Fluoride glasses are of great interest for optical applications, as low phonon energy hosts for rare-earth ions. With an increasing need for more compact optical devices that impose higher dopant concentration, research activity has been focused on the fabrication of fluoride glass planar waveguides to produce integrated lasers and optical amplifiers, especially those based on Er$^{3+}$-doped glasses. The aim of this review is to give the state of the art of fabrication technology for fluoride glasses and to present the most interesting results obtained on confined waveguides. Recent developments in fluoride transparent glass ceramic waveguides will also be mentioned.

11.1 Introduction

Fluoride glasses have been known since 1926, when it was discovered that beryllium fluoride could be cooled below the liquidus temperature without crystallization. Little further development took place until 1974, when Poulain et al. made the first synthesis of ZrF$_4$-NaF-BaF$_2$-NdF$_3$ [1]. During the past three decades, much attention has been paid to the family of fluoride glasses [2], especially fluorozirconates such as ZBLAN.
glass (ZrF$_4$-BaF$_2$-LaF$_3$-AlF$_3$-NaF), because of their potential in the development of optical fibres for long-distance telecommunication links. These applications require the absence of optical attenuation from scattering by crystals and particulates, but also ultrahigh purity materials containing no light-absorbing impurities such as transition metal (Fe$^{2+}$, Cu$^{2+}$, etc) hydroxyl (OH$^-$) ions. To date, the ultimate predicted ultralow optical loss of 0.01 dB/km compared to 0.2 dB/km for silica glasses [3] has not been reached, the biggest obstacle being in reducing transition-metal impurities and inhibiting formation of crystallites during the melt cooling operation or after reheating above the glass transition temperature (Tg). Nevertheless, fluoride glass remains an attractive material in shorter optical devices with applications lying in the visible and mid-IR spectral range, including lasers and amplifier operating at wavelengths not accessible with silica-based glasses, thank to their low phonon energy ($\sim$500–600 cm$^{-1}$) compared to silica ($\sim$1100 cm$^{-1}$). In particular, the development of optical communication necessitates the design and manufacture of integrated optic lasers and amplifiers, especially of those based on erbium-doped glasses. Integrated optical amplifiers (IOA) are used to bring the fibre to the home because they gather two complementary criteria: the high debit rate by use of wavelength distribution multiplexing (WDM) system and local network architecture. Indeed they inherit all the advantages of erbium doped fibre amplifiers (EDFA) – weak noise, weak polarization effect, absence of interference between channels in WDM application, in contrast with semiconductor optical amplifiers (SOA) [4]. The short length of integrated amplifiers imposes higher Er$^{3+}$ concentration and higher pump-power density than fibre so the choice of the glass matrix is particularly critical. Actually, the rare-earth solubility is strongly related to the crystal chemistry of the glass. Except BeF$_2$, fluoride glasses offer high coordination sites for rare earth ions and thus represent a unique optical host for rare earth ions; solubility can reach 10 mol%, depending on the ion size [5] while solubility is only a few hundred ppm in the tetrahedra-based network of silica.

In this chapter, the current status of the processing technologies in the planar waveguides fabrication and their performance as integrated optical amplifier and laser is reviewed. A special part will be dedicated to waveguides based on transparent glass ceramics, an emerging material in the field of active optics, as it may offer macroscopic glass properties and crystal-like spectroscopic characteristics [6].

11.2 Rare Earth in Fluoride Glasses

The composition and thermal and physical properties (namely, Tg, stability criteria $\Delta$T, refractive index and vibration frequency of metal-F bond) of some fluoride glasses that have been used for waveguide fabrication are given in Table 11.1. One can note the relatively high concentration of rare-earth fluorides, at least 5 mol%. (with YF$_3$ assimilated to the lanthanide family REF$_3$). Such a high concentration allows more flexibility in rare-earth combinations for active optical applications, especially for upconversion processes and enhanced pump absorption due to energy transfer between lanthanide ions.
11.2.1 Fundamentals

Rare earths (REs) are characterized by \([Xe] 4f^n 6s^2\) electronic configuration and the most stable oxidation state is \(+III\) with the 5s and 5p electrons remaining untouched. These electrons act as a screen for 4f electrons toward the surrounding environment, so that the energy levels of the ion are almost independent of the host. Unlike the energy levels, the transition probabilities between 4f states are host sensitive through phonon energy and clustering due to concentration effect. The quantum efficiency of a given transition is limited by nonradiative relaxations that may be classified as (i) multiphonon relaxations, (ii) cross relaxations and (iii) upconversion processes. The probability of multiphonon relaxations \(W_{MP}\) is a function of energy gap \(\Delta E\) to the next lower level [7]:

\[
W_{MP} = B \exp(-\alpha \Delta E)
\]

with \(B\) and \(\alpha\) as constants that depend only on the host. It is commonly admitted that \(W_{MP}\) is negligible when \(\Delta E > 7\omega\). As an example, the lack of emission at 1.3 \(\mu\)m for \(\text{Pr}^{3+}\) in silica-based glasses is a direct consequence of this, the energy gap being \(\sim3000\ \text{cm}^{-1}\).

