness at room temperature of two glasses is not appropriate.

Silica (and to some extent other similar glass formers that are continuously fourfold, three-dimensionally coordinated, e.g., germania and beryllium fluoride) is unique, although very similar to water in many ways. Because of silica’s continuous, tetrahedral, open, three-dimensional network, it has many anomalous properties—low and even negative thermal expansion coefficient, as well as positive temperature and negative pressure coefficients of elastic constants. All of these anomalous properties disappear when silica is sufficiently broken down as described above. There is an added problem in attempting to understand the continual change from anomalous to normal behavior, because phase separation makes glasses with moderate concentrations of network modifier inaccessible. (Although, recently, sol–gel techniques appear to have overcome this problem.[81]) Although it is known that germania and beryllium fluoride have structures that are very similar to silica (corner-joined tetrahedra) and also show the various anomalies that make silica unique, attempts to use these glasses as models usually fail for one or more reasons. Perhaps the most important characteristics to examine in comparing these glasses are their viscosity–temperature behavior, thermal expansion, and chemical durability. These are strikingly different in *silica* glasses on the one hand and *silicate* glasses on the other. If we have an idea of how these properties work and can

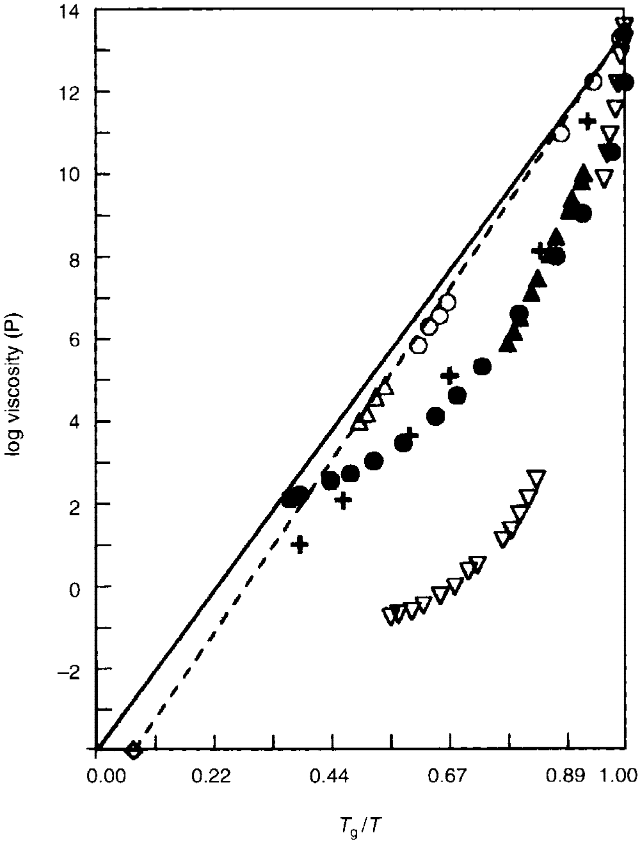

Fig. 6. Variation of the logarithm of viscosity versus T_g/T for strong and fragile liquids ((○) SiO_2, (△) GeO_2, (●) $Na_2O\cdot 2SiO_2$, (+) metallic glass, and (▽) heavy-metal fluoride glass) (modified from Ref. 83).

be controlled, in a general sense, we may be able to design a glass with some degree of success. The qualitative difference in the viscosity of silica and other normal glasses is shown in Fig. 6. Silica demonstrates Arrhenius behavior over the logarithm of viscosity range from ~1 to 14, whereas normal glasses demonstrate almost a continuously changing logarithm of viscosity, or one that can be approximated by two straight lines—one with $E \approx 35$ kJ/mol and one with $E \approx 10$ kJ/mol.[82] These viscosity behaviors are controlled by continuous Si—O—Si bonding in silica (an anomalous or strong liquid) and the breakup of this bonding by network modifiers (Na—O or Ca—O) in a normal or fragile liquid. At some high temperature (low viscosity) in the normal liquid, the flow occurs by the motion of silicate units, whereas, at lower temperature for the normal liquid and at nearly all temperatures in silica, the flow is presumably by some type of bond-interchange mechanism. Angell[83] has noted this behavior, and his plot of viscosity versus the reciprocal temperature normalized by the glass transition temperature (T_g) illustrates in a striking manner the differences just discussed (Fig. 6). His terminology for his behavior is ''strong'' (or anomalous for silica, germania, and beryllium fluoride) and ''fragile'' (for other normal glass-forming liquids).

