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Structure–property relationships of Fe_2O_3 doped novel oxyfluorophosphate glasses

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ABSTRACT

The relationship between the network structure and properties of iron containing novel oxyfluorophosphate glasses with the composition $20ZnO–20CaF_2–(60 - x)P_2O_5{:}xFe_2O_3$ with $0 \le x \le 5$ mol% has been studied. The density, molar volume, oxygen molar volume and oxygen packing density studies helped to understand the structural changes occurring in these glasses. The dissolution rate and pH of the immersion liquid are measured to explain the chemical durability of the glasses. Differential thermal analysis studies are carried out to analyze the thermal stability of the studied glasses. Deconvoluted infrared and Raman spectra of the glasses are analyzed to determine the relative areas of the vibrational bands corresponding to different structural units. Analysis of the vibrational spectra in conjunction with the other properties reveals that Fe_2O_3 enters the glass matrix in the form of Fe^{2+} and Fe^{3+} ions through the formation of more stable $P–O–Fe^{2+}$ and $P–O–Fe^{3+}$ bonds at the expense of easily hydrated $P–O–P$ bonds.

1. Introduction

Glasses exhibit a broad variety of properties which make them probable elements in the modern scientific and technological applications [1,2]. In the recent past, glasses are vital in the advancement of solid state lasers, optical glass fibers, biomaterials, imaging technologies, and glass films in microelectronic devices [3–7]. Phosphate glasses are of increasing interest nowadays because of their broad range of applications. Due to the low melting and softening temperatures, low viscosity and high thermal expansion coefficient [8], phosphate glasses possess multiple applications such as low temperature sealing materials [9], biomedical, quick ionic conductors [10], solid state electrolytes, glass-to-metal seals, optical data transmission, laser technology [11], thick film paste, low temperature enamels for metals [12] etc. However, the relatively poor chemical durability of phosphate glasses, limits them only to industrial applications. It has been proved that chemical durability of phosphate glasses can be enhanced by the addition of various modifier oxides such as ZnO, CaO, BaO, PbO, Li_2O, K_2O, and Na_2O [13–20].

Zinc oxide glasses are important due to their non-toxicity, non-hygroscopic nature, lower cost and useful optical, electrical and magnetic properties [21–23]. ZnO can act as both a six-coordinated network modifier and four-coordinated network former [24,25]. Zn^{2+} ions in oxide glasses enhance mechanical properties and chemical resistivity through the formation of tetrahedral co-ordination. ZnO is a key constituent for the preparation of multicomponent oxide glasses with a high thermal resistance against crystallization [26,27]. It has been established that ZnO in oxide glasses can lower the melting point and glass transition temperature and improve the thermal expansion coefficient [28,29]. Zinc phosphate glasses find applications in low temperature seals and can be used as luminescent ion hosts. In recent times, it has been revealed that the optical properties of zinc phosphate glasses can be tailored with a femto-second laser. Hence, these glasses exhibit a variety of applications in making optical devices [30]. Fining agents such as calcium fluoride are added to the glass mixture to remove bubbles from the melt [2,31]. Important biological applications for calcium phosphate glasses also exist as it was demonstrated that they are biocompatible as bones and dental implants [32,33]. The addition of CaF_2 into the glass atmosphere lowers the viscosity liquidus temperature to a significant amount and further it acts as a good mineralizer. Also, fluorine ions coming from CaF_2 act as co-activators and smooth the progress of the substitution of activators into the lattice [34]. The structure and properties of oxide glasses containing fluorine ions are important owing to their potential applications in the fields of infrared fiber optics, laser windows and multifunctional optical components [2].

The addition of transition metal oxide into the glass causes a change in the glass configuration in which the metal oxide acts as a modifier or network former [35]. Extensive investigations on the optical absorption, luminescence and ESR spectroscopy of different transition metal ions in a variety of phosphate glasses have been made in the recent years in view of their technological applications [36–40]. Transition metal ions are known to influence the optical, electrical and magnetic properties

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of glasses due to their high sensitive response to the changes in the surrounding actions. Further, these ions can be used as a better candidate to probe the glass structure due to their broad radial distribution of outer *d*-orbital electron functions [41]. Transition metals present in-depth knowledge about many detailed aspects like the geometry of structural units present in the glass, the character of chemical bonds as well as the coordination polyhedra [42].

Iron ions have strong bearing on electrical, optical and magnetic properties of glasses. A large number of interesting studies are available on the environment of iron ion in various inorganic glass systems viz., silicate, borate, phosphate and germinate glasses [43–49]. These ions exist in different valence states with different coordinations in glass matrices, for example as Fe^{3+} with both tetrahedral and octahedral and as Fe^{2+} with octahedral environment [50,51]. The content of iron in different forms in different valence states existing in the glass depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc. Hence, the connection between the state and the position of the iron ion and the physical properties of the glass is highly interesting. Further, it is also quite likely for iron ions to have a link with phosphate groups perhaps due to the creation of some Fe – O – P bonds [52]; strengthen glass structure and may raise the chemical resistance of the glass.