Figure 11.1 shows the energy levels of rare-earths and emissions of primary interest with regard to visible, NIR and mid-IR applications in fluoride glasses.

**Table 11.1** Chemical composition, thermal and physical properties of fluoride glasses used to achieve planar waveguides. \(\omega\) is the vibration frequency that accounts for the multiphonon absorption.

<table>
<thead>
<tr>
<th>acronym</th>
<th>Composition (mol%)</th>
<th>Tg (°C)</th>
<th>(\Delta T) (°C)</th>
<th>(n_d)</th>
<th>(\omega) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZBLAN</td>
<td>52ZrF(_4)-24BaF(_2)-5LaF(_3) 4AlF(_3)-15NaF</td>
<td>272</td>
<td>90</td>
<td>1.504</td>
<td>580</td>
</tr>
<tr>
<td>ZBLANPb</td>
<td>52ZrF(_4)-19BaF(_2)-5PbF(_2) 5LaF(_3)-4AlF(_3)-15NaF</td>
<td>254</td>
<td>81</td>
<td>1.517</td>
<td>580</td>
</tr>
<tr>
<td>ZBLA</td>
<td>57ZrF(_4)-34BaF(_2)-5LaF(_3) 4AlF(_3)</td>
<td>307</td>
<td>85</td>
<td>1.516</td>
<td>580</td>
</tr>
<tr>
<td>ZELAG</td>
<td>60ZrF(_4)-26LaF(_3)-6ErF(_3) 1AlF(_3)-6GaF(_3)</td>
<td>392</td>
<td>49</td>
<td>1.503</td>
<td>600</td>
</tr>
<tr>
<td>BIG</td>
<td>25BaF(_2)-23InF(_3)-12GaF(_3) 25ZnF(_2)-15GdF(_3)</td>
<td>324</td>
<td>145</td>
<td>1.505</td>
<td>510</td>
</tr>
<tr>
<td>BIGNa</td>
<td>15BaF(_2)-18InF(_3)-12GaF(_3)-20ZnF(_2) 10YbF(_3)-10GdF(_3)-15NaF</td>
<td>310</td>
<td>140</td>
<td>1.487</td>
<td>510</td>
</tr>
<tr>
<td>PZG</td>
<td>36PbF(_2)-24ZnF(_2)-35GaF(_3) 5YF(_3)-2AlF(_3)</td>
<td>270</td>
<td>52</td>
<td>1.577</td>
<td>560</td>
</tr>
<tr>
<td>IZSB</td>
<td>16BaF(_2)-40InF(_3)-20ZnF(_2) 20SrF(_2)-4GdF(_3)-2NaF-6GaF(_3)</td>
<td>300</td>
<td>90</td>
<td>1.503</td>
<td>510</td>
</tr>
<tr>
<td>ALF70</td>
<td>37AlF(_3)-15CaF(_2)-12MgF(_2)-6BaF(_2) 15YF(_3)-9SrF(_2)-6NaPO(_3)</td>
<td>435</td>
<td>130</td>
<td>1.432</td>
<td>&lt;650</td>
</tr>
</tbody>
</table>
11.2.2 Applications: Laser and Optical Amplifiers

In all active optics applications, rare-earth doped fibres or waveguides possess significant advantages over bulk solid-state lasers because of long interaction length in laser media [8]. Laser action in waveguiding structures occurs at a threshold well below the bulk one, thus allowing higher gain and consequently large population inversion with low pumping power. The properties of planar optical amplifiers and lasers are expected to be similar to those of the fibre because of confinement and moreover offer the possibility of integrating other optical functions. A demonstration was made for the first time in 1974 with a Nd$^{3+}$-doped integrated optical glass laser, while the same material (a borosilicate glass) was employed as an early fibre laser [9, 10].

