Structural, Optical and Dielectric Studies on Ion Exchanged Sm$^{3+}$: K-Mg-Al-Zn Fluorophosphate Glass

Abstract

The design and optimization of a novel ion exchange unit are presented. A simple system with a modified dipping mechanism and a temperature controller for ion exchange in the glass substrate with molten salt is described. The ion exchange unit is optimized with Ag$^+/Na^+$ ion exchange in commercially available soda lime glass. The present unit is adapted for Ag$^+/K^+$ ion exchange on Sm$^{3+}$-doped K-Mg-Al-Zn fluorophosphate glass. The structural studies have been carried out using EDS, XRD and TEM measurements. The crystallite size of silver was estimated to be 19 nm from the XRD and it was confirmed using TEM analysis. Assessment of the optical properties has been carried out by absorption, photoluminescence and lifetime measurements. The energy transfer mechanism from Ag to Sm$^{3+}$ and the SPR of Ag nanoparticles are discussed for the ion exchanged glass. Dielectric studies have been carried out in order to assess the influence of Ag on the dielectric properties and ac conductivity of the ion exchanged glass. Coulomb blockade effects have been discussed to clarify the enhancement in the insulating behavior of the glass by the incorporation of Ag nanoparticles. The power-law and Cole-Cole parameters were determined and the influence of Ag on these parameters is discussed.
4.1 Introduction

Ion exchange in glass is a widely used process for the fabrication of active and passive devices with desirable properties such as low propagation losses, low waveguide birefringence and excellent mode matching to optical fiber [1]. The ion exchange is a prime technique for making waveguide lasers and amplifiers due to the affinity of the glass substrate towards high rare earth ion concentration. By the proper selection of ions to be exchanged, it is possible to realize a graded refractive index in the ion exchanged glass. It can be used to fabricate graded index lenses for imaging in scanners, small photocopiers, collimation optics of high power diode lasers and in endoscopes enabling minimally invasive surgery [2, 3]. The graded refractive index as a result of the ion exchange process can also be employed to fabricate low loss planar waveguides and optical sensors [4, 5].

For photonic applications, the glasses comprised of metal nanoparticles (NPs) have drawn more attention [6]. The surface plasmon resonance (SPR) due to the confinement effect on the electronic properties of silver or gold metal particles gives specific consideration for metal-dielectric nanostructured materials [7]. The noble metal NPs with strong SPR band are used for the enhancement of photoluminescence intensity in rare earth incorporated glasses. The physics of metal NPs integrated in dielectric materials has accomplished significant consideration in the previous decade due to its remarkable properties such as quick response and higher third order optical nonlinearity [8]. On account of tunable nonlinear properties, glass matrices embedded with metal particles have enormous potential applications in optical switching and opto-electronic devices [9]. Dielectric properties of the metal and the surrounding medium have considerable influence on the nonlinear properties [10].
We here report the design, performance and optimization of the ion exchange apparatus. Since, one of the main criteria for the ion exchange process is the thermal equilibrium; the temperature can be controlled very precisely in this apparatus. Removable substrate holder and visibility of movement of the substrate are other admirable features of this apparatus. The spectroscopic and dielectric studies of Ag\(^+/K^+\) ion exchanged Sm\(^{3+}\) doped K-Mg-Al-Zn fluorophosphate glass were carried out to investigate the influence of silver NPs on optical and conductivity properties of ion exchanged glass. The EDS, XRD and transmission electron microscopy (TEM) analysis have been carried out to confirm the presence and to study the structure of silver NPs in Ag\(^+/K^+\) ion exchanged glass. The absorption, emission and excitation spectra, luminescence decay curve and dielectric profiles of the ion exchanged glass were recorded and analyzed. The results have been compared with reference to glass as substrate.

4.2 Design of ion exchange apparatus

The apparatus fabricated here is a modified version of dip coating mechanism. The usual dip coating system works on several up and down movement of the substrate to be coated. But in the ion exchange unit salient transfiguration is the precise up-down movement. In this ion exchange unit the substrate movement mechanism gives consent for a very slow dipping speed of 2\(\mu\)m/s. This lesser speed aids the immersion of glass substrate without any fracture due to thermal shock.

