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Review
Infra-red transmitting materials
Part 2 *Non-crystalline materials*

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Inorganic glasses suitable for application in the 1 to 6 μm spectral range are reviewed with reference to existing materials and fabrication techniques. Problems associated with water absorption which may limit the useful transmission of many glasses can be minimized by such techniques as vacuum melting. Glasses, in contrast to crystalline materials, usually offer good prospects for the relatively easy fabrication of homogeneous complex shapes.

1. Introduction

This survey of non-crystalline infra-red transmitting materials, in conjunction with Part 1 on crystalline materials [1], forms a comprehensive review of the present "state-of-the-art", and in addition attempts to formulate a guide for the prediction of infra-red transmission in general. The survey commences with a brief outline of the theoretical considerations appropriate to non-crystalline materials, is followed by a résumé of existing materials, and concludes with a concise consideration of the relationships between infra-red transmission and mechanical properties.

2. Theoretical considerations

A glass may be defined as a non-crystalline material, usually produced by cooling a melt, which may exhibit some short-range order on the atomic scale, but which lacks long-range periodicity. Various materials may be produced in bulk form as glasses, of which the most common are based on oxides, the other chalcogenides S, Se or Te, and certain halides. Glasses may exist in the form of three-dimensional atomic networks, as in the oxide glasses, or as two-dimensional layer structures linked by weak Van der Waal's forces or by direct cross-linking, as in many of the chalcogenides. One of the major advantages associated with glasses is the relative ease with which large complex shapes can be produced by standard glass-forming techniques, free from large-scale structural discontinuities such as grain boundaries. However, difficulties may be experienced due to volatility of components, contamination from the crucible etc., and these factors are considered later.

In addition to the general theoretical aspects, outlined in Part 1, the interpretation of the infra-red spectra of amorphous materials is further complicated by the fact that no long-range structural order exists. As a first approximation it is general to relate the observed spectra to that assumed for an isolated structural unit determined theoretically. However, not only is the basic structural unit linked to the rest of the structure, and hence not "isolated" (as in the analogous crystalline state), but also it is not an unambiguous unit and may vary locally both in shape and size. Hence, the concept of an "average" or most-probable structural unit (related to the crystalline state) must be introduced, and this is usually fairly satisfactory, although band-broadening, relative to the crystalline state, must generally be expected.

For instance, Chen and Su [2] calculated the vibrational frequencies of the normal modes of the average structural units for vitreous GeO_2 using the Wilson FG matrix technique and a group theoretical model. The average structural unit was established by comparing the calculated virbational frequencies with the experimentally determined values, and was in fact found to resemble that of the crystalline material.

Onomichi *et al.* [3] executed a Kramers–Krönig

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analysis of reflectivity data from As_2S_3 and As_2Se_3 glasses and noted that one reststrahlen band should be observed for each material, assignable to As–S and As–Se stretching modes respectively. This was found to be the case experimentally, although weaker bands were also observed which were assigned to overtones.

Lucovsky and Martin [4] also indicated that agreement between experimental results and theoretical predictions using a molecular sub-unit for the vibrational frequencies of chalcogenide glasses of the type As_2X_3 was excellent. The sub-unit was taken as AsX_3 linked by bridging X atoms, and the intermolecular coupling was assumed weak. Application of the model to elemental chalcogenide glasses is not feasible, however, because these contain two structural components in the form of ring molecules and polymeric chains. Similarly, the model is not applicable to amorphous Si or Ge, nor to III–V compounds which possess four-fold coordination at each atomic site so that it is not possible to identify a molecular unit.

Finally however, Borelli [5] determined the infra-red spectra of vitreous SiO_2–GeO_2 and concluded that since a simple superposition of the individual spectra of vitreous SiO_2 and vitreous GeO_2 was not obtained, the structure of the binary must be interconnected. Hence, the characteristic absorption regions as determined by the crystalline coordination may not always be representative of the amorphous state, and predictions must be treated with caution.

3. Materials

3.1. Oxide glasses

Bulk glasses have been prepared based on a wide variety of oxide glass-formers, including B_2O_3, P_2O_5, SiO_2, (TiO_2), V_2O_5, MoO_3, GeO_2, SeO_2, Ga_2O_3, As_2O_3, WO_3, TeO_2, In_2O_3, Sb_2O_3, La_2O_3, Bi_2O_3 as well as the binary system CaO–Al_2O_3.

Glasses based on B_2O_3 and P_2O_5 exhibit very limited infra-red transmission due to the high vibrational frequencies associated with the B–O and P–O bonds, and these glasses are not considered further.

3.1.1. Glasses based on SiO_2

The transmission of silicate glasses is generally limited to $\lesssim 4.5\,\mu m$ due to the first overtone of the fundamental Si–O vibration. Significant absorption bands may also be obtained at shorter wavelengths due to the presence of OH^-, or due directly to certain additives to the silica network.

