CHAPTER 6

Overall Conclusions and Future Perspectives

Abstract

The work presented in the thesis is mainly concerned with the structural, optical and dielectric properties of Sm$^{3+}$-doped fluoroborate and fluorophosphate glasses. In order to create planar waveguides, we have effectively incorporated silver ions in Sm$^{3+}$-doped K-Mg-Al-Zn fluorophosphate glass via Ag$^+/K^+$ thermally diffused ion exchange process. We have synthesized Er$^{3+}$-doped Li-Zn fluoroborate glass for applications in lasers and broadband optical amplifiers. Channel waveguides were created in Er$^{3+}$-doped Li-Zn fluoroborate glass using high repetition rate femtosecond laser micromachining. This chapter includes the overall conclusions and some future perspectives of the research problem investigated.
6.1 Overall Conclusions

It is well known that fluoroborate and fluorophosphate glasses are suitable hosts because of their high transparency, high thermal stability, good solubility of RE ions and interesting optical, structural and electrical properties. In view of the favorable and promising features of these glasses, we have undertaken a systematic investigation on their structural, optical and dielectric properties and ion migration in and around the channel waveguides written in the fluoroborate glass.

The Sm\(^{3+}\)-doped Li-Zn fluoroborate glasses were prepared by melt quench technique. The prepared glasses were found to be thermally stable and homogeneous without having any crystalline phase. JO intensity analysis has been carried out and the nature of intensity parameters was found to be \( \Omega_4 > \Omega_6 > \Omega_2 \). The negative value of the bonding parameter and the small value of \( \Omega_2 \) are indicative of the ionic nature of the Sm\(^{3+}\)-ligand bond. It has been found that the fluorescence quenching occurs above 0.5 mol\% Sm\(^{3+}\)-doped Li-Zn fluoroborate glasses. The results suggest that the present glass system is suitable for making fiber amplifiers and optical materials for the development of lasers and photonic devices in the visible region due to the large values of branching ratios and stimulated emission cross-sections. The predicted lifetime is found to be larger than the experimental lifetime with better luminescence quantum efficiency of 64%. The decay curves exhibit single exponential nature in the lower concentration and it turns to non-exponential behavior for higher concentrations. It has been concluded that the mechanism of energy transfer through cross-relaxation is predominantly governed by the dipole-quadrupole interaction between Sm\(^{3+}\) ions in the glass system under investigation. It is observed that the dielectric constant slightly decreases...
with the concentration of $\text{Sm}^{3+}$ ions, while the value of conductivity ranges from 0 to $1.6 \times 10^7 \ \Omega^{-1}\text{cm}^{-1}$. The values of power-law parameter ($s$) and Cole-Cole parameter ($\tau$) are found to increase with the concentration of $\text{Sm}^{3+}$ ions.

K-Mg-Al-Zn fluorophosphate glasses doped with $\text{Sm}^{3+}$ ions were prepared successfully without having any crystalline phase. The optical energy band gap ($E_g$) for PKAMZFSm10 glass has been obtained as 3.89 eV. Negative value for the bonding parameter ($\delta$), low value of asymmetric ratio and the small value of JO parameter ($\Omega_2$) have substantiated the ionic nature of $\text{Sm}^{3+}$-ligand bond in the $\text{Sm}^{3+}$-doped PKAMZF glass. Judd-Ofelt intensity analysis for 1.0 mol% $\text{Sm}^{3+}$-doped PKAMZF glass has been carried out and the nature of the JO parameters is found to be $\Omega_4 > \Omega_6 > \Omega_2$. This glass system is suitable for developing visible laser and optical fiber amplifiers due to its higher values of branching ratios and stimulated emission cross-sections. The non-exponential decay curves are well fitted to the IH model and it is found that the energy transfer between $\text{Sm}^{3+}$ ions is of dipole-dipole nature. A successful tuning of dielectric constant can be achieved by varying the concentration of $\text{Sm}^{3+}$ ions. There is a considerable progress in the insulating behavior of $\text{Sm}^{3+}$-doped K-Mg-Al-Zn fluorophosphate glasses when $\text{Sm}_2\text{O}_3$ concentration is about 1.0 mol% in the glass system. Hence these glasses are more advantageous than undoped glass for practical applications. Thus it is proposed that the investigated glass system is useful for optical communications as optical dielectric polarizers at high optical powers, photonic devices or optical energy transport devices.

