

Investigation of the Structures Properties and Applications of Phosphate Based Glasses

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ABSTRACT

Glasses based on $RO-R_2O-Na_2O-Al_2O_3-P_2O_5$ ($R= Mg, Ca, Ba$ and $RO= Li$ system has successfully been prepared and their properties and structural features have been investigated. The properties of those glasses seem to depend on the field strength of the alkali or alkali-earth ions in glasses as in silicate glasses. The density was determined by means of an ordinary principle of Archimedes and it was found that the density increases as RO and R_2O oxide was introduced replacing some amount of Al_2O_3 . The spectra of glasses have been studied within the spectral range of 4000 cm^{-1} to 100 cm^{-1} by Fourier transform infrared spectroscopy. Infrared (IR) spectroscopy indicates that the glass network is dominated by bridging P-tetrahedral present in glasses with $O/P \approx 3.0$. The variation in physical properties of the glasses seem to be closely related to the variation in structure of the glasses and could be explained by simple mechanism such as field strength and differences in mass.

(Key Words: Alumina Phosphate, Density, DTA, IR Spectroscopy)

1. INTRODUCTION

Glasses are one of the oldest as well as one of the newest materials in the world that find a variety of uses in everyday life. Applications of glass materials range from the ordinary drinking glass to the extraordinary fiber optic cables used in the communications industry [Norbert, 1990]. Glass materials can be formed into a variety of simple shapes (fibers, rods, and sheets) and exotic shapes (lightbulb casings). Research on common glasses and other less common non crystalline solids has been very active and productive in past decade. There are three primary reasons. The first was the theoretical understanding some twenty years ago which suggested that practically all liquids could be rendered into the glassy state if crystal growth could be prepared by processes other than by the cooling of melts. Secondly Vapor phase techniques to prepare ultra high purity glass fibers, rapid quenching of liquid metals to give metallic glasses, the gel method to give new oxide glasses, new halide, new chalcogenide, new phosphate, and new nitride glasses are some important examples. A third reason has been the increasing awareness of industry that from fabrication viewpoint, glasses can play an important role in electronics [Mackenzie, 1982].

The prospect of glass sciences are indeed bright. The entire periodic table is available for exploration in the research of new glass. Many scientific problems are still remain to be solved. The relationships between

chemical composition, structure and properties are still far from scientific understanding. Examples include chemical durability, especially alkali resistance, and elastic modulus. The solution of these scientific problems will undoubtedly lead to many useful glass products in the future.

In the 1960s, interest in amorphous alkali phosphate ions stimulated by their used in variety of industrial applications, including sequestering agents for hard water treatments and dispersants for clay processing and pigment manufacturing. By studying such materials, Van Wazer (1958) established the foundations for understanding of the nature of phosphate glasses. Kordes et.al (2000) re-examined the alkaline earth phosphate glasses, including UV-transmitting compositions, and noted some anomalous trends in properties which they suggested showed a compositional dependence for the coordination number of metal cations like Zn^{2+} . The advent of solid state lasers in the 1960s heralded a new era of phosphate glass research. Certain compositions have large rare-earth stimulated emission cross-sections and low thermo optical coefficients compared with silicate glasses and the materials of choice, particularly for high power laser applications [Ehrt et.al, 1991]. More recently, phosphate glasses have been developed for variety of specialty applications. Alkali alumino phosphate compositions have glass transition temperatures under $400\text{ }^{\circ}\text{C}$ and thermal expansion coefficients greater than $150 \times 10^{-7}\text{ }^{\circ}\text{C}^{-1}$ and so are used for specialty hermetic seals [Campbell et.al, 1995]. Zinc phosphate compositions are chemically durable, have processing temperatures under $400\text{ }^{\circ}\text{C}$ and can be co formed with high temperature polymers to produce unusual organic or inorganic composites [Brow et.al, 1996].

Compared with conventional oxide glasses, phosphate glasses are technologically important materials because they possess some superior physical properties such as high thermal expansion coefficients, low melting temperature, low softening temperature, low transition temperature and high electrical conductivity [Stokowski, 1982, Weber, 1990 and Wiench, 2000].