The diffusion and, thus, the electrical conductivity also are qualitatively different for these anomalous and normal glasses. The conduction in silica is by impurities, because the diffusion coefficients of silicon and oxygen are extremely small, whereas, in a sodium-glass or sodium–calcium-glass, these ions have appreciable mobility and, thus, result in substantial conductivity, although the glass remains basically an insulator. The mobility of these ions obviously can be either helpful or detrimental. In the case of a glass tube for the processing of semiconductors, or for an insulating film for the same semiconductor, the use of a sodium-containing glass can result in undesirable contamination with sodium. On the other hand, the mobility of the cations makes these glasses suitable for ion exchange, whereby the glass can be strengthened or can become a waveguide by virtue of the changes in index brought about by the ion exchange. This ion exchange, however, also results in at least one mechanism responsible for the poorer chemical durability of soda–lime–silica glasses.

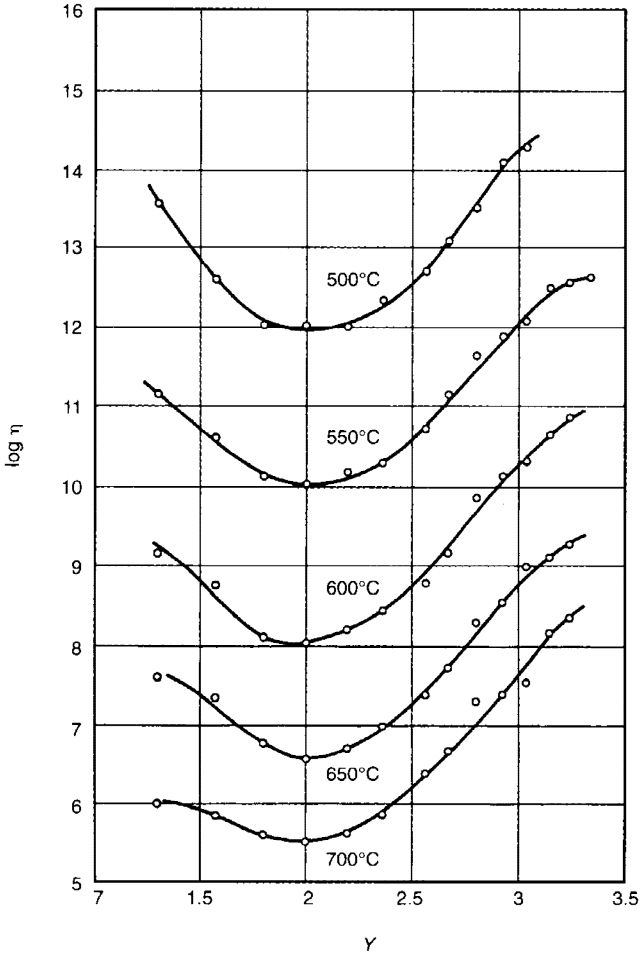

Fig. 7. Viscosity isotherms of an invert glass system (Na_2O–K_2O–CaO–SrO–BaO silicate).[84]

(3) *Invert Glasses*

The use of too great a content of flux (sodium, potassium, calcium, magnesium, etc.) results in glasses that are prone to devitrification, or that are so nondurable that they either dissolve or become undesirably clouded. This is understandable when one considers the CRN model. If too much network modifier is added, the network is no longer a network. The network and ion mobilities are so great that rearrangements can occur readily, and the possibility of crystallization is enhanced. However, in one of the many surprises in glass composition–property behavior, Trapp and Stevels[84] have developed a series of so-called invert glasses (although it has been pointed out by Weyl and Marboe[85] that Hänlein[86] had studied glasses of a very similar type many years before that had a composition (in wt%) of $35K_2O{\cdot}15Na_2O{\cdot}10CaO{\cdot}40SiO_2$). This description in terms Y (the number of bridging oxygens) is essentially the form used earlier by Stevels:

- For $Y = 4$, if O/Si $= 2$, this is a three-dimensional network, all four corners bridging;
- For $Y = 3$, if O/Si $= 2.5$, this is a two-dimensional sheet, three corners bridging;
- For $Y = 2$, if O/Si $= 3$, this is a one-dimensional chain, one corner bridging;
- For $Y < 2$, if O/Si $= 4$, this is an individual SiO_4 tetrahedra, all oxygens nonbridging.

