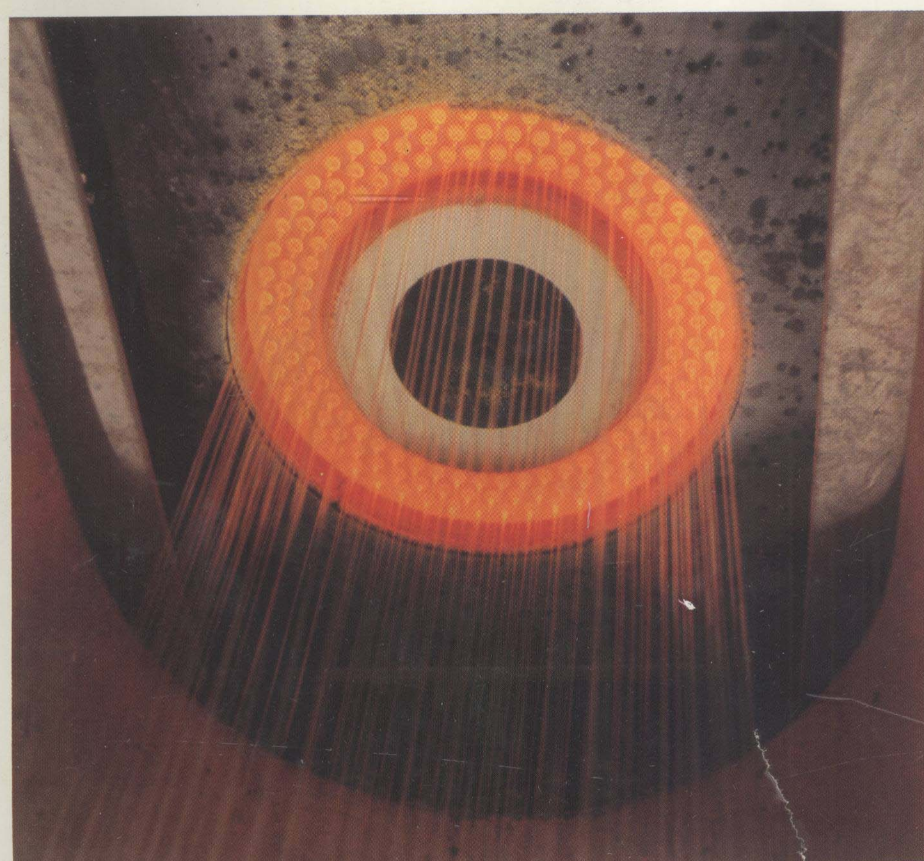
ADVANCES IN CERAMICS • VOLUME 18

COMMERCIAL GLASSES

Edited by
David C. Boyd
John F. MacDowell



ADVANCES IN CERAMICS • VOLUME 18

COMMERCIAL GLASSES

Edited by

David C. Boyd
and
John F. MacDowell
Corning Glass Works

The American Ceramic Society, Inc.
Columbus, Ohio

Proceedings of a special symposium on commercial glass held at the 1984 Fall Meeting of the American Ceramic Society, October 17–19, 1984, Grossinger, New York.

Library of Congress Cataloging in Publication Data

Commercial glasses.

(Advances in ceramics, ISSN 0730-9546 ; v. 18)
"A special symposium on commercial glass during the 1984 fall meeting of the Glass Division of the American Ceramic Society" —Pref.
Bibliography: p.
Includes index.
1. Glass—Congresses. 2. Glass manufacture—Congresses. I. Boyd, David C., 1924- . II. MacDowell, John F. III. American Ceramic Society. Glass Division. IV. Series.
TA450.C57 1986 666'.1 86-10723
ISBN 0-916094-78-2

Coden: ADCEDE

ISBN 0-916094-78-2

Coden: ADCEDE

Printed in the United States of America.

