Ceramics International 22 (1996) 535–541
© 1996 Elsevier Science Limited and Techna S.r.l.
Printed in Great Britain. All rights reserved
0272-8842/96 $15.00+.00

0272-8842(95)00129-8

Review Paper

New Inorganic Glasses for Optical Waveguides

Douglas R. MacFarlane

Department of Chemistry, Monash University,
Clayton, 3168, Victoria, Australia

(Received 5 September 1995; accepted 19 October 1995)

Abstract: Recent advances in lightwave technology, including optical fibres, optical amplifiers, optical couplers and a variety of non-linear optical effects and devices, have created the need for a new range of glass materials. These glasses may themselves have properties tailored for the application or may play the role of host for an active guest species. In this review, the types of glass systems currently being developed will be reviewed with a focus on the different properties offered by different chemical makeup. Specific examples will include recent work on Heavy Metal Fluorides and Heavy Metal Oxides. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

The revolution in photonics has created a range of important new applications for glassy materials in optical technology, including telecommunications and optical computing. The optical telecommunications application, in particular, has generated a need for a range of glass based devices which can facilitate the manipulation of the signals at various stages, including the optical fibre transmission medium itself and bulk waveguides in which the signals are handled before and after transmission. Operation in the second ($\sim 1{\cdot}3$ μm) and third ($\sim 1{\cdot}5$ μm) telecommunications windows means that the glass material must be capable of low loss transmission in this region of wavelength as well as simultaneously supporting other types of chemical and optical effects.

New applications of lasers further into the infrared, in what is often termed the eye-safe region of the spectrum (beyond 1500 nm), have also created the need for a range of waveguide materials capable of operating at these wavelengths. Applications include medical laser surgical tools operating at around 2500 nm or around 10 000 nm, chemical sensing devices operating throughout the mid infra-red and ultra-low loss communications at wavelengths in the vicinity of 2500–3000 nm. At the other end of the spectrum, fabrication of blue/green fibre lasers has been limited by the absorption bands in traditional silica fibres and this also has stimulated interest in new glassy materials for fibres.

In this article we review recent work on a range of non-classical inorganic glass systems and highlight some of the important and unique properties that makes each system attractive. In Section 3 we review some of the special glass systems which can be used to create active glassy materials which exhibit a range of effects such as lasing and photorefractivity.

2 GLASS SYSTEMS

2.1 *Halide-based systems*

Prior to 1975 only a few halide systems were known to form glasses. Two halide compounds, BeF_2 and $ZnCl_2$, were known glass formers. BeF_2 glass is extremely toxic and deliquescent. $ZnCl_2$ glass is also very hygroscopic and it tends to crystallize easily. The latter is thought to be caused by the presence of small amounts of residual water which are very difficult to remove.[1] Several studies have been made where alkali halides are mixed with $ZnCl_2$ in order to increase the stability of the glass against devitrification and to reduce the hygroscopicity of the glass.[2,3] However, the effect of these additions has usually resulted in a lowering of the glass transition temperature (in some cases to an unacceptably low value ≈40°C).

A significant breakthrough occurred in 1974 when a group at the University of Rennes unexpectedly prepared glassy materials from fluorides of the heavy metals zirconium and barium.[4] These are now known as heavy metal fluoride glasses (HMFG). The significance of this discovery was

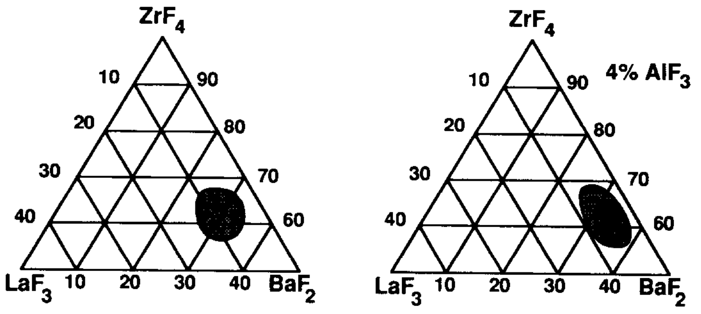

Fig. 1. (a) Glass forming area (shaded) in the ZrF_4–BaF_2–LaF_3 ternary (mol%). (b) Glass forming area (shaded) in the ZrF_4–BaF_2–LaF_3 ternary stabilized with 4%AlF_3 (mol%).

soon realised and major R and D programs are currently underway in many laboratories around the world. Numerous families of HMFG have now been discovered, details of some of which are summarized in the following. They include:

