

# Optical and Photonic Glasses

## Lecture 19: New Optical Glasses – Fluorides and Chalcogenides

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# Preparation of fluoride glasses and related problems

In general, the fabrication of halide glasses and, in particular, fluorides, requires special installations.

For example, in the case of  $\text{BeF}_2$  or  $\text{BeF}_2$ -based glasses, there is the problem of *toxicity* and *hygroscopicity*. In the case of other fluoride glasses, like the HMFG, or the lower halide glasses (chlorides and bromides, such as those of zinc), although toxicity is not generally a problem, hygroscopicity, or the possible contamination with oxide and hydrogen species, are problems which require adequate facilities to be prevented.

Therefore, most halide glasses are normally melted in controlled atmosphere glove-boxes, with residual  $\text{H}_2\text{O}/\text{O}_2$  contents not exceeding a few ppm. The glasses are melted and annealed inside the glove-box, or, alternatively, they may be melted in a furnace attached to the bottom of a glove-box, also under a controlled atmosphere and then the melt is raised into the glove-box, where it is cast and annealed. Pt crucibles are normally used, although vitreous carbon or gold are possible alternatives.

For the preparation of optical components such as lenses, prisms or light pipes, the grinding and polishing operations have to be performed with the use of non aqueous liquids such as the organic ones.

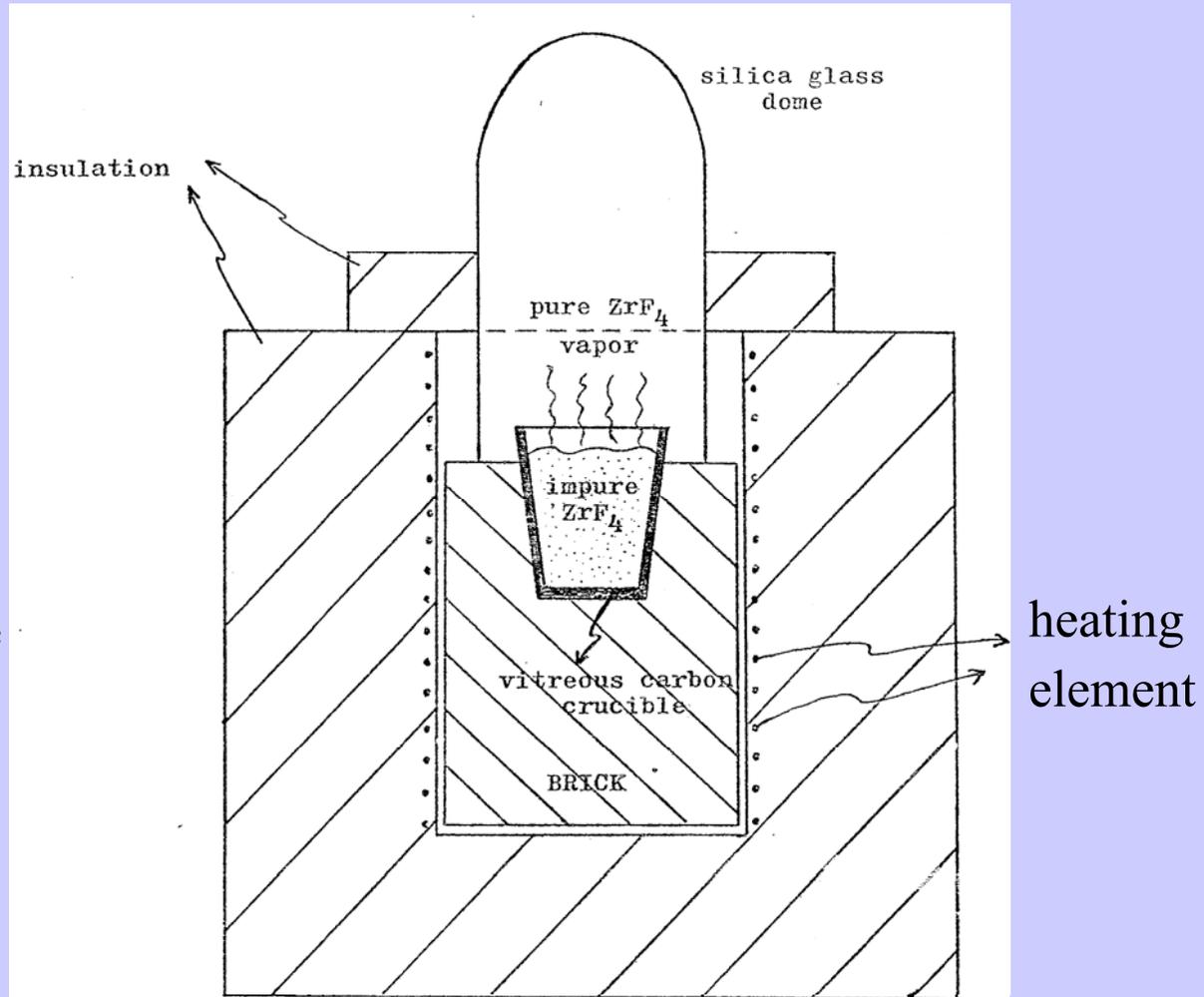
In addition to melted optical glass components, fiberoptic preforms may also be fabricated by melting, e.g. by the rod-in-tube or rotational casting methods (to be discussed later) and HMFG films and waveguides for integrated optics may be deposited by thermal evaporation (physical vapor deposition, or PVD), eventually coupled with ion-exchange techniques for waveguide definition.

