PREFACE

The present thesis deals with the studies on “Spectroscopic and electrical properties of Na$_2$SO$_4$–BaO–P$_2$O$_5$: Fe$_2$O$_3$ glass system & Role of modifier oxide in emission spectra and kinetics of Sm$^{3+}$ and Er$^{3+}$–Ho$^{3+}$ co-doped Na$_2$SO$_4$–MO–P$_2$O$_5$ glasses”. This work has been carried out in the Department of Physics, Acharya Nagarjuna University – Dr. M.R.A.R Campus, Nuzvid. The thesis contains the methods of preparation, studies on electric and spectroscopic properties of Na$_2$SO$_4$–BaO–P$_2$O$_5$ glass systems doped with varying concentration of Fe$_2$O$_3$ and also the influence of different modifiers (MgO, CaO and BaO) on spectroscopic properties of Sm$^{3+}$ and Er$^{3+}$–Ho$^{3+}$ co-doped Na$_2$SO$_4$–MO–P$_2$O$_5$ glasses.

Alkali sulphate mixed phosphate glasses are considered as appropriate materials for the immobilization of radioactive waste. These glasses exhibit unique electrolytic properties that make them suitable for several solid-state electrochemical devices such as high temperature solid-state sodium–sulphur batteries, high density micro-batteries, sensors, smart card and medical appliances etc. A material to be used as solid electrolyte should exhibit high electrical conductivity, purely ionic, compatible with the electrode materials and should be thermally and chemically stable. In sulpho-phosphate glasses, SO$_4^{2-}$ ions largely dissolve in the phosphate glass matrix. However, these ions and metaphosphate ions appear to be weakly interacting and resulting in a
small dynamic concentration of dithiophosphate (DTP) units. Such weak and variable interaction between these two ions is expected to influence the electrical properties to a large extent.

Usually electrical conductivity of alkali phosphate glasses is inhibited due to their relatively poor chemical stability. The addition of transition metal ions like iron to these glasses is expected to improve their electrical properties. Regardless of the original oxidation state of the iron in the starting glass batch, the final glass contains Fe$^{3+}$ (in both tetrahedral and octahedral environments) and Fe$^{2+}$ ions in octahedral environment. The concentration of Fe$^{2+}$ (or Fe$^{3+}$) which will have a strong bearing on electrical properties of these glasses depends primarily upon the melting temperature, other constituents of the glass and to some extent on the melting time.

In view of this we have devoted initial part of the thesis to investigate the influence of Fe$_2$O$_3$ on electrical properties of Na$_2$SO$_4$–BaO–P$_2$O$_5$ glasses. The studies cover electrical conductivity and dielectric dispersion (dielectric constant $\varepsilon'$ and loss tan $\delta$) over a wide frequency range from 0.01 Hz to 1 MHz and in temperature range from 303 to 523 K. To have some pre-structural understanding for explaining the conduction phenomenon, we have also included the data on optical absorption, ESR, IR and Raman spectral studies on these glasses.
Although a large number of studies are available in the literature on alkali sulphate–phosphate glasses mixed with different modifiers, majority of them are focused mainly on conductivity studies.

Weak and variable interaction between sulphate and phosphate ions is a welcoming facet for the incorporation of rare earth ions to give high luminescence efficiencies with minimal non radiative losses in these glasses. The interaction between sulphate and phosphate ions can further be modified with the introduction of different modifier oxides. As it is well known that, the incorporation of alkali-earth oxides (viz., MgO, CaO and BaO) in the glass structure leads to a disruption of the glass network and promotes the formation of non-bridging oxygens (NBO) groups. The ionic field strengths $I (I = Z/r^2$ where $Z$ is the charge number and $r$ is the ionic radius) for $\text{Mg}^{2+}$, $\text{Ca}^{2+}$ and $\text{Ba}^{2+}$ ions are $4.73 \ A^{\circ-2}$, $2.04 \ A^{\circ-2}$ and $1.49 \ A^{\circ-2}$ respectively, indicating that the network modifier cation, $\text{Mg}^{2+}$ has larger ionic field strength than the other two ions. In view of these facts, when sodium sulphate-phosphate glasses are mixed with these network modifying ions there will be structural modifications and local field variations around the rare earth ion dopant in the glass matrix; in other words the symmetry and or covalency of the glass at the rare earth ion should be different for different modifier mixed glasses. Such variations will have strong bearing on various luminescence transitions of the lanthanide ion.

