

# CHAPTER 1 INTRODUCTION

## 1.1 Background

Recently, glasses play an important role in various human being activities e.g. scientific equipment, decorate buildings or even as jewelry. There are several types of glass such as silicate, borate and phosphate glass which are used for appropriate purposes. Therefore, the development of inorganic glasses has been attracted both academic and industrial interest in recent years.

Soda lime silicate glass is a glass type that is popular and used widely. Soda lime silicate glass is primarily made of a glass former like silica, alkalis like soda and potash to change the state from solid to liquid, stabilizers like CaO, MgO and Al<sub>2</sub>O<sub>3</sub> to reduce weathering, refining agents like Na<sub>2</sub>O, K<sub>2</sub>O and CaSO<sub>4</sub> to remove bubbles, reduce the melting temperature of silicate melts, where the melting point of silica is usually (>2000°C), although adding large amounts of alkali fluxes can degrade chemical durability. The composition of the substance to a glass container can be adjusted as appropriate. This may depend on environment in the combustion glass.

The viscosity of a glass melt, as a function of temperature, is the most important variable affecting the melting rate and pour ability of the glass. The viscosity determines the rate of melting of the raw feed, the rate of gas bubble release (foaming and fining), the rate of homogenization, and thus the quality of the final glass product. The slowest cooling rate that produces a glass is deemed the critical cooling rate. Glass stability is often characterized by the difference between the onset of the glass transition region (T<sub>g</sub>) and the first occurrence of a crystallization peak (T<sub>p</sub>) [1-23].

The colors of this glass system which give from additional transition elements depend on the composite of glasses system, the types and concentrations of transition metal ions, and the characteristic of the transition metal ions in environment. Fe, Mn, Cu, V or Cr, etc., are famous transition elements. Each 3d-transition metal can exist in two or more oxidation or coordination states within the glass matrix and the equilibrium between such states depends on the glass type and composition and also on the melting conditions. Each state normally gives rise to specific absorption spectra, which have been measured and explained by the application of ligand field and molecular orbital theories [24-31].

The manganese, <sup>55</sup>Mn, ions have been frequently used as paramagnetic probes for exploring the structure and properties of vitreous systems which their ions have strong bearing on the optical and magnetic properties of glasses. A large number of interesting studies are available on the environment of manganese ion in various inorganic glass systems [32-44]. In this work, all samples are soda lime silicate glass system containing manganese ions which were one type of chemical composition of glass system.

## 1.2 Motivation

A study of the color of the glass is important in the manufacture of glass. Because of the color in the glass resulted in glass color distortion resulting in the loss of both manufacturing cost and reliability. Factors affecting the color of the glass are contamination of transition metals. Manganese is often found to have contaminants in the materials used in the manufacture of glass.

However, a little information is available on physical and optical properties of soda lime silicate glasses containing manganese ions. Therefore, the aim of the present study is to prepare the  $Mn^{2+}$  doped soda-lime-silicate glass with different  $MnO_2$  concentrations and difference melting temperature. The effect of  $MnO_2$  content on the density, molar volume, refractive index and optical absorption were studied. In addition the optical basicity and polarizability were theoretically determined.

## 1.3 Objective

The first objective of this dissertation is to study the preparation of  $MnO_2$ -doped soda lime silicate glass by the normal melt-quenching technique. The second objective is to investigate the physical-, optical-, structural properties, and the color of prepared glass.

## 1.4 Thesis Significance

This thesis is important to study the basic behavior of the glass with the addition of manganese. In order to describe the effect of the additives in the production of manganese in the glass industry level. In addition, the data obtained can be applied to improve the use of glass as imitation gem.

## 1.5 Literature Reviews

Rao [4] studied the effects of alkali fluorides in unmixed form:  $40(NaPO_3)_6 + 10BaF_2 + 9ZnF_2 + 20B_2O_3 + 20RF + 1NdF_3$ , where  $RF = LiF, NaF$  and  $KF$ . On the basis of the measured values of densities and refractive indices, the dielectric constant, reflection losses, molar refraction,  $Nd^{3+}$  ion concentration in glasses and several other physical properties were determined.