Another problem which needs to be taken into account is the purity of the starting raw materials themselves. The major compound utilized in the fabrication of HMFG is, by far,  $\text{ZrF}_4$ . This is often found to be contaminated with OH, oxide and transition metal impurities, which may be strongly deleterious to the final glass quality, e.g. for IR transmission and fiberoptic applications. One way to minimize this is to add a fluorinated compound like  $\text{NH}_4\text{F}\cdot\text{HF}$  to the batch, or to use “Reactive Atmosphere Processing” (RAP), e.g. in the presence of  $\text{CCl}_4$  or  $\text{NF}_3$ , to remove oxide and hydroxide species from the melt.

A particular aspect concerning  $\text{ZrF}_4$  is that, at 1 atm of pressure, rather than melting like most glass-forming compounds, it sublimates at  $\sim 900\text{ }^\circ\text{C}$ , exhibiting an appreciable vapor pressure at temperatures above  $600\text{ }^\circ\text{C}$ . This is a nuisance for the melting procedure, as it tends to lead to excessive  $\text{ZrF}_4$  evaporation losses from the melt, at the usual melting temperatures  $\sim 900\text{ }^\circ\text{C}$ .

## Purification of $\text{ZrF}_4$ by sublimation

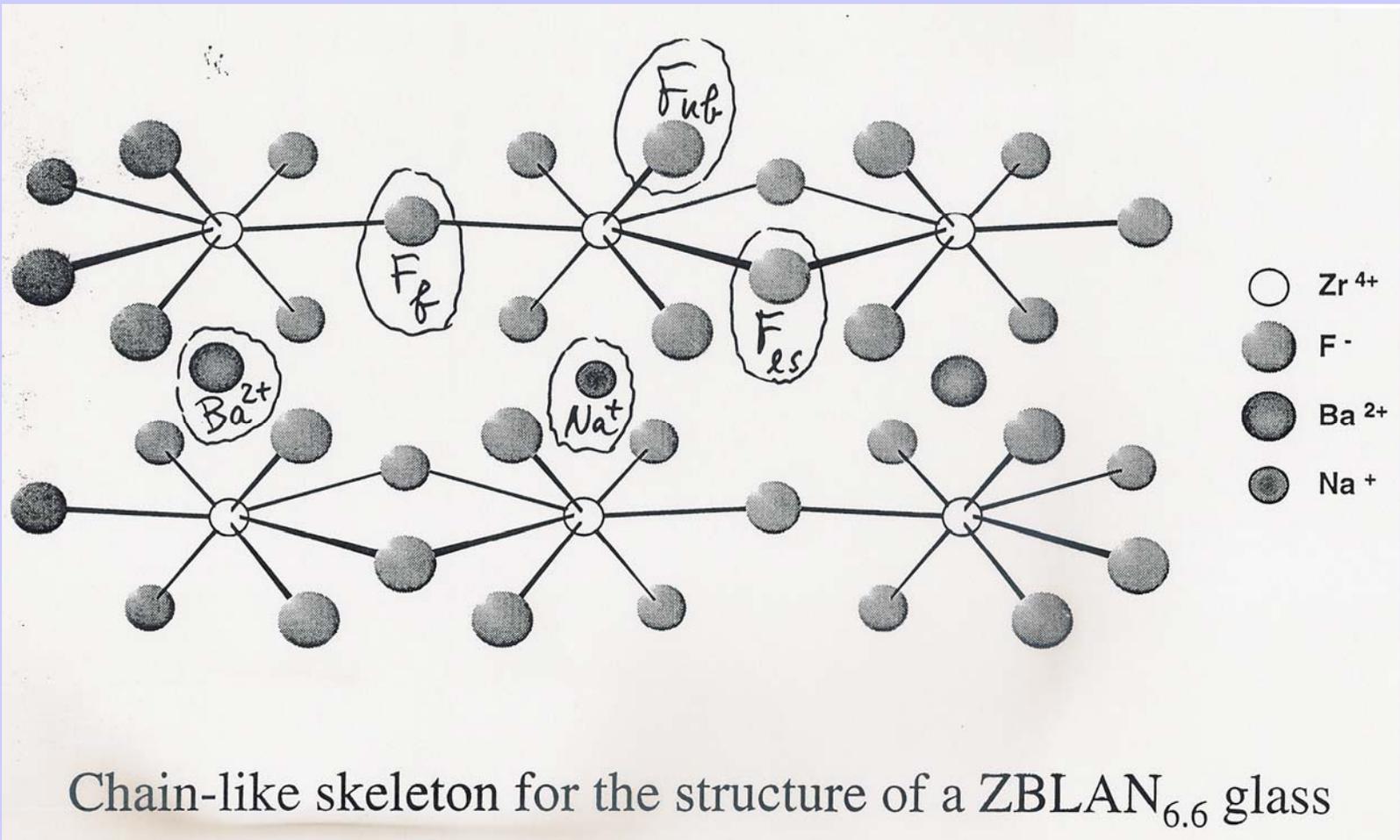
The high vapor pressure of  $\text{ZrF}_4$  provides a rather simple way for a major purification step, by sublimation, of an impure raw material, using simple equipment, since most of the impurities have significantly lower vapor pressures than  $\text{ZrF}_4$  itself.