Iron doped phosphate glasses are technologically as well as biologically important as they are used as biomaterials with modified rates of degradation in aqueous environment [53] and are used for the arrest of nuclear waste [54]. The addition of iron to phosphate glasses shows a momentous effect on the glass transition temperature and thermal expansion coefficient and enhances the chemical durability considerably. The addition of Fe_2O_3 into the glass environment causes a depolymerization of the phosphate chains complex. Also, iron phosphate glasses show corrosion-resistance, reinforcing fibers for composite materials [55]. Depending on the redox state and coordination number of Fe, iron phosphate glasses demonstrate fascinating electrical and magnetic properties [56–58].

Detailed literature survey shows that work has been carried out by researchers on the preparation, characterization, physical, vibrational and magnetic properties of phosphate glasses containing iron ions [59–63]. However, no effort appears to have been made to investigate the structure and properties of ZnO–CaF_2–P_2O_5 glasses doped with Fe_2O_3.

The objective of the present work is to study the influence of Fe_2O_3 addition on the structure of ZnO–CaF_2–P_2O_5 glass and the mechanism of the conversion of different phosphate units in this glass with the aid of density, molar volume, infrared and Raman spectral studies. The importance of the present study is that it establishes the foundation for the structure of phosphate based glasses useful for industrial, biomedical and technological applications. Also, it is proposed to study the thermal parameters of the ZnO–CaF_2–P_2O_5:Fe_2O_3 glasses using differential thermal analysis which determines the qualitative estimation of the thermal stability and glass forming ability.

2. Experimental methods and characterization

2.1. Glass preparation

Glasses of the composition 20ZnO–20CaF_2–(60 − x)P_2O_5:xFe_2O_3 with $0 \leq x \leq 5$ were prepared from appropriate amounts (all by mol%) of reagent grades of ZnO, CaF_2, P_2O_5 and Fe_2O_3; among various compositions, this range seems to have formed a relatively clear and transparent glass. The powders of the raw materials were thoroughly mixed in an agate mortar and melted in a sealed silica crucible at 1173 K and kept in a microcontroller regulated pit furnace (Krishna Enterprises, Hyderabad, India) for about 30 min until a bubble free liquid was formed. The resultant melt was then poured in a graphite mold and subsequently annealed at 573 K for 24 h. The samples were then ground and optically polished. It may be noted here that, to fix the base or parent glass to which doping is performed, actually different combinations of ZnO–CaF_2–P_2O_5 glasses are prepared and among these combinations it is found that 20ZnO–20CaF_2 glass sample is found to be more stable and chemically more durable and hence in the present study we preferred to this ratio of ZnO and CaF_2 in the parent glass.

2.2. Bulk glass characterization

2.2.1. ICP analysis

To analyze the final composition of the glasses, inductively coupled plasma atomic emission spectroscopy (Philips XL-30 spectrophotometer) was used. The nominal and analyzed glass compositions along with the codes of the glass samples under study are presented in Table 1.

2.2.2. Density and chemical durability measurements

The macroscopic density (ρ/kgm^{-3}) of the glasses at room temperature was determined to an accuracy of ± 4 kg m^{-3} by standard principle of Archimedes using *o*-xylene (99.99% pure) as the buoyant liquid using the relation [39]:

$$\rho = \rho_b \frac{W_a}{W_a - W_b} \tag{1}$$

where $_b$ is the density of the buoyant liquid, and W_a and W_b are the weights of the samples in air and in the buoyant liquids respectively. The measurements were done with a digital balance (Shimadzu AUY 220 accuracy 0.0001 g) and the experiment was repeated a number of times for each composition and the average value was taken.

The chemical durability of the bulk glasses was determined from the average weight loss of the samples immersed in distilled water (pH = 6.8 ± 0.1) for few minutes to 10 days. The glass samples of 1 cm × 1 cm × 0.6 cm were cut, ground, polished to 600 grit finish with SiC paper, cleaned with acetone, weighed (±0.01 mg) and suspended by a weightless strand in polyethylene bottles filled with 100 ml of distilled water. The bottles were introduced in a constant temperature oven at

Table 1
Sample codes, nominal and analyzed batch compositions (±0.1%), average dissociation rate of ZnO–CaF_2–P_2O_5:Fe_2O_3 glasses and pH of the immersion liquid.

Sample code	Nominal (mol%)				Analyzed (mol%)				Avg diss rate (±10%) (D_R/g cm^{-2} min^{-1})	pH (±0.1)
	ZnO	CaF_2	P_2O_5	Fe_2O_3	ZnO	CaF_2	P_2O_5	Fe_2O_3		
ZCP	20	20	60	0	19.8	19.6	60.6	0	3.4×10^{-7}	5.4
ZCPFe 0.5	20	20	59.5	0.5	20.1	19.9	59.6	0.4	5.5×10^{-7}	5.3
ZCPFe 1.0	20	20	59	1.0	19.8	20.2	58.9	1.1	7.2×10^{-7}	5.0
ZCPFe 1.5	20	20	58.5	1.5	19.9	20	58.5	1.6	1.0×10^{-6}	4.8
ZCPFe 2.0	20	20	58	2.0	20	19.7	58.4	1.9	5.4×10^{-7}	5.2
ZCPFe 3.0	20	20	57	3.0	19.9	19.9	57.1	3.1	3.1×10^{-8}	5.6
ZCPFe 4.0	20	20	56	4.0	20.3	19.8	56	3.9	9.1×10^{-9}	5.8
ZCPFe 5.0	20	20	55	5.0	20.2	20.1	54.9	4.8	2.5×10^{-9}	6.1