For instance, Stair *et al.* [6] noted that additions of certain rare earth or transition metal oxides to soda-lime glass could produce prominent absorption bands, although others produced little or no change in the transmission. Hence, small additions of Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Gd_2O_3, Er_2O_3, V_2O_5, CoO and NiO all gave rise to strong absorption bands, whilst Y_2O_3, Cr_2O_3 and MnO_2 gave little change in the transmission.

The OH^- band is very prominent in silicate glasses produced from standard materials melted and cast in air, although certain compositions are more prone to hydroxyl absorption than others. Hence, Florence *et al.* [7] observed that for glasses of the type R_2O–MO–SiO_2, where R = Li or Na, and M = Be, Mg, Ca, Sr or Ba, the intensity of the OH^- absorption band decreased marginally with increasing molecular weight of the alkaline earth, M. It was also noted that better transmission was obtained when nitrates rather than carbonates or hydrated materials were used in the batch.

Compositions based on SiO_2–TiO_2–BaO are less prone to hydroxyl absorption than silicate glasses containing alkali oxides, and Cleek *et al.* [8] noted that glasses formed from this ternary were colourless up to about 15 mol% TiO_2. Various additions, including La_2O_3, PbO, ThO_2, ZrO_2, Ta_2O_5, Cd_2O_5, and WO_3 could be included to improve the chemical resistance of the material, and provide glasses of low hygroscopicity [9].

Certain non-oxide additives have also been found useful in reducing or eliminating the OH^- absorption band. For instance, Cleek *et al.* [10] noted that fluoride additives made to certain glasses of the type SiO_2–TiO_2–BaO, SiO_2–La_2O_3–BaO, and SiO_2–Ta_2O_5–La_2O_3–BaO by substituting BaF_2 or AlF_3 for BaO and SiO_2, effectively removed the hydroxyl band completely. Dumbough [11] also noted that glasses in the system CaO–Al_2O_3–SiO_2 could be produced free from the OH^- band by mixing the batch with a reactive fluorine-containing agent, and fusing at 1500 to 1650° C in a flowing dry atmosphere.

3.1.2. Glasses based on GeO_2

The long-wavelength cut-off of germanate glasses is greater than that of the silicates, but the effect of hydroxyl absorption may still be very prominent. However, this can be minimized by methods appropriate to silicate systems including halide additions to the batch, or by melting and casting in vacuum or in a flowing dry atmosphere.

For instance, Cleek *et al.* [12] studied glasses in the system $BaO-TiO_2-GeO_2$ with additions of BaF_2 which effectively removed the OH^- band. The best materials transmitted adequately to about 5.7 μm with the total cut off >6 μm. Florence *et al.* [13] prepared glasses in the system GeO_2-PbO by melting in dry air and noted that additions of BaO or BeO gave better transmission >3.6 μm but reduced transmission <3.6 μm.

An extensive investigation of germanate glasses was carried out by Colborn *et al.* [14] who noted that although hydroxyl bands were observed in the spectra of the materials, they could be minimized by melting the batch in flowing argon. Their investigation was designed to consider the feasibility of producing dual-mode domes which could operate at both radar and infra-red frequencies simultaneously, and they studied systematically the effect of various oxide additions on the physical properties and infra-red transmission of the resultant glasses. General trends predicted by theory, such as increase in thermal expansion with additions of higher expansion oxides were observed.

Water-free germanate glasses in the system $CaO-Al_2O_3-GeO_2$ have been prepared by Dumbaugh [15] by mixing the batch with anhydrous $CaCl_2$ and melting in a dry atmosphere; the resultant glasses transmitted well to about 5.2 μm.

It has also been observed that the fundamental Ge–O absorption can be shifted to higher frequencies either by inducing the GeO_2 to switch from four-fold to six-fold coordination so that the structure contains GeO_6 octahedra substituted for GeO_4 tetrahedra, or by "depolymerizing" the network so that the GeO_4 tetrahedra become isolated. Obviously both of these techniques are limited by the need to maintain a glassy structure.

Hence, Murthy *et al.* [16] observed that the main Ge–O absorption band centred at 875 cm^{-1} for pure GeO_2 glass was shifted to longer wavelengths with increasing alkali content for R_2O-GeO_2 glasses, and this was attributed to a change of coordination. Murthy *et al.* [17–19] also investigated glasses in the system $R_2O-X_2O_3-GeO_2$, where X is Al, Ga or In. It was noted that glass formation in the $X = Al$ system was restricted to compositions in which the R:Al ratio was $\geqslant 1$, and hence the glass-forming region did not extend beyond the $R_2O \cdot Al_2O_3-GeO_2$ boundary. When the ratio is <1 glasses do not form because AlO_6 groups cannot be accommodated in a glassy structure due to the presence of GeO_6 groups. Glass formation in the $X = Ga$ system was found to extend beyond the $R_2O \cdot Ga_2O_3-GeO_2$ composition line, and the glass-forming region also increased with increasing molecular weight of R_2O. However, the glass-forming regions were found to be less extensive in the $R_2O-In_2O_3-GeO_2$ system due to the restrictive coordination requirements of the larger In ion. The effect of Tl^+ and Ag^+ additions on alumino-germanate glasses has been investigated by Riebling [20] who noted that $\geqslant 9\%$ Ag_2O shifted the main absorption from 875 to 780 cm^{-1}, whereas a minimum of 20% Tl_2O or 26% K_2O was required to produce a similar effect, and this was attributed to modification of the polyhedral network via substitution of non-bridging oxygens for bridging oxygens.