Novel ion exchange unit with a modified dipping mechanism and temperature controller was designed, fabricated and optimized. Silver ions
were effectively incorporated in $\text{Sm}^{3+}$-doped K-Mg-Al-Zn fluorophosphate glass via $\text{Ag}^+$/K$^+$ thermally diffused ion exchange process. The crystallite size of the Ag NPs, in the ion exchanged glass was estimated to be 19 nm. The energy transfer mechanism from silver to $\text{Sm}^{3+}$ ions causes a slight decrease in the absorption and an enhancement in the photoluminescence intensity of $\text{Sm}^{2+}$ ions in PAgSm glass. Lifetime of $^4\text{G}_{5/2}$ level of $\text{Sm}^{3+}$ ions in PAgSm glass was less than that in PKSm glass. This reduction in the lifetime of PAgSm glass indicates that the total transition probability and $\text{Sm}^{3+}$-$\text{Sm}^{3+}$ electric-dipole interactions are higher for PAgSm glass. The dielectric constants for silver incorporated glass increased due to the lack of restrictions for dipoles to line up in the field direction whereas the intrawell hopping of charge carriers and large surface scattering resulted in a reduction in conductivity at higher frequencies. It is suggested that regions near to the surface of the $\text{Ag}^+$/K$^+$ ion exchanged $\text{Sm}^{3+}$-doped K-Mg-Al-Zn fluorophosphate glass is suitable for optical communications in the visible region as planar waveguides, optical amplifiers, sensors or optical dielectric polarizers at high optical powers.

$\text{Er}^{3+}$-doped Li-Zn fluoroborate glass has been synthesized with good optical quality and transparency. The ionic nature of the $\text{Er}^{3+}$-ligand bond in the glass network was confirmed by bonding parameter evaluation. Judd-Ofelt parameters $\Omega_t$ ($t = 2, 4, 6$) were found to be larger than those reported in the literature for different host materials. JO intensity analysis reveals the nature of JO parameters as $\Omega_2 > \Omega_6 > \Omega_4$. In this study, the small value of quality factor and 1.53 $\mu$m broad emission with large emission cross-sections point out that the present glass system is an appropriate material for lasers and broadband optical amplifiers. Femtosecond laser written optical channel waveguides were fabricated in the glass with different energies and scan conditions. The interplay among
the pulse repetition rate, average laser power and the scan speed affects strongly the waveguide characteristics. The waveguides have revealed good guiding properties like highly confined single mode profiles and good propagation losses which indicate promising potential applications for waveguide amplifiers, lasers and sensors. The guiding of 980 and 1640 nm wavelengths through the waveguides indicates the potential for fabricating waveguide lasers in the near-IR region. The investigation on elemental distribution demonstrates migration behavior of the boron, zinc and fluorine ions in the laser irradiated zone. The migration of boron and fluorine within a laser written waveguide is reported for the first time. These results possibly will be supportive for the control of shape and dimension of laser inscribed structures that may show potential applications in integrated photonic devices.

6.2 Future Perspectives

The hunt for novel luminescent materials has been intensified in recent years for various optical device applications. RE$^{3+}$ ions in glasses exhibit narrow absorption/emission lines in the UV-Visible and near infrared regions which make them attractive for use in lasers and fiber amplifiers. The work presented in this thesis opens the door to several future research and applications. Some of the future perspectives are:-

- Fabrication of optical planar waveguides in Sm$^{3+}$-doped Li-Zn fluoroborate glass via Ag$^+/Li^+$ ion exchange.
- Profiling of silver concentration and refractive index in the ion exchanged glass.
- Investigations on sensing properties of optical planar waveguides in the ion exchanged glass through evanescent coupling.
Synthesis and characterizations of Er$^{3+}$-doped K-Mg-Al-Zn fluorophosphate glasses for the applications in optoelectronic devices and broadband optical amplifiers.

Fabrication of optical channel waveguides in Er$^+$-doped K-Mg-Al-Zn fluorophosphate glasses via femtosecond laser writing and a detailed investigation of ion migration in and around the waveguides.

Photoluminescence studies of femtosecond laser written optical channel waveguides.