

CHEMISTRY OF GLASS



W. Vogel

translated by N. Kreidl

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Translated and edited by
N. Kreidl

Associate Editor
Esther Lense

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Foreword

Glass chemistry represents a relatively young branch of chemistry. It comprises a boundary area between chemistry, physics, mineralogy, biology, and, recently, medicine as well. It is difficult to present this area with the proper balance and well-placed accents.

No doubt chemistry and also physics—the latter particularly in its technological aspects—occupy a central position in the treatment of glass problems.

Glass technology is not treated within the framework of this book, although a glass chemist or physicist certainly cannot manage without sufficient background in glass technology, nor a glass technologist without one in glass chemistry. In the area of glass technology, excellent older texts are available, such as those by R. Guenther, F. Tooley, J. J. Kitaigorodski, etc.

Glass chemistry represents a special branch of high-temperature chemistry in which chemical processes of transformation of matter take place. They have, during the past 20 years, led to results hardly believed possible before.

The importance of glass and silicate chemistry for mankind is going to increase considerably at the turn of this century. This is because, once the classical sources of raw materials such as oil, natural gas, and ores begin to be exhausted as a basis for materials development and production, the supply of raw materials for the glass and silicate industry will remain indefinitely.

This book has been conceived as a text for university-level students of glass science and industry. Its content is largely the core of a course at the Friedrich-Schiller-University in Jena, offered since 1961 and updated annually. In some cases, the book goes beyond educational needs and thus might be useful to those already active in glass science or production.

The introductory sections of the book have been guided by the impulses emerging in Jena from Otto Schott, pioneer of modern glass research. The main thrust is the elucidation of the relation of composition, structure, and properties. Only thorough understanding in this respect will lead from the empiricism which has governed glass investigation for so long toward a firm foundation for systematic development and production control.

Of the many modern methods applied in contemporary studies of the structure of glasses, nuclear magnetic resonance spectroscopy and electron microscopy have been singled out for more detailed coverage. These two complementary methods have significantly advanced glass research during the past 20 years. While nuclear magnetic resonance provided closer insight into atomic interaction and the coordination of ions, electron microscopy revealed structure-property relations in glasses over a range orders of magnitude larger than those accessible through magnetic resonance. Many examples demonstrate the utilization of both methods in practice.

The book uses SI units consistently with some reference to older units still in use, particularly in the industry. To facilitate adjustment of SI units, a conversion table precedes the text.

The section on nuclear magnetic resonance spectroscopy was written by Professor P. J. Bray, Physics Department, Brown University, Providence, Rhode Island, USA. Professor Bray is known worldwide as an expert in the

field of nuclear magnetic resonance and as an outstanding teacher. I thank him for his collaboration.

I also thank Ing. Lothar Horn, my expert and dedicated collaborator for nearly 30 years in the field of electron microscopy. He has given me excellent support in the production of the illustrations for this book.

Mr. Martin Brand, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, German Democratic Republic, has greatly supported me in the preparation of the German first and second editions by his excellent counsel and assistance.

The present edition has been published by the American Ceramic Society. Special thanks are due to Norbert J. Kreidl for translating, editing, and updating the book. More than 100 references were added (Nos. 828-947). No better translator than Dr. Kreidl, who is also a glass scientist and teacher, could have been found anywhere in the world for this project.

My special thanks are due, too, to Mrs. Esther Lense, American Ceramic Society, who has given splendid support in proofreading the translation and in editing the text.

Last, but not least, I wish to offer my sincere thanks to the American Ceramic Society for making possible so successful an English edition of my book.

W. Vogel

Otto-Schott-Institut

Jena, German Democratic Republic

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1 Historical Development of Glass Chemistry

The Beginnings of Glass Research

The history of glass is quite old, that of its scientific exploration very young. During formation of the earth, highly siliceous melts of rocks occasionally froze to natural glasses such as obsidian. Water, dissolved homogeneously under high pressure, evaporated rapidly if such melts penetrated the surface, e.g., in a volcanic eruption; and, when cooled quickly, the foaming melt became a solid natural glass foam, since high viscosity prevented the escape of bubbles. Modern industrial technologies may be considered variations of this basic process.