Riebling [21] also found that addition of 40 mol% Bi_2O_3 to a GeO_2 glass can completely depolymerize the random three-dimensional network and shift the main absorption from 878 cm^{-1} to as low as 675 cm^{-1}. The effect of additions of CaO and PbO to $GeO_2-Bi_2O_3$ glasses has also been investigated by Riebling [22], and the absorption was found to be shifted due to the formation of isolated GeO_4 tetrahedra. Small crystals were observed to precipitate in certain compositions but this could be suppressed by the addition of Al_2O_3, although excess Al_2O_3 caused the precipitation of $Ca_3Al_2Ge_3O_{12}$ garnet crystals. The glasses were prepared in air, and up to 6 wt% loss was observed due to the volatility of CaO and Bi_2O_3, but compositions could be adjusted to take this loss into account.

It has been noted by Topping *et al.* [23] that Bi_2O_3 can be reduced to metallic Bi when melting $Bi_2O_3-SiO_2-GeO_2$ glasses in air, and this may subsequently attack platinum crucibles. Melting in an oxygen-rich atmosphere did not alleviate this problem, but use of a silica crucible was found to be satisfactory.

Crystals of $PbGe_2O_5$ have been found to precipitate in a 45% $PbO-GeO_2$ glass but other compositions were crystal-free [24] and exhibited useful transmission to 6 μm. Transparent glass-ceramics have been produced by Hasegawa *et al.* [25] by crystallization of GeO_2 glasses containing 58 to

65 mol% PbO to yield a crystalline phase of ferroelectric $Pb_5Ge_3O_{11}$.

More refractory and abrasion-resistant germanate glasses have been produced based on La_2O_3–Al_2O_3–GeO_2. However, Dumbaugh [26] noted that these glasses are difficult to work due to their high liquidus temperature (1300 to 1600° C), although additions of Ta_2O_5 or ZnO improved the stability of the glasses in addition to lowering the liquidus temperature to between 1196 and 1290° C; the resultant glasses exhibited useful transmission to about 5.3 μm, coupled with relatively low thermal expansion. Dumbaugh [27] also noted that the transmission range is further increased by additional substitution of Ta_2O_5 and ZnO for Al_2O_3, and the best compositions exhibited 59% transmission at 5.5 μm.

Finally however, a limitation of the germanates may be their water solubility – it has been reported that vitreous GeO_2 powder is very soluble in water (10 $g l^{-1}$ in "cold" water) [28].

3.1.3. Glasses based on Ga_2O_3–SrO

Glasses containing a minimum of 50% of Ga_2O_3–SrO, together with other oxides including those of Pb, Li, Na, K, Ca, Mg, Cu, Zn, Cd, La, Ti, Zr, Th, Ge, Ta, As or Sb, have been prepared by Burton and Reid [29]. The glasses exhibited good transmission to beyond 6 μm in addition to moderate softening points $\geqslant 650°$ C. The most promising composition, based on Ga_2O_3–SrO–PbO, gave 35% transmission at 6.5 μm. All these glasses exhibited an OH^- band at 2.7 μm, but addition of a fluoride to the batch was effective in its removal, although it was considered preferable to melt in vacuum.

However, despite the apparently promising nature of these glasses, no further work has been carried out on similar compositions [30].

3.1.4. Glasses based on TeO_2

Various glass compositions based on TeO_2 have been reported to yield stable materials. For instance, Ulrich [31] investigated glasses in the system TeO_2–Bi_2O_3, and observed that materials containing 75 or 90 wt% TeO_2 formed stable glasses, whilst compositions $\leqslant 65 > 90$ wt% TeO_2 crystallized on cooling. The glasses were prepared in 100 g batches at 900° C and cast slabs were annealed at 250° C. All the glasses were opaque to the visible but transmitted well in the infra-red up to 6.3 μm, although an absorption band was observed at 3.5 μm which reduced transmission from 80% to about 65%, and this was attributed to the presence of water. It was noted that the glasses crystallized on heating to 550° C and became opaque to the infra-red.