Fluorozirconates. Zirconium tetrafluoride does not exist in the vitreous form. At a minimum, binary combinations such as ZrF_4–BaF_2 and ZrF_4–ThF_4 will vitrify, although very high cooling rates are required. Ternary compositions are required in order to prepare glass samples thick enough for optical testing. These include ZrF_4–BaF_2–NaF,[4,5] ZrF_4–BaF_2–ThF_4[6] and ZrF_4–BaF_2–LaF_3[7] (Fig. 1(a)). In all these compositions, hafnium may replace zirconium with no significant change in physical properties except for a decrease in refractive index.[8] An important development was the discovery that a few mole percent of AlF_3 increased glass stability.[9] This led to glasses with the general formulation ZrF_4–BaF_2–MF_n–AlF_3, where MF_n = LaF_3 (Fig. 1(b)), NaF, LiF, CaF_2, YF_3, GaF_3, NdF_3 and ThF_4.[10] While these formulations were adequate for preparing large samples such as discs for optical testing, crystallization invariably occurred when optical fibre preforms were prepared. The association of ZrF_4–BaF_2–LaF_3–AlF_3 and ZrF_4–BaF_2–NaF–AlF_3 led to the much investigated ZrF_4–BaF_2–LaF_3–AlF_3–NaF (ZBLAN) composition.[11] This composition exhibits one of the lowest critical cooling rates observed for fluorozirconate glasses.

Some typical compositions (mol%) of fluorozirconate glass include: $57ZrF_4$–$34BaF_2$–$5LaF_3$–$4AlF_3$ (ZBLA); $60{\cdot}5ZrF_4$–$31{\cdot}5BaF_2$–$4GaF_3$–$4AlF_3$ (ZBGA); $53ZrF_4$–$20BaF_2$–$4LaF_3$–$3AlF_3$–20NaF-(ZBLAN20); $52ZrF_4$–$21BaF_2$–$5LaF_3$–$3AlF_3$–19LiF-(ZBLALi). A computer simulation approach developed in our laboratories has met with some success in predicting the maximum in stability as a function of composition in these complex multicomponent systems.[5,12–15]

Various other fluorides may be incorporated as additional components in order to change certain glass characteristics such as refractive index, thermal expansion coefficient or to allow the glass to be used as an active optical material. The influence of additives on crystallization is sometimes substantial, however, and empirical rules have been formulated to maintain reasonable stability.[10]

Fluoride melts tend to have low viscosities at their liquidus temperatures and their tendency to crystallize is high.[16–18] They must be prepared using stringent atmospheric control to prevent oxide/hydroxide contamination which leads to absorption in the mid-IR and possible nucleation of the glass. Ultra high purity starting materials are required in order to reduce scattering and absorption losses. Recent work has developed methods for the *in situ* purification of the melt by electrochemical means immediately prior to pouring.[19–23]

Many compositions of HMFG are continuously transparent from around 0·25–0·3 μm in the near UV to around 5–6 μm in the mid-IR.[24] The multiphonon edge depends, to a first approximation, on the concentration of the most absorbing cation, according to the sequence: Al, Li, Zr, Hf. For this reason, Hf based glasses are transparent to slightly longer wavelengths, than Zr based glasses, as are In based glasses in comparison to either fluorozirconates or fluorohafnates. Figure 2 shows transmission curves of fused silica, ZBLA and HBLA glass.

The thermal expansion coefficient α of HMFG $(\approx 200 \times 10^{-7}\ K^{-1})$ is higher than typical oxide

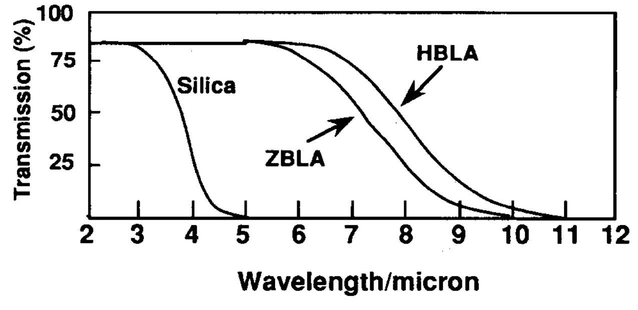

Fig. 2. Transmission of silica, ZBLA and HBLA glass.