Volume 1 Grain Boundary Phenomena in Electronic Ceramics

Volume 2 Physics of Fiber Optics

Volume 3 Science and Technology of Zirconia

Volume 4 Nucleation and Crystallization in Glasses

Volume 5 Materials Processing in Space

Volume 6 Character of Grain Boundaries

Volume 7 Additives and Interfaces in Electronic Ceramics

Volume 8 Nuclear Waste Management

Volume 9 Forming of Ceramics

Volume 10 Structure and Properties of MgO and Al_2O_3 Ceramics

Volume 11 Processing for Improved Productivity

Volume 12 Science and Technology of Zirconia II

Volume 13 New Developments in Monolithic Refractories

Volume 14 Ceramics in Heat Exchangers

Volume 15 Fourth International Conference on Ferrites, Part I

Volume 16 Fourth International Conference on Ferrites, Part II

Volume 17 Fission-Product Behavior in Ceramic Oxide Fuel

Preface

The challenge of glass commercialization encompasses the art and science of formulating an optimum glass composition, discovering and/or creating a need for it in the marketplace, and then manufacturing it profitably. A special symposium on commercial glass during the 1984 Fall Meeting of the Glass Division of the American Ceramic Society brought together technical leaders in all three of these areas of endeavor. This book contains most of the papers from that symposium.

Commercial glass is classified by use into flat, container, fiber, and specialty glass. The flat and container companies produce over ten million tons of soda-lime glass per year. The specialty glass and fiberglass companies melt hundreds of different compositions to produce pressed, blown, and fiberglass for the optical, television, lighting, consumer, communications, and electronics industries. Following a treatise on the history of glass manufacturing, the first section of this book discusses the glass industry as classified by its product.

Glass is a product, but glass is also a material. Because its properties can be tailored to precisely fit its intended use, glass enjoys a unique versatility. The technology of glasses ranges from the ultrapure and low optical loss waveguide materials to the highly strengthenable aluminosilicates to the myriad of phase-separated glasses such as opal glasses, photosensitive glasses, and glass-ceramics. Glass, a most ancient material, has taken its place as one of the leading materials of our modern society. The second section of this book describes the most important of the glass composition types.

Just as our materials scientists invent more sophisticated glass compositions in our laboratories, so must our engineers and process scientists develop more sophisticated methods for the manufacture of these materials in our plants. To do so profitably and competitively is becoming the challenge of the decade. The third section describes some aspects of glass manufacture and the control of the manufacturing process.

We are indebted to the authors who prepared these papers for their willingness to share their expertise with the rest of us in the industry. We hope that this volume will be especially valuable to scientists and engineers in industries peripheral to glass, such as electronics, telecommunications, information, space exploration, and national defense. Although glass-derived materials are used only sparingly in products from these industries, the unique properties of glass often constitute a most vital element in the operation of their complex product systems. We also wish to thank the American Ceramic Society for affording us the opportunity to publish this collection of knowledge on commercial glasses.

David C. Boyd
John F. MacDowell
Corning Glass Works

Contents

SECTION III: GLASS MANUFACTURE

3500 Years of Glassmaking

George B. Hares

Corning Glass Works
Corning, NY 14831

The evolution of commercial glassmaking from its beginnings in ancient Egypt to present-day practice is traced. The relationships between raw material availability, changes in melting and forming processes, expanding technological needs, and glass chemistry are emphasized.

As scientists involved in commercial glass manufacture, we are possessors of a long and rich technological heritage, reaching back some 3500 years. This paper is only a brief and cursory overview of the evolution of commercial glassmaking from its beginnings to present-day practice.

The origins of glassmaking are lost in antiquity. Dates as early as 2600 B.C. have been claimed for some glass beads, but at least some of these dates are questionable.

The immediate predecessor of glass may have been a material known as Egyptian faience, which was used to make small objects such as statuettes or jewelry. This material appeared as early as 4000 B.C. and was prevalent throughout the Egyptian empire from 2700 to 350 B.C. It consisted of a porous, silica body with a surface of alkali silicate glass, often colored green or blue. This surface probably was not produced by a classical glazing technique, but was rather the result of chemical reactions with a mixture of sand and alkali salts in which the object was buried during firing. The maximum temperature during firing was probably no higher than 900°C, judging from X-ray evidence of the crystalline phases of silica present in the body.