Figure 4.1 shows the schematic of the ion exchanger unit. The most important parts of the system are programmable translation unit, mechanical setup consisting of a substrate holder, inner chamber with heater coil, an enclosed outer chamber and a digital temperature controller. The translational unit consists of a programmable micro controller based stepper motor control drive for translation of the substrate holder. The
translational rate can be controlled by varying the speed 2 - 9000 $\mu$m/s. In this setup linear translation is accomplished by directly coupling the motor shaft with a metal rod arrangement for ultra-smooth and vibration free up-down movements. The number of dipping and the length of dipping can be adjusted using this arrangement and can be controlled programmably. The maximum translational length is 240 mm. Dipping length specifies how far the substrate should be moved downwards for a dip and it is varied from 0 to 240 mm.

Figure 4.1 The Ion Exchange apparatus
Mechanical setup consists of removable substrate holder which can be fitted to the end of the metal rod. Depending on the size and shape of the substrate used, the substrate holder can be changed. Ion exchanging can be done either vertically or horizontally by placing the substrate either in X or Y plane using different types of substrate holders.

The inner chamber is made up of stainless steel with 90 mm depth and 85 mm diameter. This chamber acts as a top loading furnace in which a beaker can be slowly introduced. The height is limited to 9 cm so that the pyrex beaker (of 115 mm height) can be placed by hand while it is being put into the chamber. Its top has a circular opening to insert the beaker. It has heating elements (nicrome coil) around the walls and also at the bottom. This helps to provide a uniform heating inside the chamber. The temperature of the heater can be controlled by a digital temperature controller to which a thermocouple is attached. The temperature of the inner chamber can be controlled in the range 30 to 500°C with an accuracy of 1°C.

There is also an outer chamber which encloses the inner chamber, translational unit and the thermocouple. This outer chamber also prevents the heat radiation. This chamber has a front door with a glass window in order to see the movement of substrate before dip. Visibility of the melt beaker makes it possible to ensure proper melt conditions and also to remove any impurities present before introducing the sample. There is another glass window on the top side of the outer chamber, to see whether the substrate is completely dipped. After the temperature is raised to the desired level, the user can start the dip process. The dip speed and the dwell time can be controlled by microcontroller.
4.3 Performance of ion exchange apparatus

The substrate is inserted between the plates of the substrate holder and the knob is fastened to hold it firm. Proper composition of chemicals to be melted is taken in a pyrex beaker and is inserted in the inner chamber. Using the temperature controller keys, temperature is set to a predefined value and waits until it reaches the same. Hence the sample is sandwiched between the plates which is an extension of suspension mechanism, through which the sample is slowly immersed into the molten salt (The sample is very slowly introduced into the beaker and is kept just above the melt to attain a thermal equilibrium and can avoid any thermal shocks). The immersed sample remains there for a certain amount of time. After that, it is withdrawn from the salt and held above the molten salt to avoid thermal shocks. The above translation of substrate is controlled programmably by parameters entered through the keyboard which is connected to the microcontroller. By entering the dip start position and dipping length, the substrate can be moved from 0 to 240 mm along the vertical direction. For example, if the dip start up position is 40 mm and the dipping length is 120 mm, the substrate reaches 40 mm from the reference point and it travels 120 mm along the vertical direction. Dip duration can be set, which specifies how long the substrate should remain dipped in the solution. The sample is then transferred into a beaker containing deionised water in order to wash the salt residues completely and make the surface clean. Finally the exchanged surface is cleaned up with deionised water and acetone using soft and lint-free Kodak lens paper.

