Photonic glasses for IR and mid-IR spectral range

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Abstract— The mid-IR spectral range is of particular interest for optical spectroscopy as many molecules exhibit signature optical absorptions in this wavelength range. Detection of these chemical species is essential for many applications in space research such as in-situ and remote sensing of gases in planets’ atmosphere, isotope detection and identification of the soil composition of planetary surfaces. Moreover, in this wavelength region specific transmission windows are available in the Earth’s atmosphere. The development of mid-IR optical spectrometers has been delayed by the lack of compact, reliable, high power mid-IR optical sources, either narrowband or broadband. This limitation resides in the difficulty of finding glass or crystal host materials that are both sufficiently transparent in the mid-IR wavelengths range and sufficiently stable, robust and easy to fabricate.

A promising option to engineer such sources relies on the use of mid-IR transmitting glass, in the form of an optical fiber. This solution will extend into the mid-IR the considerable advantages of fiber technology such as simplified thermal management, light weight, minimum occupied volume and distributed system architecture. The optical confinement reduces the need for free space optics which are sensitive to misalignment; in addition light in fibers is totally confined within the core-cladding structure and thus completely shielded from environmental conditions like dust, vibration, and moisture.

Several RE trivalent ions (e.g. Er$^{3+}$, Ho$^{3+}$, Tm$^{3+}$, Dy$^{3+}$) possess fluorescence emissions in the mid-IR spectral range which can potentially be made to lase in mid-IR glasses. For instance, fiber laser, in these glass host, with emission around 2 μm have already been successfully demonstrated [3] [4].

An alternative technology relies on microstructured mid-IR transmitting glass optical fiber in order to generate a very broadband supercontinuum (SC) light emission spanning the optical range from near to-mid-IR wavelength [5]. This fiber generated SC light possesses the characteristics of coherence, bandwidth and brightness requested by spectroscopic applications in the mid-IR region.

The aim of this short review is to present the relevant glass host materials suitable for the development of IR and mid-IR coherent sources based on RE doping. Moreover the current state of the art in mid-IR fiber laser and supercontinuum sources is presented.

I. INTRODUCTION

Photonic technologies present numerous intrinsic advantages particularly well suited for space applications, such as light weight, low volume (resulting in much reduced payload), immunity to electromagnetic interference, capability of operating in harsh environments and practically unlimited bandwidth [1]. It is thus not surprising that in the last decade photonic technologies have had an increasing role in the engineering of space systems.

Among photonic materials, glass plays an important role thanks to its unique structural and thermodynamic features. Besides stability, glass presents an excellent homogeneity, good thermo-mechanical properties and a viscosity–temperature relationship that allows for fiber drawing. Moreover glass has the potential for doping with rare earth (RE) ions and a wide range of properties can be chosen to meet the needs of different applications.

Silica based glasses are the most widespread material used for photonic systems, especially for data transmission. However, other applications depend on optical amplification (through dopants or nonlinear optical processes), infrared (IR) light transmission or high optical nonlinearities that require alternative glass systems with suitable properties. Silica based glasses, in fact, exhibit high intrinsic absorption beyond 2.4 μm, which precludes their use in the mid-IR range (2–5 μm), and possess low nonlinear index compared to other glass families (e.g. tellurite and chalcogenide) [2].

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II. GLASS SYSTEMS

The choice of a suitable glass composition for a photonic component based on a fiber or a planar structure involves the evaluation of series of parameters related to the glass: the maximum phonon energy, the chemical durability, the fiber drawing ability and the purity of the starting materials.

Active devices, such as fiber amplifiers and lasers, rely on the presence of RE dopants in the glass. This places further requirements on glass compositions and properties, like a homogeneous distribution of RE in the glass matrix and a stable oxidation state of the optically active ion.

For certain RE transitions, particularly those in the mid-IR, it is important to use glass host with low phonon energy. In fact, the maximum phonon energy sets the overall infrared transparency range and the multiphonon relaxation rates which influence the quantum efficiency. Lower phonon energy results in a lower non-radiative transition rate between adjacent RE energy levels, leading to fluorescence and laser emission from additional energy levels that are not possible for high phonon energy glasses.