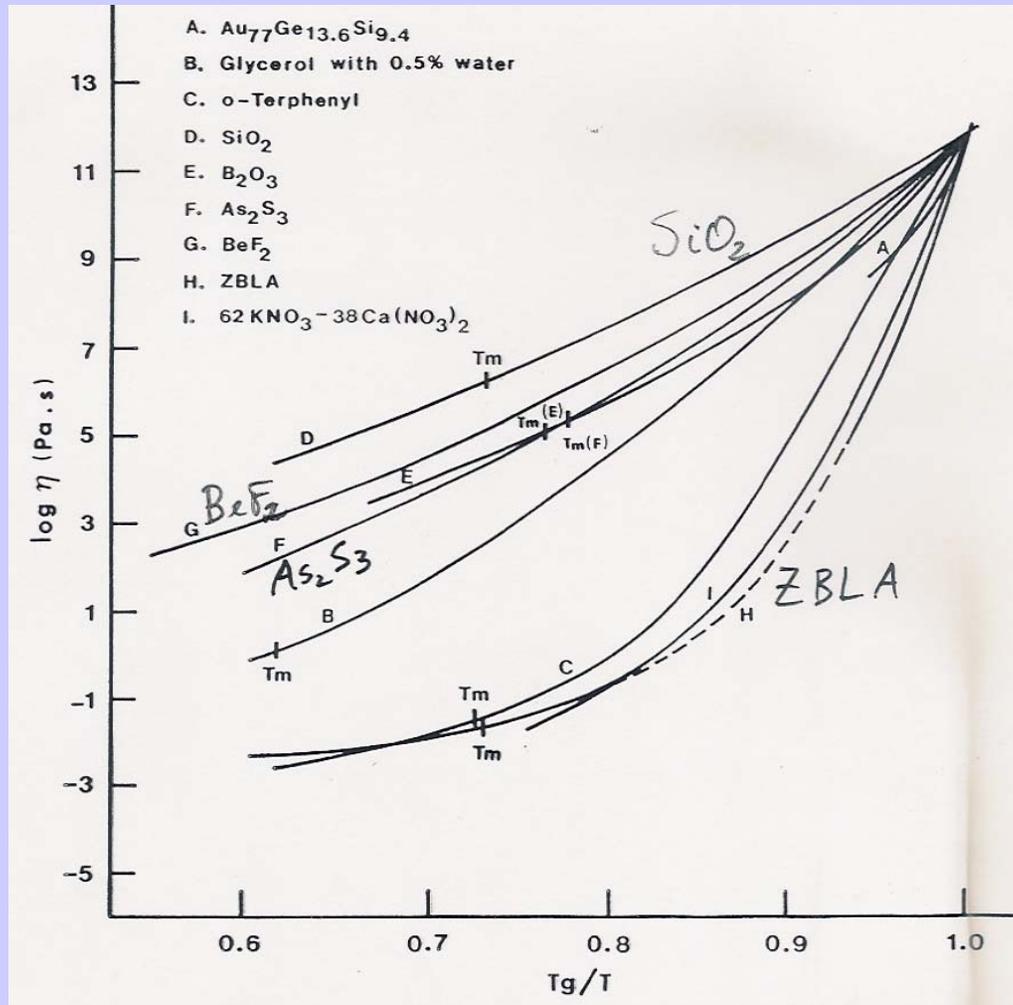
Set-up for the distillation of impure commercial  $\text{ZrF}_4$ . The process is carried out in an electric furnace operating in a dry  $\text{N}_2$  atmosphere.

