Optical Properties of Calcium Sodium Phosphate Glasses Doped With Strontium

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Abstract. Strontium doped calcium phosphate sodium oxide glasses are prepared by a conventional melt quenching technique with different concentrations. XRD Spectra reveals that these glasses are amorphous in nature. The absorption spectrum of these glass samples exhibited broad band at about ~230nm. Optical band gap were determined by drawing Tauc plot. On the basis of the measured values of density, molar volume, optical band gaps and refractive index, properties like Ca2+ ion concentration, electronic polarizabilities, oxide ion polarizabilities, inter ionic distance, polaron radius, molar refraction and optical basicity of glass systems were estimated. All the variation can be attributed to the formation of Non bridging oxygens (NBO) with the increase of CaO composition in the glass network.

1. Introduction

Glass can be formed from materials in which the nature of bonding can be of several types such as ionic, covalent, metallic, Van der Waals and hydrogen (bonds) or a combination of them. A wide variety of multi-component glasses of desired composition can be prepared by changing the chemical composition. The complex chemical components of a glass are as a result of mixing of network former, network modifier and a dopant salt in different proportions. The complex chemical components of a glass are as a result of mixing of network former, network modifier and a dopant salt in different proportions. Glasses consisting of more than one component are enormous in nature and multicomponent systems are found to form glasses more easily. Doped materials are interesting and technologically relevant subject of research because of their unique optical properties and potential applications. The addition of cation to the glass network leads to the Bridging Oxygen (BO) and Non Bridging Oxygen (NBO) conversion. The surge of the NBO species in the glass matrix leads to the general depolymerization of the network that can be linked to the modifications of the chemical and physical properties.

Phosphate glasses possess remarkable functional properties such as low viscosity, low dispersion, high refractive indices and high transparency in the ultraviolet range [1]. The properties of the phosphate glasses can be tailored and the chemical durability can be enhanced by adding alkali and alkaline earth metal oxides into the glass network [2]. Phosphate glass is special type of optical glass which is composed of metaphosphates of different metals. Phosphate glasses are used due to its noticeable properties like biocompatibility, water solubility etc. They exhibit low dispersion and high refractive index compared to silica glasses. [3].

The basic building blocks of crystalline and amorphous phosphate glasses are PO4 – tetrahedral. They arise from the formation of sp3 hybrid orbitals of the p – outer electrons [4]. In the glass system
under consideration, CaO, Na$_2$O and SrO are modifiers and P$_2$O$_5$ is a glass former. Strontium containing glasses are found to possess homogenous composition and controllable degradation and ion release rates. Besides that Strontium is found to be naturally present in bone tissue and improves the mechanical properties of bone and is suggested as a daily oral supplement for the treatment of osteoporosis [5]. Phosphate Based Glasses containing Ca$^{2+}$ and Na$^+$ ions have prospective applications in both soft and hard tissue engineering, since the ions released from these glasses are natural constituents of human body and are accepted by it [6].

The knowledge of the structural aspects, transport and optical properties are necessary for pointing out the possible applications of glasses, Optical spectroscopy has been considered as one of the important analytical tool for studying the nature of glasses, especially to find the potential applications in the production of optical components and commercial filter glasses. It is one of the beneficial tools used to figure out the electronic structure of amorphous materials. This paper deals with the study of optical properties of calcium sodium phosphate glasses doped with strontium.

2. Experimental
2.1. Sample Preparation
Glasses with composition 45P$_2$O$_5$- xCaO- (50-x) Na$_2$O- 5SrO with x =20, 25, 30, 35mol% were synthesized by conventional melt-quenching technique using the high purity chemicals supplied by Sigma Aldrich. An appropriate quantity of weighed chemicals were mixed and thoroughly ground to homogenize the mixture using an agate motor and kept in a silica crucible inside a muffle furnace with furnace temperature set to 1100$^\circ$C. Uniform glass melts formed at 1100$^\circ$C were plate quenched using brass plates. The glasses formed were annealed in the furnace at 200$^\circ$C for about 2 hours to remove air bubbles and thermal strains formed in the glasses during their quenching process.