In Table 1 a comparison between typical values of selected properties of main glass system is reported. These values can vary with changing the glass compositions.

A. Silica based glasses

Silica based glasses exhibit high intrinsic absorption beyond 2.4 μm, which make them ideal for use in the visible and near infrared (NIR), but precludes their use in the mid-IR beyond 2.4 μm.

Silicate glasses, in particular aluminosilicate and germanosilicate, have been largely employed for the realization of active devices, such as fiber lasers or amplifiers, thanks to the possibility of directly connecting the active fiber component to a silica telecommunications fiber by fusion splicing with low insertion loss and low reflectivity.

Because of the low solubility of rare-earth oxides in silica, concentration can be increased only to ~ $10^{19}$ ions/cm$^3$, before concentration quenching effects take place, resulting in a degradation of the laser efficiency [13]. Therefore, silica is not the best choice in order to realize compact active devices.

The highest values of output power and efficiency from a fiber laser, have been achieved using an Yb$^{3+}$-doped silicate fiber emitting at a wavelength of ~ 1 μm. Commercial system able to supply output powers up to 50 kW are used for a variety of industrial applications, especially in material processing [19].

Silica based glasses possess low nonlinear index compared to other glass families, which is beneficial in many cases where nonlinear effects can be detrimental but limits its use in devices based on nonlinear optical processes.

<table>
<thead>
<tr>
<th>Glass family</th>
<th>Silica</th>
<th>Phosphate</th>
<th>Tellurite</th>
<th>ZBLAN</th>
<th>Chalcogenide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission range [μm]</td>
<td>0.2 – 2.5</td>
<td>0.2 – 4</td>
<td>0.4 – 5.0</td>
<td>0.2 – 6</td>
<td>0.8 – 20</td>
</tr>
<tr>
<td>Maximum phonon energy [cm$^{-1}$]</td>
<td>1100</td>
<td>1200</td>
<td>800</td>
<td>600</td>
<td>350</td>
</tr>
<tr>
<td>Glass transition temperature [°C]</td>
<td>1000</td>
<td>461</td>
<td>300</td>
<td>260</td>
<td>300</td>
</tr>
<tr>
<td>Thermal conductivity [W/(mK)]</td>
<td>1.38</td>
<td>0.57</td>
<td>1.25</td>
<td>0.628</td>
<td>0.2</td>
</tr>
<tr>
<td>Expansion coefficient [10$^{-6}$/K]</td>
<td>0.55</td>
<td>13.4</td>
<td>12 – 17</td>
<td>17.2</td>
<td>14</td>
</tr>
<tr>
<td>Density [g/cm$^3$]</td>
<td>2.2</td>
<td>2.59</td>
<td>5.5</td>
<td>4.33</td>
<td>4.51</td>
</tr>
<tr>
<td>Young’s modulus [GPa]</td>
<td>70</td>
<td>47</td>
<td>33.6</td>
<td>58.3</td>
<td>21.5</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.458</td>
<td>1.507</td>
<td>2</td>
<td>1.499</td>
<td>2.9</td>
</tr>
<tr>
<td>@0.589 μm</td>
<td>@0.587 μm</td>
<td>@1.55 μm</td>
<td>@0.589 μm</td>
<td>@ 10.6 μm</td>
<td></td>
</tr>
<tr>
<td>Abbe number</td>
<td>68</td>
<td>68</td>
<td>10 – 20</td>
<td>76</td>
<td>NA</td>
</tr>
<tr>
<td>Nonlinear index [m$^2$/W]</td>
<td>$10^{-20}$</td>
<td>$10^{-16}$</td>
<td>2.5 * $10^{-19}$</td>
<td>$10^{-21}$</td>
<td>$10^{-18}$</td>
</tr>
<tr>
<td>@ 1.06 μm</td>
<td>-4.7</td>
<td>-16.4</td>
<td>-14.75</td>
<td>@ 1.06 μm</td>
<td>@ 10.6 μm</td>
</tr>
<tr>
<td>Thermo-optic coefficient [10$^{-15}$/K]</td>
<td>12</td>
<td>-4.7</td>
<td>50</td>
<td>0.65</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>@ 1.06 μm</td>
<td>@ 1.2 μm</td>
<td>@ 1.2 μm</td>
<td>@ 2.59 μm</td>
<td>@ 3 μm</td>
</tr>
<tr>
<td>Fiber loss [dB/Km]</td>
<td>0.2</td>
<td>1.5</td>
<td>50</td>
<td>0.65</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>@ 1.5 μm</td>
<td>@ 1.05 μm</td>
<td>@ 1.2 μm</td>
<td>@ 2.59 μm</td>
<td>@ 3 μm</td>
</tr>
<tr>
<td>RE solubility</td>
<td>$10^{15}$ ions/cm$^3$</td>
<td>$10^{21}$ ions/cm$^3$</td>
<td>$10^{21}$ ions/cm$^3$</td>
<td>$10^{21}$ ions/cm$^3$</td>
<td>0.1 mol%</td>
</tr>
</tbody>
</table>
B. Non-silicate oxide glasses