Glass was first produced by man about 4000 years ago, apparently in furnaces used in the ancient art of pottery, as, for example, in ancient Egypt. As with most materials, such as bronze or iron, the first application was to jewelry. However, the favorable shaping properties of glass were soon utilized in other fields, such as containers, windows, and lenses. Yet, during the long first period of application to life and progressing technology, the nature of glass remained unexplored.

For a long time, too, systematic studies of the relation of composition to properties and the development of new glasses remained inhibited by the inability to produce glass of sufficient homogeneity. For this reason, the first significant progress waited until about 1800, when Guinand and Fraunhofer devised special stirring methods. Thus, Fraunhofer was able to determine that a glass containing lead refracted and dispersed light quite differently than a glass containing lime. The spectrometer invented by Fraunhofer enabled the study of the change in refraction with wavelength for varying compositions. His experiments with 7 elements besides oxygen (Si, Na, K, Ca, Pb, Al, and Fe) were extended to over 20 by Harcourt, an English clergyman, and Stokes (Li, Tl, Be, Mg, Sr, Ba, Zn, Cd, As, Sb, Sn, Ti, W, Mo, V, B, P, and F). This was not only the beginning of glass chemistry, but also the first step anticipating later optical glassmaking, since a platinum crucible was used to avoid contamination. Hydrogen was developed in a lead bomb, led via a washing bottle and copper tubing to a spiral platinum point, where it was burned. The platinum crucible was suspended on platinum wires above the platinum nozzle and turned by clockwork to ensure uniform heating. Unfortunately, Harcourt did not live to see the success of his more than 35 years of labor. The homogeneity of his 166 prisms did not suffice to measure dispersion with the required accuracy, and some of the glasses were hygroscopic and unstable.

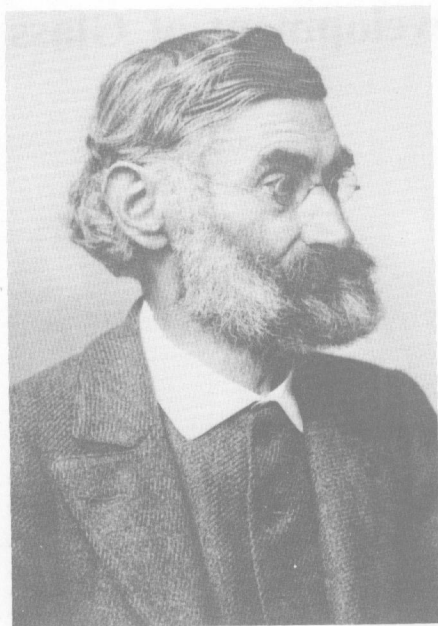


Fig. 1.1. Ernst Abbe. Born January 23, 1840 in Eisenach, Thuringia; died January 14, 1905 in Jena.



Fig. 1.2. Otto Schott. Born December 17, 1851 in Witten, The Ruhr; Died August 27, 1935 in Jena.

Yet, qualitative comparison suggested future production of telescopes free from chromatic aberration, particularly by combinations with glasses in which SiO_2 would be replaced by B_2O_3 or P_2O_5 .

Much earlier attempts sponsored by the famous German poet Goethe, then prime minister of a German duchy, deserve to be recorded. On March 28, 1829, Goethe wrote to the noted chemist Dobereiner at Jena University that "it would be most important to determine the relation of refraction and dispersion in your (Ba and Sr) glasses . . . I should be pleased to contribute modest funding . . ."

History of the Chemistry of Optical Glass

The decisive chapter in the history of optical glass as a practical product was shaped by two people: chemist Otto Schott and physicist Ernst Abbe, both at Jena, and their fortuitous collaboration.