The boundaries of glass formation of various tellurite glasses were established by Yakhkind [32], who noted that stable glasses were formed in the binary systems TeO_2–(Li_2O, Na_2O, K_2O, BeO, CaO, WO_3, Ta_2O_5, Tl_2O, Sb_2O_3 and V_2O_5), and in the ternary systems TeO_2–WO_3–(Ta_2O_5, BaO, Tl_2O). The glasses were prepared in 200 g batches in gold crucibles at 700 to 1000° C, and transmitted adequately to about 5.5 μm, although hydroxyl bands were observed. Apparently platinum crucibles are not suitable for melting TeO_2-containing glasses due to the reduction of TeO_2 to metallic Te, and its subsequent reaction with Pt.

The system TeO_2–ZnO has been studied by Redman *et al.* [33] in the range 20 to 40 mol% ZnO, and the glasses obtained transmitted well to about 5.5 μm, although water absorption bands were evident at 3.35 and 4.5 μm.

3.1.5. Glasses based on Sb_2O_3

Glass-forming compositions in the system R_2O–Al_2O_3–Sb_2O_3 were determined by Hedden *et al.* [34]. Subsequently, in a later investigation [35], they found an improved composition, 63 wt% Sb_2O_3–15 wt% Al_2O_3, with additions of Na_2O, K_2O, PbO, As_2O_3 and Fe_2O_3 and noted that the addition of PbO imparted good moisture resistance to the glass. The glass transmitted adequately to 5.4 μm, with 10% transmission up to 6 μm. Domes 152 mm diameter were easily fabricated in the glass, but they were apparently opaque to the visible.

3.1.6. Glasses based on Bi_2O_3

Glass formation in bismuthate systems has been reported despite the fact that Bi_2O_3 is not normally regarded as a network-former, and the glasses transmit reasonably well to relatively high wavelengths.

For instance, Rao [36] prepared glasses in the systems Bi_2O_3–CdO–(B_2O_3, SiO_2 or GeO_2), and stable glasses could be produced with low concentrations of the normal network-former. It was suggested that, B_2O_3, SiO_2 or GeO_2 act as *network-modifiers* in this instance, and produce a distorting influence on Bi^{3+} and Cd^{2+} ions, there-by holding the material in a vitreous condition.

Dumbaugh [37] has reported stable glasses in the system Bi_2O_3–PbO–(BaO, ZnO, Tl_2O), and in this instance there is a complete absence of conventional glass-formers. Similarly, Berleue and Dumbaugh [38] have reported the stabilization of lead and cadmium bismuthate glasses with Fe_2O_3. Depending on the composition employed the glasses transmitted to about 7 μm; however, they exhibited relatively low softening points in the range 360 to 630° C and were observed to crystallize if heated below the softening point.

3.1.7. Glasses based on CaO–Al_2O_3

Although neither CaO nor Al_2O_3 are network-formers, a narrow composition range centred around $12\,CaO \cdot 7\,Al_2O_3$ has been found to form fairly stable glasses. An early comprehensive investigation was reported by Kreidl *et al.* [39], who studied the effect of numerous oxide additions on the stability of calcium aluminate glasses. All these glasses were found to be difficult to prepare without some devitrification, particularly if formed in large batch size, and all exhibited a strong water absorption band at 3 μm. However, it was noted that MgO, SrO, ZnO and BaO were useful additions to the base composition, whilst Fe_2O_3 could be directly substituted for Al_2O_3 in small amounts up to about 15 mol%, and produced relatively stable glasses, although transmission was slightly reduced. It has also been observed [40] that small additions of Cu_2O to Fe_2O_3-containing glasses may improve the transmission.

Florence *et al.* [13] investigated the effect of additions to CaO–Al_2O_3–SiO_2 glasses based near the low silica eutectic composition, and noted that substitution of BeO for SiO_2 produced more stable glasses but also lowered the transmission. It was found that glasses in the system CaO–Al_2O–BaO–BeO–PbO were easy to produce devitrification-free, and transmitted usefully to about 5 μm, although a water absorption band was evident.

Dumbaugh [11] has also prepared stable CaO–Al_2O_3–SiO_2 glasses, and stable glasses based on CaO–Al_2O_3–GeO_2 have been studied by Dumbaugh [15] and by Florence *et al.* [13].

3.1.8. Miscellaneous glasses

Various other glasses have been reported based on complex systems composed of several network-formers, or on other systems not normally regarded as glass-formers.

For instance, King *et al.* [41] prepared glasses in the systems PbO–Bi_2O_3–WO_3–In_2O_3, RO or R_2O_3–Bi_2O_3–TiO_2, Cs_2O–CuO–Bi_2O_3–TiO_2, as well as the binaries K_2O–Sb_2O_3 and K_2O–In_2O_3. However, the transmittance of all the resultant glasses was fairly low (<40%) in the wavelength range of interest.

Bromer *et al.* [42] successfully prepared glasses from 63 to 98 wt% of at least two members selected from WO_3, MoO_3, Bi_2O_3, As_2O_3, plus other oxide additions including Sb_2O_3, ZrO_2, ThO_2, MgO, PbO, Ta_2O_5, TeO_2 and fluoride additions including MgF_2, PbF_2 and BaF_2. Water absorption at 3 μm could be removed by moistening the batch with a halogen-containing organic liquid, such as CCl_4. The best glass was prepared in the system As_2O_3–PbO–Bi_2O_3 and transmitted adequately to 6 μm.