Margaryan [11] studied on luminescence, absorption and electron spin resonance (ESR) spectroscopic measurements are performed for two new  $Mn^{2+}$  doped fluorophosphate glass systems containing bismuth and lead, respectively, i.e.,  $45Ba(PO_3)_2-55BiF_3$  and  $45Ba(PO_3)_2-55PbF_2$ .

Manal [13] studied different optical properties of  $xTiO_2-(60-x)SiO_2-40Na_2O$  ( $(5 \leq x \leq 20$  wt%) optical glasses are determined.

Thiemsorn [19] studied the changes in glass structure and redox ratio, R (reduced ion to oxidized ion) of  $Mn^{2+}-Mn^{3+}$ ,  $Cu^+-Cu^{2+}$ ,  $Cr^{3+}-Cr^{6+}$ ,  $Ni^{2+}-Ni^{3+}$  and  $Co^{2+}-Co^{3+}$  couples and optical absorption due to  $Mn^{3+}$ ,  $Cu^{2+}$ ,  $Cr^{3+}$ ,  $Ni^{2+}$  and  $Co^{2+}$  ions in industrial soda-lime-silica glass were investigated as a function of  $Na_2O$  concentration in the range 11–19 mol%.

Sreekanth [21] studied electron paramagnetic resonance (EPR) and optical absorption studies of iron doped mixed alkali borate glasses,  $x\text{Na}_2\text{O} - (30 - x)\text{K}_2\text{O} - 70\text{B}_2\text{O}_3$  ( $5 \leq x \leq 25$  mol%) have been investigated as a function of alkali content to look for the 'mixed alkali effect' on the spectral properties of the glasses.

Macalik [28] studied the effect of mechanical stretching upon room temperature - coloration of soda-lime silicate (SLS) glasses has been investigated. Optical absorption measurements were performed to follow the formation and thermal bleaching of the induced color centers.

Scott B [29] studied iron commonly exists as an equilibrium mixture of ferrous ions,  $\text{Fe}^{2+}$ , and ferric ions,  $\text{Fe}^{3+}$ , in soda-lime-silicate glasses.

Lakshminarayana [30] studied on the spectral properties of  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions doped  $\text{B}_2\text{O}_3$ -ZnO-PbO glasses.

Elisa [31] studied optical and electronic properties of the aluminophosphate glasses containing Fe-Mn and Fe-Cr ion pairs in different concentration.

Sreekanth [35] studied EPR and optical absorption spectra of 0.5 mol%  $\text{MnO}_2$  doped  $x\text{Li}_2\text{O} - (30 - x)\text{Na}_2\text{O} - 69.5\text{B}_2\text{O}_3$  ( $5 \leq x \leq 25$  mol%) glasses

Brian [36] studied the solarization on soda-lime-silicate glasses containing manganese, manganese and antimony, and manganese and iron were exposed to an ultraviolet light source.

Krishna [37] studied electron paramagnetic resonance (EPR) and optical absorption structural investigations of  $\text{Mn}^{2+}$  ions in alkali barium borophosphate glasses at room temperature.

Thiemsorn [38] studied the redox interactions of iron, manganese, and copper ion pairs including absorption characteristics in a multicomponent soda-lime-silica glass, were investigated. Glasses containing 11-19 mol %  $\text{Na}_2\text{O}$  were melted under an air atmosphere in an electric furnace at  $1450^\circ\text{C}$  for 8 h.

Thulasiramudu [39] studied on the development and optical characterization of heavy metal oxide (HMO)-based transparent glasses in the chemical composition of  $15\text{PbO} - 40\text{B}_2\text{O}_3 - (45-x)\text{ZnO} - x\text{TM}^{2+}$  ( $= \text{Mn}^{2+}$  or  $\text{Ni}^{2+}$  or  $\text{Co}^{2+}$ ) (where  $x = 0.2, 0.5$  mol%).