With this view have devoted the second part of the thesis to the studies on the
influence of modifier ions (Mg$^{2+}$, Ca$^{2+}$ and Ba$^{2+}$ ions) on the emission characteristics of three interesting rare earth ions viz., Sm$^{3+}$, Ho$^{3+}$ and Er$^{3+}$ in Na$_2$SO$_4$–BaO–P$_2$O$_5$ glasses.

The compositions of the glasses used for the present studies are:

1. $(20-x)$Na$_2$SO$_4$–20BaO–60P$_2$O$_5$: xFe$_2$O$_3$ $(0 \leq x \leq 2.0$ in the steps of 0.5))

2. 19 Na$_2$SO$_4$–20 MO–60P$_2$O$_5$: 1.0 Sm$_2$O$_3$/ 1.0 Ho$_2$O$_3$/ 1.0 Er$_2$O$_3$

3. 18 Na$_2$SO$_4$–20 MO–60P$_2$O$_5$: 1.0 Ho$_2$O$_3$ + 1.0 Er$_2$O$_3$

where M = Ba, Ca & Mg) (all in mol %).

The studies carried out are:

a) Studies of Na$_2$SO$_4$–BaO–P$_2$O$_5$: Fe$_2$O$_3$

(i) differential scanning calorimetric studies and the evaluation of glass transition temperature $T_g$ and crystallization temperature $T_C$

(ii) infrared and Raman spectral studies in the wavenumber range 400–2000 cm$^{-1}$ and the study of the effect of concentration of iron ions on the position and intensity of various vibrational bands;

(iii) optical absorption studies in the wavelength range 300–2100 nm, identification of various electronic transitions of iron ions;

(iv) electron spin resonance measurements and the identification of the positions and valence states of iron ions in the glass network;

(v) dielectric properties viz., dielectric constant $\varepsilon'$, dielectric loss tan $\delta$ and
ac conductivity $\sigma_{ac}$ and impedance spectra in the frequency range 0.01 Hz to 1 MHz and in temperature range from 173 to 523 K.

b) Studies of Na$_2$SO$_4$–MO–P$_2$O$_5$ glasses

(vi) optical absorption, fluorescence studies of Sm$^{3+}$, Ho$^{3+}$, Er$^{3+}$ ions doped Na$_2$SO$_4$–MO–P$_2$O$_5$ glasses.

For the sake of convenience, the thesis is divided into six chapters.

**CHAPTER–I** presents the General Introduction, Scope, Contents and the Aim of the present work. In this chapter, the basic theory related to electrical and spectroscopic properties of Na$_2$SO$_4$–BaO–P$_2$O$_5$: Fe$_2$O$_3$ and spectroscopic properties of Na$_2$SO$_4$–MO–P$_2$O$_5$: Sm$^{3+}$/Ho$^{3+}$/Er$^{3+}$ glasses are presented systematically.

**CHAPTER–II** gives the description of experimental methods employed in the preparation and characterization of Na$_2$SO$_4$–MO–P$_2$O$_5$. The details of the apparatus used and the techniques adopted for characterization and for measuring electrical properties, optical absorption, ESR, IR, Raman and photoluminescence are described in detail in this chapter.

**Chapter-III** deals with the studies of Na$_2$SO$_4$–BaO–P$_2$O$_5$ glasses doped with different concentrations of Fe$_2$O$_3$. 

Na$_2$SO$_4$–BaO–P$_2$O$_5$ glasses mixed with different concentrations of Fe$_2$O$_3$ (ranging from 0.5 to 2.0 mol%) were synthesized. A complex spectroscopic (optical absorption, ESR, IR and Raman) electrical and dielectric studies have
been carried out. The thermal analysis of these samples has indicated that the glass containing 1.5 mol % (glass BF$_{15}$) possesses lower stability against devitrification. The optical absorption and ESR studies indicated that iron ions exist in Fe$^{2+}$ and Fe$^{3+}$ local states. The results of these studies have confirmed that with the increasing concentration of Fe$_2$O$_3$ up to 1.5 mol%, there is a gradual increase in the redox ratio Fe$^{2+}$/Fe$^{3+}$. The IR and Raman spectral investigations have revealed higher degree of disorder in the network of BF$_{15}$ glass. This is understood as being due to higher depolymerization of the glass network by the Fe$^{2+}$ ions present in larger concentration in this glass matrix.