The compositions of the glasses under investigation are listed out in Table 1.

| Sample code | CaO mol% | Composition |
|-------------|----------|-------------|
| Sr1         | 20       | 45P$_2$O$_5$- 20CaO- 30 Na$_2$O- 5SrO |
| Sr2         | 25       | 45P$_2$O$_5$- 25CaO- 25 Na$_2$O- 5SrO |
| Sr3         | 30       | 45P$_2$O$_5$- 30CaO- 20 Na$_2$O- 5SrO |
| Sr4         | 35       | 45P$_2$O$_5$- 35CaO- 15 Na$_2$O- 5SrO |

2.2. XRD Analysis
X – Ray Diffraction studies for the glass samples were performed using Rigaku Ultima 4 PXRD in the diffraction angle 2$\theta$ ranging from 5$^\circ$ to 85$^\circ$. The synthesized samples were crushed in an agate mortar to fine powders and analyzed using X-ray diffractometer (Model: Rigaku DMAC-1C) by employing Cr-K$\alpha$ radiation.

2.3. Density and Molar Volumes
The density of the glasses free from air bubbles was determined by the Archimedes principle using toluene ($\rho_{toluene}= 0.860$ gm/cc) as the immersion liquid. By applying Archimedes principle, the weight of the prepared glass samples was measured in air and in toluene using a 4-digit sensitive microbalance (Denver, Pb214). Then, the density ‘$\rho$’ was determined using the relation

$$\rho = \frac{W_a}{W_a-W_t}\rho_t$$  \hspace{1cm} (1)

where $W_a$ is the weight of the sample in air, $W_t$ is the weight of the sample in toluene and $\rho_t$ is the density of toluene ($\rho_t= 0.860$ gm/cc ). The corresponding molar volume ($V_M$) was calculated using the relation,

$$V_M = \frac{M_T}{\rho}$$  \hspace{1cm} (2)

where $M_T$ is the total molecular weight. The relative error in the measurement of density was about $\pm$ 0.005g/cm$^3$. 


2.4. Optical Absorption Measurement
The Ultraviolet and Visible spectroscopy is a valid and precise analytical laboratory experimental technique that allows the analysis of a substance. Specifically, the absorption, transmission and emission of ultraviolet and visible light by matter is measured by the ultraviolet and visible spectroscopy. The wide ranging electromagnetic radiation spectrum consists of only a small portion of the Ultraviolet and visible light. In the practical sense, spectroscopy measures the absorption, emission or scattering of electromagnetic radiations by atoms or molecules. UV–Visible Absorption spectra of synthesized glasses was recorded using Perkin Elmer (Lambda 35) spectrometer in the UV-Vis-NIR region in the range 200 to 900 nm.

2.5. Refractive Index Measurement
In order to understand the lasing action of optical materials, refractive index is a vital parameter. Hence, many investigations are done to establish this correlation. The determination of refractive index is essentially important in connection with the theory of electronic structure of amorphous materials. Refractive indices of these glasses have been measured at wavelength 589.3 nm using Digital Abbe Refractometer (DR-A1) with methylene iodide containing sulfur solution as the contact layer between the sample and prism of the refractometer by using sodium vapor lamp as the light source. Refractive index measurement was performed using Digital Abbe Refractometer (DR-A1).

3. Results and Discussions
3.1. Results on X–Ray Diffraction
XRD patterns of the glass samples are shown in Figure 1 and all the samples show a hump in the low 2θ region which is the characteristic feature of amorphous structure. This indicates the absence of long range periodicity of the three dimensional network.

![XRD spectra of glass samples](image)