If the stiffness of the network is decreased gradually by replacing the bridging oxygens by nonbridging oxygens until only individual, isolated tetrahedra remain, crystallization occurs very readily. However, Trapp and Stevels, as Hänlein before them, has shown that, by the incorporation of many modifiers, crystallization can be frustrated. In fact, as shown in Fig. 7 and as is evident from the ''invert'' name, some properties show an inversion in their trend at $Y \approx 2$. In such cases, although the kinetics of crystallization are enhanced, the probability of crystallization may be made more difficult because of the lack of a simple, most stable structure. More-recent work in glasses with mixed anions shows that they increase the glass-forming range and produce a variety of behaviors.

(4) *Metallic Glasses*

Only recently has it been possible to produce bulk amorphous metals, i.e., metals that can be retained in the glassy state while cooling at rates of the order of degrees per minute. This means that samples centimeters in all dimensions can be produced. This is possible using essentially the same technique used in the case of the invert glasses. The liquidus temperature is decreased at the same time that the compositional complication is increased. As a result, crystallization is frustrated.

The first glassy metals were produced at California Institute of Technology by a group directed by Duwez,[87] who was studying the formation of metastable metal phases by splat cooling. For the following many years, this group and others led by Turnbull[88] at Harvard University produced a variety of amorphous metals and studied their properties and structure. However, all of these glass compositions required cooling rates of at least hundreds of degrees celsius per second. Recently, Inoue[89] and co-workers in Japan (La−Ni−Cu, Mg−Y−Cu−Ni, and Zr−Ni−Cu−Al) and Johnson[90] and co-workers at California Institute of Technology (Zr−Ti−Cu−Be) succeeded in producing the bulk glassy metals described above. These

Neri/Merrett on the Brittleness of Glass

Although other Neri/Merrett comments about the structure of glass might be subject to some differences in interpretation, the following statements are quite unequivocal: ‘‘tis of its own nature the most brittle thing in the world, and to make it malleable a quality quite contrary to it’s nature must be introduced. Besides, diaphaneity is a property not communicated to anything malleable, and who would call that Glass, that were not transparent? As well may one name that Gold which is not ponderous nor malleable, as that Glass which is malleable and not transparent. Add hereunto, that the nature of malleability consists in a close and throughout adhaesion of parts to parts, and a capacity to the change of Figure in the minutest parts. Both which are inconsistent with the nature of Glass.’’[25]

glasses could be maintained in the glassy state by cooling at moderate rates, and their viscosity behavior was more reminiscent of silica than of other less-stable glasses. In fact, these new glasses were as strong as normal soda–lime–silica or $Na_2O{\cdot}2SiO_2$ glasses—i.e., a network glass with three of the four doubly bonded oxygens intact (Fig. 8).

(5) Nonnetwork and Noninvert Glasses—Some New and Interesting Optical Glasses

Most of the commercial glass compositions that we have considered so far contain a traditional glass former. They have been developed for rather general purposes—windows, containers, high-temperature and thermal shock applications, and optical applications. Although properties have to be tailored so that optical glasses can be worked, the main consideration has been the optical properties—refractive index and dispersion. It is somewhat understood what types of atoms and/or ions are required to obtain the desired property—the refractive index is controlled by both the electronic and atomic contributions to refraction, whereas the dispersion is controlled by the position and magnitude of the intrinsic ultraviolet absorptions. Therefore, the idea essentially has been to find a glass solvent that can dissolve the required quantity and type of solute. Until 1936, according to Weyl and Marboe,[85] ‘‘. . . all glasses made commercially contained, as a major constituent, a compound which, by itself, could form a glass.’’