4.4 Optimization with Ag⁺/Na⁺ ion exchange

The silver ions are introduced into the glass network by an isothermal ion exchange for the optimization of the ion exchanger apparatus. Slices of commercially available soda lime glasses are used for
the exchange of ions, by keeping it in a molten salt with a composition of 5% AgNO$_3$ and 95% NaNO$_3$. Figure 4.2 shows the photographs of the ion exchanged soda lime glass along with the substrate glass. It is noted that color of the soda lime glass becomes yellowish due to the Ag$^+$/Na$^+$ ion exchange in it. Ion exchange in soda lime glass had been carried out for 10 seconds duration at 400$^\circ$C. The dipping and withdrawal speed of the substrate was 150 µm/sec. The parameters like temperature, dip duration, dipping and returning speed for the ion exchange process were optimized by trial and error method to get the crack free ion exchanged glass.

![soda lime glass](image)

**Figure 4.2** Photographs of the soda lime glasses

The ion exchange process can be represented by the following chemical reaction,

$$\text{Ag}^+_{\text{melt}} + \text{Na}^+_{\text{glass}} = \text{Ag}^+_{\text{glass}} + \text{Na}^+_{\text{melt}} \quad \ldots \ldots (4.1)$$

where subscripts ‘melt’ and ‘glass’ represent the cations in the melted salt and in the glass substrate respectively. The soda lime glass used here
contains sodium, magnesium, aluminum, silicon and calcium, and it is verified by EDS analysis. Figure 4.3 shows that EDS spectrum of the ion exchanged soda lime glass. Appearance of peak at 3.1 keV in the EDS spectrum reveals the presence of Ag$^{+}$ ions in the ion exchanged glass [11].

![EDS spectrum of ion exchanged soda lime glass for 10 seconds at 400°C](image)

**Figure 4.3** EDS spectrum of ion exchanged soda lime glass for 10 seconds at 400°C

Figure 4.4 (a) shows the UV-Vis absorption spectrum of an ion exchanged soda lime glass after annealing for 5 hours at a temperature of 450°C. After the annealing process, the sample changes its color to pale red [12]. SPR band with a maximum of 422 nm in the absorption spectrum indicates the presence of silver NPs in the ion exchanged glass substrate due to the annealing process [12, 13]. The SPR band is a phenomenon noticed in solid or solution phase due to the existence of metal NPs and it can be elucidated via the collective resonance of the conduction electrons of the NPs [14].
Figure 4.4(a) Absorption spectrum of ion exchanged soda lime glass

The SPR is prompted by pairing among the incident electromagnetic wave in quasistatic regime and oscillation of conduction band electrons cloud on the surface of Ag NPs as shown in Figure 4.4 (b). In general, silver and gold particles with a diameter greater than 5 nm manifest strong SPR band [15]. By assuming the free particle behavior of the conduction electrons, diameter \( d \) of the silver NPs can be calculated using the expression [16]

\[
d = \left( \frac{2h\nu_f}{\Delta E_{1/2}} \right)
\]

where \( h \) is Planck’s constant (in eV s), \( \nu_f \) (1.39×10^6 m/s) is the Fermi velocity of electrons in bulk silver and \( \Delta E_{1/2} \) is the FWHM of SPR band (in eV). In the case of bulk silver, the mean free path of electrons is about 27 nm at room temperature [16]. The above expression is effective only for the particle size less than the mean free path of electrons [16]. For ion exchanged soda lime glass, the values for \( \Delta E_{1/2} \) and the particle size of Ag were obtained as 0.69 eV and 17 nm, respectively.
4.5 Experimental

4.5.1 Ag$^+/K^+$ ion exchange for Sm$^{3+}$:K-Mg-Al-Zn fluorophosphate glass

The molar composition of the Sm$^{3+}$-doped K-Mg-Al-Zn fluorophosphate glass preferred to carry out the Ag$^+/K^+$ ion exchange was

\[ 52P_{2}O_{5} + 15K_{2}O + 13MgO + 10ZnF_{2} + 8Al_{2}O_{3} + 2Sm_{2}O_{3} \]  