Abbe (1840–1905) (see Fig. 1.1) professor of mathematics and physics at the University of Jena, Director of the Observatory, and a collaborator of Carl Zeiss, the University's optician and microscopist, recruited Schott when he learned of his experiments with glass compositions and brought him to Jena.

Schott (1851–1935) (see Fig. 1.2) was the descendant of a glassmaking family. His father founded and operated a window glass plant and purposefully encouraged his son's career as a scientist, recognizing the need to supplement practical expertise by fundamental knowledge. Schott first became

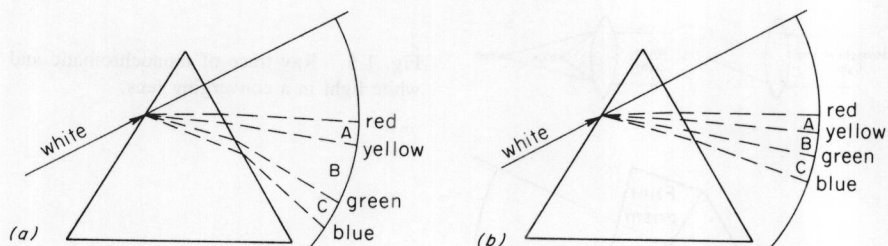


Fig. 1.3. Ray trace in a crown and a flint prism. Difference in dispersion of white light (a) flint glass prism and (b) crown glass prism.

interested in “pyrochemistry,” the chemistry of high-temperature melts, and deduced similar behavior for homogeneous melts of silicates, borates, and phosphates. Concerning glass, his attention first centered on lithium as a component, being intrigued by the possible effects of its low specific weight. For this reason, on March 27, 1879, Schott approached Abbe with a request that he determine refraction and dispersion for the lithium glass sample Schott had prepared. His hope was that optical instruments could be improved by the use of glasses with unusual dispersion-refraction relations.

When, once more, homogeneity was found to be insufficient for exact refractometry, Schott found a suitable stirrer in the form of the thin, white refractory clay tubing used in Dutch tobacco pipes. Abbe immediately appreciated the enormous step represented by the homogeneous lithium glass, even though it did not exhibit the expected property variations. However, Schott, encouraged by publications on the additivity of atomic refraction, proposed the investigation of melts containing B_2O_3 and P_2O_5 .

Soon Abbe reported that “the experimental melts indicated a variability in optical character hardly ever hoped for on the basis of the uniformity in optical relations in older silicate glasses” and that “the versatility of P_2O_5 was truly fabulous!”

The transition to large-scale production had to overcome many difficulties—obviously large volumes crystallize more easily. Jena Glass Works of Schott and Associates was founded. This enterprise pioneered a social attitude resulting in the statutes of the Zeiss-Schott foundation, which was unique in its time (profit sharing, retirement, severance pay, etc.).

The scientific and technological progress achieved during these few years of collaboration may be summarized as follows. In the past, only two types

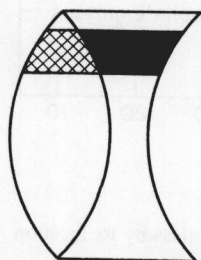


Fig. 1.4. Lens combination of converging and diverging lens. Each lens may be imagined as built up from an infinity of small prisms.

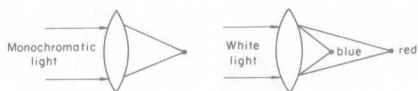


Fig. 1.5. Ray trace of monochromatic and white light in a converging lens.