Faience had been manufactured for at least a thousand years before the earliest glass objects appeared, in the form of "sandcore" glass vessels used as containers for cosmetics, and so forth. Although these glasses were most often deep blue (probably an imitation of lapis lazuli), the base glass composition differed little from lime-glass compositions used in the flat-glass industry today. While analyses of the ancient compositions show them to be very complex mixtures, actually only a few readily available raw materials were probably used: Sands in the Nile valley contain a large amount of limestone, and either natron or plant ash, both of which contain considerable quantities of lime and magnesia, as well as alkali, was used for fluxes.

The melting process was probably carried out in two stages: First, at comparatively low temperature, the sand and alkali were converted into a frit; and second, the frit was converted to glass in crucibles in the melting furnace. The highest fritting temperature was probably about 750°C, while the melting temperature was no higher than 1100°C and the practical temperature was about 1050°C. (If pieces of the crucibles are heated to 1150°–1200°C, they themselves form a glass!) At 1050°C these compositions were very viscous, so that forming a glass vessel was a problem. Unfortunately, no written record of Egyptian glass-forming technique survives; thus, the technique has been subject to much speculation over the years.

Since most of the vessels show traces of a sand or clay core material adhering to the inside surface, we must assume that the vessels were formed around a core. This core was possibly preshaped and, by some process, dipped or rolled in the softened glass. It was decorated by applying threads of colored opaque glass, usually yellow or white, which were then rolled flat into the surface. Reheating the decorated vessel and then "combing" the surface with a pointed tool produced more elaborate decorations. Opaque glasses were probably obtained by adding a white pigment (calcium antimonate) or a yellow one (lead antimonate) to the base glass used for the body of the vessels.

In any event, glass objects in this historical period were available only to the wealthy or powerful. It was not until the Roman period and discovery of the blow pipe, to make thin-walled vessels, that glass products became more universal. The introduction of the blow pipe may have resulted from new techniques for achieving higher glass-melting temperatures: As iron implements became more widespread, higher smelting temperatures than those used for copper smelting became mandatory. These newer methods of glass melting allowed temperatures at which the glass was fluid enough to gather on a hollow rod, so that a glass bubble could be formed by blowing through the tube.

The blow-pipe technique made possible the rapid production of utilitarian vessels, and glass became a household commodity. A middle-class Roman family probably owned glass storage containers, looked through crude glass windows, and could even buy glass souvenir cups of their favorite gladiator. Everywhere the Romans went, glass went, too. Glass objects from Roman times have been found in abundance to the ends of the empire, as far north and west as Scandinavia and Britain, and as far east and south as eastern Syria and Ethiopia.

These early glasses used two primary raw materials, sand and plant ash, neither of which had a fixed chemical composition. Sand varied in content of iron, alumina, lime, and other impurities. Plant ash, derived from burning of various plants or trees, varied widely in constitution, reflecting not only the type of plant, but also the soil in which the plant grew: For instance, plants that grew near the sea or on salt desert land had a high proportion of soda to potash, while inland plants were much richer in potash than in soda. With universal availability of the chief glassmaking raw materials, sand and ash, it is easy to see that growth and decline in glass technology closely paralleled growth and decline of the individual civilizations and empires. In addition, the easy workability of glass as an artistic medium resulted in forms very characteristic of the locale or of the origin of the craftsman himself.

After the fall of the Roman Empire, the main glassmaking centers returned to the eastern Mediterranean area. Islam was on the rise, and enameling and copper- and silver-staining techniques were applied to produce beautifully decorated mosque lamps.