Morey[91] then discovered and patented the Kodak glasses. While developing a series of rare-earth borate glasses that greatly expanded the dispersion–refractive index region (see Fig. 2), Morey learned that some glasses can be produced without B_2O_3. An example is (in wt%) $15ZrO_2{\cdot}45Ta_2O_5{\cdot}40TiO_2$. These glasses were described after Hänlein published on his invert glasses, and, even so, they were equally as unexpected, if not more so, because, although some of them contained a small amount of B_2O_3 as the glass former, many of these particular compositions contained *no* traditional glass former, per se. Somewhat after the development of these Kodak glasses, K. H. Sun,[92] a collaborator of Morey’s, patented an equally unexpected type of glass. Again, although some of these glasses used beryllium fluoride, which was Goldschmidt’s and Zachariasen’s model glass former, some of them contained only aluminum fluoride as the apparent glass former (in mol%): $34A1F_3{\cdot}50PbF_2{\cdot}10MgF_2{\cdot}10SrF_2{\cdot}2BaF_2{\cdot}1CaF_2{\cdot}1LaF_3{\cdot}1CeF_3{\cdot}1ThF_4$.

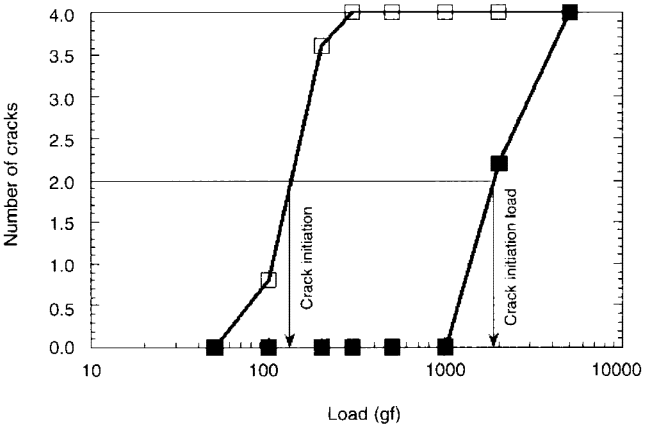

Fig. 8. Probability of crack initiation in a (□) standard and a (■) less-brittle soda–lime–silica glass.[103]

Besides the unusual glasses described above, glasses in several aluminate, gallate, tungstate, molybdate, titanate, niobate, and tantalate systems, i.e., glasses with no real glass former, have been produced. These glasses often have unexpected properties, and it is interesting that glasses can be formed in such systems.

(6) Heavy-Metal Fluoride Glasses

There is an obvious similarity between the aluminum fluoride glasses of Sun and the heavy-metal fluoride (HMF) glasses discovered accidentally at the University of Rennes, in France, in 1975.[93] At the time of their discovery, indeed even until now, although there has been speculation about the structure, etc., of the two types of glasses discovered by Morey and Sun, little real structural work has been done. On the other hand, because of the possibility of a major use for the HMF glasses as lightguides and also because of the much larger glass science/technology population in 1974, an enormous amount of research of all types has been conducted on these glasses. Despite the very substantial efforts expended on this topic, the issue of the structure of HMF glasses is yet more elusive than that of most oxide glasses. This is caused in part because there is no really fixed structural unit, as, for instance, a SiO_4 tetrahedron. Although it generally is accepted that zirconium is the network former, it has variable coordination with fluorine (7–8). Also, as opposed to the corner sharing of silica tetrahedra that is known in both crystalline and glassy silicates, both edge and corner sharing are known in crystalline HMF crystals.

(7) Phosphate Glasses

Phosphate glasses have an interesting history. It was discovered very early that phosphorus pentoxide is a glass former. It differs from the other classic glass formers in that, although it forms a tetrahedral three-dimensional network (because phosphorus is pentavalent), one of the four oxygen ions is doubly bonded, that is, not coupled to the network. Although a silica-like structure is possible, as in aluminum phosphate, normal alkali and alkaline-earth glasses tend to have chainlike structures because of this pentavalency.