Several key photonic devices are made of non-silica based oxide glasses belonging to the phosphate, borate, germanate or tellurite systems. Although these glass systems are not applied to mass production due to the higher cost of raw material (compared to silicate), lower chemical durability and mechanical strength, they possess unique properties that cannot be obtained for silicate glasses.

Phosphate glasses are the most resistant to quenching concentration effect. They enable extremely high doping level of RE ions (up to $10^{21}$ ions/cm$^3$) and thus more compact active devices. In fact the length of the phosphate fiber laser can be substantially decreased even below ten centimeter in order to have an output power in the order of watt level, in a single frequency operation. Moreover, phosphate glasses offer a higher photo-darkening threshold than silica and low nonlinear refractive index, that make them suitable for the realization of high power, high brilliance single-frequency laser source [14].

Another important feature of phosphate glasses is their thermal and mechanical strength, that allows for the realization of optical fibers that can be cleaved and fusion spliced with commercial optical fiber components based on silicate glasses [20].

Tellurite glasses have a wide transmission bandwidth in the infrared wavelength region (up to 5 μm) that makes them suitable for the mid-IR spectral range. Compared to other non-oxide glasses operating in this range, they demonstrate higher glass stability and corrosion resistance. Furthermore, they are non-hygroscopic, which allows storage in ambient air without degradation.

Tellurite glasses also show advantages as host materials for RE ions: high doping level can be achieved without clustering (up to $10^{21}$ ions/cm$^3$) [3,18], and RE ions show broad emission bands in this glass host. In addition tellurite glasses also exhibit the lowest phonon energy among conventional oxide glasses.

Among all oxide glasses, tellurites are the ones that exhibit the highest linear and nonlinear refractive indices: the first is beneficial in obtaining efficient radiative transitions, the second makes them attractive for supercontinuum generation devices.

C. Fluoride glasses

The most common form of heavy-metal fluoride glass is the fluorozirconicate (ZrF$_4$) composition and the most widespread fluoride fiber material is the so-called ZBLAN glass (56ZrF$_4$-19BaF$_2$-6LaF$_3$-4AlF$_3$-15NaF, atomic %). Compared to other halide glasses (like the BeF$_2$ based glasses), ZrF$_4$-based multicompontent fluoride glasses have been extensively investigated thanks to the fact that they are neither toxic nor hygroscopic [15].

The high transparency of ZBLAN up to about 6 μm along with chemical stability comparable with a sodium silicate glass, make this glass an excellent candidate for fiber lasers in visible and mid-infrared regions where emissions are hard to be obtained from silicate and phosphate fibers.

A drawback of fluorides is the fact that their fabrication process requires extremely pure starting material (infrared-absorbing impurities below 1 ppb) and absolute absence of water and contamination in all synthesis stage. Moreover fluoride glasses are particularly prone to crystallization because of the low viscosity of the melt and the small stability parameter (difference between the glass transition and crystallization temperature).

D. Chalcogenide glasses

Chalcogenide glasses are based on the chalcogen elements (sulfur, selenium and tellurium) usually formulated with other elements to build up robust glass matrices.