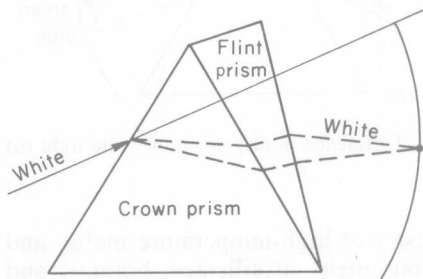


Fig. 1.6. Ray trace of white light in a combination of crown and flint prisms.

of optical glass could be distinguished: (1) crown (soda-lime) glass, with low index and low dispersion, named after the shape worked into the final product in a British process, and (2) flint (lead) glass, with high index and high dispersion, named after the pure British "flint stone" used as a source of SiO_2 in its production.

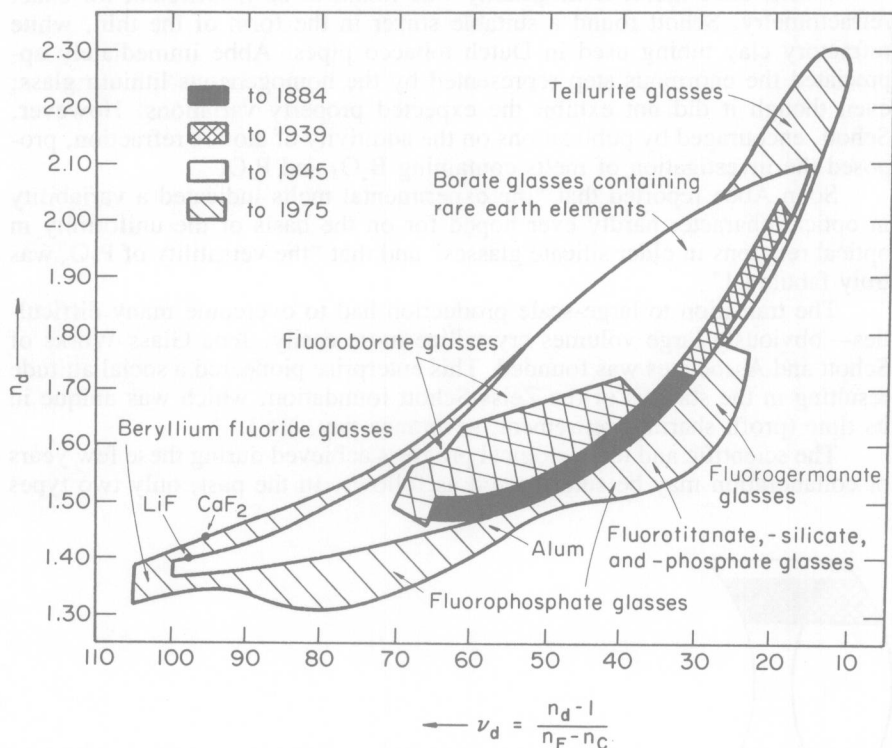


Fig. 1.7. State of development of optical glass, characterizing an optical glass by its location in the $n_d - \nu_d$ diagram, as proposed by Abbe.

The change of refraction with wavelength and the resulting dispersion in prisms and lenses are illustrated in Figs. 1.3 and 1.4. The result is a superposition of blurred images, since the focus changes with wavelength (chromatic aberration, Fig. 1.5).

In the first approximation, the theory allows for correction by joining an inverted flint glass (high index, high dispersion) prism (lens) with a smaller angle to a crown glass (low index, low dispersion) prism (lens). However, the relation of index to wavelength is not the same in crown and flint glass (Fig. 1.6), so that correction may be possible for two spectral ranges only (e.g., red, blue), not for all. A colored rim remains in the image ("secondary spectrum").

The secondary spectrum can be removed only if the partial dispersions of glasses with different indices become identical. Fraunhofer recognized this need, but the few elements considered did not permit him to foresee the solution.

Schott's introduction of B_2O_3 , leading to borosilicate crown glass, solved the problem for microscopes, telescopes, binoculars, and photographic applications. The Abbe microscope conquered a world market serving science and medicine. Quality fabrication was made possible by technological improvements such as Schott's introduction of better refractories, the Siemens regenerative furnace, or the process of casting into preheated molds ("Jena process").