Phosphate glass with low dispersion and relative indices, compared with silicate-based optical glasses have been developed for achromatic optical elements about 100 years ago. Subsequent interest in alkaline earth phosphate glasses stemmed from their high transparency for ultraviolet light [Todd, 1999]. The technological development of phosphate glasses containing rare-earth as host material for lasers have attracted many researchers to exploit these glasses for other applications such as sensors, detectors and receivers [Brow et.al, 2000]. These devices are used for research, communication, medical and other applications. A lead iron phosphate glass has been found to be suitable as a stable medium for storage of high-level nuclear waste [Sales et.al, 1984]. Phosphate glasses doped with high ionic conductivity silver and find application in batteries [Ravaine, 1985].

Meanwhile, the phosphate glasses are less important commercially because of their poor chemical durability [Wei et.al, 2001]. Several studies have shown that the chemical durability of phosphate glasses can be improved by addition of various oxides such as Al_2O_3 , Fe_2O_3 , PbO and ZnO [Carol et.al, 2002]. The ZnO containing phosphate glasses incorporating Na_2^+ and Ba^{2+} are interest in connection with the ionic conductivity.

In this study, phosphate glass was used as the host glass in the system. Although phosphate is poor chemical durability, the criterion that allows it to be used in many applications is closely related to glass molecule structure [Uwe, 1996]. The basic building block in phosphate glasses is the phosphorous-oxygen tetrahedron [Karabulut et.al, 2001]. According to Brow et.al (1996) when alkali or alkali earth oxide are added to P_2O_5 , the phosphate network is presumably broken into chain or ring network. The additional of other glass forming oxides or modifiers would then contribute in the change of the physical and chemical characteristic of

the glass.

The main interest of this study is to investigate the effect of adding the R and Ro to the alumina phosphate glass system, to see how it could control the properties. Although the fundamental interest in the glassy state and the many new challenges posed by new non crystalline solids have been growing, it will be difficult to divorce glass research from the issues of practical relevance. The use of alkali earth oxide as additive material would contribute knowledge in glass development. Furthermore, the great expansion of scientific and technical literature on this material provides evidence of their continuing importance during the intervening years

2. EXPERIMENTAL PROCEDURE

2.1 Sample preparation

Glasses were synthesized by melting dry mixtures of 25 g according to the composition $20(\text{RO-R}_2\text{O})-5\text{Na}_2\text{O}-5\text{Al}_2\text{O}_3-70\text{P}_2\text{O}_5$ (R= Mg, Ca, Ba and RO= Li). To react the constituents, the mixed powders were heated in an electrical furnace at 350°C for 1h, and then melted in another furnace at 1300°C . To ensure proper mixing and homogeneity, the molten liquid was shaken frequently and vigorously. After being checked, the melt was cast by pouring as fast as possible into a hot steel split mould to quench it to form a glass. The glass was immediately transferred to an annealing furnace at 250°C where it was kept for 3 h to relieve any residual stress which could cause embrittlement. At the end of this annealing process, the furnace was switched off and the glass left to cool down to the room temperature gradually by controlled thermal treatment at cooling rate of $0.5^\circ\text{C}/\text{min}$. The sample were selectively cut, ground, and polished. After preparation, samples were stored in plastic containers in a desiccators until the FTIR and DTA measurement was performed. The amorphous nature of the samples was checked by X-ray diffraction.

A relatively fine powder is placed on the aluminum holder and the XRD analysis was done using a Philips Analytical X-Ray Instrument with $\text{CuK}\alpha$ radiation ($\lambda = 1.5408 \text{ \AA}$) at $2\theta = 10^\circ - 80^\circ$, the step size is 0.020° and time per step was 0.5s. The non existence of any peaks would verify that the sample is in the amorphous state

2.2 Density measurement

The density of the glass samples was measured by simple Archimedes principle using toluene as an immersion liquid. Toluene ($\rho_l = 0.8690 \text{ g cm}^{-3}$) was used because it does not reactive to glass samples. The densities were calculated using the relation,

$$\rho_g = \rho_l W_a / (W_a - W_l)$$

where W_a , W_l are the weights of the sample in air and in toluene respectively and ρ_l is the relative density of the toluene.