One of the most important features of these glasses is their good transparency in the IR region up to 20 μm, therefore they can be used for the realization of optical elements for infrared rays such as prism, windows, waveguides, etc. Furthermore chalcogenide can be used for active applications in the near- and mid-IR range when doped with RE ions. The low phonon energy of chalcogenide glasses activates many mid-IR transitions for RE ions that are normally not present in materials with higher phonon energies.

In spite of all the studies on RE doped chalcogenide fiber lasers and amplifiers, their efficiencies and output powers are still relatively low due to the poor RE doping level (~0.1 mol%) achievable, the large background loss, and the fragility of chalcogenide glasses [6]. Significant long term efforts are needed before the realization of high output power chalcogenide fiber lasers for practical applications.

Another important feature of chalcogenides is their high optical non-linearity that makes these glasses promising candidates for all-optical switching applications.

III. MID-IR FIBER LASER

A promising option to engineer compact, reliable, high power mid-IR laser sources relies on the use of mid-IR transmitting glass, in the form of an optical fiber. This solution will extend into the mid-IR the considerable advantages of fiber technology such as simplified thermal management, light weight, minimum occupied volume and flexible remote delivery. Another key advantage of this new technological approach is the possibility of developing the whole laser resonator using only fiber components (all-fiber setup), and so avoiding the use of free-space optics, which can be critical in some applications, like space missions, due to mechanical vibrations and large temperature variations.

Several RE trivalent ions (e.g. Er$^{3+}$, Ho$^{3+}$, Tm$^{3+}$, Dy$^{3+}$, etc.) emit in the mid-IR spectral range and can potentially be made to lase in mid-IR glasses. See for example Fig. 3 in [21] which shows all the laser transitions responsible for IR emission longer than 1.5 μm from RE doped fiber lasers. However, efficient radiative processes involving these transitions require host material with low phonon energies and transparent to both the pump and the lasing wavelengths. In addition, the host material should be sufficiently robust and easy to fabricate.
Emission at ~2 μm from Tm\(^{3+}\) and Ho\(^{3+}\) ions into silicate glasses is highly developed, primarily because of the robustness and convenience offered by the silica glass host. From a Tm\(^{3+}\)-doped silica fiber laser, probably the most mature technology among the mid-IR fiber laser, an output power of ~1 kW has been recently reported [22]. The longest laser wavelength from a silicate glass fiber laser is currently 2.188 μm; lasing at longer wavelengths is not expected to be possible in the majority of silicate glasses.

A promising option for extending the emission wavelengths into the mid-IR domain is offered by ZBLAN fiber laser. For instance, 2μm, 2.9 μm, 3.22 μm, and 3.9 μm emissions were obtained from Ho\(^{3+}\) doped ZBLAN fiber lasers, 2.7 μm and 3.45 μm emissions from Er\(^{3+}\) doped ZBLAN fiber lasers, and 1.94 μm and 2.3 μm emission from Tm\(^{3+}\) doped ZBLAN fiber lasers [6]. Considerably high output powers have been reached for some of these transitions. For example, 24 W have been obtained from an Er\(^{3+}\) doped fluoride fiber at 2.7 μm [23]. This emission is close to the highest absorption peak of water around 3 μm and therefore has been extensively investigated for its application in laser surgery. From a Tm\(^{3+}\)-doped ZBLAN fiber laser, an output power of 20 W at 1.94 μm has been measured [24]. Although the output power of Tm\(^{3+}\)-doped fluoride fiber laser are not comparable with the silica fiber laser, these results indicate that ZBLAN fiber lasers with an output power in the order of tens of watts are feasible using suitable fiber design and novel pumping schemes. An extensive overview of fluoride fiber lasers can be found in [6].

Despite the promising results obtained so far, fluoride glass has not been widely accepted by industry because of the relatively poor stability and difficulty of fabrication, so alternative solutions are continuously sought. Among the oxide glasses, a promising solution to engineer mid-IR fiber laser is offered by tellurite and germanate glasses, thanks to their relatively low phonon energy and good stability, as already discussed in section II.A.