The ac and dc conductivities have exhibited maximal effect, whereas the activation energy for the conduction exhibited minimal effect at 1.5 mol% of Fe$_2$O$_3$. This is understood as follows: the divalent iron ions that present in larger proportions act as modifiers and increase the concentration of dangling bonds. This leads to a decrement in the electrostatic binding energy and the strain energy facilitating for the easy passage of conducting ions which ultimately cause to a substantial decrement in the jump distance of these ions. The analysis of the results of dc conductivity has indicated that when T > $\theta_D$/2, the small polaron hopping model is appropriate and the conduction is adiabatic in nature. These results further indicated that there is a mixed conduction both ionic and electronic in these glasses. The ac conductivity in the low temperature region is explained based on quantum mechanical tunneling model.
The variations of dielectric constant, $\varepsilon'(\omega)$, and loss, tan $\delta$, with temperature have been analyzed on the basis of dielectric polarization. The frequency and temperature dependence of the electrical moduli as well as dielectric loss parameters have exhibited relaxation character. The relaxation effects have been analyzed quantitatively using Cole-Cole plots and spreading of relaxation times has been established.

The main objective of **CHAPTER-IV** is to characterize the optical absorption and the fluorescence spectra of Sm$^{3+}$ ion in Na$_2$SO$_4$–P$_2$O$_5$ glasses mixed with three interesting alkaline earth modifier oxides, viz. MgO, CaO and BaO, and to shed some light on the relationship between the structural modifications in the glass network and luminescence efficiencies. For this study, a particular composition, 19Na$_2$SO$_4$–20MO–60P$_2$O$_5$: 1.0Sm$_2$O$_3$, is chosen.

The optical absorption spectra of these glasses recorded at room temperature in the wavelength range 300–2200 nm, have exhibited the following absorption bands:

$^6H_{5/2} \rightarrow ^4P_{3/2}, ^4G_{9/2}, ^4H_{9/2}, ^4D_{5/2}+^4H_{7/2}, ^6P_{7/2}, ^4L_{15/2}, ^4F_{7/2}+^6P_{3/2}, ^6P_{5/2}+^4K_{11/2}, ^4G_{9/2},

^4I_{13/2}, ^4I_{11/2}, ^4M_{17/2}, (UV-visible region)

$^6F_{11/2}, ^6F_{9/2}, ^6F_{7/2}, ^6F_{5/2}, ^6F_{3/2}, ^6F_{1/2}, ^6H_{15/2} (NIR region)$
The pattern of the absorption spectra for the entire three modifier mixed glasses remains the same; however, the absorption strength under given peak is found to vary with the change of modifier oxide.

By performing least square fitting analysis the J-O parameters for these samples are computed and are found to show the following order for the Pr$^{3+}$ doped glasses: $\Omega_4 > \Omega_6 > \Omega_2$ for all the three glasses.

The luminescence spectra of all the three glasses doped with Sm$^{3+}$ ions were recorded at room temperature in the visible and NIR regions; the spectra exhibited the following prominent emission bands:

$$^4G_{5/2} \rightarrow ^6H_{5/2}, ^6H_{7/2}, ^6H_{9/2} \text{ and } ^6H_{11/2}$$

The comparison of the spectra of the three glasses indicate that the intensity and the half width of the band due to $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition are significantly higher for BaO mixed glass than that observed in CaO and MgO mixed glasses. This is identified as being due to the low phonon energy and the large refractive index of BaO mixed glass.

Branching ratio, $\beta$, (that defines the luminescence efficiency of the transition) of yellow emission ($^4G_{5/2} \rightarrow ^6H_{7/2}$) among various transitions originated from $^4G_{5/2}$ is found to be the highest ($\sim 50\%$). Further, the comparison of $\beta$ values for the glasses viz., NSMgP, NSCaP and NSBaP, suggests the highest value for the glass NSBaP. The quantum efficiency is also found to be the highest for BaO mixed glasses. From these studies it is
identified that modifier BaO is more appropriate modifier in this glass matrix to produce high luminescence efficiency.