During the Middle Ages (A.D. 500–1500), glassmaking in central Europe declined, but did not disappear completely. The glassmakers were itinerant, setting up their furnaces near a supply of sand and a forest. The wood from the forest supplied two needs: fuel for the furnaces and ashes, which could be leached to provide raw material for the glass batch. Because the impurities in the sand, particularly iron, were very high (compared to the sand of the Mediterranean beaches), this glass had a characteristic dark green, almost black, color. Glass of this type has come to be known as "Waldglas" or forest glass. Since the forest was quickly depleted, these glassmakers then gathered up all their necessary tools and moved on to another spot, where the supply of sand and wood was adequate.

Following the Crusades, and with the beginning of the Renaissance, the artistic glassmaking pendulum swung back from Asia Minor to the western Mediterranean, particularly to Venice. Not only was this a period of great artistic activity, but it was also a period in which technical emphasis shifted to obtaining ever purer raw materials, resulting in the almost colorless, transparent Venetian "cristallo" of the sixteenth century.

The traditions of luxury glassmaking, carried by Italian craftsmen, spread through Europe like wildfire in the sixteenth and seventeenth centuries. The Venetian tradition, established in England by 1575, remained more or less active through the Puritan period and into the Restoration (1660). At that time, in England, there was a great effort toward establishing national self-sufficiency. Since most glassmaking ingredients were still imported, in 1673 George Ravenscroft was engaged by the Glass-Sellers Company to begin research on eliminating foreign ingredients. By about 1676 he had developed a potash lead glass that was insusceptible to atmospheric moisture. Ravenscroft was permitted to use a raven's head seal as his device on glassware of this composition. For silica, English flints, a very hard form of quartz, low in iron, were used. The flints were pulverized before mixing with the potash and lead, and these potash lead glasses became known as flint glasses due to their color clarity.

There were two basic processes for making window glass: the cylinder process and the crown process. In the cylinder process, a long, cylindrical bubble was blown and the end heated, then opened to form a cylinder. The entire piece was next reheated, slit lengthwise, and opened out and allowed to sag into a flat sheet. This process was used (with some mechanization) until the beginning of the twentieth century.

The crown process, on the other hand, consisted of first forming a spherical bubble. A pontil rod was then attached to the surface of the sphere, diametrically opposite the blowpipe. The blowpipe was cracked off and the sphere reheated and opened where the blowpipe had been attached. Then the sphere was reheated, and when the glass fluidized the pontil rod and sphere were rotated very rapidly. Centrifugal force opened the sphere into a more-or-less flat disk. The round sheet or "table" was then cracked off, annealed, and cut up for window panes. In ninteenth-century England, sheets made by this process were as large as five feet in diameter.

Two characteristics of glass made by the crown process were a thickness that decreased with increasing distance from the center, and a large mass of clear glass, known as a bull's-eye, or crown, in the center of the "table," where it had been attached to the pontil iron. The bull's-eyes themselves were shaped somewhat like lenses; indeed, in sixteenth-century Venice, spectacles were made using bull's-eye glass.

The seventeenth century brought great activity in the science of astronomy. Galileo built his first telescope in 1609, and larger and larger telescopes were built for higher magnifications. It was difficult, however, to obtain sharp images, since eliminating the color fringes at the edge of the image seemed impossible. Then in 1666, Newton discovered that a beam of sunlight passing through a glass prism would bend and form the different colors of the spectrum. He concluded that "all refractive substances diverged the prismatic colors in a constant proportion to their mean refraction" and drew the natural conclusion that refraction could not be produced without color.

Newton's assumption, however, was incorrect. Chester Moor Hall argued that the humors of the eye refract rays of light to produce a color-free image on the retina, and he argued reasonably that combining lenses of different substances might produce a similar result. After some time, he discovered a combination of two glasses that would indeed accomplish this purpose. This achromatic lens was perfected by John Dollard in 1758, using a combination of window (crown) glass for the positive component and lead-crystal (flint) glass for the negative component. The terms "crown" and "flint" are used in optical-glass designations to this day. This combination of a convex lens of crown glass and a concave lens of flint glass decreased the color fringes on the image formed by a telescope, but the colors did not disappear completely: A much smaller, colored edge, the so-called secondary spectrum, remained.