Some activity on RE-doped fluoride glass is telecommunication oriented with research devoted to broad-band optical amplification, within the loss-low window (1.2–1.6 $\mu$m) of silica optical fibre. The attenuation curve of highly transparent silica fibre (termed ‘allwave’) shown in Figure 11.2 reveals Pr$^{3+}$, Tm$^{3+}$ and Er$^{3+}$ to be of great interest. Erbium-doped amplifiers (EDFA) based on silica can cover the 1.5–1.6 $\mu$m band but signal amplification in the entire 1.2–1.6 $\mu$m window cannot be achieved; fluoride glass host is required at 1.3 $\mu$m with Pr$^{3+}$ and 1.48 $\mu$m with Tm$^{3+}$. Moreover, fluoride erbium-doped fibres are of practical interest because they possess a flat and broadband gain bandwidth as a function of signal wavelength [8]. This property is fundamental for wavelength division multiplexing (WDM), which allows the transmission of several wavelengths simultaneously over a wide range of energy. It is expected that WDM transmission will also be present in local networks, with integrated optical devices allowing complementary functions such as amplification, division and multiplexing.

**Figure 11.1** Energy level diagram of RE$^{3+}$ ions (RE = Pr, Er, Tm, Nd, Yb) of main interest for visible and IR applications. Yb$^{3+}$ is used as a sensitizer because of its high absorption cross-section and the possible energy transfer to its neighbouring ions.

![Energy Level Diagram](image-url)
Besides telecom applications, RE-doped fluoride glass waveguides can also be used as planar lasers in the area of high range power diode-pumped solid-state lasers. The idea is to improve the beam quality by delivering a diffraction-limited beam from a single-mode waveguide. Lasings have been obtained for a large number of rare-earth transitions in fluoride glass fibres from blue to the mid-IR (see Table 11.2), including several three-level systems that hardly lase in bulk configuration. As already noted, fluoride glass fibre allows

![Figure 11.2](image_url)  
*Figure 11.2* Attenuation of silica optical fiber and operation wavelengths for optical amplification. “Allwave” refer to OH free fiber developed by Lucent Technology.

<table>
<thead>
<tr>
<th>RE$^{3+}$</th>
<th>$\lambda$ (µm)</th>
<th>transition</th>
<th>$\lambda_{\text{exc}}$ (µm)</th>
<th>$\Delta E$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>1.3 (IR)</td>
<td>$^1G_4 \rightarrow ^3H_6$</td>
<td>1.02</td>
<td>2900</td>
</tr>
<tr>
<td></td>
<td>0.605–0.635 (red)</td>
<td>$^3P_0 \rightarrow ^3H_6 \rightarrow ^3F_2$</td>
<td>0.48, 0.85&lt;sub&gt;apte&lt;/sub&gt; (Yb cod.)</td>
<td>3800</td>
</tr>
<tr>
<td></td>
<td>0.52 (green)</td>
<td>$^3P_1, ^1I_6 \rightarrow ^3H_5$</td>
<td>0.48, 0.85&lt;sub&gt;apte&lt;/sub&gt; (Yb cod.)</td>
<td>4400</td>
</tr>
<tr>
<td></td>
<td>0.49 (blue)</td>
<td>$^3P_0 \rightarrow ^3H_4$</td>
<td>(1.02 + 0.83)&lt;sub&gt;uc&lt;/sub&gt;</td>
<td>3800</td>
</tr>
<tr>
<td>Tm</td>
<td>1.48 (NIR)</td>
<td>$^3H_4 \rightarrow ^3F_4$</td>
<td>1.4</td>
<td>4100</td>
</tr>
<tr>
<td></td>
<td>0.45 (blue)</td>
<td>$^1G_4 \rightarrow ^3H_6$</td>
<td>1.12, 0.98&lt;sub&gt;apte&lt;/sub&gt; (Yb cod.), 0.65&lt;sub&gt;uc&lt;/sub&gt;</td>
<td>6100</td>
</tr>
<tr>
<td>Er</td>
<td>3.45 (mid-IR)</td>
<td>$^4F_{9/2} \rightarrow ^4I_{9/2}$</td>
<td>0.65</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>2.79 (mid-IR)</td>
<td>$^4I_{13/2} \rightarrow ^4I_{11/2}$</td>
<td>0.98</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>1.54 (NIR)</td>
<td>$^4I_{13/2} \rightarrow ^4I_{15/2}$</td>
<td>1.48&lt;sub&gt;apte&lt;/sub&gt; (Yb cod.)</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>0.65 (red)</td>
<td>$^4F_{9/2} \rightarrow ^4I_{15/2}$</td>
<td>1.48&lt;sub&gt;uc&lt;/sub&gt;</td>
<td>2200</td>
</tr>
<tr>
<td></td>
<td>0.545 (green)</td>
<td>$^4S_{3/2} \rightarrow ^4I_{15/2}$</td>
<td>1.48, 0.98&lt;sub&gt;et&lt;/sub&gt; (Yb cod.), 0.80&lt;sub&gt;uc&lt;/sub&gt;</td>
<td>2800</td>
</tr>
<tr>
<td>Ho</td>
<td>3.9 (mid-IR)</td>
<td>$^5I_5 \rightarrow ^5I_6$</td>
<td>0.65</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>0.55 (green)</td>
<td>$^5S_2, ^5F_4 \rightarrow ^5I_6$</td>
<td>0.88&lt;sub&gt;uc&lt;/sub&gt;</td>
<td>3000</td>
</tr>
<tr>
<td>Nd</td>
<td>1.34 (NIR)</td>
<td>$^4F_{3/2} \rightarrow ^4I_{13/2}$</td>
<td>0.80</td>
<td>5500</td>
</tr>
<tr>
<td></td>
<td>1.06 (NIR)</td>
<td>$^4F_{3/2} \rightarrow ^4I_{11/2}$</td>
<td>0.80</td>
<td>5500</td>
</tr>
</tbody>
</table>