Glass-formation in the system PbO–CdO–Fe_2O_3–Tl_2O has been studied by Dumbaugh [43] who noted that stable glasses could be produced despite the fact that a conventional glass-forming oxide was not present. Although transmission was only about 30%, this extended to approximately 8.5 μm. The glasses exhibited relatively low softening points in the range 560 to 640° C, and crystallized at 310 to 405° C.

The system $(K\text{ or }Cs)_2O$–$(Nb\text{ or }Ta)_2O_5$–Al_2O_3 has been studied by Kokubo *et al.* [44], but these glasses were hygroscopic. Substitution of Li or Na for K or Cs reduced the glass-forming ability, whilst materials containing Ba or Pb oxides could not be produced as glasses.

Stable glasses corresponding to the molecular compositions R_2TiO_3 and $R_2Ti_2O_5$ have been prepared in the R_2O–TiO_2 system by Rao [45]. The glasses were made in small 1 to 5 g batches by quenching, and could be heat-treated to form opal-like glasses. Strong absorption centred around 7.1 μm, and weak sharp bands at 9.4 and 11.4 μm were exhibited which White [46] attributed to the presence of carbonate impurity. The mechanical and physical properties of many of the glasses just reviewed are summarized in Table I.

3.2. Non-oxide glasses

Glasses based on the other chalcogenides S, Se or Te have been extensively reported in the literature [47]. In general, these materials are difficult to prepare in bulk form completely free from oxide-

TABLE I Properties of selected glasses

Glass	Transmission 50% cut-off (μm)	Sample thickness (mm)	E (GN m^{-2})	Knoop hardness (kg mm^{-2})	MOR (MN m^{-2})	T_s (° C)	α (10^{-6} ° C^{-1})	Density (g cm^{-3})	n	Comments and references
Based on SiO_2										
Fused SiO_2	4.2 3.5	1 10	71.72	640	55.2	1670	0.54	2.2	1.458	
SiO_2–BaO	4.5	2.01								[13]
SiO_2–PbO	4.5	2.0								[13] Strong water absorption band – reduced by vacuum melting
SiO_2–BaO–TiO_2	4.5	2.0				767–791	9–10			[8]
SiO_2–Al_2O_3CaO	4.6	2.0		658		981	5.95 (25–300° C) 7.2 (25–700° C)	2.798	1.613 at 0.4861 μm	[11] $CaCl_2$ additive and flowing dry atmosphere – no water band observed
SiO_2–BaO–TiO_2–La_2O_3	4.6	2.0				>800			1.914	[9]
SiO_2–BaO–La_2O_3–BaF_2	4.5	2.0				735–780	9–10			[10]
SiO_2–Al_2O_3–ZnO–CaO–ZrO_2	4.8	1.0			180					[63] Transparent glass-ceramic ~ 25% crystalline
Based on GeO_2										
GeO_2–PbO	5.5	2.07							1.91	[13] water absorption removed by dry-air treatment
GeO_2–MgO–ZnO	5.3	1.83					6.67 (20–300° C)		1.717	[14] Moderate water absorption band
GeO_2–PbO–Ga_2O_3	5.5	2.0				506			1.81	[29]
GeO_2–Al_2O_3–CaO	5.2	2.0		560		758 (Tann)	6.36 (250–300° C)	3.354	1.660 at 0.5893 μm	[15] CaF_2 additive and flowing dry atmosphere – no water absorption
GeO_2–BaO–TiO_2–ZnO	5.7 4.3	2.04 8.02				725	9.3 (100–600° C)		1.883 at 0.4861 μm	[12] Strong water absorption band
GeO_2–BaO–TiO_2–ZnO–BaF_2	5.5 4.9	2.03 8.04	93.88			700	10.0 (100–600° C)		1.875 at 0.4861 μm	[12] Minor water absorption band
GeO_2–BaO–TiO_2–La_2O_3	5.3	2.0							1.976	[9] Moderate water absorption band
GeO_2–La_2O_3–Ta_2O_5–ZnO	5.0–5.6			555			6.2–7.4			[27]

TABLE I continued.