Once Newton's tenet that all glasses exhibit equal, or at best equally rising, dispersion ("law of the iron-clad line") was disproved, the way was open to the rapid development of new types of glass. The new types introduced by Schott were:

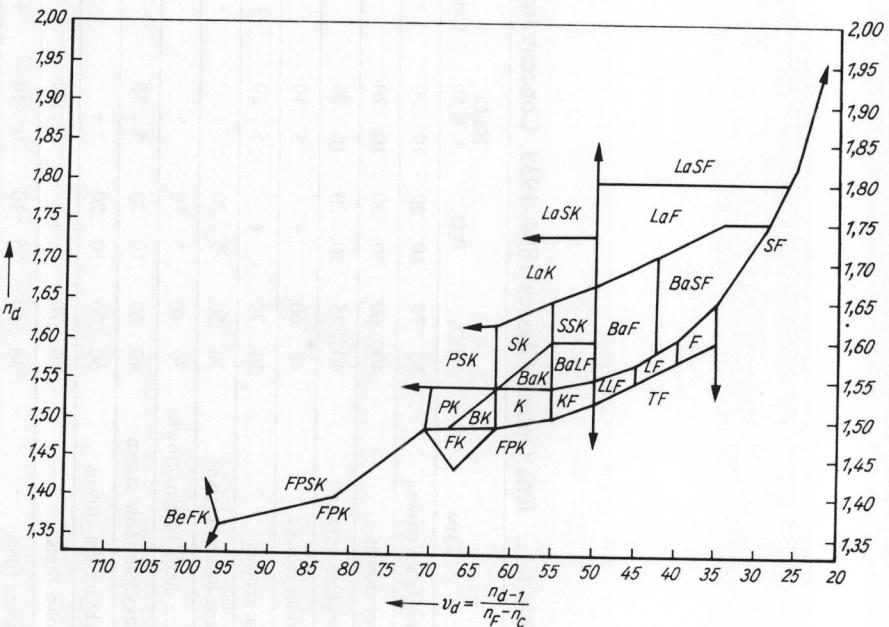


Fig. 1.8. Delineation of various optical glass types in the $n_d - v_d$ diagram.

Table 1.1. Jena Optical Glasses 1884–1939. Concentrations in Mass %

Type	SiO ₂	B ₂ O ₃	Na ₂ O + K ₂ O	CaO	BaO	Al ₂ O ₃	F	ZnO	TiO ₂	PbO	Sb ₂ O ₃
Borosilicate crowns	50...70	10...20	10...20	+	+	+					
Fluor crowns	40...60	10...30	10...20			5...20	5...10				
Phosphate crowns	40...75	10...20	10...20		+	+	+	+			
Barium crowns	40...60	+	5...10		15...30	+		5...15			
Zinc crowns	50...70	+	5...20	+		+		5...25			
Dense barium crowns	30...50	5...20	+	+	30...40	+		+	+		
Extra dense barium crowns	30...40	5...10	+		30...50	+		+		+	
Heavy phosphate crown	40...60	10...20	5...15		20...30	+					
Light barium crowns	60...70	10...20	+		5...15			+			
Crown flints	50...70	+	5...20				+	+	+	5...20	
Barium flints	30...50	5...10	0...10	+	10...40	+		+	+	5...20	

Table 1.2. Basic Kodak Patent "Optical Glass" (G. W. Morey) 1936, Registered as DRP 691 356, Brit. Pat. 462 304, US Pat. 2 206 081, French Pat. 810 442, and Swiss Pat. 206 664 Composition in Mass % (Examples)