In 1941, Kreidl and Weyl[94] discussed the history of these glasses. As indicated above, phosphates were added by many early investigators, and, in fact, it appears that Vernon Harcourt[39] did most of his work on these glasses. The first Schott catalog, in 1886,[1] included so-called phosphate crown glasses. In 1894, Elder and Valenta[95] found that phosphate crowns had much better ultraviolet transmission than other optical glasses, and, when the beneficial physiological effects of ultraviolet radiation were discovered in 1925, research increased. At about the same time, it was discovered that phosphates were only slightly soluble in hydrofluoric acid. American Optical[96] developed glasses containing high concentrations of iron, but which were relatively colorless in the visible, while absorbing harmful infrared wavelengths. The low melting and processing temperatures and low viscosity of phosphate glasses made them useful as solder glasses.

A very important use of phosphate glasses emerged in 1988. Although silicate glasses were usually preferred for laser glasses because of their superior thermomechanical properties, phosphates were found to have superior laser characteristics—line widths, laser cross section, etc., as well as low, nonlinear refractive index and essentially zero dependence of optical path length on temperature. However, perhaps their most interesting property, in this case, is their ability to dissolve ionic platinum,[97] and, thus, such phosphate glasses could be produced essentially free of inclusions. This is a very necessary quality of a high-power laser glass.[98] Michael Faraday was probably the first glassmaker to use platinum to contain molten glass: ''Platina also was ultimately found to answer perfectly the purpose of retaining the glass, ... Neither the glass nor any of the substances entering into its composition, separate or mixed, had the slightest action on it.''[37]

Often it is desirable to have a glass with a very low softening point as well as a high thermal expansion coefficient, for instance, for sealing glass to aluminum. Phosphate glasses have been developed for such purposes. The high expansion coefficient with the associated low T_s is quite reasonable, because it is expected that, by increasing the amount of flux and, thus, decreasing the melting or glass temperature (decreasing the bond strength in the solid), the thermal expansion coefficient also increases for the same reason. Unfortunately, the usual additional consequence of this reduced bond strength is a decrease in chemical stability—an increase in solubility or corrosion rate.

Perhaps even more interesting, then, is the set of glasses recently discovered by Tick.[99a] Incredibly, Tick discovered a fairly wide range of glass formation in the lead tin fluorophosphate system. Certain compositions in this field, developed for ophthalmic applications, show a valuable combination of properties—low melting temperature, T_m, low glass temperature, T_g, and high expansion coefficient, while retaining respectable chemical durability, less than 50 times greater weight loss than soda–lime float glass (0.02 versus 1 mg/(cm^2·d)). The durability depends strongly on the amount of lead and tin, but not strongly on the amount of fluorine. Small changes in lead content have a very strong impact on the durability. It is, first of all, surprising that, in such a system where there are probably at least two glass formers, the system had not been discovered and studied earlier. Even more surprising is that these glasses can be melted at $T \approx 400$°C with $T_g \approx 100$°C, and yet have chemical durabilities comparable to soda–lime–silica glasses. Although several structural models have been proposed, that of Brow *et al.*[99b] seems most likely. In a modification of Tick's original model, they find extensive P—F bonding and suggest that the reason for the special properties of these glasses is the result of unusual electron lone-pair structures associated with the Sn^{2+} and Pb^{2+} sites.

(8) New Transparent Glass-Ceramics

Another exciting, unexpected, and, to some extent, unexplained area is that of transparent glass-ceramics. Although such materials were discovered by Stookey quite early in the history of glass-ceramics, these new materials show transparencies that are of a completely different order. In 1993, Wang and Ohwaki[100] reported efficient infrared-to-green up-conversion using Er^{3+} in a transparent oxyfluoride glass-ceramic. The rare earth (Er^{3+}) apparently dissolves preferentially in these crystals, and, thus, the absorption–emission behavior is that of a crystalline rather than a glassy host. Although this is useful, the more important effect is that the transmission of the combined glass-ceramic is comparable to that of the glass host itself. That is, the scattering caused by the presence of these small crystals, 20–30 vol% of crystals ~9–18 μm average size, is small. Further work on such systems by Tick, Borelli, and co-workers[101] has shown that this effect can be more or less explained using a model proposed by Hopper.[102] His model assumes that, rather than small crystals in a continuous glass matrix, the system can be approximated as a continuum with spatial variations of refractive index. The development of these materials is another example of the unexpected.