Glass	Transmission 50% cut-off (μm)	Sample thickness (mm)	E (GN m^{-2})	Knoop hardness (kg mm^{-2})	MOR (MN m^{-2})	T_s (° C)	α (10^{-6} ° C^{-1})	Density (g cm^{-3})	n	Comments and references
Based on $CaO–Al_2O_3$										
Al_2O_3–CaO–(SiO_2, Na_2O, Fe_2O_3, Cu_2O)	4.5	2.0								[40] Moderate water absorption band
CaO–Al_2O_3–Na_2O	5.5	2.15								[39] Strong water absorption band
	4.5	4.16								
CaO–Al_2O_3–SiO_2	5.0	2.18	103.4				9–11			[13] Strong water absorption band
CaO–Al_2O_3–GeO_2		2.0								[13] Strong water absorption band
Based on Ga_2O_3–SrO										
Ga_2O_3–SrO–PbF_2	35% at 6.5 μm	2.0				>650	~13			[29] Water absorption removed by vacuum melting
Ga_2O_3–SrO–PbO	6.0					>600			1.71–1.82	[29]
Ga_2O_3–SrO–(miscellaneous oxides)	35% at 6.5 μm									[29]
Based on TeO_2										
TeO_2–Bi_2O_3	6.3	1.0								[31] Moderate water absorption band
TeO_2–ZnO	5.5	1.7		263		355		3.55		[33] Strong water absorption band
TeO_2–(miscellaneous oxides)	5.5							4.5–6.6	2.07–2.2	[32]
TeO_2–ZnO–BaO	6.2				22			5.6	~2.0	
Based on Bi_2O_3										
Bi_2O_3–PbO–(BaO, ZnO, Tl_2O)	7.5	1.0						7.88	2.5	[37] Moderate water absorption band
Bi_2O_3–PbO–CdO–Fe_2O_3	7.0					360–630	11.3–13.6			[38] Only minor water absorption band
Bi_2O_3–Sb_2O_3–As_2O_3–PbO	5.5	1.94								[42] Moderate water absorption band

TABLE I continued.

Glass	Transmission 50% cut-off (μm)	Sample thickness (mm)	E ($GN\,m^{-2}$)	Knoop hardness ($kg\,mm^{-2}$)	MOR ($MN\,m^{-2}$)	T_s (° C)	α (10^{-6} ° C^{-1})	Density ($g\,cm^{-3}$)	n	Comments and references
Miscellaneous glasses										
As_2O_3–PbO–Bi_2O_3	5.7	2.05								[42] Moderate water absorption band
PbO–CdO–Tl_2O_3–Fe_2O_3	30% at 8.5 μm					560–640				[43] Maximum transmission only ~30% – no water absorption
Fe_2O_3 WO_3–MoO_3–Bi_2O_3–As_2O_3	5.1	1.94							1.87–1.91 at 1.5 μm	[42] Batch material moistened with CCl_4 – no water absorption
Commercial glasses										
Silicates										
GEC fused quartz	3.6	10							1.463 at 0.486 μm	Strong water absorption band
Corning 7906	3.2	10	65.5	532 (100) 477 (500)	49.2	1500	0.8 (0–300° C)		1.449 at 1.0 μm	
Schott 1RGN6 calcium alumino-silicate	4.3	5.0	103.2	623 (200)			6.3 (20–300° C) 7.2 (20–600° C)	2.81	1.615 at 0.486 μm	Minor water absorption
Germanates										
Corning 9754	5.2	2.0	84.1	560 (100)	49.9		6.2 (25–300° C)		1.65 at 1.0 μm	Minor water absorption
Schott 1RG2	5.2	5.0	95.9	481 (200)			8.8 (20–300° C) 9.6 (20–600° C)	5.00	1.916 at 0.486 μm	Negligible water absorption
Calcium aluminates										
Schott 1RG11	5.0	5.0	107.5	608 (200)			8.2 (20–300° C) 8.6 (20–600° C)	3.12	1.693 at 0.486 μm	Minor/moderate water absorption
Barr and Stroud BS 37A	5.2 4.7	2.0 5.0	107.0		83		8.35 (20–300° C) 9.5 (20–600° C)	2.9	1.679 at 0.486 μm)	Minor/moderate water absorption
Barr and Stroud BS 39B	5.5 5.0	2.0 5.0	139.0		69		9.7 (20–500° C)	3.1	1.687 at 0.486 μm	Minor/moderate water absorption
Miscellaneous										
Barr and Stroud Tellurite	6.2	2.0			22		14	5.6	2.03 at 0.6 μm	
Barr and Stroud As_2S_3	10.5	3.0		109 (100)	17	200				
Barr and Stroud As_2Se_3	17.8	2.0			14		22	4.25	2.72 at 13 μm	Minor water absorption

impurity, and they exhibit low softening points, often <300° C. Hence, they are of limited applicability, and cannot be used for applications which may encounter temperatures approaching or exceeding this in service. Nevertheless, the excellent infra-red transmission of many chalcogenide glasses has warranted detailed investigations aimed at improving their mechanical properties or increasing their softening points, and some of the more prominent investigations are reported below.

For instance, Aggarwal *et al.* [48] attempted to improve the properties of Ge–As–Se glasses by additions of heavy metal selenides. Glass-formation was investigated for each system, and phase separation was found to occur over wide compositional ranges. It was concluded that these systems are unlikely to be superior to the base composition in the glassy state, although it was suggested that controlled crystallization to produce glass-ceramics may lead to satisfactory materials.