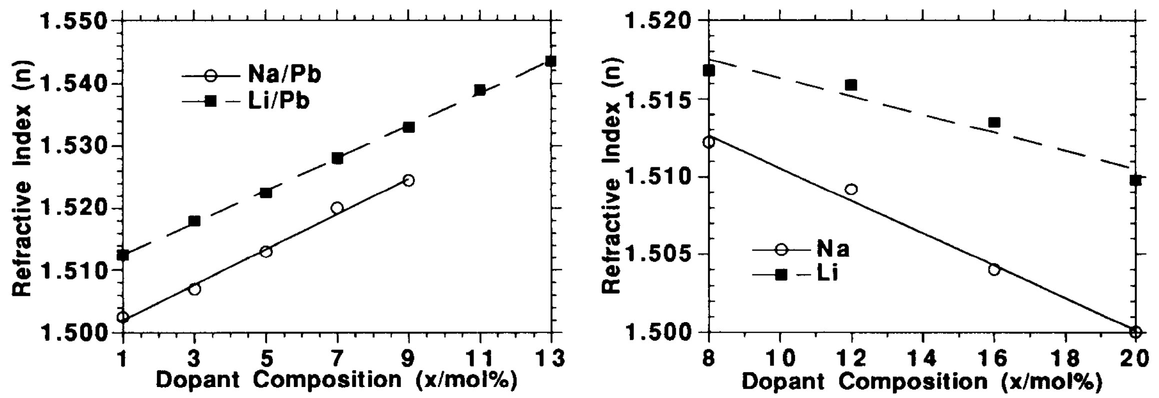

Fig. 3. (a) Variation in refractive index with composition in the lead substituted HMF glass sytem. (b) Variation in refractive index with composition in the alkali substituted HMF glass system.

glasses;[25,26] their density is also high (4–6 gcm^{-3}) as a consequence of the heavy cations,[10] while typical refractive indices fall in the range 1·47–1·53. Substitution with heavy polarizable cations (e.g. Pb) gives higher n values, while substitution of Na for Li and Hf for Zr lowers the refractive index.[27–29] The variation in refractive index with composition in the systems $53ZrF_4$–$(20\text{-}x)BaF_2$–$4LaF_3$–$3AlF_3$–$20MF$–$xPbF_2$, where M = Li or Na, and $53ZrF_4$–$(20\text{-}x)BaF_2$–$4LaF_3$–$3AlF_3$–xMF, where M = Li or Na, is shown in Fig. 3(a) and (b).[28,29]

Fluoroaluminates. The first glasses in this group (AlF_3–PbF_2–SrF_2–MgF_2) were reported by Sun.[30,31] More stable compositions were reported by Poulain[32] (AlF_3–BaF_2–YF_3–ThF_4), Kanomori[33] (AlF_3–YF_3–BaF_2–CaF_2) and Tick[34] (AlF_3–CdF_2–LiF–PbF_2). The latter glasses are stabilized by a small amount of oxygen.[35] Research into these glass systems has been less developed compared to the fluorozirconates, firstly because crystallization was a problem when slow cooling rates were used and secondly because they exhibited slightly higher theoretical minimum losses.

Recently a new glass system was described by Izumitani *et al.* in which a small amount of ZrF_4 was added to a complex fluoroaluminate glass.[36] This multi-component glass, $30{\cdot}2AlF_3$–$10{\cdot}2BaF_2$–$13{\cdot}2SrF_2$–$20{\cdot}2CaF_2$–$3{\cdot}5MgF_2$–$8{\cdot}3YF_3$–$3{\cdot}8NaF$–$10{\cdot}2ZrF_4$, exhibited a low crystallization rate and was found to be more durable against water and acids than ZBLAN glass. This offers the potential for using this type of glass for optical components and windows without the requirement of applying a protective coating to the glass surfaces. Sigel *et al.* recently prepared fluoroaluminate glass fibres and achieved a 40-fold reduction in the optical loss through the use of high purity materials and advanced processing techniques.[37] Due to the excellent chemical durability of these fibres, they can be used in evanescent sensing applications in aqueous environments, a situation in which a fluorozirconate fibre would fail completely.