(9) Less-Brittle Glasses

One of the most active areas of glass research over the years always has been that of glass strength. It is very interesting and surprising, therefore, that, in all of the thousands of papers dealing with the strength of glasses, as far as the authors are aware, not one specifically has suggested that the resistance of the glass surface to *crack initiation* might be improved by changes in the bulk glass composition. Reduction in damage to the surface has been accomplished by the generation of a compressive stress in the surface, either by thermal or chemical means or by the application of coatings.

A recent publication, presentation, and patent from Ito, Sehgal, and co-workers[103] reveals the interesting possibility of a substantial improvement in the abrasion resistance of silicate glasses by rather modest compositional changes. Figure 8 shows that, by small compositional changes (see Table II), marked improvements in cracking susceptibility have been produced. Although these workers have proposed a model to explain the effects that they observed, the model certainly appears to deserve much more fundamental study.

(10) Other Special Glasses

Glass R&D over the years has produced an array of glass compositions–properties that have been unexpected and that initially have been used in special applications. As technology has changed, however, occasionally these uses also have changed. Often limited uses become, if not extensive, at least more commercially important. Chalcogenide glasses that were used first as index-matching liquids have become important because of their infrared transparency. This transparency is the result of low vibrational (phonon) frequencies. These low phonon frequencies, in turn, make these glasses important for fiber lasers. Fiber lasers were discovered by Koester and Snitzer[104] in the mid-1960s and were of virtually no interest until the development of suitable diode lasers in the mid-1990s. Diode lasers are now a critical component in long-distance telecommunications systems. Although the final choice of the glass host for diode lasers has not been made (clearly, there will be more than one such material), heavy-metal fluoride glasses and sodium–zinc–telluride glasses may be the host of choice in some cases.

Finally, a special category of glasses is bio-glass. Bioglasses are useful and interesting because they do not fit into the criteria described in the Introduction—they are *nondurable*!

Table II. Glass Compositions[†]

Oxide	Composition (wt%)
Standard soda–lime–silica glass	
SiO_2	66–75
MgO	0–5
CaO	7–12
Na_2O	12–20
K_2O	0–3
Al_2O_3	0–4
Scratch-resistant glass	
SiO_2	75.5–85.5
RO	1–8
R'_2O	10–23.5
$RO + R'_2O$	11–24.5
Al_2O_3	0–5
RO/R'_2O (weight ratio)	0.5 (at most)

[†] Reference 103. The authors of this work recently have indicated that, in a dry nitrogen environment, the loads necessary to produce two cracks increases to 350 g for the standard glass and to 3500 g for the scratch-resistant glass.

Their reactivity, which allows the rapid formation of surface gels, apparently is the reason for their suitability.

VI. New Era of Optical Fibers

The impact of optical communications technology has been so swift and pervasive that life without it is all but forgotten. Those who are in the glass industry are perhaps more conscious of this development than the average person, and, therefore, only a short discussion of this phenomenon is necessary. However, as one of the present authors has recently emphasized, the importance of the work of early glass researchers to this industry should not be underestimated.[105]

The main body of this article has been concerned with a discussion of rather complex silicate and, in one instance, phosphate glasses, and the rather natural and ordinary properties that are obtainable in such systems. In the case of lightguide fibers, almost the opposite characteristics are seen: the compositions and structures are rather simple, natural, and ordinary, but the properties that are observed are very unpredicted and, in some cases, at least as yet, unexplained. The history of the origins of the glass lightguide have been well documented. After early theoretical and experimental work by Kao and coworkers[106,107] at the Standard Telecommunications Laboratory in Harlow, England, in 1970, Maurer and co-workers[108] at Corning produced the first fiber with low optical loss (20 dB/km). This fiber consisted of a titania–silica core glass and a pure-silica cladding. The core material, as required for lightguiding, had a higher refractive index than the core glass. The primary reason that the loss is not lower than 20 dB/km is that the titanium in the core is easily reduced from 4+ to 3+ at the high processing temperatures. This results in ultraviolet absorption with a tail in the visible and near infrared.