<sup>uc:</sup> up-conversion pumping.  
<sup>apte:</sup> addition of photon by energy transfer pumping.
emission at wavelengths not achievable with oxide glasses [11]; for example mid-IR emissions located in the 3–5 \( \mu \text{m} \) atmospheric window are specific to fluoride glasses doped with \( \text{Er}^{3+} \) at 2.8 \( \mu \text{m} \) and \( \text{Ho}^{3+} \) ions at 3.9 \( \mu \text{m} \), taking advantage of fluoride glasses’ transparency at wavelengths greater than 5 \( \mu \text{m} \) while silica transmission starts decreasing at ~3 \( \mu \text{m} \). Because of the strong confinement of the light in fibre or channel configuration, upconversion processes can be nicely optimized to achieve powerful and compact new visible laser sources, i.e. blue (with \( \text{Tm}^{3+} \) at 453 nm), green (with \( \text{Er}^{3+} \) or \( \text{Ho}^{3+} \) at 550 nm) and red (with \( \text{Er}^{3+} \) at 650 nm). A low phonon energy material is generally required to give access to most of the involved metastable excited states. This is why only RE-doped fluoride materials have been successfully used. Some applications require the simultaneous generation of the three primary light colours (red, green and blue) allowing additive synthesis of light in the visible spectrum [12], to be used for miniature video-projection; in this case, \( \text{Pr}^{3+} \) or \( \text{Tm}^{3+}, \text{Er}^{3+} \) codoped fluoride glasses appear attractive.

Table 11.2 gathers interesting wavelengths for laser action and optical amplification in visible and IR observed in fluoride glasses. An exhaustive list of results can be found in [13].

11.3 Fabrication of Waveguides: A Review

There is no single waveguide fabrication process that is universally applicable to the whole range of glass materials. Various techniques are available and some have been used to produce fluoride glass planar waveguiding structures: ionic exchange, chemical and physical vapour deposition (CVD and PVD), pulsed laser deposition (PLD), radio frequency (RF) magnetron sputtering and electron-beam sputtering (EB). The main difficulties encountered in these processes are (i) to reproduce the composition and optical properties of multicomponent fluoride glass; (ii) to avoid crystallization during the quenching step or after reheating the glass (over \( T_g \)) needed for ion-diffusion and sintering, (iii) to get low propagation losses. Moreover the film thickness has to be achievable in a reasonable processing time for a mass production. The main advantages and drawbacks of the processes mentioned above as applied to fluoride glasses are listed below:

- **Ionic exchange.** The \( F^- \) ion is replaced by \( Cl^- \), \( OD^- \) coming from gaseous phase [14,15] or alkali cations (\( \text{Li}^+ \), \( \text{K}^+ \), \( \text{Ag}^+ \)) are exchanged from a molten salt [16,17] or by dry interdiffusion [18]. The maximum refractive index gradient achieved by anionic and cationic diffusion on fluoride glass is given in Table 11.2. The optical properties of the starting glass may be affected by the change in size of the exchanged ions by generating stress at the surface.
- **CVD.** After its success in the preparation of low-loss silica based fibres, this process has been adapted to fluoride materials using volatile fluoride containing organometallic precursors (\( \beta \) diketonates) and HF or SF\(_6\) fluorinating gases to prepare ZrF\(_4\)-based fluoride glasses [19]. Direct synthesis of transparent thin film on a substrate has been achieved by plasma-enhanced CVD [20]. The main disadvantage of using precursor organic ligands is the presence of residues containing carbon and/or oxygen that cause quenching of luminescence and defect centres.
• **PVD.** The noncongruent evaporation of multicomponent glass restrains the choice in fluoride glass composition [21, 22]. As for all deposition techniques, the thermal expansion coefficients of the substrate and of the deposit have to be close to avoiding film cracking. The technique allows high growth rate (~0.1 μm/min).