2.3 Thermal Analysis

The equipment used to carry out the thermal measurement was a Perkin-Elmer Pyris Diamond TG/DTA Series system, which was operated under standard atmospheric conditions. The maximum temperature that could

be reached by the instrument was approximately 1400°C. The same weight of fine standard and sample (± 5 -20 mg) were loaded in an alumina crucibles and were heated at a rate of 10 °C/min for all samples. With the combination of built-in computer and UNIX operating system. It was possible to obtained DTA curves and the required data for analysis

2.4 Fourier Transform Infra Red

A Perkin Elmer spectrum GX Fourier Transform infra-red have been used to investigate all sample prepared using the KBr pellet technique. Typically around 2 mg of a finely ground sample is mixed with 200 mg of KBr powder and the mixture then pressed for 4 minutes, in evacuable die under 10 tons of pressure to give a transparent disk with a surface area of 1 cm². Samples were placed in the spectrometer then scanned at radiation at wave numbers in the spectral range of 4000 – 400 cm⁻¹.

(Wave numbers = reciprocal of wave length, usually expressed in cm⁻¹).

3. RESULTS AND ANALYSIS

3.1 Introduction

Glasses containing alkali earth ions in high concentration have considerable potential for applications in optical data transmission, detection, sensing and laser technology [Bowron et.al, 1998]. For example neodymium phosphate glasses have been widely used in lasers. In rare earth systems the energy of the $4f^{n+1} \rightarrow 4f^n d^1$ transition governs the systematics of the cohesive energy changes and determines the rare earth ion valence. The lanthanide element samarium has a marked tendency to exhibit valence instability in many of its crystalline compounds. Application of hydrostatic pressure can induce a transition from divalent (semiconducting) state to compounds exhibit extraordinary behaviour. The transition from the divalent state involves a sharp reduction of the ionic radius in the intermediate valence state. Anomalous elastic behaviour is associated with this valence instability. Application of pressure induces a marked decrease in the bulk and longitudinal moduli [Bowron et.al, 1996].

Phosphate glasses are characterized by low viscosity at the melting temperature which facilitates manufacture and so are useful host for studies of the properties of rare earth ions in a glassy matrix. Their microscopic structures are quite well known and their FTIR spectra have been characterized in terms of the vibration of simple structural components [Sidek et.al, 1988].

3.2 Glass Composition and Formation

Series of glass based on $20(\text{RO-R}_2\text{O})-5\text{Na}_2\text{O}-5\text{Al}_2\text{O}_3-70\text{P}_2\text{O}_5$ glasses, has successfully been made and the result is given in Table 3.1. Samples that were well formed were examined using the XRD analysis. This analysis is used to detect the presence of any crystallinity in the glass sample. The XRD spectra of the glasses are

shown in Figure 3.. It is found that there was no crystalline phase occurs as there was no significant peak in the spectra obtained.

Table 3.1. Composition and some measured parameters of $20(\text{RO-R}_2\text{O})\text{-}5\text{Na}_2\text{O}\text{-}5\text{Al}_2\text{O}_3\text{-}70\text{P}_2\text{O}_5$ glasses

| RO (mol) | R ₂ O (mol%) | Na ₂ O (mol%) | Al ₂ O ₃ (mol%) | P ₂ O ₅ (mol%) | Density (gcm ⁻³) | Molar Volume (cm ³ /mole) | Glass Transition(°C) |
|----------|-------------------------|--------------------------|---------------------------------------|--------------------------------------|------------------------------|--------------------------------------|----------------------|
| 20 | - | 5 | 5 | 70 | 3.12 | 44.29 | 370 |
| 20 | - | 5 | 5 | 70 | 2.56 | 46.44 | 405 |
| 20 | - | 5 | 5 | 70 | 2.52 | 45.87 | 440 |
| | 20 | 5 | 5 | 70 | 2.38 | 47.69 | 330 |