Intensive R&D work followed worldwide on all aspects of this technology. There were two primary difficulties. First, not many organizations were familiar with the handling and processing of fused silica. Second, even if the organization had such a capability, it was neither immediately obvious what glass could be substituted for the titania-doped silica first used by Corning nor what procedures could be used to fabricate such composite, or glass-clad glass, fibers. As indicated, the core had to have a refractive index higher than the cladding, and few, if any, known glasses had a refractive index less than silica. Thus, although silica was known to be rather easily obtained in high-purity, high-transmission form, it could not be used as the core—the light-carrying portion of the waveguide. For these reasons, most initial work was directed at the purification of multicomponent silicate glasses. It proved extremely difficult to purify these glasses sufficiently, and, consequently, most workers eventually turned their attention to the ‘‘silica’’ glasses first shown by the Corning workers to be so promising.

Three processes have been developed to produce lightguide fibers, which are now mainly germania-doped silica as the core material and pure silica as the cladding.[109] In the first process (OVD), the glasses are built up on the outside of a ‘‘bait’’ rod in the form of a powder or soot by depositing them from a torch moving in the axial direction. Thus, the preform is built up radially, layer by layer. This preform is sintered in a subsequent operation. In a second process (MCVD), the (core or core and deposited cladding) glasses are laid down again layer by layer, on the inside of a silica tube, which itself may act as the cladding glass. The layers are sintered *in situ* as a part of this operation. In the third process, the preform is built up in an axial rather than in a radial direction and is thus called vapor axial deposition (VAD). In the first two processes, the index gradient is produced stepwise by depositing layers, each with constant refractive index. In the VAD process, the composition and, thus, the desired refractive index variation, can be produced and maintained across the gas stream.

To date, ~100 × 10^6 km of lightguide fiber have been deployed worldwide, with ~5 × 10^6 km of fiber being deployed per year.[110] This fiber has ~0.2 dB/km loss, essentially the intrinsic optical loss for fused silica. The fiber usually has a germania–silica core glass and a silica or fluorine-doped silica cladding, and operation is at 1300 or 1550 nm. Although handling, connecting, and deploying of such brittle fibers has presented a challenge, rather outstanding success has been achieved.

The use of lightguide fibers requires a variety of devices for the control and manipulation of the light signals. Here, we briefly describe the role of glass fibers as active components. As indicated in an earlier section, there are areas of rather intense R&D that should be mentioned here, because they reinforce our earlier premise that these relatively simple glasses show some quite remarkable effects. One of these effects is the formation of fiber Bragg gratings by laser irradiation.[111,112] These devices are extremely useful for the control of optical signals and for the detection of a variety of environmental effects when used as sensors (the sensor area itself is one of enormous activity at the moment, but one that we have no space to discuss).[113] The mechanism of the formation of gratings is not yet completely understood. Although the ordinary refractive index difference produced by this irradiation is of the order of 10^{-4}, by using special techniques, such as hydrogen loading or flame brushing, index increases of up to 10^{-2} can be realized. It initially was believed that the generation of Ge-E′ centers and the associated absorption resulted in the refractive index change through the Kramers–Kronig transform. However, it now is believed that the observed increases in refractive index are too large to be the result only of such a mechanism, and structural changes with associated volume compaction also have been shown to be involved.

As a final indication of the complexity of the effects that have been demonstrated in these glasses, an effect that continues to receive attention, but that also continues to defy complete understanding, is second harmonic generation (SHG). This effect—the production of light of twice the energy (half the wavelength) of the generating light—was first discovered in 1986 by Osterberg and Margulis.[114] When it was first observed in lightguide glasses, its discovery was quite unexpected, because it requires a noncentrosymmetric medium. The mechanism that seems best to describe this effect is the freezing-in of a periodic direct-current field. This field is probably the result of the asymmetric photoionization of defects in the glass.[115] Although this direct-current field was initially produced by the interaction of the fundamental and the induced or applied second harmonic beams, such SHG also has been found to be formed by poling.[116,117] In this technique, a direct-current of >10 kV is applied to a sample at ~200°–300°C to form the grating. The exact model to explain this effect or the maximum magnitude of the effect has not yet been determined completely.