Sreekanth [42] studied the mixed alkali borate  $x\text{Na}_2\text{O} - (30 - x)\text{K}_2\text{O} - 70\text{B}_2\text{O}_3$  ( $5 \leq x \leq 25$  mol%) glasses doped with 1 mol% of manganese ions were investigated using EPR and optical absorption techniques as a function of alkali content to look for 'mixed alkali effect' (MAE) on the spectral properties of the glasses.

Machado [44] studied spectroscopic studies of optical properties of manganese ions in barium phosphate glasses prepared by adding 1-20 mol% of  $\text{Mn}_2\text{O}_3$  in the glass composition was performed.

Vaidhyanathan [45] studied EPR spectra of microwave-prepared  $7\text{ONaPO}_3:30\text{PbO}$  glasses containing different weight percentages of manganese ions have been studied.

**Table 1.1** Literature Reviews

Glasses	Mn Doped							Reference
	Physical Properties	Optical Properties	Structural Properties	Electrical Properties	Magnetic Properties	Etc.		
$40(\text{NaPO}_3)_6\text{-}10\text{BaF}_2\text{-}9\text{ZnF}_2\text{-}20\text{B}_2\text{O}_3\text{-}20\text{RF-}1\text{NdF}_3$ (RF= LiF, NaF and KF)	<ul style="list-style-type: none"> <li>• Density</li> <li>• Polaron radius</li> <li>• Interionic distance</li> <li>• Field strength</li> <li>• Basicity</li> </ul>	<ul style="list-style-type: none"> <li>• UV-Visible</li> <li>• Refractive Index</li> <li>• Reflection losses</li> <li>• Molar refraction</li> <li>• Molecular electronic polarizability</li> </ul>	-	<ul style="list-style-type: none"> <li>• Optical dielectric constant</li> <li>• Dielectric constant</li> </ul>	-	-	4	
$45\text{Ba}(\text{PO}_3)_2\text{-}55\text{BiF}_3$ and $45\text{Ba}(\text{PO}_3)_2\text{-}55\text{PbF}_2$	-	<ul style="list-style-type: none"> <li>• UV-Visible</li> <li>• Luminescence</li> </ul>	-	-	<ul style="list-style-type: none"> <li>• EPR</li> </ul>	-	11	
$\text{SiO}_2\text{-Na}_2\text{O-CaO-MgO-Al}_2\text{O}_3$ (doped MnO, CuO, Cr <sub>2</sub> O <sub>3</sub> , NiO and CoO)	<ul style="list-style-type: none"> <li>• Density</li> <li>• Basicity</li> </ul>	<ul style="list-style-type: none"> <li>• UV-Visible</li> <li>• Refractive Index</li> </ul>	<ul style="list-style-type: none"> <li>• XRD</li> </ul>	-	<ul style="list-style-type: none"> <li>• NMR</li> </ul>	-	19	