R= Ba, Ca, Mg

R₂= Li

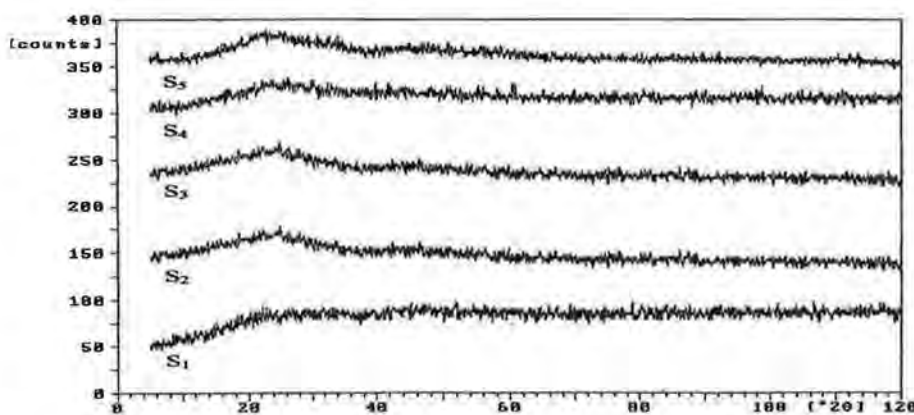


Figure 3.1: XRD spectra of $20(\text{RO-R}_2\text{O})\text{-}5\text{Na}_2\text{O}\text{-}5\text{Al}_2\text{O}_3\text{-}70\text{P}_2\text{O}_5$ glasses

3.3 Density

As shown in Table 1. the densities of the $20(\text{RO-R}_2\text{O})\text{-}5\text{Na}_2\text{O}\text{-}5\text{Al}_2\text{O}_3\text{-}70\text{P}_2\text{O}_5$ glasses with no substitution, where R is Ba, Ca, Mg and R₂O is Li increased in order $\text{Li} < \text{Mg} < \text{Ca} < \text{Ba}$ as expected from the relative masses of the alkaline-earth and alkali ions.

The molar volumes of the glasses also showed a similar trend. The variation in the molar volume as well as the density in this glass system is very hard to explain using a simple mechanism. It should be noted that the molar volume $20\text{CaO}-5\text{Na}_2\text{O}-5\text{Al}_2\text{O}_3-70\text{P}_2\text{O}_5$ glass was lower than that the $20\text{MgO}-5\text{Na}_2\text{O}-5\text{Al}_2\text{O}_3-70\text{P}_2\text{O}_5$ glass, which is discussed below in terms of the structure of the glass.

Komiyama et.al (2002) explained that although the introduction of R_1O or R_2O elements into glasses causes the expansion of the network due to the increasing ratio of non-bridging oxygen ions, they tend to develop a more tightly packed glass structure thereby compacting the electron clouds surrounding these oxygen ions owing to their high charge and co-ordination number. Further, the $\text{Al}-\text{O}-\text{Al}$ bonds are broken and hence the formation of unstable bond may take place. The introduction of coordinated defect bonds known as dangling (broken) bonds results in softening of the glass network. Thus, an increase in the volume results in a decrease in density.

3.4 Thermal Analysis

The glass transition temperature of the above mentioned glass system, as shown in Table 3.1, the glass transition temperature decreased in order of $\text{MgO} > \text{CaO} > \text{BaO} > \text{Li}_2\text{O}$. This is also attributed mainly to the lower field strength of the Na^+ than that of the alkali and alkaline earth ion, resulting in a loosely bonded structure. A similar trend in variation of properties in the alkali, alkali-earth metaphosphate glasses has been observed by Wilder et.al [1984].