• **Sol gel.** The synthesis usually involves wet chemistry reactions and is based on the inorganic polymerization of molecular precursors – either organic like alkoxides or inorganic like nitrate – for active optical application. Thin films are produced directly from the solution by dip or spin coating and can be converted in a fluoride glass film by fluorination with HF at temperature below the Tg (~200 °C) [23, 24]. The critical step is the drying to remove OH groups.

• **Spin casting.** The low viscosity of fluoride glass at its melting point allows to use this technique, provided that the glass is rapidly quenched to avoid crystallization of the molten glass layer [25]. Fast quenching enhances thermal stress at the film-substrate interface. To overcome this difficulty, the substrate is heated close to the glass transition temperature. The main drawback of the technique is the great dependence of film thickness and uniformity with spin speed parameters.

• **Sputtering.** Ar⁺ plasma or electron beam are used to sputter atoms from the target to the substrate. Fluoride thin film coatings are generally difficult to deposit by sputtering processes because deposition rates are low and coating quality is also generally low compared to films deposited by evaporation [26]. The evaporation of the glass has to be congruent for electron beam sputtering [27] unlike RF sputtering. Processing gas (SF₆, ...) is introduced during deposition in order to compensate fluorine that is frequently deficient at the surface target [28].

• **PLD.** This is a versatile materials fabrication technique that enables to preserve the stoichiometry of multi-component targets. The films are grown by ablation of fluoride glass, resulting in a congruent vaporization. Fluorine F₂ is used as processing gas [29].

A basic glass waveguide consists of a guiding core glass surrounded by a smaller refractive ‘cladding’ material (fluoride glass or single crystal like CaF₂, ...). The refractive index difference Δn between the core and the clad is an important parameter because it governs the guiding properties of the waveguide. Often, the top surface of the waveguide is left open to the air to make the fabrication simpler. In order to minimize coupling loss between the optical fibre and the waveguide, single-mode structure is preferred. For which the maximum waveguide thickness e is given by:

\[
\frac{e \pi}{\lambda} \sqrt{n_g^2 - n_s^2} = \frac{e}{\lambda} \sqrt{\Delta n(2n_g - \Delta n)} \leq \frac{\pi}{2}
\]

with \(n_g\) and \(n_s\) the guide and substrate refractive indices. Flexibility in Δn is achieved by using core and clad glasses with close compositions. Despite a refractive index that often does not match the required index, single crystal is chosen because it provides injection faces of optical quality by cleavage.

Table 11.3 compares the optical properties of different fluoride glass waveguides. Although being the most promising materials owing to their low phonon energy, production of InF₃-based channel waveguides with acceptable loss has been unsuccessful due to
the low Tg compared to the temperature required for the diffusion mechanism [16]. The process based on spin casting of fluoroaluminate glass currently holds the record for the minimum propagation losses, of less than 0.1 dB/cm.

Table 11.3  Comparison of fabrication methods and characteristics (refractive index change, thickness and propagation loss) of fluoride glass planar waveguides

<table>
<thead>
<tr>
<th>Technique</th>
<th>Waveguide glass</th>
<th>Substrate</th>
<th>Δn core/clad</th>
<th>e (μm)</th>
<th>Loss (dB/cm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVD</td>
<td>PZG</td>
<td>CaF$_2$</td>
<td>0.14</td>
<td>1–10</td>
<td>0.4</td>
<td>[32]</td>
</tr>
<tr>
<td>Zela</td>
<td>CaF$_2$</td>
<td>0.10</td>
<td>1–5</td>
<td>1.2</td>
<td></td>
<td>[22]</td>
</tr>
<tr>
<td>CVD</td>
<td>60ZrF$_4$-35BaF$_2$-5PrF$_3$</td>
<td>CaF$_2$</td>
<td>0.09</td>
<td>4–7</td>
<td>15.9</td>
<td>[36]</td>
</tr>
<tr>
<td>EB</td>
<td>79ZrF$_4$-8AlF$_3$-13NaF$^{(b)}$</td>
<td>BaF$_2$</td>
<td>0.09</td>
<td>&lt;5</td>
<td></td>
<td>[28]</td>
</tr>
<tr>
<td>sol gel</td>
<td>ZBLA</td>
<td>CaF$_2$</td>
<td>0.08</td>
<td>25</td>
<td></td>
<td>[24]</td>
</tr>
<tr>
<td>spin casting</td>
<td>ALF70</td>
<td>ALF101$^{(c)}$</td>
<td>0.21</td>
<td>2–10</td>
<td>0.1</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td>ZBLANPb</td>
<td>ZBLAN</td>
<td>0.02</td>
<td>50</td>
<td></td>
<td>[33]</td>
</tr>
<tr>
<td>PLD</td>
<td>ZBLAN</td>
<td>MgF$_2$</td>
<td>0.10</td>
<td>1</td>
<td>5.1</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>exchanged ions</td>
<td>Max. Δn gradient</td>
<td>20</td>
<td>2.4 (dB/cm)</td>
<td></td>
</tr>
<tr>
<td>IZSB</td>
<td>Ag$^+$/Na$^+$</td>
<td>0.03</td>
<td>2–300°C</td>
<td></td>
<td></td>
<td>[18]</td>
</tr>
<tr>
<td>ionic exchange</td>
<td>BIGNa</td>
<td>Li$^+$/Na$^+$</td>
<td>0.19</td>
<td>5</td>
<td>very high</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16 h–300°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BIG</td>
<td>OD$^-$/F$^-$</td>
<td>0.07</td>
<td>100 h–347°C</td>
<td>22</td>
<td>~5</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>Cl$^-$/F$^-$</td>
<td>0.07</td>
<td>10.5 h–250°C</td>
<td>8</td>
<td>0.3</td>
<td>[14]</td>
</tr>
</tbody>
</table>