The introduction of Ag into Si–As–Te glasses was reported by Anthonis *et al.* [49] to permit the incorporation of Se, which is otherwise volatile in Si-containing chalcogenide glasses. Phase separation occurred, manifest in two glass transition temperatures, and the most stable composition was 10 Ag–30 Se–35 Si–15 As–10 Te. However, transmission was severely restricted, (only about 35% at 6 μm, and presumably even lower at <6 μm). Relatively stable Si–As–Ag–Te–Se glasses with softening points at around 676° C have also been reported by Amrhein *et al.* [50].

Chalcogenide glass-ceramics produced from a Ge–As–Se glass with PbSe additions have been reported by Mecholsky *et al.* [51]. The material was first phase-separated, and then subsequently crystallized. However, the short wavelength cut-on was significantly increased from approximately 3 μm for the glass to about 6 μm for the 50% crystalline material. A slight increase in MOR and hardness was reported, but it seems unlikely that such materials could ever be suitable for producing satisfactory transmission in the near infra-red.

Halide glasses are also feasible, but their mechanical and physico-chemical properties are inadequate for all but low-performance applications.

Finally, certain non-oxide additions have been made to oxide glasses in order to improve certain properties. Hence, fluorides have been extensively employed to minimize hydroxyl absorption, but too high a concentration of fluorides can lead to opalescence [10–12, 15]. It has also been reported [52] that additions of 0.75 to 2.9 wt % of a carbide, such as B_4C, to a silicate glass is successful in improving the wear-resistance.

3.3. Strengthening methods

Chemical methods of strengthening glass, with particular reference to large-for-small ion-exchange which results from treatment in a molten salt bath at temperatures less than the annealing temperature, have been reviewed by Norberg *et al.* [53].

Physical alteration of the surface of materials has also been employed to improve the resultant strength. Hence, Duke *et al.* [54] strengthened glass-ceramics by application of compressive glazes. Glasses in the system Na_2O–BaO–Al_2O_3–SiO_2–TiO_2 were crystallized and then coated with an Na_2O–CaO–PbO–B_2O_3–Al_2O_3–SiO_2 glaze of lower thermal expansion. The glaze bonded well on firing, and yielded a typical increase in strength from about 84 to 345 MN m^{-2}.

Surface crystallization has also proved to be effective in increasing the strength of certain glasses. For instance, Davy [55] has made reference to techniques for forming crystalline surface layers on calcium aluminate glass.

Similarly, Bloor *et al.* [56] reported that surface crystallized glasses in the CaO–Al_2O_3–ZnO–MgO–GeO_2 system had been prepared with mechanical properties in excess of those measured for the glasses prior to surface crystallization. Micro-hardness, impact strength and rain-erosion resistance were also significantly increased by the surface crystallization process, with little decrease in the transmission over the 2 to 5 μm wavelength range.

Finally, the properties of silicate glasses may often be significantly improved by controlled crystallization to yield glass-ceramics, and it has been noted that certain compositions retain their transparency to the visible [57–63]. Transparent glass-ceramics may be feasible in other systems based on network-formers other than SiO_2, and of particular interest may be materials based on GeO_2, which is chemically similar to SiO_2.

4. Relationships between infra-red transmission and mechanical and physical properties

Prediction of the infra-red transmission of glasses is complicated by the fact that there is no discretely defined structural unit. However, reference to the diatomic oscillator model [1], (frequency of vibration, $\bar{\nu} \propto (f/\mu)^{1/2}$) does suggest that infra-red transmission will decrease as the value of the force constant, f, increases, or as the reduced mass, μ, decreases. Therefore, glass-formers of high reduced mass and low field strength are required for maximum transmission.

Hence, oxide glass-formers may be placed in a series of decreasing cation charge-to-mass ratio, in which oxides higher in the series are expected to exhibit improved infra-red transmission relative to those lower in the series:

B_2O_3–P_2O_5–SiO_2–(CaO–Al_2O_3)–V_2O_5–

TiO_2–MoO_3–GeO_2–SeO_2–Ga_2O_3–As_2O_3–

WO_3–TeO_2–In_2O_3–Sb_2O_3–La_2O_3–Bi_2O_3

The most useful glass compositions are based on several oxides, and additions of network modifiers and intermediates are usual, so that the overall structure may be extremely complex. However, in general, the useful transmission will be set by addition of the oxide that exhibits the lowest transmission characteristics. Hence, glasses containing SiO_2 generally do not transmit well $\gtrsim 4.8\,\mu m$. There are insufficient data available to attempt to predict infra-red transmission on the basis of the simple diatomic oscillator model utilizing "average" interatomic distances and E or hardness values.