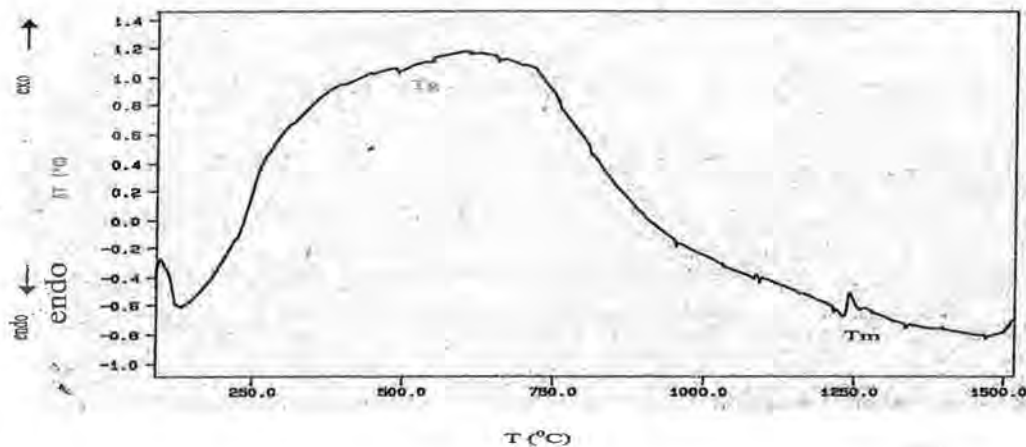


Figure 3.2 : DTA curve for a $20\text{MgO}-5\text{Na}_2\text{O}-5\text{Al}_2\text{O}_3-70\text{P}_2\text{O}_5$ glasses

3.5 Vibrational Spectra

The IR spectra of $20(\text{RO}-\text{R}_2\text{O})-5\text{Na}_2\text{O}-5\text{Al}_2\text{O}_3-70\text{P}_2\text{O}_5$ glasses is shown in Fig.3.3. The spectra is similar to those reported for various metaphosphate glasses [Byun et al, 1996, Abe et al, 1976]]. In general, there

are seven major bands observed at around 1365, 1268, 1062, 954, 864, 744, and 470 cm^{-1} . These bands can be assigned to the

P-O-P sym.str unperturbed, P-O-P bending ν_{as} PO_2 , ν_s PO_2 , ν_{as} POP, ν_s POP, and δ PO_2 modes of $(\text{PO}_3)_n$ chain groups, respectively [Abe et al, 1976]. The intensity of strong bands observed around 1365, 1268, 1062 and 954 cm^{-1} for the glasses of $20(\text{RO-R}_2\text{O})\text{-}5\text{Na}_2\text{O}\text{-}5\text{Al}_2\text{O}_3\text{-}70\text{P}_2\text{O}_5$ decreases as the relative mass of alkali or alkali – earth increases, and their frequencies shift to lower values. However, there are no significant structural changes to the metaphosphate network and there is no evidence for the presence of significant concentrations of terminal PO_3 groups, These observations are consistent with the analyzed compositions which yield O/P ratio of ≈ 3.0 .

However there are no significant structural changes to the network and there is no evidence for the presence of significant concentrations of terminal groups (ν_{as} PO_3 at 1255.51 cm^{-1}). These observations are consistent with the analyzed compositions which yield O/P ratio of ≈ 2.69 and so PO_3 groups as indicated by the presence of the IR band at 1255.51 cm^{-1} . In addition to the relatively low frequency position of the band at 481 cm^{-1} , are in part due to cross linked three dimensional phosphate structure. This observation is an agreement with those obtained by Ilieva et.al (2001a). The band at 776.5 cm^{-1} is assigned to P-O-P ring frequency in the part of three dimensional network relatively free of chain. Generally the structure of the ν_s POP band is considered as the most characteristic one in the spectra of metaphosphate since it appears in a frequency range free from other vibrational frequencies [Junmo Koo et.al, 1997]. In addition, the ν_s POP bands are very sensitive to changes since the frequency is strongly dependent on POP bond angle.

A slight shift in the position of some band is observed. The absorption band at 470 cm^{-1} has shifted to 476 cm^{-1} as the rare-earth content is changes from sample to sample. Wong and Angell (1971) found that in binary phosphate glasses, the P=O band occurred at 1310 cm^{-1} . However, Muller (1972) argued that the principal absorption of the P=O group lies at 1282 cm^{-1} to 1250 cm^{-1} in a polymeric phosphate chain. In both our series of glasses the absorption of the P=O group agreed with the results of Muller (1969).