$^{(a)}$refractive index of single crystal $n_D$: CaF$_2$ = 1.434; BaF$_2$ = 1.474; MgF$_2$ = 1.378.
$^{(b)}$ZBLAN target.
$^{(c)}$modified ALF70 composition with low refractive index: $n_D$ = 1.417.

11.4 Performance of Active Waveguides

The successful fabrication of planar waveguides with proper spectroscopic properties and low propagation loss is not the ultimate goal. Demonstration of efficient laser or optical amplification requires a channel waveguide configuration, with lateral and transverse confinement. This supplementary step often generates extra propagation loss.

Figure 11.3 shows the possible geometries of confined structures. Except in the case of laser writing and micromachining, processing using photolithography is necessary to achieve these geometries. Photolithography, which is well established for silica, is not directly transferable to fluoride material because of (i) incompatibility between the glass and the solvent used to develop the resin; and (ii) thermal resistance and chemical inertia of the mask toward the glass components and sometimes reactive atmosphere. Obviously, this is one main reason why the literature on the production of fluoride glass-channel waveguides is not as extensive as that for planar waveguides.
For $\text{F}^-/\text{Cl}^-$ exchange, the use of a silica mask leads to the best results in terms of optical quality of the guide [30] owing to its chemical inertia against the glass and the reactive atmosphere, in comparison to a metallic mask; final burial by HF treatment results in an elliptical waveguide. In deposition techniques, a resin mask is acceptable when deposition temperature is low (i.e. $< 200 \, ^\circ\text{C}$); as an example, the ‘lift-off’ process have been successfully applied to get PZG strip waveguides by PVD [31]. For ridge waveguide fabrication, wet (chemical) or physical etching are available techniques. Wet etching of fluoride glass requires specific solutions, i.e. $\text{ZrOCl}_2/\text{HCl}$ for $\text{ZrF}_4$-based glass [32, 33], $\text{AlCl}_3/\text{HCl}$ for $\text{AlF}_3$-based glass, which prevent precipitation by forming a stable fluoride complex. The

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**Figure 11.3** Different geometries of confined waveguides (WG): (a) laser written WG (direct writing or self writing), (b) exchanged WG (buried or not buried), (c) strip WG (“lift-off” process), (d) ridge WG and (e) charged WG. The resist mask in (b), (c), (d) and (e) is obtained by standard photolithography. RIE is reactive ion etching.
main problems encountered with wet etching are the nonrectangular profile and the extensive roughness of the edges [34]. Micromachining has been applied to generate ridge-like waveguides between two parallel grooves structured by laser ablation [29], also leading to poor edge quality. One alternative may be to use reactive ion etching (RIE), but a test performed on ZrF$_4$-based glass was not conclusive [35]. On the whole, ionic exchange is considered to be the most suitable low-cost technique to fabricate channel waveguides.

To complete the overview, laser writing of channel waveguides has to be mentioned. This is a very fast and powerful technique that can be applied both to films and bulk materials. Irradiation of an area in the glass is used to achieve photo-induced refractive index changes, up to 0.01. Practically, waveguides are written in glass with focused femtosecond laser pulses (i.e. $\lambda = 800$ nm [36]), or continuous waves in the case of films to avoid damage (i.e. $\lambda = 244$ nm [37]). Another possibility is to create a confined waveguide between two photothermal expansion ridges (i.e. $\lambda = 244$ nm [38]); this way, the guiding zone is sheltered from possible radiation damage that can strongly affect the guiding properties.