In tellurite glass system Ho\(^{3+}\), Er\(^{3+}\), Tm\(^{3+}\) ion emissions in mid-IR range have been investigated [3,18,25,26]. One issue in these glasses, like most oxide glasses fabricated from solid-state precursor materials, is the presence of hydroxyl ions (OH\(^-\)), which have absorption in the wavelength region of interest. For example, 3 μm emission from Er\(^{3+}\)-doped tellurite glass is suppressed by energy transfer from excited Er\(^{3+}\) ions to OH\(^-\) impurities, combined with the low radiative efficiency of the upper laser level in this host. A watt level output power at ~2 μm from a Tm\(^{3+}\)-doped tungsten tellurite fiber laser has been recently reported [27], while in germanates the highest output power reported from a Tm\(^{3+}\)-doped fiber laser is 64 W at 1.9 μm [28].

Despite the fact that these results show efficient emission at ~2 μm, no demonstration of laser operation beyond ~2 μm in tellurite or germanate glasses has been reported so far.

Chalcogenide glasses, as discussed in section II.D, possess a great potential as host materials for mid-IR fiber laser. However, the purity and toxicity of the starting materials and the difficulty of making ultra-low loss fiber currently limit the widespread use of these glasses for mid-infrared fiber-laser applications. Studies of mid-infrared luminescence of RE ions in chalcogenides have been reported for several ions including Ho\(^{3+}\), Tm\(^{3+}\), Tb\(^{3+}\), Dy\(^{3+}\), Pr\(^{3+}\) and Er\(^{3+}\) [9] with emission wavelengths as long as 4.3 μm [21]. However, the only example of fiber-laser action in chalcogenides so far is a Nd\(^{3+}\)-doped GaLaS (GLS) glass operating at a wavelength of 1.08 μm [29].

So far, the 3.95 μm wavelength emitted from a Ho\(^{3+}\)-doped ZBLAN fiber laser under cryogenic conditions is currently the longest laser wavelength that has been generated from a fiber laser.

IV. SUPERCONTINUUM LIGHT SOURCES

Spectroscopy in the molecular fingerprint regions of the mid-IR spectral range requires an optical source of sufficient brightness whose wavelength range extends from near-IR into the mid-IR region. Laser sources provide brightness and coherence, but have very limited bandwidth. Other sources, such as thermal sources, have very high bandwidths but low coherence and low brightness. Fiber generated SC light provides an useful balance of brightness, coherence and bandwidth making it a promising optical source for investigations in this spectral region.

SC generation is a physical process leading to an extensive spectral broadening of a laser beam while it propagates through a strongly nonlinear medium. Optical fiber, and especially microstructured fibers, are promising options for SC generation thanks to their significant length of interactions.

So far, most of the investigations have been carried out on silica fibers and thus the upper limit of the SC light spectrum was limited to ~2 μm, the multiphonon edge of silica glass. In order to extend the emission in the mid-IR spectral range other materials are preferable as host medium.

One option is ZBLAN glass thanks to its low background loss and wide transparency window in the mid-IR region, although this glass has the nonlinearity even less than that of silica glass (see Table 1). On the other hand, other soft glasses, such as tellurites or chalcogenides, besides having high transparencies in the mid-IR range, show strong nonlinear properties as well. This latter feature allows for shorter fiber length, providing the additional advantage to mitigate the high losses of these specialty glasses.

In the past years several mid-IR SC source lab versions have been demonstrated; however, no off-the-shelf products are yet commercially available, nor are all relevant information published. The best published result so far is the SC generation from a ZBLAN fiber presenting a spectral coverage from ~1.9 to 4.5 μm with an average power of 2.6 W [30].

A recent result reported in tellurite glass is the generation of SC light with a bandwidth of 4080 nm extending from 789 to 4870 nm obtained using a sub-cm (8 mm) length of highly nonlinear microstructured photonic crystal fiber (PCF). This bandwidth is comparable with previously reported spectra for
other nonlinear glass fiber formulations despite the significantly shorter fiber length [5].

V. CONCLUSIONS
In this paper the main properties of the different glass system useful for the development of IR and mid-IR optical sources are briefly reviewed. Main achievements in the research of fiber laser and SC sources operating in the mid-IR spectral range are reported. In spite of the remarkable results obtained so far, the development of coherent sources in the mid-IR spectral range, remains an open research field that still has to face several issues and challenges.

REFERENCES
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