Trifluoride glasses. Jacobini has investigated the preparation and properties of fluoride glasses containing substantial amounts (≈25–45 mol%) of transition metal fluorides.[38,39] Numerous and quite large vitreous domains have been found for the systems PbF_2–MF_2–XF_3 and AF–MF_2–XF_3, where A represents an alkali metal and M and X are transition metals: Fe, Co, Ni. These glasses require rapid quenching and the hygroscopic nature of some of the TM fluorides necessitates very dry preparative conditions. However, their stability may be enhanced via addition of further fluorides to the basic ternary composition. These glasses have IR properties similar to fluorozirconates but exhibit interesting magnetic behaviour including "spin glass" properties at very low temperatures.[40]

Glasses based on InF_3 form a group of growing importance. The InF_3–BaF_2–YF_3 system was discovered by Videau *et al.* in 1983.[41] Recent studies by Poulain,[42] Lucas[43–45] and Nishii *et al.*[46] have identified glasses with low critical cooling rates, extended IR transmission (50% transmission at 9 μm) and superior chemical durability compared with fluorozirconate glass. Extended IR transmission will allow fibres to carry CO_2 laser power and enable thermal imaging at room temperature. Examples of these multi-component glasses include: $40InF_3$–$20ZnF_2$–$5SrF_2$–$25BaF_2$–$10PbF_2$; $30BaF_2$–$30InF_3$–$20ZnF_2$–$10ThF_4$–$10YbF_3$ and $30BaF_2$–$18InF_3$–$12GaF_3$–$16ZnF_2$–$10YbF_3$–$10ThF_4$–$4MnF_2$.

Divalent metal fluoride glasses. Multi-component glasses based on divalent fluorides ZnF_2, SrF_2, MnF_2, CaF_2 and BaF_2 show extended transmission into the IR and considerable resistance to corrosion provided the zinc content is low.[47,48] However, the stability of these glasses is still not comparable to fluorozirconate glass.

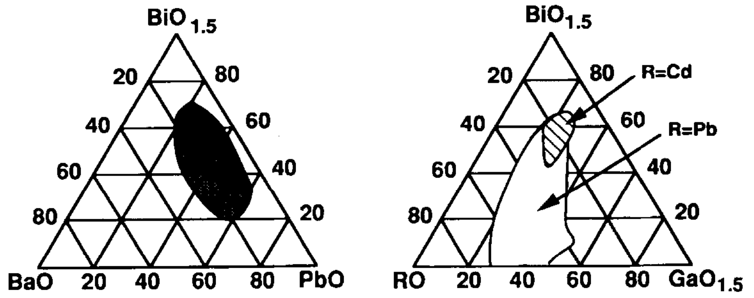

Fig. 4. (a) Glass forming area (shaded) in the BaO–PbO–Bi_2O_3 ternary incorporating 10 cat% ZnO. (b) Glass forming areas in the ternary Bi_2O_3–Ga_2O_3–RO, where R = Pb or Cd.

2.2 Oxide-based systems

Germanates. Although germanate glasses have been known for some time, considerable progress was made possible when chemical vapour deposition technology was applied to the glass making process. High purity GeO_2 based glasses are now generally fabricated using the vapour phase axial deposition (VAD) process.[49] One of the difficulties in preparing high grade germanate glass is that OH contamination is difficult to overcome. Strong absorption peaks at 1·4 and 2·2 μm are thought to be due to water.[50] However, GeO_2 glasses possess important non-linear optical properties.[51]

Tellurates. TeO_2 is a conditional glass former, requiring at least one other oxide for glass stability. Binary glasses based on TeO_2 and a wide range of alkali, alkali earth and transition metal oxides have been reported.[52] They are easily melted at temperatures $< 1000°C$ using conventional crucible techniques but are more prone to devitrification than silicates. These glasses have quite high refractive indices ($n > 2$) and transmit well into the infrared. Recently, ternary tellurates with constituents TeO_2–BaO–ZnO, TeO_2–WO_3–Ta_2O_5, TeO_2–WO_3–Bi_2O_3 and TeO_2–BaO–PbO have been reported by Boniort *et al.*[53]

Calcium aluminates (CA). These glasses have been prepared close to the eutectic composition 43CaO–57$AlO_{1·5}$. Pure CA glasses are rather difficult to prepare as they require a rapid quench to prevent devitrification and also tend to be moisture sensitive.[52] However CA glasses can be stabilized against devitrification by the addition of SiO_2, BaO, Na_2O or K_2O. The transmission spectrum of a 10μm thick sample of 43CaO·57$AlO_{1·5}$ with 5 wt% SiO_2 glass showed a window between 0·3 and 5·6 μm.[54] The multiphonon absorption thus occurs at longer wavelengths in CA glasses than in high-silica glass. One drawback of this glass system is that temperatures in excess of 1600°C are required for melting and the melts are quite basic. Hence corrosion of both platinum and ceramic crucibles is observed.[31]