# Structure of HMFG

Basic chain-like structure of  $ZrF_4$ -based HMFG

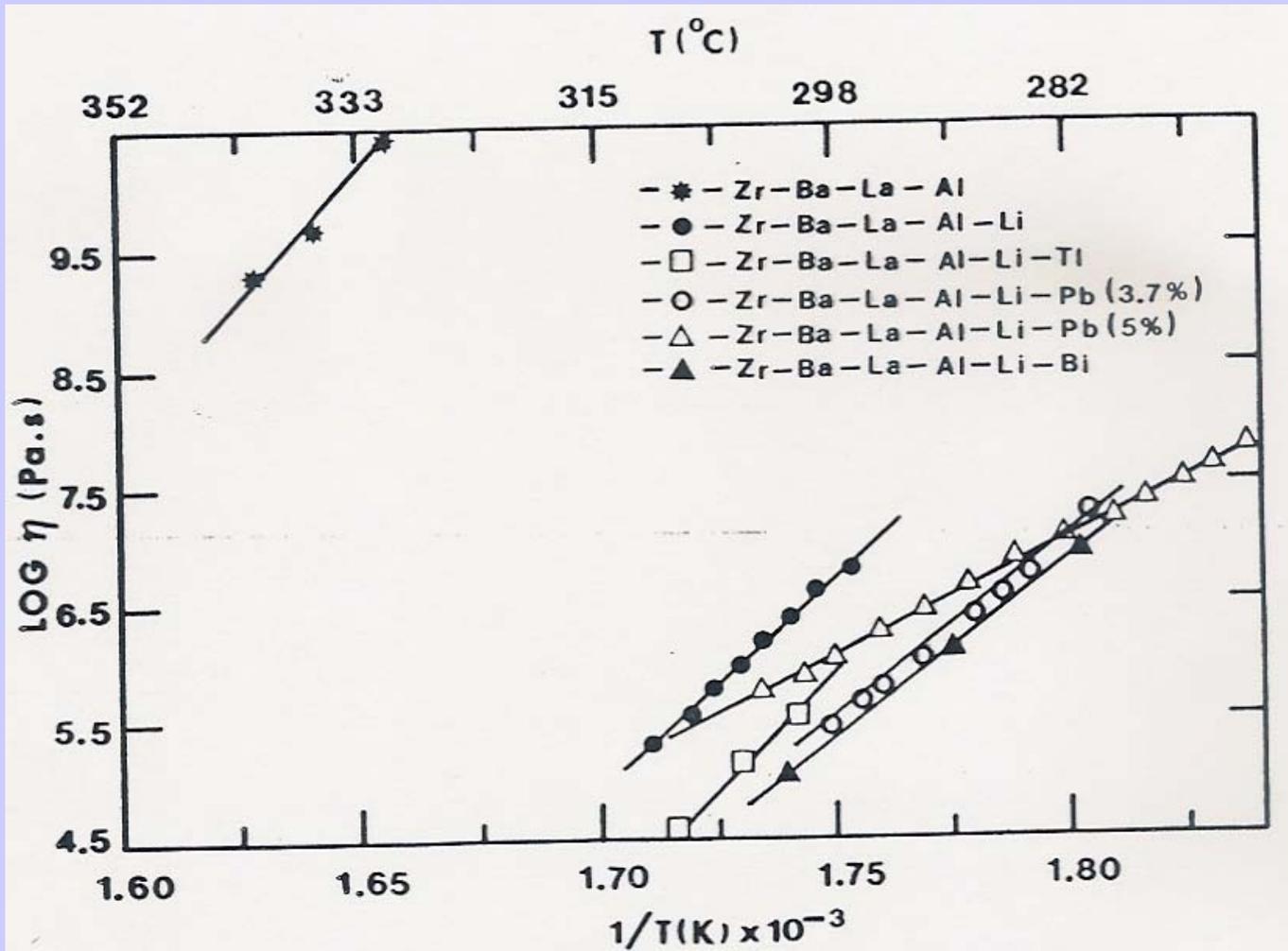


# Arrhenius plots of the **viscosity** of different glass-forming melts



(Adapted from: *J.D. Mackenzie et al., in: Halide Glasses for Infrared Fiberoptics*, ed. R.M. Almeida, Martinus Nijhoff, 1987)

# Viscosities of different HMFG glass-forming melts



(Adapted from: D.C. Tran et al., Mat. Res. Bull. 17(1982)117)

Steep viscosity vs. temperature curves (corresponding to “short glasses”) may lead to crystallization during cooling of the melt. The addition of compounds like  $\text{PbF}_2$  or  $\text{BiF}_3$  decreases the activation energy for viscosity, making the glass “longer” and more stable.