Glass Compo- nent	A	C	D	E	F	I	J	K	L	M	P	R	S	T	U	V
B ₂ O ₃		12	10	12.5	14	22.7	22.6	9.8	12.5	16.6	20	33.4	40	26	22	20
La ₂ O ₃		42	51	60	50	26.3	27.2	49.2	60	37.5	36	22.2	60	33	28	28
ThO ₂						20.2	8.5	9.8		16.7	16	22.2		41	14	14
Ta ₂ O ₅	50	28				26.3	27.2	23.0		29.2	28	22.2			28	28
ZrO ₂		6	11	8.5	10			4.9	8.5							
WO ₃			15		14											
TiO ₂	50	12	13	17	12				17							
Li ₂ O															8	10
Na ₂ O				2												
Na ₂ B ₄ O ₇						4.5	4.5	3.3	2.0							
n _d	2.002	2.008	1.893	1.842	1.995	1.805	1.800	1.809	1.848	1.898	1.85	1.7175	1.7227	1.7667	1.8119	1.8037
v _d	19.1	25.2	38.8	35.5	26.6	40.3	38.4	35	32.5	36.9	42	53.5	54.1	51.4	41.2	42.4

Significant Element		Designation		Index	Relative Dispersion
		German*	English†		
B	Borosilicate crown	(BK)	(BSC)	Very low	Very low
F	Fluor crown	(FK)	(FC)	Lowest	Lowest
P	Phosphate crown	(PK, PSK)			Rel. low
Ba	Barium crown	(BaK, SK, SSK, LBaK)	(EDBC, DBC, LBC)	High	Low
Ba, Pb	Barium flint	(BaSF, BaF, BaLF)	(BF)	High	Medium
B, Pb	Short flint	KzF	KzF		Small in blue
Adding to the older types which were extended to comprise:					
CaNa	Crown	K	C	Low	Low
CaPb	Crown flint	KF	CF	Low	Medium
Pb	Flint	LLF, LF, F, SF	ELF, LF, DF, EDF	High	High

* (In German the scale LL, L, S, SS is used to indicate increased index.)

† (In English the scale EL, L, D, ED, is used to indicate increased index.)

A complete list of properties and compositions of optical glasses (Schott, Dsa) is presented in Table 1.1. Corresponding glasses can be found in the catalogs of optical glass companies throughout the world. After Schott's innovations, it was not until 1936 that another major period of progress was initiated, this time in the United States.

This advance is chiefly due to G. Morey, at the Geophysical Laboratory in Washington, who, since 1936, has reported compositions containing small amounts of the glass-former B_2O_3 in combination with the oxides of the rare elements La, Th, Zr, Nb, Ta, W, Mo, etc. In particular, glasses with low concentrations of B_2O_3 and high concentrations of La were found to have much lower dispersion at high indices (Table 1.2). Melting of these glasses necessitated the transition to a technology involving platinum-lined containers and electrical heating. Several other developments extended the list.¹⁻⁵ Patents published between 1936 and 1958 are listed in Tables 1.3 and 1.4. Glass types, including those novel glasses, are mapped in Fig. 1.7, which, for comparison, includes crystalline LiF, CaF_2 , and alum. The names and conventional codes for the new glasses are:

Significant Element	Name	Designation	Index	Dispersion
La	Lanthanum crown	LaK, LaSK, LaC	Very high	Low
La, Pb	Lanthanum flint	LaF, LaSF,	Very high	Medium
F, P	Fluorophosphate crown	FPK, FPSK	Very low	Very low
F/(Be)	(Beryllium) fluoride crown		Lowest	Lowest
F, Ti, P	Fluorotitanophosphate			
F, Ti, Si	Fluorotitanosilicate			

History of the Chemistry of Technical Glass

The history of technical glass, particularly Schott's development of borosilicate compositions, is closely associated with that of optical glass. Schott soon became aware of the fact that B_2O_3 is much more compatible with SiO_2