Heavy metal oxide (HMO) glasses. These glasses contain over 50 cation percent bismuth and/or lead. They have been extensively studied by Dumbaugh and co-workers.[55] Many different compositions are now known including: 55Bi_2O_3–25PbO–10ZnO–10BaO; 26·2Bi_2O_3–40·9PbO–16·4CdO–16·4Al_2O_3; 20Bi_2O_3–30PbO–50GeO_2; 12Bi_2O_3–12PbO–35GeO_2–41Tl_2O. Sizeable areas of glass formation were discovered in the PbO–Bi_2O_3 systems containing BaO and ZnO.[56] Figure 4(a) shows the BaO–PbO–Bi_2O_3 ternary incorporating 10 cat% ZnO, while Fig. 4(b) shows the ternary Bi_2O_3–Ga_2O_3-RO, where R = Pb or Cd.[57]

Several interesting properties arise in these glasses due to their high density (> 6 gcm^{-3}), low bond strength and high polarizibility of Pb and Bi ($n \approx 2·5$).[55] They transmit into the infrared; in fact, these glasses transmit to the longest wavelength of any oxide glass. One of the most promising applications of HMO glasses is in the field of non-linear optics (optical isolators and optical switches). The Bi_2O_3–Ga_2O_3–(Pb,Cd)O glasses have high Verdet constants[58] and high third-order non-linear optical susceptibilities.[59]

2.3 Chalcogenides

The chalcogenide glasses are defined as materials containing at least one of the elements S, Se and Te. A large number of compositions are now known, e.g. As–S, Ge–S, Ge–P–S, As–Se, As–Ge–Se, Ge–Se, Ge–As–Se, La–Ga–Ge–Se, Ge–Sb–Se, Ge–Se–Te, As–Ge–Se–Te and As–Se–Te.[60] The most important feature of these glasses is their extended transmission in the IR (to ≈10 μm for sulphide glasses, to ≈14 μm for selenide glasses and to ≈20 μm for telluride glasses). The optical losses of these glasses are considerable due to contamination by water and other hydrogen-containing impurities. The first IR optical fibre (As_2S_3) was prepared by Kapany and Simms in 1965.[61] However, the losses were greater than 10000 dBkm^{-1}. This has been reduced to $\approx$100 dBkm^{-1} but further reduction is thought to be difficult because of the existence of an intrinsic absorption tail in the IR.[62] Several selenide and telluride glasses have been drawn into fibres, but in all cases high transmission losses have been recorded.[63–65]

2.4 Chalcohalide glasses

This family of glasses has received little attention compared to HMFG and chalcogenides. They are prepared from mixtures of chalcogenides and halides (Cl, Br and I) and are usually stabilized with As, Ge, or Sb,[42–44] although stable Te–halide binaries are known.[66] The IR transmission of these glasses is generally high, they possess good glass forming ability, an excellent resistance to crystallization and some glasses show very good chemical durability.

3 OPTICALLY ACTIVE GLASSES

3.1 Lasing[67]

Fluorescence and non-linear phenomena form the basis of active optical devices. Many rare earth (RE) ions possess low lying energy levels which will produce strong fluorescence when pumped with light from a suitable source. It is therefore possible to design a laser waveguide from an intentionally doped-glass waveguide structure. Fibre lasers, in particular, have a number of practical attractions, including the long length of the fibre which results in low pump power threshholds and high efficiencies, simple cavity optics and the laser is compact, lightweight and durable. This makes them very important for optical communications applications, i.e. optical amplification.

At present, Er^{3+} doped silicate fibres are being used as optical amplifiers in the 3rd communications window at 1.54 μm. A Pr^{3+} doped fluoride glass fibre amplifier is potentially useful in the 2nd communications window at 1.3 μm.[68] In this particular application, fluoride glasses offer two important advantages over more traditional silicate systems. Firstly, relatively high concentrations of RE ions can be easily incorporated into the fluoride host, since RE fluorides are a common component in the glass formulation. Secondly, the lifetime of the excited state is longer in fluoride glass as a result of non-radiative decay processes. These processes, which depopulate the excited state, are slower in glasses in which only low energy phonon modes are possible. In order to overcome the problem of dopant ions having only weak pumping bands, another dopant ion (e.g. Yb^{3+}), which absorbs strongly at the pump wavelength, has been added.