A fundamental absorption band at about 500 cm^{-1} which appears in glasses and crystalline P_2O_5 is known to be associated with the $(\text{PO}_4)^{3-}$ group [Karmakar et.al, 2001], probably the wagging mode. As can be seen from Figure 5.17 the $(\text{PO}_4)^{3-}$ group absorption band in binary phosphate glass appears around 470 cm^{-1} to 476 cm^{-1} .

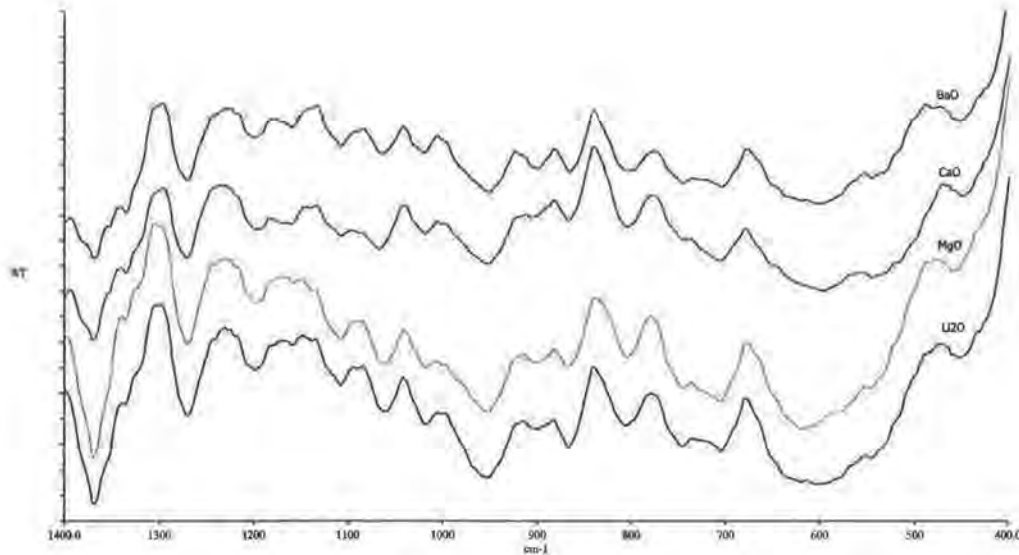


Figure 3.3. IR spectra of $20(\text{RO-R}_2\text{O})\text{-}5\text{Na}_2\text{O}\text{-}5\text{Al}_2\text{O}_3\text{-}70\text{P}_2\text{O}_5$ ($\text{R} = \text{Mg, Ca, Ba}$ and $\text{R}_2\text{O} = \text{Li}$). glasses

4. CONCLUSIONS AND SUGGESTIONS

4.1 Conclusions

In this study various experiments have been carried out to determine the structural and properties of Alkali Earth Alumina phosphate glasses.

Their x-ray diffraction measurements showed only a continuous haloes pattern rather than sharply defined peaks which confirmed that these materials are amorphous.

Density measurements for the system was found that the density increases as R_2O and R_2O oxide was introduced replacing some amount of Al_2O_3 . The increase in density is associated with changes in the structural re-arrangement as the R_2O and R_2O ions are introduced. The FTIR spectra of these glasses show a great similarity in their general shape. This indicate that most of the absorption bands seem to be mainly characteristic of the phosphate tetrahedra. The addition of small amount of R and R_2O oxide also effects the absorption band positions. The additional bands could be attributed to the formation of R-O groups. This confirms that the R and R_2O oxides in these glasses play some role in the formation of the strong and broad peak for these glasses.

4.2 Suggestion

This research is only based on structural and properties of R and R_2O Alumina phosphate glasses. Other glass properties such as thermoelectric power, magnetic properties and thermal conductivity are yet to be done. Further work has to be carried out so as to understand better about the glasses by further investigating the other properties. For a comparison, the glass preparation can be altered to sol-gel, CVD and PECVD technique.

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