11.4.1 Optical Amplifier

The most important characteristic to indicate the performance of an optical amplifier is the net or external gain that takes into account the coupling loss (C), propagation loss ($\alpha$) and RE-absorption $\sigma_a$. It is given by the following equation:

$$G_{\text{net}}(\text{dB}) = G_{\text{on/off}} - 2C - (\alpha L + \sigma_a NL)$$

where $L$ is the waveguide length and $N$ the RE concentration. The relative gain $G_{\text{on/off}}$, i.e. the ratio of the output signal when the laser pump is on and off, is a quicker measurement and thus gives a preliminary estimation of amplifier performance (Figure 11.4).

![Figure 11.4](image)

**Figure 11.4** ‘On/off’ gain at 1.53 $\mu$m as function of the incident pump power in Er$^{3+}$-doped ZBLA and PZG fluoride glass waveguides pumped at 980 nm. Inserted in the graph, near field images showing single mode (ZBLA) and multimode (PZG) waveguides at this wavelength.
Table 11.4 summarizes the most interesting results for fluoride glass integrated amplifiers. As can be noted, both PVD and ionic exchange technologies, developed simultaneously by two French teams in Rennes and Le Mans, have shown an ability to make waveguide amplifiers. Although waveguides produced by PVD exhibit similar or even higher relative gain, net gain has been observed only for Cl\(^-\)/F\(^-\) exchanged ZBLA in a single-mode channel waveguide (\(G_{\text{net}} = 2.5 \text{ dB for } L = 1.9 \text{ cm with } 1.48 \mu\text{m pumping}\)). This can be partially explained by the mismatch between the optical modes of the coupling fibre and the smaller mode of the PZG ridge waveguide.

It is known that pump absorption is strongly enhanced at 980 nm with Yb\(^{3+}\) codoping. To take advantage of this in fluoride hosts, Er\(^{3+}\)/Yb\(^{3+}\)/Ce\(^{3+}\) tridoping is necessary to prevent upconversion of Er\(^{3+}\) by emptying the \(4I_{11/2}\) level. With this tridoping, the simulated gain could reach nearly 10 dB, even for waveguides as short as 4–5 cm [39] thus coming near the best performance reported on exchanged phosphate glass (i.e. 13 dB for a waveguide 5.5 cm long [40]). To emphasize the quality of these structures, it is worth recalling the performance of a ZBLAN fibre (33 dB for a fibre 10 m long [41]).

### 11.4.2 Lasers

Turning now to lasers, the only demonstration of laser action comes from a fluoride glass channel waveguide obtained by direct UV writing of a negative index change close to 0.01 in a fluoro-aluminate glass layer fabricated by dip casting [38]. The negative index change induced by photothermal expansion of the glass produces lateral confinement. Table 11.4 gives the characteristics of this laser and compares them to oxide glass waveguides. As can be seen, the performances are not as good but they could be largely improved considering the highly multimode structure.

Green upconversion lasing was unsuccessful in a ridge ZBLAN waveguide obtained by pulse laser deposition and laser micromachining [30]; possible reasons are large scattering and coupling loss inside the resonator. However, simulation predicts that a conversion efficiency of 13% is possible with a loss by scattering reduced down to 1 dB/cm (the actual value is 5 dB/cm).
It is clear that the results are not as good as expected, considering the intrinsic advantage of fluoride in comparison to oxide glasses. Unfortunately, the channel waveguide with the lowest propagation loss (i.e. 0.1 dB/cm) is achieved by lateral confinement for which control of the waveguide width (~10 μm) is not as accurate as for the photolithography process.

### Table 11.5 performance of fluoride glass waveguide lasers at 1.05 and 1.3 μm (pumping @ 800 nm). The oxide waveguides exhibiting the best performance are given for comparison

<table>
<thead>
<tr>
<th>λ (μm)</th>
<th>Glass</th>
<th>WG section (type)</th>
<th>slope efficiency</th>
<th>power threshold</th>
<th>length (cm)</th>
<th>loss (dB/cm)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.05</td>
<td>ALF70Nd³⁺</td>
<td>10 × 100 μm²</td>
<td>27%</td>
<td>60 mW</td>
<td>1.6</td>
<td>0.1</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>BK7*Nd³⁺</td>
<td>10 × 5 μm²</td>
<td>42%</td>
<td>~10 mW</td>
<td>2.4</td>
<td>0.2</td>
<td>[44]</td>
</tr>
<tr>
<td>1.3</td>
<td>ALF70Nd³⁺</td>
<td>10 × 100 μm²</td>
<td>2%</td>
<td>32 mW</td>
<td>1.6</td>
<td>0.1</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>SiO₂-P₂O₅</td>
<td>8 × 12 μm²</td>
<td>2.6%</td>
<td>20 mW</td>
<td>5.9</td>
<td>&lt;0.8</td>
<td>[45]</td>
</tr>
</tbody>
</table>