Recent work in our laboratories has concentrated on producing HMFG with very high levels of REs for use in optically-pumped single-longitudinal-mode lasers operating in a micro-chip configuration.[69] Micro-chip lasers operating in the "eye-safe" region offer great promise for a number of practical applications including remote sensing, lidar applications, vehicle guidance and robot vision. The very small size of these lasers necessitates much higher dopant levels than fibre lasers. We have reported[69] for the first time a ZBLAN glass doped with as much as 18 mol% Er^{3+}.

3.2 Photorefractive glasses

Photorefractivity, that is the effect whereby the refractive index of a glass is altered by the action of exposing the material to UV/vis radiation, can be used to generate a number of important devices including waveguides and diffraction gratings, the latter both in bulk materials and *in situ* in optical fibres.

In the classic photorefractive effect,[70] as observed in germano-silicate systems, irradiation of the glass with 200–300 nm radiation produces a bond rearrangement process in the glass structure such that the refractive index is slightly altered. The effect is usually quite small ($\Delta n < 10^{-3}$) except under the most extreme conditions. Nonetheless useful optical fibre gratings have been produced by this process. In a recent development in our laboratories a photorefractive effect has been discovered based on dopant species in the glass.[71]

The effect is clearly not limited to only one family of glasses and by adjustment of the dopant level can be used to generate effects as high as $\Delta n > 10^{-2}$. With changes in refractive index of this order of magnitude available, not only are high selectivity gratings possible in both optical fibres and bulk waveguides, but the effect can also be used to generate a waveguide in an otherwise uniform glass material.

The generation of a waveguide by photorefractive effect printing can be achieved by a process in which the waveguide profile is masked by traditional methods and then the photorefractive change generated by exposure to UV/vis light. Alternatively, a focused visible laser beam could be used to print the desired waveguide structure.

4 CONCLUSIONS

The search for glasses having a wide range of properties has produced families based on almost every one of the elements in groups 6 and 7 of the periodic table. Nonetheless, the fact that glass formation is often enhanced by the inclusion of more than one periodically similar element, by mixing cations of differing size to charge ratio and by mixing, in some cases, of the anions, guarantees that chemical and materials science research will continue in the future to discover new glass systems of varied properties.