\text{(PKAMZFSm20).}  

It is one of the set of glasses we have investigated for the visible laser applications and optical fiber amplifiers [17]. The glass was incised into two segments and one piece was heat treated at 350°C for 24 h, which is referred to as PKSm hereafter. The second piece of glass was isothermally ion exchanged to introduce silver ions into the glass network. It was carried out by dipping it in a molten salt batch of composition 95% KNO$_3$ + 5% AgNO$_3$ at 350°C for 24 h using ion exchange apparatus. The dipping and withdrawal speed of the glass substrate for Ag$^+/K^+$ ion exchange was 150µm/s. To eliminate AgNO$_3$ adhering to the glass surface, this silver exchanged glass was cleaned with distilled water. This ion exchanged glass
Chapter 4                         Structural, Optical and Dielectric Studies on Ion Exchanged……

will be referred to as PAgSm hereafter. The ion exchange process is represented by the following chemical reaction,

\[ \text{Ag}^{+}_{\text{melt}} + \text{K}^{+}_{\text{glass}} = \text{Ag}^{+}_{\text{glass}} + \text{K}^{+}_{\text{melt}} \]  

\[ \ldots..(4.3) \]

4.5.2 Measurements

The EDS spectrum of the glass was recorded using Oxford instrument attached with TEM. The TEM analysis along with selected area electron diffraction (SAED) pattern and High Resolution TEM (HR-TEM) was done by using JEOL 2100 at an operating voltage of 200 kV. Absorption spectra of the glasses were recorded in transmittance mode using UV-Vis spectrophotometer (Perkin Elmer Lambda 650) with a spectral resolution of 0.5 nm in the wavelength range 200-900 nm by keeping air as reference. Excitation and emission spectra of the glasses were measured using spectrophotofluorometer (Shimadzu-RFPC 5301) with a spectral resolution of 1 nm. The XRD, lifetime and dielectric measurements were carried out as discussed in the second chapter (section 2.2.2).

4.6 Results and Discussion

4.6.1 Energy Dispersive Spectrum analysis

Figure 4.5 shows the EDS spectrum of thermally diffused Ag\(^{+}\)/K\(^{+}\) ion exchanged glass. The presence of silver was clearly confirmed by the peak at 3.3 keV in the EDS spectrum of ion exchanged glass [11]. The presence of Cu in the EDS spectrum is owing to the grid of the TEM instrument.
4.6.2 X-ray diffraction

Figure 4.6 shows the XRD patterns of PKSm and PAgSm glasses. Broad humps present in the region 20-35° in the XRD patterns indicate the amorphous nature of the glass matrix. The ion exchanged glass exhibits the characteristic peaks in the XRD pattern at 38°, 44°, 64° and 77° corresponding to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of FCC structure of silver, respectively (ICDD No: 89-3722 Silver). The crystallite size of the silver was estimated from the (2 0 0) plane of the XRD spectrum of PAgSm glass using the well-known Debye-Scherrer formula [18]

\[ t = \frac{0.9 \lambda}{\beta \cos \theta} \]  

……(4.4)  

and the crystallite size was obtained as 15 nm.
Due to lattice distortion, there is a possibility of FWHM ($\beta$) broadening which may lead to an inaccuracy in the crystallite size calculation. Therefore, we used the Williamson-Hall plot for crystallite size estimation by employing the improved equation [18]

$$\beta \cos \theta = \frac{k\lambda}{D} + \eta \sin \theta$$

$$\ldots (4.5)$$

where $\eta$ is the effective strain and $D$ is the effective particle size. By using this equation, crystallite size and the effective strain were evaluated as 19 nm and 0.024 (i.e. 2.4%), respectively.

### 4.6.3 TEM analysis

Morphology, strain, particle size and crystalline nature of the Ag NPs in PAgSm glass were evaluated using TEM analysis. Figures 4.7 (a) and (b) show the TEM images at a scale of 10 nm along with SAED pattern (inset of Figure 4.7 (a)) and HR-TEM image at a scale of 2 nm of the
PAgSm glass, respectively. It is observed from the TEM image of the PAgSm glass, the silver NPs are formed as clusters and the average size of the silver NPs is estimated as 21 nm (Figure 4.7 (a)). The bright spots present in the SAED pattern (see inset) at a scale of 2-1/nm indicate the crystalline nature of the silver NPs. The d-spacing values corresponding to these bright spots are identified as (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of the Ag NPs using ImageJ software. HR-TEM micrograph clearly reveals the surface planes of Ag NPs. The fringes of Ag nanocrystallite in HR-TEM were used to estimate the d-spacing value and this is identified as (2 0 0) plane of silver nanocrystal.