# HMFG properties

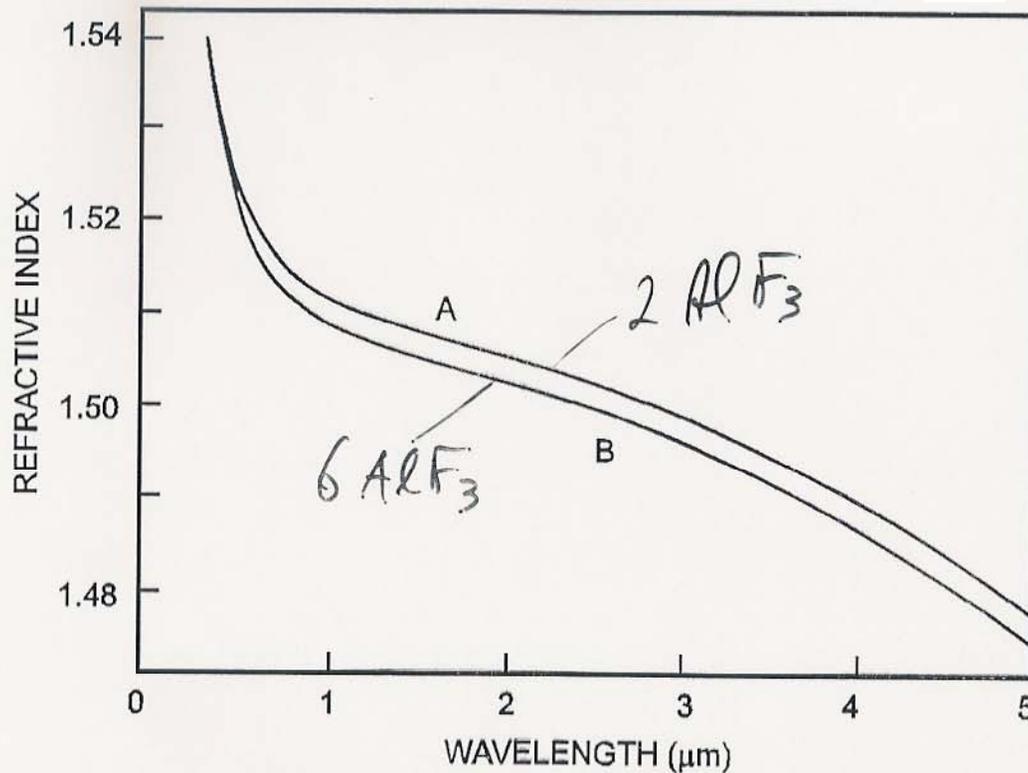
	HBLA	ZBLA	ZBLAN	BZnLuT
<b>MOL %</b>				
ZrF <sub>4</sub>	—	57	55.8	—
HfF <sub>4</sub>	57	—	—	—
BaF <sub>2</sub>	36	36	14.4	19
LaF <sub>3</sub>	3	3	5.8	—
AlF <sub>3</sub>	4	4	3.8	—
NaF	—	—	20.2	—
ZnF <sub>2</sub>	—	—	—	27
LuF <sub>3</sub>	—	—	—	27
ThF <sub>4</sub>	—	—	—	27
<b>DENSITY (gm/cm<sup>3</sup>)</b>	5.88	4.61	~4.52	6.45
<b>T<sub>g</sub> (°C)</b>	325	310	263	353
<b>T<sub>x</sub> (°C)</b>	426	403	~386	429
<b>REFRACTIVE INDEX n<sub>D</sub></b>	1.504	1.521	1.480	1.534
<b>EXPANSION COEFFICIENT (°C<sup>-1</sup>)</b>	173 x 10 <sup>-7</sup>	187 x 10 <sup>-7</sup>	175 x 10 <sup>-7</sup>	151 x 10 <sup>-7</sup>

Fluoride glass compositions and selected properties.

(Adapted from: *M.G. Drexhage, in: Halide Glasses for Infrared Fiberoptics*, ed. R.M. Almeida, Martinus Nijhoff, 1987)

# Dispersion of HMFG

$ZrF_4 - BaF_2 - GdF_3$  glasses



CG { Sulfides ~ 2.3  
Tellurides ~ 3-3.5

Index dispersion in gadolinium fluoroaluminate glasses: A - 2% AlF<sub>3</sub>; B - 6% AlF<sub>3</sub>. (Adapted from MITACHI & MIYASHITA, 1983)

*Appl. Optics* 22 (1983) 2419.

## Fabrication of ChG

During the preparation of chalcogenide glasses, one has to avoid their contamination by O and H elements and care must be taken with the toxicity of elements such as As and Sb.

Because of this and because the ChG batch volumes used are normally much smaller than those encountered in typical oxide glass industrial manufacturing, ChG are usually melted inside sealed v-SiO<sub>2</sub> ampoules of variable sizes. Depending upon the initial purity of commercially available elements like Ge, As, Se or Te, the batch materials may be further purified by distillation before sealing of the ampoule (e.g., As<sub>2</sub>O<sub>3</sub> is more volatile than As<sub>2</sub>S<sub>3</sub>). Melting is normally carried out inside a rocking furnace, to allow efficient melt homogenization and the furnace itself is often encased in a mechanically robust structure, in order to protect the technical personnel involved, since explosions may occur during melting!

Once the glass is melted, it is annealed usually inside the ampoule and it is finally removed from it. Once the glass is formed and as long as it is not ground to a powder, toxicity is not a problem.