REFERENCES

1. GOLDSTEIN, M. & NAKONECZNYJ, M., *Phys. Chem. Glasses*, **6** (1965) 126.
2. YAMANE, M., KAWAZOE, H., INOUE, S. & MAEDA, K., *Mater. Res. Bull.*, **20** (1985) 905.
3. ALMEIDA, R. & SANTOS, L. F., *J. Am. Ceram. Soc.*, **72** (1989) 2065.
4. POULAIN, M., POULAIN, M., LUCAS, J. & BRUN, P., *Mater. Res. Bull.*, **10** (1975) 243.
5. UHLHERR, A. & MacFARLANE, D. R., *J. Non-Cryst. Solids*, **161** (1992) 98.
6. POULAIN, M., CHANTHANASINH, M. & LUCAS, J., *Mater. Res. Bull.*, **12** (1977) 151.
7. LECOQ, A. & POULAIN, M., *J. Non-Cryst. Solids*, **34** (1979) 101.
8. DREXAGE, M. G., BENDOW, B. & MOYNIHAN, C. T., *Laser Focus*, **10** (1980) 62.
9. LECOQ, A. & POULAIN, M., *J. Non-Cryst. Solids*, **41** (1980) 209.
10. POULAIN, M., Fluoride glass composition and processing. In *Fluoride Glass Fibre Optics*, ed. I. D. Aggarwal & G. Lu. Academic Press, San Diego, USA, 1991, p. 1.
11. OHSAWA, K. & SHIBATA, T., *J. Lightwave Technol.*, **LT2** (1984) 602.
12. INOUE, S. & MacFARLANE, D. R., *J. Non-Cryst. Solids*, **95** (1987) 585.
13. MacFARLANE, D. R., INOUE, S., BROWNE, J. O. & UHLHERR, A., *Mater. Sci. Forum*, **32/33** (1988) 125.
14. UHLHERR, A., MacFARLANE, D. R. & BASTOW, T. J., *J. Non-Cryst. Solids*, **123** (1990) 42.
15. UHLHERR, A., MacFARLANE, D. R., MOORE, L. J. & THOMAS, P. D., *Mater. Sci. Forum*, **65/66** (1991) 431.
16. MacFARLANE, D. R. & MOORE, L. J., Nucleation and crystallization. In *Heavy Metal Fluoride Glasses*, Crit. Revs. Appl. Chem. Vol. 27, ed. A. Comyns. John Wiley and Sons, UK, 1989, pp. 49–64.
17. MacFARLANE, D. R. & FRAGOULIS, M., *Mater. Sci. Forum*, **5** (1985) 237.
18. MacFARLANE, D. R. & MOORE, L. J., *Mater. Sci. Forum*, **19/20** (1987) 447.
19. ZHOU, Z. & MacFARLANE, D. R., *J. Non-Cryst. Solids*, **140** (1992) 215.
20. ZHOU, Z., NEWMAN, P. J., WONG, D. K. Y. & MacFARLANE, D. R., *J. Non-Cryst. Solids*, **140** (1992) 297.
21. ZHOU, Z., NEWMAN, P. J. & MacFARLANE, D. R., *J. Non-Cryst. Solids*, **161** (1993) 27.
22. ZHOU, Z., NEWMAN, P. J. & MacFARLANE, D. R., *J. Non-Cryst. Solids*, **161** (1993) 36.
23. BAO, S., NEWMAN, P. J., ZHOU, Z., VOELKEL, A. & MacFARLANE, D. R., 9th Int. Symp. Nonoxide Glasses, Extended Abstract, Hangzhou, P.R.C., May 1994, *J. Non-Cryst. Solids*, **184** (1995) 194.
24. DREXHAGE, M. G., Optical properties of fluoride glass. In *Halide Glasses for Infrared Fibreoptics*, ed. R. M. Almeida. Martinus Nijhoff, Dordrect, The Netherlands, 1987, pp. 219–235.
25. CLARE, A. G. & PARKER, J. P., *Phys. Chem. Glasses*, **30** (1989) 205.
26. ROWE, R., ROSMAN, G. & BYRNE, C., 9th Int. Symp. Nonoxide Glasses, Extended Abstract, Hangzhou, P.R.C., May 1994. *J. Non-Cryst. Solids*, **184** (1995) 79.
27. POIGNANT, H., LE MELLOT, J., LEVÉ, A., LE CABEC, P. & RIVIÈRE, D., *J. Non-Cryst. Solids*, **161** (1993) 192.
28. MacFARLANE, D. R., NEWMAN, P. J., ZHOU, Z. & JAVORNICZKY, J., *J. Non-Cryst. Solids*, **161** (1993) 182.
29. JAVORNICZKY, J., NEWMAN, P. J. & MacFARLANE, D. R., 9th Int. Symp. Nonoxide Glasses, Extended Abstract, Hangzhou, P.R.C., May 1994. *J. Non-Cryst. Solids*, **184** (1995) 336.
30. SUN, K. H., *J. Am. Ceram. Soc.*, **30** (1947) 277.
31. SUN, K. H., US Patent 2,466,509, 1949.
32. POULAIN, M., POULAIN, M. & MATECKI, M., *Mater. Res. Bull.*, **16** (1981) 555.
33. KANOMORI, T., OIKAWA, K., SHIBATA, T. & MANABE, T., *Jpn J. Appl. Phys.*, **20** (1981) L326.
34. TICK, P. A., *Mater. Sci. Forum*, **32/33** (1988) 115.
35. MITACHI, S. & TICK, P. A., *Mater. Sci. Forum*, **32/33** (1988) 197.
36. IZUMITAMI, T., YAMASHITA, T., TOKIDA, M., MIURA, K. & TAJIMA, H., *Mater. Sci. Forum*, **19/20** (1987) 19.
37. IQBAL, T., SHARRIARI, M. R., FOY, P., ULBRICH, R. & SIGEL, G. H., *Electron. Lett.*, **27** (1991) 110.
38. MIRANDAY, J., JACOBINI, C. & DEPAPE, R., *J. Non-Cryst. Solids*, **43** (1981) 393.
39. JACOBINI, C., LE BAIL, A. & DEPAPE, R., *Glass Technology*, **24** (1983) 164.
40. RENARD, J. O., MIRANDAY, J. & VARRET, F., *Solid State Commun.*, **35** (1980) 41.
41. VIDEAU, J. J., DUBOIS, B. & PORTIER, J., *C. R. Acad. Sci. Paris*, **297** (1983) 483.
42. MESSADDEQ, Y., DELBEN, A., BOSCOLO, M., AEGERTER, M. A., SOUFIANE, A. & POULAIN, M., *J. Non-Cryst. Solids*, **161** (1993) 210.
43. ADAM, J. L., SMEKTALA, F. & LUCAS, J., *J. Non-Cryst. Solids*, **140** (1992) 31.
44. RIGOUT, N., ADAMS, J. L. & LUCAS, J., *J. Non-Cryst. Solids*, **161** (1993) 161.
45. CHARRON, C., FONTENEAU, G. & LUCAS, J., *J. Non-Cryst. Solids*, **161** (1993) 213.
46. NISHII, J., KAITE, Y. & YAMAGISHI, T., *Phys. Chem. Glasses*, **30** (1989) 55.
47. POULAIN, M. & MESSADDEQ, Y., *Mater. Sci. Forum*, **32/33** (1988) 131.
48. MESSADDEQ, Y. & POULAIN, M., *J. Non-Cryst. Solids*, **140** (1992) 41.
49. TAKAHASHI, H., SUGIMOTO, I. & SATO, T., *Electron. Lett.*, **18** (1982) 398.
50. TAKAHASHI, H. & SUGIMOTO, I., *J. Lightwave Tech.*, **LT2** (1984) 613.
51. KATSUYAMA, T. & MATSUMURA, H., *Infrared Optical Fibres*. Adam Hilger, UK, 1989.
52. RAWSON, H., *Inorganic Glass-Forming Systems*. Academic Press, UK, 1967.
53. BONIORT, J. Y., BREHM, C., DOPONT, P. H., GUIGNOT, D. & LE SERGENT, C., *Proc. 6th European Conf. Opt. Commun.*, IEEE Conf. Publ., 1980, p. 61.
54. LINES, M. E., MacCHESNEY, J. B., LYONS, K. B., BRUCE, A. J., MILLER, A. E. & NASSAU, K., *J. Non-Cryst. Solids*, **107** (1989) 251.