The objective of the **Chapter-V** is to investigate and to characterize the optical absorption and the fluorescence spectra of Ho\(^{3+}\) and Er\(^{3+}\) ions as well as upconversion fluorescence during the energy transfer from Ho\(^{3+}\) to Er\(^3\) in Na\(_2\)SO\(_4\)–P\(_2\)O\(_5\) glasses mixed with three alkaline earth modifier oxides, viz. MgO, CaO and BaO and to clarify the relationship between the structural modifications in the glass network and luminescence efficiencies.

The optical absorption spectra of holmium and erbium doped Na\(_2\)SO\(_4\)–MO–P\(_2\)O\(_5\) glasses recorded at room temperature in the spectral range 300−2500 nm exhibited several following absorption bands:

**Ho\(^{3+}\) glasses:**

\[ ^{5}I_{8} \rightarrow ^{5}G_{2}, ^{3}K_{6}, ^{3}H_{6}, ^{3}K_{7} + ^{5}G_{4}, ^{5}G_{5} + ^{3}G_{5}, ^{5}G_{6}, ^{3}K_{8}, ^{5}F_{2} + ^{5}F_{3}, \]
\[ ^{5}F_{4} + ^{5}S_{2}, ^{5}F_{5}, ^{5}I_{6}. \]

**Er\(^{3+}\) glasses:**

\[ ^{4}I_{15/2} \rightarrow ^{2}G_{7/2}, ^{4}G_{11/2}, ^{2}G_{9/2} + ^{2}H_{9/2}, ^{4}F_{3/2}, ^{4}F_{7/2}, ^{2}H_{11/2}, ^{4}S_{3/2}, \]
\[ ^{4}F_{9/2}, ^{4}I_{9/2}, ^{4}I_{11/2}, ^{4}I_{13/2}. \]

The absorption spectra of Ho\(^{3+}\) and Er\(^{3+}\) co-doped glasses retained the bands caused by transitions of both the ions. However some of them exhibited some overlap. Applying JO theory, the values of JO parameters \(\Omega_{\lambda}\) are evaluated and they are found to be in the following order for the Ho\(^{3+}\) doped glasses: \(\Omega_{4} > \Omega_{2} > \Omega_{6}\) and for Er\(^{3+}\) the order is \(\Omega_{2} > \Omega_{4} > \Omega_{6}\) for all the three modifier mixed glasses.
The fluorescent spectra of individual ion doped Na$_2$SO$_4$–BaO–P$_2$O$_5$ glasses recorded at room temperature exhibited the following prominent emission bands:

Ho$^{3+}$ glass ($\lambda_{\text{exc}} = 448$ nm): $^5F_3 \rightarrow ^5I_8$, $^5S_2(^5F_4) \rightarrow ^5I_8$, $^5F_5 \rightarrow ^5I_8$, $^5G_5 \rightarrow ^5I_6$, $^5F_4 \rightarrow ^5I_7$, $^5G_5 \rightarrow ^5I_5$, $^5F_2 \rightarrow ^5I_6$, and $^5F_3 \rightarrow ^5I_6$.

Er$^{3+}$ glass ($\lambda_{\text{exc}} = 379$ nm): $^2H_{9/2} \rightarrow ^4I_{15/2}$, $^4F_{5/2} \rightarrow ^4I_{15/2}$, $^4F_{7/2} \rightarrow ^4I_{15/2}$, $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$, $^4F_{9/2} \rightarrow ^4I_{15/2}$ and $^2G_{9/2} \rightarrow ^4I_{11/2}$.

The spectra of the co-doped glasses (excited at 890 nm) exhibited red, blue and green emissions with enhanced intensities. The comparison of the spectra for different modifier oxide mixed glasses have indicated the highest intensity of all the luminescence transitions for BaO mixed glasses.

**CHAPTER-VI** reports brief summary and conclusions drawn from the investigation carried out on a variety of properties viz., dielectric and spectroscopic properties of Na$_2$SO$_4$–BaO–P$_2$O$_5$ glasses doped with different concentrations of Fe$_2$O$_3$ and also the spectroscopic properties Na$_2$SO$_4$–MO–P$_2$O$_5$ glasses doped with Sm$^{3+}$, Ho$^{3+}$ and Er$^{3+}$ ions.

References closely related to the present work have been compiled to the extent possible and given at the end of the relevant chapter.