In the early nineteenth century, chemists began introducing oxides other than lead and lime into glass, hoping to discover new types of optical glass. Fraunhofer had determined that, if chromatic aberrations were to be eliminated, new glasses, with different ratios of partial dispersion than the ordinary crown and flint glasses, would have to be found. Most of the search, however, was fruitless, because of difficulty in obtaining experimental melts suitable for optical measurements.

Not until Otto Schott (who was perhaps the first chemist to present a doctoral dissertation on a glass-related subject) approached Ernst Abbe in 1879, asking him to determine the optical properties of an experimental lithium glass he had made, did the quality of small glass melts become acceptable. Schott joined forces with Abbe, and by 1884 the Jenaer Glasswerke Schott and Genossen was formed. By 1886, 44 glass types were on the market. Among the new glass types were phosphate and borate crowns, barium silicate crowns, borosilicate crowns, zinc and potash silicate crowns, and borate flints. Minor variations proliferated over the years. One significant advance was the development of the high-index, low-dispersion glasses based on lanthanum borate.

Along with advances in optical-glass compositions came continued improvement in the quality of optical-glass melts, but this aspect of optical glass must be discussed elsewhere. Other Schott developments included glass compositions for thermometry and borosilicate compositions for chemical ware.

The first commercial laboratory in the United States devoted to glass research was founded at Corning Glass Works in 1908. One of its first problems was the thermal shock breakage of railroad lantern globes and signal lenses. A soft, lead-containing, low-expansion borosilicate glass was developed for this purpose. A clear version, known as Nonex,* was used for battery jars because of its chemical stability. The bottom of one of these battery jars was used to bake the famous cake that resulted in the use of borosilicate glass for consumer baking ware.

At this same time, World War I cut off the supply of German borosilicate chemical ware, and a new borosilicate glass was developed to meet the need. Lower in expansion and much more difficult to melt than Nonex, this composition has now become the standard for laboratory ware around the world. One of the characteristics of the borosilicate family is the wide range of properties available using different proportions of alkali and boric oxides: Extremely low-expansion glasses such as those used in the 200-inch Mt. Palomar telescope, moderate-expansion glasses for sealing to molybdenum and Kovar,† and higher-expansion glasses such as those used in optical borosilicate crowns are typical illustrations of this family.

---

*Corning Glass Works, Corning, NY.
†Westinghouse Electric Co., Pittsburgh, PA.

Among the problems associated with borosilicate glasses is the tendency of many such glasses to separate into a silica and a borate phase, the latter having poor chemical durability. This tendency, however, has been capitalized on by adjusting the composition so that the separated borate phase is an interconnected network. Subsequent leaching of this phase in dilute acids, followed by firing at about 1250°C, produces a hard, clear glass, more than 96% silica, that is marketed and known in the trade as Vycor.[‡] It has a low thermal expansion (8×10^{-7}/°C) and can withstand much higher temperatures than can the borosilicate family.

In the nineteenth century, two families of glass were widespread: The lime-glass family was used for windows, bottles, dinnerware, and such decorative ware as vases. Some lime glasses were called "flint" glasses, for their color clarity (low iron content), rather than their optical properties. The other family was the alkali-lead silicate family. The alkali was most often potash, and two lead-oxide contents were prevalent, one at ≈24 wt% lead oxide, the other at ≈30 wt%. These compositions were used in the cut-glass industry.

Edison's first light bulbs were made from lead-glass tubing, and the practice of using lead glass for lamp envelopes continued until World War I, when the supply of lead oxide was severely curtailed. A switch was made to a lime-glass composition containing about 8 wt% dolomitic lime, in contrast to the 10–12 wt% lime used in the container and window-glass industries. Later, tubing for fluorescent lamps was made from the same composition.