55. DUMBAUGH, W. H. & LAPP, J. C., *J. Am. Ceram. Soc.*, **75** (1992) 2315.
56. DUMBAUGH, W. H., *Phys. Chem. Glasses*, **19** (1978) 121.
57. DUMBAUGH, W. H., *Phys. Chem. Glasses*, **27** (1986) 119.
58. BORRELLI, N. F. & DUMBAUGH, W. H., Infrared optical materials and fibres V. *SPIE Proc.*, **843** (1987) 6.
59. HALL, D. W., NEWHOUSE, M. A., BORRELLI, N. F., DUMBAUGH, W. H. & WEIDMAN, D. L., *Appl. Phys. Lett.*, **54** (1989) 1293.
60. SAVAGE, J. A., *Infrared Optical Materials and their Antireflection Coatings*. Adam Hilger, UK, 1985.
61. KAPANY, N. S. & SIMMS, R. J., *Infrared Phys.*, **5** (1965) 69.
62. KANOMORI, T., TERUNUMA, Y., TAKAHASHI, S. & MIYASHITA, T., *J. Non-Cryst. Solids*, **69** (1985) 231.
63. KATSUYAMA, T. & MATSUMURA, H., *Appl. Phys. Lett.*, **49** (1986) 22.
64. SANGERA, J. S., HEO, J. & MacKENZIE, J. D., *J. Non-Cryst. Solids*, **103** (1988) 155.
65. GAN, F., *J. Non-Cryst. Solids*, **140** (1992) 184.
66. LUCAS, J. & ZHANG, X. H., *J. Non-Cryst. Solids*, **125** (1990) 1.
67. QUIMBY, R. S., Active phenomena in doped halide glasses. In *Fluoride Glass Fibre Optics*, ed. I. D. Aggarwal & G. Lu. Academic Press, San Diego, USA, 1991, pp. 351–393.
68. DAVEY, S. T., SZEBESTA, D., WILLIAMS, J. R., WHITLEY, T. & WYATT, R., *J. Non-Cryst. Solids*, **161** (1993) 262.
69. JAVORNICZKY, J., NEWMAN, P. J., MacFARLANE, D. R., BOOTH, D. J. & BOGDANOV, V., 9th Int. Symp. Nonoxide Glasses, Extended Abstract, Hangzhou, P.R.C., May 1994. *J. Non-Cryst. Solids*, **184** (1995) 249.
70. MAXWELL, G. D., KASHYAP, R., AINSLIE, B. J., WILLIAMS, D. L. & ARMITAGE, J. R., *Electron Lett.*, **28** (1992) 2106.
71. MacFARLANE, D. R., BAO, S., JAVORNICZKY, J. & NEWMAN, P. J., 9th Int. Symp. Nonoxide Glasses, Extended Abstract, Hangzhou, P.R.C., May 1994.