FIGURE 1. XRD spectra of glass samples

3.2. Results on Density and Molar Volumes
The variation of density and molar volumes with CaO concentration is represented in Fig 2. As shown in the figure, the density increases with increase in concentration of CaO. The increase in density is in good agreement with the results reported on the density of calcium phosphate glasses [7]. Since the relative error in the measurement of density is about ± 0.005 gcm⁻³, the error is found to be around 0.179%. Both the modifiers CaO and Na₂O causes the formation of non-bridging oxygens (NBOs) in the phosphate matrix. As the concentration of Strontium Oxide is fixed , with increase in CaO and decrease in Na₂O , the NBOs formed will consist of isolated PO₄ tetrahedron bonds linked together by ionic CaO bonds . The higher density can also be attributed to the much higher density of SrO (4.7gcm⁻³) than that of CaO (3.34 gcm⁻³). Accordingly, the increase of the calcium content in the glasses studied is responsible for increasing the number of the non-bridging oxygens and this may cause a decrease in the free space in the glass network structure and is the reason for the increase in the value of density and decrease in the value of molar volume in the glasses studied. Since CaO in
different concentrations is used as modifier in the glasses, it leads to formation of NBOs in the matrix. Hence, structural changes in the phosphate units are attributed to the NBOs.

![FIGURE 2](image_url). Variation of density and molar volume

3.3. Results on Optical Absorption in UV and Visible Regions

The absorption spectra of strontium doped calcium sodium phosphate glasses are shown in Figure 3. The optical absorption edges are not well defined in the investigated glasses and this is in accordance with the amorphous nature of the samples. The UV spectrum revealed a peak at 230 nm and that the absorption intensity of the bands is found to increase with increase in CaO content.

**TABLE 2.** Physical and optical properties of glass samples

| Physical Property                  | Sample codes     | Sr1        | Sr2        | Sr3        | Sr4        |
|-----------------------------------|------------------|------------|------------|------------|------------|
| Density \(\rho\) (g/ cm\(^3\))    |                  | 2.6190     | 2.6725     | 2.7260     | 2.7795     |
| Molecular Weight M (g)            |                  | 97.6593    | 97.0645    | 96.4697    | 95.8749    |
| Molar Volume VM (cm\(^3\))       |                  | 37.2887    | 36.3197    | 35.3887    | 34.4935    |
| No. of Ca\(^{2+}\) ions N \((\times 10^{-21}\) per cm\(^3\)) | | 3.23       | 4.15       | 5.11       | 6.11       |
| Polaron Radius \(r_p\) \((\times 10^{-8}\) m) | | 2.73       | 2.51       | 2.34       | 2.20       |
| Internuclear distance \(r_i\) \((\times 10^{-8}\) m) | | 6.76       | 6.22       | 5.81       | 5.47       |
| Refractive Index n                |                  | 1.4482     | 1.4871     | 1.5260     | 1.5650     |
| Dielectric constant E             |                  | 2.0971     | 2.2215     | 2.3288     | 2.4492     |
| Reflection Loss R                 |                  | 0.0335     | 0.0384     | 0.0434     | 0.0485     |
| Molar Refractivity \(R_m\) \((\text{cm}^3)\) | | 9.9852     | 10.4477    | 10.9634    | 11.2354    |
| Molar Polarizibility \(\alpha_m\) \((\text{Å}^3)\) | | 3.9624     | 4.1459     | 4.3108     | 4.4585     |
| Optical Basicity                  |                  | 0.801      | 0.796      | 0.791      | 0.786      |

The physical properties [8] provide an insight into the atomic arrangements in a glass network. Based on the measured density and molar volume, various physical properties like calcium ion concentration (N), polaron radius \(r_p\), inter-nuclear distance \(r_i\) and field strength (F) were determined using the standard relations (3) to (6) as described below

\[
N (\text{ions/cm}^3) = ({\% \text{ mol of CaO}}) \times \frac{(\text{Avagadro's number} \times \text{Density})}{(\text{Average Molecular Weight})} \tag{3}
\]

\[
Polaron\ radius, r_p (\text{Å}) = \left(\frac{1}{2} \left(\frac{\pi}{6N}\right)\right)^{1/3} \tag{4}
\]

\[
Inter\ nuclear\ distance, r_i (\text{Å}) = \left(\frac{1}{N}\right)^{1/3} \tag{5}
\]
Field strength, \[ F(c m^2) = \left( \frac{Z}{r_f^2} \right) \] (6)

**FIGURE 3:** UV Visible spectra of samples

The concentration of the alkali earth ions is an important parameter as the physical properties provide an insight into the atomic arrangements. It is noticed that the calcium concentration \( N \) increases whereas the polaron radius and internuclear distance of alkali earth ions are found to decrease with the increase in calcium oxide content in the compositions. The increase in density observed is attributed to increase in the rigidity of glass and increase in field strength tends to attract the oxygen ions, leading to a decrease in the size of the interstices.