* BK7: exchanged Na⁺/K⁺ borosilicate glass

### 11.5 Fluoride Transparent Glass Ceramics: An Emerging Material

A new kind of material doped with rare-earth ions have been intensively investigated in the last decade – transparent glass ceramics (GC). These materials are obtained by controlled crystallization of a fraction of glasses by thermal process to get the active ions embedded in the crystal phase (see also Chapter 9 in the present book). Glass ceramics are thus of great importance in photonics because they can offer higher cross sections compared to glass that can be exploited in order to fabricate more compact devices. While the spectroscopic efficiency of GCs has been demonstrated in bulk, published works on rare-earth-doped GC waveguides remain very few, even for oxide materials [46]. The major obstacle concerns the crystallite size which has to be sufficiently small (a few nanometers) to keep Rayleigh scattering losses to an acceptable low level. Jestin et al. succeeded with SiO₂-HfO₂ glass made by sol-gel with propagation loss around ~1 dB/cm after thermal treatment [47].

The first rare-earth-doped transparent CG containing fluoride was reported by Auzel et al. [48], combining pure oxide components with PbF₂. A few years later, they obtained a totally fluoride transparent GC starting from ZELA or ZELAG glasses [49, 50] (see Table 11.1 for composition). The particularity of these glasses is to show only one crystalline phase through a spinodal decomposition, unlike ZBLAN glass, which gives nontransparent GC. It is also worth noticing that this glass is not significantly affected by concentration quenching up to ~10 mol%.

Recently, ZELA glass waveguides have been successfully obtained by PVD, through coevaporation of a LaF₃-ErF₃ mixture and ZBNA (ZrF₄-BaF₂-NaF-AlF₃) glass [22]. Figure 11.5 illustrates the process by showing the vapour pressure curves of the fluoride compounds involved in the system. With a suitable thermal treatment, vitreous
thin films deposited on a substrate heated slightly above Tg crystallize in a single phase with composition close to the glass one, in a similar way to the bulk (two-step process). When increasing deposition temperature, GC containing LaF$_3$ nanocrystals (doped with 30 mol% Er$^{3+}$) are obtained without any thermal treatment (one-step process).

**Figure 11.5** Vapour pressure curves of fluorides entering ZELAG et ZBNA glass compositions

**Figure 11.6** Luminescence spectra of Er$^{3+}$ at 1.5$\mu$m upon 514.5 nm excitation of ZELA waveguides containing either LaF$_3$ (one-step process) or LaZr$_3$F$_{15}$ (two-steps process) nanocrystals. The spectra of the pure crystalline phases and glass are given for comparison.
it is likely that small ‘aggregates’ of ErF$_3$ and LaF$_3$ formed in the vapour state and quenched on the substrate act as nucleation agents. Guiding properties in infrared are not affected by the presence of nanocrystals in the waveguide with respect to the glassy waveguide for which propagation loss is 1.3 dB/cm, consistent with the dimension of the nanocrystals (<50 nm). The changes in the Er$^{3+}$ environment in the precursor glass and GC are visible on the luminescence spectra at 1.5 $\mu$m (Figure 11.6) with Er$^{3+}$ both in glassy and crystalline parts [51]. For LaF$_3$ containing GC this results in a flatter and broader emission band (71 nm at half height width) close to the highest value reported in oxyfluoride bulk GC containing PbF$_2$ crystals [52]. Concerning emission efficiency, some more work is necessary to optimize Er$^{3+}$ doping to avoid concentration quenching in the crystalline phase.

11.6 Conclusion

In this chapter, we have shown that fluoride glass-confined waveguides with an acceptable propagation loss level (i.e. <0.5 dB/cm) can be obtained by suitable combination of composition and fabrication technique. This was a real challenge knowing the low thermal stability of fluoride glasses toward crystallization in comparison to oxide homologues.

Actually, the performance of planar optical waveguides is less impressive than in fluoride glass optical fibre amplifiers or lasers; it partially reflects the time taken to establish reliable processes before achieving the required guiding structure. However, it is hoped that the performance as well as the integration may be further improved by the increasing number of laboratories working in this field, driven by the need for low-cost and reliable devices, particularly in the fibre telecommunication industry. In this regard, the recently emerged fluoride glass-ceramic waveguide appears as a promising structure in terms of bandwidth and flatness of the Er$^{3+}$ emission band at 1.55 $\mu$m for optical amplification. Rare-earth doped glass waveguides may also find applications in realizing efficient compact visible laser sources, using upconversion processes by energy transfer, favoured by high doping rate and/or codoping.

References

Fluoride Glasses and Planar Optical Waveguides