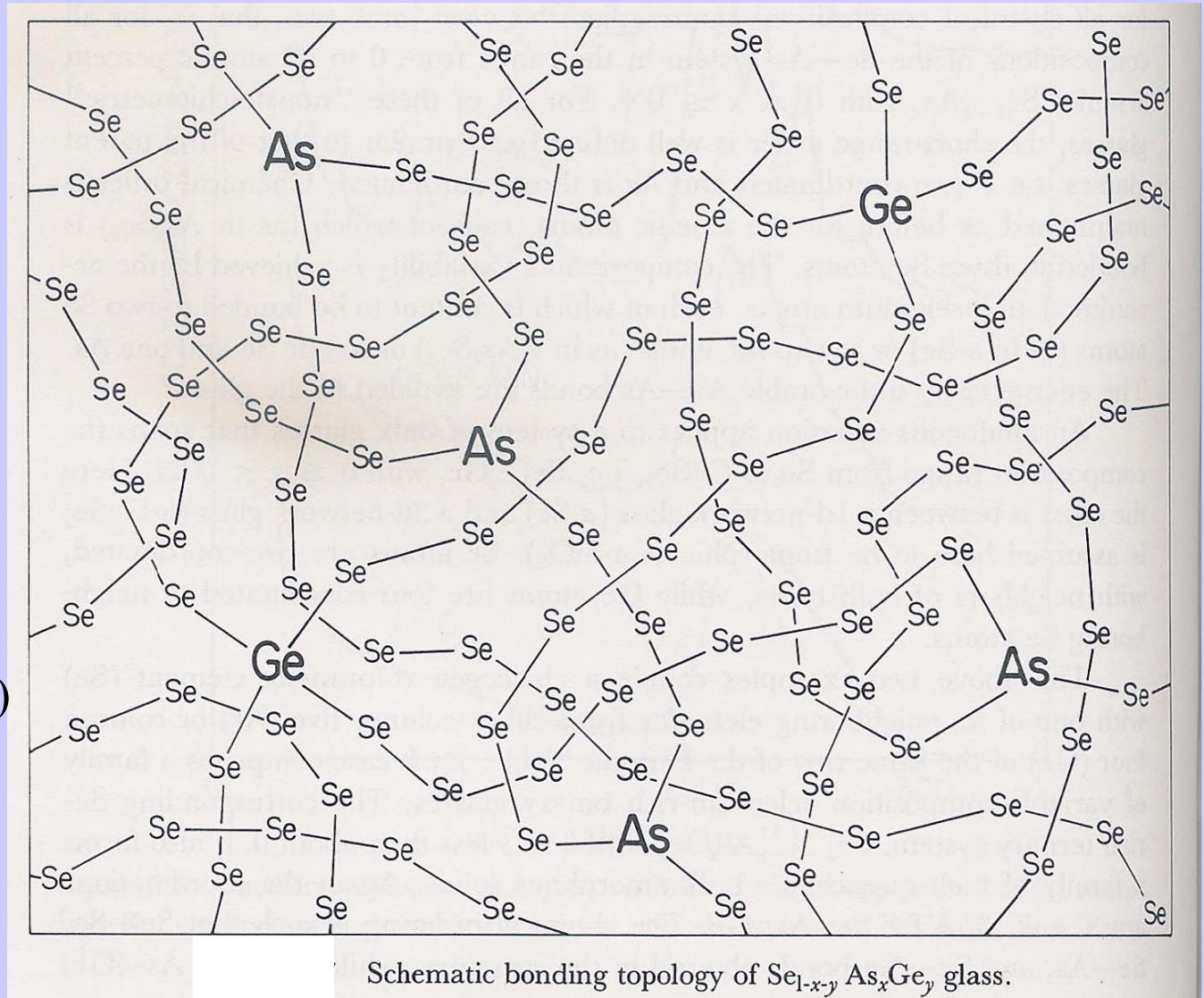
# Typical structure of a ChG in the Ge-As-Se system

v-Se → 1 - D

v-As<sub>2</sub>S<sub>3</sub> → 2 - D

v-GeSe<sub>2</sub> → 3 - D

(As<sub>2</sub>S<sub>2.5</sub> phase separates)



(Adapted from: *The Physics of Amorphous Solids*, R. Zallen, John Wiley, 1983)

## Properties of ChG

### *Thermal properties of Ge–As–S glasses* (Savage 1985)

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Composition	T <sub>g</sub> °C	Thermal expansion coefficient. (×10 <sup>-7</sup> /°C)
As40. S60	165	261
Ge15. As25. S60	—	194
Ge25. As15. S60	425	128
Ge30 As15 S55	400	96
Ge40 As15 S45	—	77