Glasses	Mn Doped							Reference
	Physical Properties	Optical Properties	Structural Properties	Electrical Properties	Magnetic Properties	Etc.		
$\text{Li}_2\text{O}-\text{BaO}-\text{Al}_2\text{O}_3-\text{La}_2\text{O}_3-\text{P}_2\text{O}_5$	-	<ul style="list-style-type: none"> <li>UV-Visible</li> <li>Refractive Index</li> </ul>	<ul style="list-style-type: none"> <li>FTIR</li> </ul>	-	-	-	31	
$20\text{ZnO}-40\text{Sb}_2\text{O}_3-40\text{B}_2\text{O}_3$	<ul style="list-style-type: none"> <li>Density</li> <li>Polaron radius</li> <li>Interionic distance</li> </ul>	<ul style="list-style-type: none"> <li>UV-Visible</li> </ul>	-	-	<ul style="list-style-type: none"> <li>Magnetic susceptibility</li> <li>ESR</li> </ul>	-	32	
$\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{B}_2\text{O}_3$	<ul style="list-style-type: none"> <li>Basicity</li> </ul>	<ul style="list-style-type: none"> <li>UV-Visible</li> <li>Indirect optical band gap</li> <li>Urbach energy</li> </ul>	<ul style="list-style-type: none"> <li>XRD</li> </ul>	-	<ul style="list-style-type: none"> <li>EPR</li> </ul>	-	35	
$72\text{SiO}_2-17\text{Na}_2\text{O}-11\text{CaO}$	-	<ul style="list-style-type: none"> <li>UV-Visible</li> <li>Solarization</li> </ul>	-	-	-	-	36	
$50\text{P}_2\text{O}_5-20\text{B}_2\text{O}_3-10\text{M}_2\text{O}-20\text{BaO}$ (M = Li, Na, K, Li-Na, Na-K, K-Li)	<ul style="list-style-type: none"> <li>Basicity</li> </ul>	<ul style="list-style-type: none"> <li>UV-Visible</li> </ul>	-	-	<ul style="list-style-type: none"> <li>EPR</li> </ul>	-	37	
$\text{SiO}_2-\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3$	<ul style="list-style-type: none"> <li>Density</li> </ul>	<ul style="list-style-type: none"> <li>UV-Visible</li> </ul>	-	-	-	-	38	

Glasses	Mn Doped							Reference
	Physical Properties	Optical Properties	Structural Properties	Electrical Properties	Magnetic Properties	Etc.		
$40\text{B}_2\text{O}_3\text{-}15\text{PbO}\text{-}(45\text{-}x)\text{ZnO}\text{-}x\text{MnO}_2$	<ul style="list-style-type: none"> <li>Density</li> <li>Polaron radius</li> <li>Interionic distance</li> <li>Field strength</li> </ul>	<ul style="list-style-type: none"> <li>UV-Visible</li> <li>Refractive Index</li> <li>Direct optical band gap</li> <li>Indirect optical band gap</li> </ul>	<ul style="list-style-type: none"> <li>XRD</li> <li>FTIR</li> <li>Glass transition temperature</li> <li>Crystallization temperature</li> <li>Temperature of melting</li> </ul>	-	-	-	39	
$x\text{Na}_2\text{O}\text{-}(30\text{-}x)\text{K}_2\text{O}\text{-}70\text{B}_2\text{O}_3$	<ul style="list-style-type: none"> <li>Density</li> <li>Ionic radius</li> <li>Interionic distance</li> <li>Basicity</li> </ul>	<ul style="list-style-type: none"> <li>UV-Visible</li> <li>Refractive Index</li> <li>Molar refraction</li> <li>electronic polarizability</li> <li>Direct optical band gap</li> <li>Indirect optical band gap</li> <li>Urbach energy</li> </ul>	<ul style="list-style-type: none"> <li>XRD</li> <li>Hyperfine splitting</li> <li>Zero-field splitting parameter</li> </ul>	<ul style="list-style-type: none"> <li>Optical dielectric constant</li> </ul>	<ul style="list-style-type: none"> <li>EPR</li> <li>Number of spins</li> </ul>	-	42	
$40\text{BaO}\text{-}60\text{P}_2\text{O}_5$ doped $\text{Mn}_2\text{O}_3$	-	<ul style="list-style-type: none"> <li>UV-Visible</li> <li>Luminescence</li> </ul>	-	-	-	-	44	
$x\text{TiO}_2\text{-}(60\text{-}x)\text{SiO}_2\text{-}40\text{Na}_2\text{O}$	-	<ul style="list-style-type: none"> <li>UV-Visible</li> </ul>	<ul style="list-style-type: none"> <li>FTIR</li> </ul>	-	<ul style="list-style-type: none"> <li>EPR</li> </ul>	-	45	