However, based on the cation charge-to-mass ratio, it is possible to estimate which oxides are likely to be the best infra-red transmitters. Hence, glasses based on Bi_2O_3 at one extreme of the scale exhibit the highest infra-red transmission of the oxide glasses so far reported, with 50% cut-off values up to about 7.5 μm. At the other extreme, B_2O_3 glasses exhibit the lowest transmission limit at $<4\,\mu m$. Glasses based on SiO_2 have a limit of useful transmission $<4.8\,\mu m$, MoO_3/WO_3 $<5.1\,\mu m$, GeO_2 $<5.7\,\mu m$, Ga_2O_3 $<6\,\mu m$, As_2O_3 $<5.7\,\mu m$, and TeO_2 $<6.3\,\mu m$, and hence the qualitative trend is realized.

A survey in 1968 [64] considered that it was not possible to predict accurately the infra-red transmission and mechanical properties of hypothetical glasses due to a lack of fundamental understanding of the relationships between crystalline materials and glasses, and this conclusion must still stand at the present time. It was also pointed out that certain materials such as ThO_2 exhibit a large force constant, reflected in high melting point, together with a large reduced mass, and hence can be expected to give a good compromise between infra-red transmission and mechanical properties, but unfortunately ThO_2 fails to satisfy network-forming conditions and consequently does not form a glass.

However, when the charge-to-mass ratio is considered for the oxide glass-formers, it is apparent that many network formers high in the series do exhibit high melting points, e.g. La_2O_3 at 2315° C and Ga_2O_3 at 1900° C, and these may be expected to exhibit useful mechanical properties in addition to high infra-red transmission. The melting points and charge-to-mass ratios of several oxide glass-formers and additions are summarized in Table II.

Hence, although in general silicate glasses exhibit the best overall mechanical and physicochemical properties (but at the expense of infra-red transmission) certain oxides higher in the charge : mass series may provide very useful materials. Data from the literature indicates that glasses based on (MoO_3–WO_3), SeO_2, TeO_2, Sb_2O_3, and As_2O_3 are limited due to their relatively low softening temperatures, and hence the useful known glass-formers are probably limited to (CaO–Al_2O_3), GeO_2, Ga_2O_3, WO_3, La_2O_3 and possibly In_2O_3 and Bi_2O_3.

5. Conclusions

(1) Oxide glass-formers may be placed in a series of decreasing cation charge-to-mass ratio, in which oxides higher in the series generally exhibit superior infra-red transmission, and this forms a useful qualitative guide for the prediction of infra-red transmission.

(2) Glasses based on CaO–Al_2O_3 are the most serviceable materials at the present time, exhibiting useful transmission to $\sim 5.5\,\mu m$ coupled with reasonable mechanical properties.

(3) Glasses based on Bi_2O_3 have been successfully prepared and these exhibit the highest overall transmission of the oxide glasses investigated to date, although their softening points are relatively low (820–860° C maximum).

(4) Glasses based on the chalcogenides S, Se or Te, or on the halides, are not generally suitable for application in the 1 to 6 μm spectral range due to a combination of high thermal expansion, high water solubility, low softening point, poor mechanical properties, or because they are opaque

TABLE II Melting point and charge-to-mass ratio of oxide glass-formers and additives

Oxide	T_m (° C)	Charge-to-mass ratio	Structure in crystalline state
B_2O_3	460	0.278	rhombic
P_2O_5	580	0.161	monoclinic
SiO_2	1728	0.142	hexagonal (quartz)
Al_2O_3	2045	0.111	hexagonal
U_2O_5	690	0.098	rhombic
TiO_2	1830–1850	0.084	tetragonal (rutile)
MoO_3	795	0.063	orthorhombic
GeO_2	1115	0.055	hexagonal or tetragonal
SeO_2	340–350	0.051	monoclinic or tetragonal
Ga_2O_3	1300	0.043	hexagonal or rhombic
As_2O_3	193*	0.040	monoclinic or cubic
WO_3	1473	0.033	rhombic
TeO_2	733	0.031	orthorhombic or tetragonal
In_2O_3	850	0.026	cubic or trigonal
Sb_2O_3	656	0.025	cubic or orthorhombic
La_2O_3	2315	0.022	cubic or rhombic
Bi_2O_3	820–860	0.014	cubic or rhombic
Li_2O	>1700	0.144	cubic
MgO	2800	0.082	cubic
Nb_2O_5	1460	0.054	rhombic
Fe_2O_3	1565	0.054	trigonal
ZrO_2	2700–2715	0.044	monoclinic or cubic
Na_2O	1275*	0.044	–
ZnO	1975	0.031	hexagonal
Ta_2O_5	1470	0.028	orthorhombic
K_2O	350†	0.026	cubic
SrO	2415	0.023	cubic
CdO	900†	0.018	cubic
BaO	1923	0.015	cubic

*Sublimes.
†Decomposes.

or only translucent to the visible and near infra-red.

(5) As a materials class, glasses undoubtedly offer the best prospect for the fabrication of homogeneous complex shapes. Hydroxyl absorption can be minimized by vacuum melting, or by melting and casting in a flowing dry atmosphere, or by adding certain halides to the batch (the latter two techniques are particularly suitable when volatile components are used which cannot be satisfactorily vacuum melted).

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