Although all of the above devices or effects have been discovered more or less outside of the glass industry and basically not by traditional glass scientists, as described by one of the authors in another report,[105] basic work done earlier, as usual, will form the basis for the ultimate understanding of these effects. The study of defects in silica and in other glasses, as well as the study of direct-current conductivity and electrode polarization over the years will be extremely valuable.

The glass compositions used in the lightguide industry, although extremely simple, had not been the subject of very much experimental or theoretical work prior to the interest in lightguides. As indicated in an earlier section, very little data were available on any of the interesting properties—such as refractive index, density, or viscosity—and this hampered progress in the development of both waveguides and associated devices (behavior of RE ions, defects for gratings, etc.). Although few surprises have resulted in this regard from the work that followed, it continues that very little detailed study has been conducted on these glass-former glasses, except on those properties of direct interest to lightguides.

VII. Conclusions

The history of glass composition has been a very long and extremely interesting one and one that has many lessons. Although there are apparently many constraints on what can be done within the framework of an amorphous inorganic material (i.e., materials that lack a periodic lattice), we do not fully understand the theories that govern such behavior, and, thus, many surprises can be expected in this fascinating field. Historically, we have seen that progress has been cyclic and spotty at best. Ideas often have appeared ahead of their time. For instance, fiber lasers were invented by Snitzer in 1963 and attracted almost no attention until the mid 1990s, when the necessary associated electronics (appropriate diode lasers) were developed to make them commercially viable. Metallic glasses, on the other hand, were more or less continuously studied for 25 years before compositions were discovered that allowed bulk metallic glasses to be produced, and now hopefully to be more generally useful commercially. The tin lead fluorophosphate glasses that defy the natural law of low T_m, low T_g, and low chemical durability are not really extraordinary compositions—in fact they are quite ordinary CRN glasses—and yet they were discovered only recently because of the need for such very-low-melting glasses.

In the past, glass scientists have studied the behavior of many simple and moderately complex glasses and have a reasonably good qualitative idea of the role of various oxide constituents in the determination of the behavior of these glasses. Also, we have available reasonably good empirical models that allow quantitative prediction of some aspects of their behavior. However, such understanding and models are able to predict behavior only over relatively narrow compositional ranges.

Also, although many interesting properties have been discovered in a variety of glass systems, perhaps only in the recent case of lightguide fibers has such a discovery been the basis for a major new industry. This development has had an enormous impact on both the industry and the science of glass. A whole new generation of glass optical fiber scientists has appeared. An important final question is whether we can expect that another such major development may occur in the future, or whether we have only to look forward to small, interesting developments in glass science and technology.

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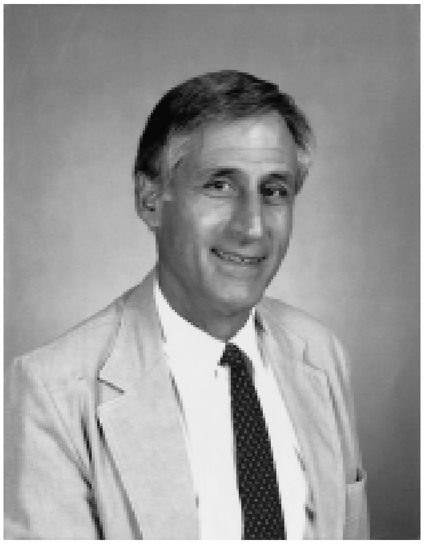

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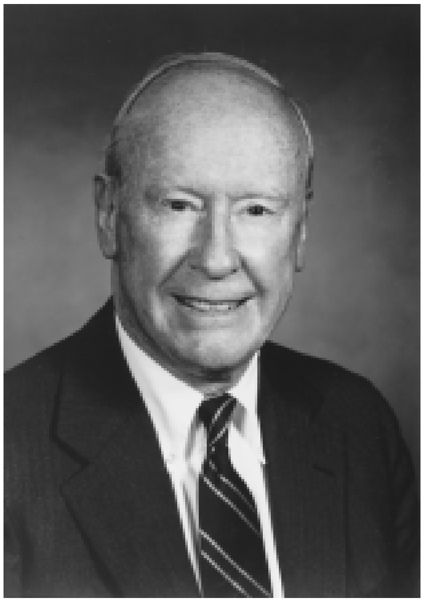

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