The search for glasses compatible with high-temperature applications, where the borosilicate family would be unsuitable, led to development of the aluminosilicate family. This family was originally used for combustion tubes. The compositions were essentially alkaline earth aluminosilicates, with a small amount of alkali. While the annealing point was about 150°C higher than that of the low-expansion borosilicates, the viscosity–temperature relationship was much steeper, so that the glasses could be melted in conventional units. High annealing and strain points permitted tempered items of these glasses to be used for top-of-the-stove cooking. Other aluminosilicate glasses include the high-soda aluminosilicates, which are chemically strengthened by a potassium for sodium-ion exchange below the strain point, and the alkaline earth glasses used in the fiberglass industry.

The ultimate in low-expansion and high-temperature capability is vitreous silica itself, which can be prepared by heating silica and/or quartz crystals to above the melting point of silica (>1725°C). However, the glass is so viscous that good quality vitreous silica is extremely difficult to obtain in this manner. An alternative technique is a vapor-deposition process, in which silicon tetrachloride is reacted with oxygen above 1500°C. A finely divided, particulate vitreous silica is formed, which can be consolidated on a substrate above 1800°C. This procedure (developed in the 1930s) is the basis for the processes used to make vitreous silica optical waveguide fibers, because of the extreme purity achievable by the vapor-deposition process.

The evolution and development of glass compositions and forming methods for television picture tubes would require a separate paper, but the original composition used in small black and white tubes was a potash lead silicate, followed rather quickly by an alkali barium glass with very similar physical and electrical properties. The advent of color television required development of a higher-

‡Corning Glass Works.

expansion barium glass for the panel, a lead-containing glass for the funnel, the original alkali lead glass for sealing to the electrical leads, an intermediate-expansion lead glass for the neck, and a solder-glass frit to seal the panel and funnel together after the phosphors, etc. were processed. Subsequent high-voltage requirements resulted in substitution of strontium oxide for barium oxide to increase the X-ray absorption of the substrate.

Opal glasses have been common since the earliest times. Early opacifying agents were calcium antimonate (white), lead stannate (yellow), and cuprous oxide (red). Phosphates and arsenates came into use much later. Fluoride opals first came into use in about the middle of the nineteenth century.

What can be said about colored glasses? They have been with us since the beginning of glass technology. Indeed, it seems that every time a chemist (or alchemist) discovered a new material, he tried it in a glass-composition matrix to see what color he would get. The story and evaluation of colored glasses is beyond the scope of this paper.

A variation of colored glass is the silver- and/or gold-containing glasses which respond to ultraviolet light. Among these are the photosensitive clear glasses; the photosensitive opal glasses, where silver particles act as nuclei for a crystallization phase; glass-ceramics, either photonucleated or internally nucleated; and the photochromic silver-halide–containing glasses.

As glass scientists, we must continually realize that glass is an extremely versatile material with a long history, an exciting present, and a promising future.

Section **I**

The Glass Industry

Optical Glasses

EMIL W. DEEG

AMP Incorporated
Harrisburg, PA 17105

Material properties, critical for meeting performance requirements of passive and active optical elements in specific applications, and important manufacturing aspects are discussed. A brief historic review, primarily of glass composition development, is included.

Optical glasses are the first of what we call today "high-technology materials." Since their introduction as regular commercial products more than a century ago, they have had to meet exceptional and continuously increasing requirements for actual values and melt-to-melt reproducibility of physical properties, as well as quality and forms of supply. High transmittance in the visible spectrum, or, in the case of optical filter glasses, well-defined "color," freedom from cords, striae, bubbles, seeds, and solid inclusions are synonymous with optical-quality glass. Producing such materials requires a thorough knowledge of the quantitative relationships between composition and properties. History shows that optical-glass production also required first the skills and later the technology for monitoring and controlling both reliably and precisely the melting, forming, and annealing processes.