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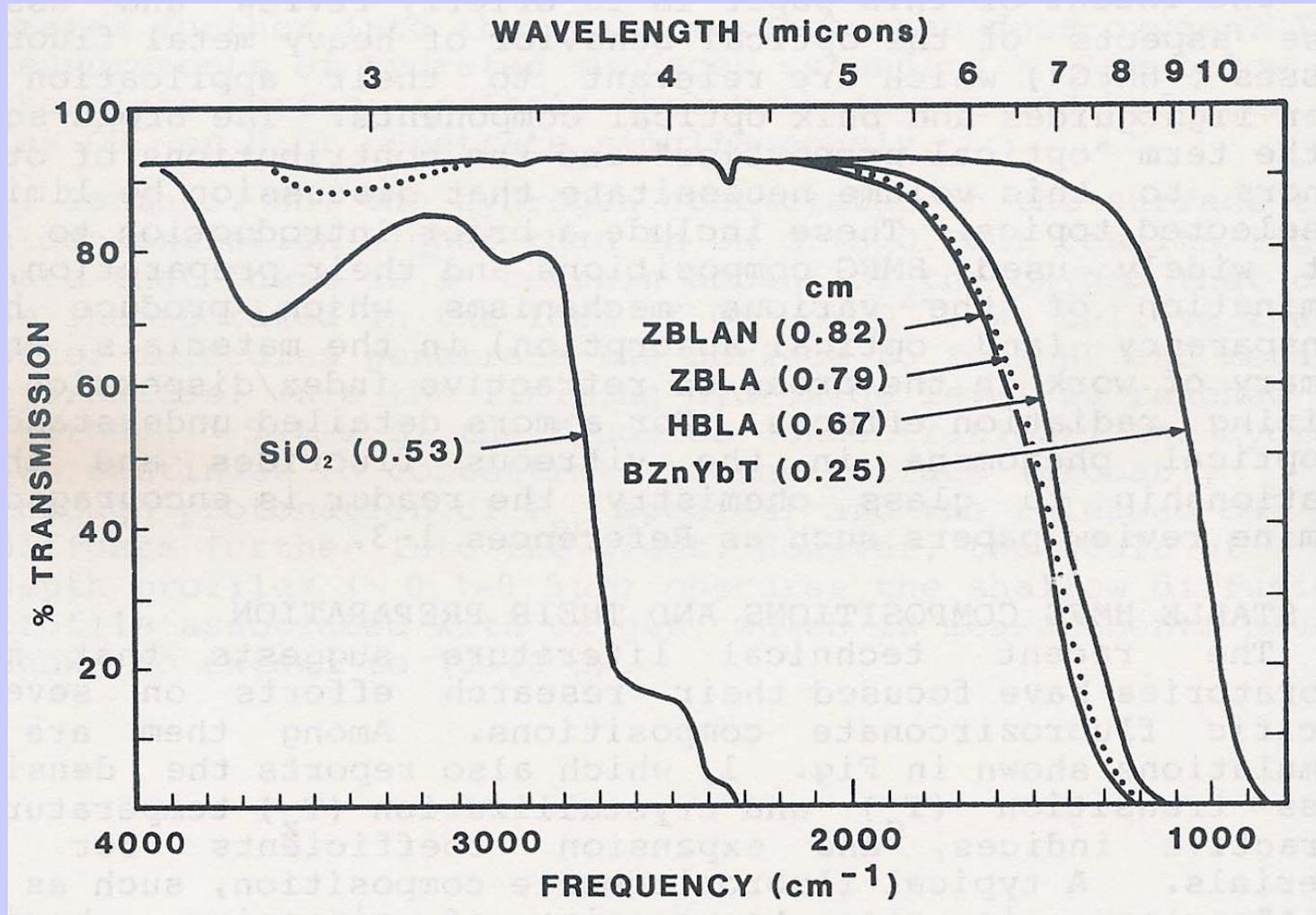
(Adapted from: J.A. Savage, 1985)