The refractive index \( (n) \) values of the strontium doped glasses measured using digital Abbe Refractometer (DR-A1) are listed in Table 2. The increment in the refractive index leads to increase in optical density and also increase in dielectric constant. The dielectric constant \( (\varepsilon) \) was calculated using the relation

\[ \varepsilon = n^2 \] (7)

The reflection loss of each sample was computed from the refractive index by using the Fresnel’s formula

\[ R = \left( \frac{n-1}{n+1} \right)^2 \] (8)

The molar refraction \( (R_m) \) [9] was calculated by using the equation

\[ \frac{n^2-1}{n^2+2} = \frac{M}{\alpha_m} \] (9)

The molar refraction lie in the range 9.98 to 11.23 and increases with increasing concentrations of CaO. Molar refraction is related to the structure of the glass and is proportional to the molar electronic polarizability of the material, through the Clausius–Mossotti [10] relation

\[ \alpha_m = \left( \frac{3}{4\pi N} \right) R_m \] (10)

where \( N \) is the number of polarizable ions per mole and is assumed to be equal to the Avogadro’s number \( (N_A) \). The value \( 4\pi/3 \) is known as a constant in Lorentz function. With \( \alpha_m \) in \( (10^{-24} \text{cm}^3) \), Eq.(10) can be transformed to \( R_m = 2.52 \alpha_m \).

The molar refraction increased with the increase in refractive index which in turn increased oxide ion polarizability and electronic polarizability. The increase in molar refraction \( (R_m) \) and refractive index \( (n) \) accompany increase in polarizability. Hence refractive index of the present glasses under study not only depends on the density values but also on the polarizability values of the glasses. The increase in the values of \( R_m \) and \( \alpha_m \) with the replacement of Calcium ions in the glass network confirms increase in the number of NBOs in the glass which in turn caused increment in refractive index values. The measured refractive indices are used for the determination of electronic polarizability \( (\alpha_e) \) and optical basicity and the values are given in Table 2.
The substitution of alkali earth ion has increased the breakage of glass network and increase the concentration of NBOs. The addition of network modifiers such as alkaline earth oxides breaks these bridges and creates non-bridging oxygens (NBOs). These oxygen ions carry a partial negative charge and are connected to structural unit only at one end in the glass network. Optical basicity of an oxide glass will reflect the ability of the glass to donate negative charge to the probe ion. The theoretical values of optical basicity of the glass was estimated using the relation

\[ \Lambda_{TH} = X_{P_2O_5} \Lambda(P_2O_5) + X_{CaO} \Lambda(CaO) + X_{Na_2O} \Lambda(Na_2O) + X_{SrO} \Lambda(SrO) \]  

(11)

Where \( \Lambda(P_2O_5), \Lambda(CaO), \Lambda(Na_2O) \) and \( \Lambda(SrO) \) are the optical basicity values associated with constituent oxides and \( X_{P_2O_5}, X_{CaO}, X_{Na_2O} \) and \( X_{SrO} \) are the proportion of contribution of respective oxides to the glass system. The values of optical basicity are read from literature [11].

The theoretical values of optical basicity were calculated for all the glass samples and are listed in Table 2. It is observed that the optical basicity decreases linearly with increasing concentration of CaO. Optical basicity is used to classify the covalent / ionic character of the glass, since decreasing basicity indicates increasing covalency.

4. Conclusions

The physical and optical properties of strontium doped calcium sodium phosphate glasses have been investigated. The density and refractive index are found to increase with the increase in CaO content. The variations in the optical band gap can be attributed to the increase in concentration of CaO which represent the modifier behaviour of Ca ion that creates NBOs in glass network. The role of Strontium also cannot be ruled out and can lead to bioactive properties. Phosphate glasses are most suitable for bioactive applications in general and bone tissue engineering in specific. The glass samples were tested for preliminary analysis of bioactivity by immersing in Seminal Body Fluid (SBF) for a prolonged duration of about 90 days. The solution showed a white coloured bone like formation which has paved an insight for further exploration about bioactivity.

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