Table 1.3. Highly Refractive Optical Glasses (Developed after 1939).
Concentrations in Mass %

	n_d	v_d	B ₂ O ₃	La ₂ O ₃	ThO ₂	Ta ₂ O ₅	Nb ₂ O ₅	TiO ₂	MoO ₃
US Pat. 2 150 694 March 14, 1939 G. W. Morey and C. C. Chase Eastman-Kodak Co.	1.70...2.02	19...58	10...40	20...60	10...41	20...45		0...40	
US Pat. 2 206 081 March 2, 1940 L. W. Eberlin Eastman-Kodak Co.	1.70...1.85	35...53	16...33	22...50	16...28	14...27			
US Pat. 2 241 249 March 6, 1941 L. W. Eberlin and P. F. De Paolis Eastman-Kodak Co.	1.70...1.75	45...50	28...37	15...35	5...15	10...20			
US Pat. 2 466 392 March 1, 1945 P. F. De Paolis Eastman-Kodak Co.	1.65...1.68	52.5...57	36	12	12				
US Pat. 2 472 447 March 19, 1946 K. H. Sun Eastman-Kodak Co.	1.9...2.1	16...18	10					12	
US Pat. 2 434 148 March 6, 1948 P. F. De Paolis Eastman-Kodak Co.	1.75...1.80	37...40	20...30	18...25	12...18			Σ 12...18	
FRG Pat. 949 686 March 12, 1951 G. Weissenberg and O. Ungemach Schott-Glaswerk-Mainz	1.60...1.73	51...60	30...96	31...68		0.5...20			
FRG Pat. 1 008 455 March 26, 1953 G. Weissenberg and O. Ungemach Schott-Glaswerk-Mainz	1.77...1.85	34...37	24...27	35...52		0...15	0...30		
FRG Pat. 1 008 456 March 16, 1953 G. Weissenberg and O. Ungemach Schott-Glaswerk-Mainz	1.75...1.80	42...49	27...30	45					
FRG Pat. 1 054 209 March 16, 1957 W. Geffken and M. Faulstich Schott-Glaswerk-Mainz	1.70...1.82	50...56	35...48	33...54	4...28		Σ Nb ₂ O ₅ , Ta ₂ O ₅ , WO ₃		
FRG Pat. 1 061 976 March 19, 1958 E. Leitz, H. Brömer, and N. Meinert Fa. Leitz, Wetzlar	1.66...1.90 (n_e)	38...57 (v_e)	4...42	22...64		Σ 0...15			0...5
FRG Pat. 1 075 807 March 7, 1958 W. Geffken and M. Faulstich Schott-Glaswerk-Mainz	1.70...1.79	46...53	6...36	50...67					
FRG Pat. 1 143 974 March 6, 1960 M. Faulstich Schott-Glaswerk-Mainz	1.90...1.96	30...38	13...20	12...35	15...30	5...25	2...27		

(continued)

WO ₃	ZrO ₂	Li ₂ O	SiO ₂	Al ₂ O ₃	PbO	MgO	CaO	SrO	BaO	ZnO	CdO	Y ₂ O ₃	In ₂ O ₃
5...20		0...50	Σ BaO, SrO, Li ₂ O, Y ₂ O ₃ , WO ₃ , HfO ₂ 0...20										
0...5	0...10												
10...20	Σ Alkaline Earth Oxides 0...15				5...25								
					0...20	0...20		20					
				78									
			0...3	Σ CaO, SrO, BaO, CdO 15...27									
0.5...20	4...18		(SnO ₂ 0.5...5)	13...45	27...60	30...69	(GeO ₂ 0.5...10)	0...68	0...70				
0...5	8...16	Σ 0...5			5...7	Σ 0...15							
0...5	3...12.5	0...1		0...10	0...12.5 0...15								
ZrO ₂ , SnO ₂ 0...12	Σ 0...10			Σ 0...6.5									
0...8	0...13	8...30	0...7.5	0...10	Σ 0...18					0...15	0...15	0...7.5	
		7...37	7...21	Additions of ZrO ₂ , BaO, WO ₃ , Ta ₂ O ₃ , CdO, PbO, ZnO, TiO ₂									
0...8	0...10												