THERMAL AND MECHANICAL PROPERTIES OF CHALCOGENIDE GLASSES

Glass Composition Atomic %	T <sub>g</sub> °C	Thermal Expansion Coefficient x 10 <sup>-6</sup> /°C	Density Kg/m <sup>-3</sup> x 10 <sup>3</sup>	Hardness K=Knoop V=Vickers Kg/mm <sup>2</sup>	Thermal Conductivity Cal/cm Sec °K	Rupture Modulus MPa	Young's Modulus GPa	K <sub>Ic</sub> N mm <sup>-3/2</sup>	Viscosity Fulcher Equation 10 <sup>5</sup> - 10 <sup>13</sup> P
As40 S60 type B.	-	26.1	3.15	109 (K)	-	-	-	-	-
Ge15 As25 S60	-	19.4	3.05	159 (K)	-	-	-	-	-
Ge25 As15 S60	425	12.8	3.00	200 (K)	-	-	-	-	-
Ge30 As15 S55	400	9.6	3.17	216 (K)	-	-	-	-	-
Ge40 As15 S45	-	7.7	3.53	276 (K)	-	-	-	-	-
As40 Se60	178	21.0	4.62	-	-	-	-	-	log <sub>10</sub> η = -4.44 + 2764/(T°C - 22.25)
Ge20 Se80	154	24.8	4.37	147 (V)	-	-	-	-	-
Ge10 As20 Se70	159	24.8	4.47	154 (V)	-	-	16.5	6.7 ± 0.4	-
Ge10 As30 Se60	210	19.0	4.51	176 (V)	-	-	18.0	7.1 ± 0.6	-
Ge10 As40 Se50	222	20.9	4.49	173 (V)	-	-	15.9	7.4 ± 0.8	-
Ge20 As10 Se70	209	20.5	4.41	186 (V)	-	-	16.1	-	-
Ge30 As10 Se60	345	13.7	4.36	236 (V)	-	-	18.6	7.7 ± 0.4	-
Ge30 As15 Se55	351	12.8	4.42	245 (V)	-	-	-	-	-
Ge30 As20 Se50	361	11.7	4.47	266 (V)	-	-	21.3	-	-
Ge33 As12 Se55	-	13.0	4.40	170 (K)	0.60	17.2	22.1	-	-
Ge28 Sb12 Se60	277	15.8	4.67	150 (K)	0.72	17.3	21.8	-	log <sub>10</sub> η = -4.97 + 2824/(T°C - 122.41)
Ge30 As13 Se57	342	13.0	4.40	237 (V)	-	-	-	-	log <sub>10</sub> η = -4.71 + 4070/(T°C - 116.13)
Ge30 As13 Se47 Te10	308	13.2	4.56	234 (V)	-	-	-	-	log <sub>10</sub> η = -5.91 + 4627/(T°C - 67.49)
Ge30 As13 Se37 Te20	285	12.9	4.77	228 (V)	-	-	-	-	log <sub>10</sub> η = -9.74 + 6466/(T°C - 5.06)
Ge30 As13 Se27 Te30	262	12.8	4.91	226 (V)	-	-	-	-	log <sub>10</sub> η = -8.19 + 4868/(T°C - 35.52)
Si25 As25 Te50	-	13.0	4.76	167 (K)	-	-	-	-	-
Ge10 As20 Te70	-	18.0	-	111 (K)	-	-	-	-	-
Si15 Ge10 As25 Te50	-	10.0	-	179 (K)	-	-	-	-	-

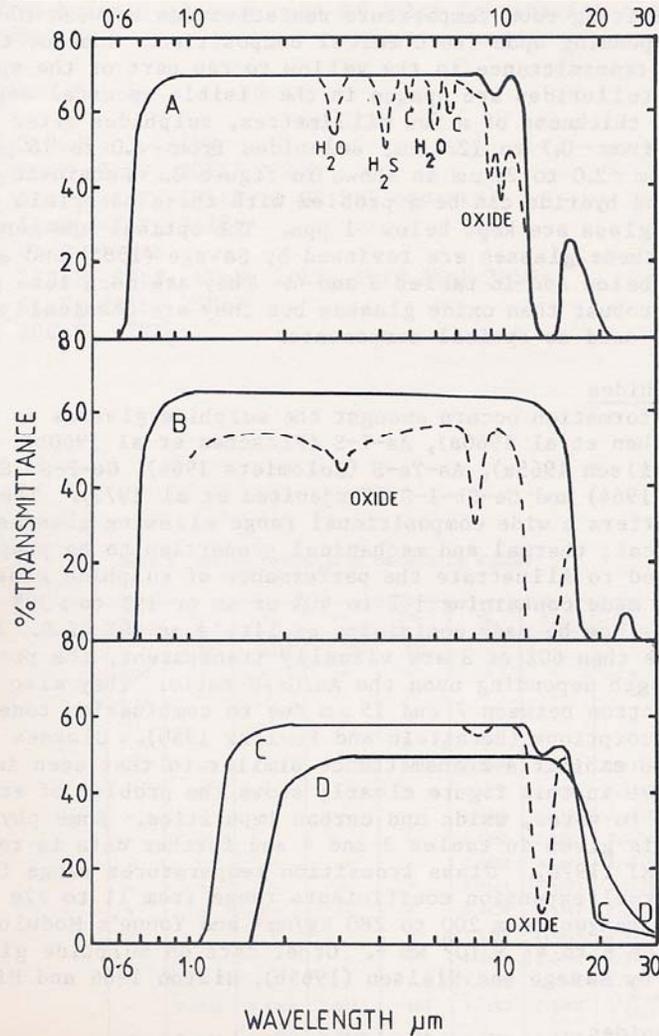
(Adapted from: J. Savage, in: *Halide Glasses for Infrared Fiberoptics*, ed. R.M. Almeida, Martinus Nijhoff, 1987)

# IR transmission of HMFG



(Adapted from: M.G. Drexhage, in: *Halide Glasses for Infrared Fiberoptics*, ed. R.M. Almeida, Martinus Nijhoff, 1987)

# IR transmission of ChG



(Adapted from: J.A. Savage, in: *Halide Glasses for Infrared Fiberoptics*, ed. R.M. Almeida, Martinus Nijhoff, 1987)

A comparison of the transmittance ranges of sulphide, selenide, selenide-telluride and telluride glasses also showing the effects of extrinsic absorption.

A	Ge 30 As 20 S 50	atomic %	1.86 mm thick
B	Ge 34 As 8 Se 58	atomic %	1.80 mm thick
C	Ge 30 As 13 Se 27 Te 30	atomic %	2.3 mm thick
D	Ge 10 As 50 Te 40	atomic %	1.62 mm thick.