This paper attempts to introduce optical glasses, emphasizing properties important for optical instruments. Compositions, given in round numbers only to demonstrate their variety, represent mature glasses available in commerce for more than 20 years. Not considered are fiber optics, glass-ceramics for reflective optics, secondary manufacturing operations (i.e., grinding, curve generating, polishing, slumping/sagging, toughening, surface modification by chemical treatment, and vacuum deposition of thin films), use of optical glasses for nonoptical purposes (e.g., ultrasonic delay lines), optical cells for laboratory apparatus, etc., or illuminating and lighting optics. Results of recent glass compositional research, although interesting, are not included, for reasons implicit in the historical highlights.

An "optical glass" must meet certain minimum requirements, i.e.,

1. Identifiability by the customary set of optical properties.
2. Satisfactory chemical durability.
3. Manufacturability in acceptable quality and in pieces large enough for preparing useful optical elements.

Quality of the highest level compatible with performance and cost is a concern also for ophthalmic glasses, which usually are not considered "optical." In that case, the consumer benefits directly from the vast knowledge and expertise accumulated by the optical-glass industry. In addition, the manufacture of filter glasses and the preparation, in reasonable sizes, of the more advanced amorphous materials, such as laser glasses, used in optics would be impossible without optical-glass technology.

Historical Highlights

This review highlights the major technical events leading to the optical-glass industry as we know it today. For details, especially regarding commercial aspects, see Refs. 1–9. More recent acquisitions of products and product lines also have been reported in trade and business journals.

At the beginning of the eighteenth century, dispersion was considered a property of light, and not of an optical material.[10] Although flint glass was about to emerge, Newton and his scientific contemporaries recognized only one "glass," the alkali-lime-silicate crown. Its composition was determined by locally available raw materials and the traditional, jealously guarded glassmaking recipes. Melting technology was still essentially as described in Agricola's *De re metallica* (ca. 1500).

Publications of Neri in 1612 and 1681 and by Kunckel in 1679 and 1689 opened the field of glass chemistry considerably but had no immediate, direct effect on optical-glass development. Early in the nineteenth century, Joseph von Fraunhofer needed improved glasses for his optical instruments and experiments; at that time it was already known that a combination of crown and flint lenses reduced the chromatic aberration of a lens system. Fraunhofer, working with Utzschneider, the owner of a glass factory, not only found that the chemical durability of a glass depends on its composition, but also prepared a new crown glass. This glass, in combination with flint glass, permitted a better correction for chromatic aberration than did the regular crown available at the beginning of the nineteenth century. Pierre-Louis Guinand, who introduced mechanical stirring of the glass melt, also worked with Fraunhofer and Utzschneider.

In 1824 the Royal Society elected a commission charged with experimental studies of flint glasses. The members were Michael Faraday, John Dollond (optician), and Sir John F. W. Herschel (astronomer). In Faraday's laboratory a lead-borosilicate flint was prepared with refractive indexes of 1.8521 in the red spectrum, 1.8735 in the yellow, and 1.9135 in the violet. With available equipment, no large high-quality pieces could be made, and melting still used batch fritting, although fining was done in platinum.

The most radical step away from conventional nineteenth-century glass chemistry was taken by William Vernon Harcourt[11] in the first half of that century. For studying the effect of different glass constituents on optical properties, he designed a laboratory "furnace" permitting glass melting in air, free from the effects of combustion gases above the melt surface. This device consisted of a rotating platinum crucible heated directly from the outside by a hydrogen-fed ring burner with platinum nozzles. The conical crucible was not contained in a furnace. In cooperation with G. G. Stokes, Harcourt used this device to explore the effect of glass composition on optical properties. The impressive list of new glass constituents introduced by Harcourt during these experiments was published in 1871 by Stokes.[12]

Biological and medical scientists needed a wider selection of new, high-quality glasses for optical instruments to build microscopes with improved resolution. By the last quarter of the nineteenth century microscopic theory had developed enough to permit quantitative specification of what were, at that point, hypothetical glasses. The status of the optical-glass industry, as seen in 1876 by its prime "customer," the instrument designer, was summarized by Ernst Abbe:

> . . . some experiments in the production of glasses with small secondary dispersion conducted by Stokes in England a few years ago, though barren of direct practical result, gave useful hints as to the specific effects of certain