**Figure 4.7(a)** TEM image at a scale of 10 nm along with SAED pattern (inset) of PAgSm glass
4.6.4 Optical Absorption spectrum

UV-Vis absorption spectra of PKSm and PAgSm glasses are displayed in Figure 4.8 along with the smoothed absorption spectrum of PAgSm glass as inset in order to clearly identify the SPR band. The sharp peaks obtained at 401 nm in absorption spectra belong to the transition from ground level $^6\text{H}_{5/2}$ to excited level $^6\text{P}_{3/2}$ of Sm$^{3+}$ ions in glasses. In the absorption spectrum of Ag$^+/K^+$ ion exchanged glass, a broad absorption band results from the SPR of Ag NPs and is observed around 375 nm (inset of Figure 4.8), which in turn is an indication of silver NPs in PAgSm glass. The broadness of SPR band might be caused by the size distribution of silver particles. The NPs exist in PAgSm glass were developed by migration and aggregation of silver atoms in the glass at the time of Ag$^+/K^+$
ion exchange process. By assuming the free particle behavior of the conduction electrons, diameter \(d\) of the silver NPs in the PAgSm glass is calculated using Eq. (4.2). For PAgSm glass, the values for \(\Delta E_{1/2}\) and the particle size of Ag were obtained as 0.57 eV and 20 nm, respectively. The reduction in the absorption peaks of Sm\(^{3+}\) ions due to the incorporation of silver NPs is clearly observed from the absorption spectra (Figure 4.8). This effect is attributed to the mechanism in which silver can serve as a sensitizer for Sm\(^{3+}\) ions [19].

**Figure 4.8** Absorption spectra of PKSm and PAgSm glasses. Inset shows the smoothed absorption spectrum of PAgSm glass in order to clearly identify the SPR band
4.6.5 Excitation and Emission spectra

Figures 4.9 (a), (b) and (c) show the PL excitation spectra, emission spectra and photograph of Sm$^{3+}$ luminescence in the investigated glass system, respectively. The excitation spectra consist of 15 peaks corresponding to the transitions from ground level $^6\text{H}_{5/2}$ to the various excited levels $^4\text{P}_{3/2}$, $^4\text{G}_{9/2}$, $^4\text{D}_{7/2}$, $^4\text{H}_{7/2}$, $^4\text{D}_{3/2}$, $^6\text{P}_{7/2}$, $^6\text{P}_{3/2}$, ($^6\text{P}$, $^4\text{P}$)$_{5/2}$, $^4\text{G}_{9/2}$, $^4\text{F}_{5/2}$, $^4\text{F}_{7/2}$, $^4\text{I}_{13/2}$, $^4\text{I}_{11/2}$ and $^4\text{G}_{7/2}$ of Sm$^{3+}$ ions at the wavelengths 318, 332, 344, 354, 361, 374, 389, 401, 416, 438, 450, 462, 470, 487 and 500 nm, respectively. It is observed that emission peaks exist at wavelengths 565, 601 and 648 nm corresponding to energy relaxations of Sm$^{3+}$ ions from the emitting level $^4\text{G}_{5/2}$ to lower lying levels $^6\text{H}_{3/2}$, $^6\text{H}_{7/2}$ and $^6\text{H}_{9/2}$, respectively. The asymmetric ratio of the transition intensities for $^4\text{G}_{5/2}$$\rightarrow$$^6\text{H}_{9/2}$ to $^4\text{G}_{5/2}$$\rightarrow$$^6\text{H}_{7/2}$ is obtained as 0.23 for both PKSm and PAgSm glasses.

![Figure 4.9(a) Excitation spectra of PKSm and PAgSm glasses](image-url)
Figure 4.9(b) Emission spectra of PKSm and PAgSm glasses

Figure 4.9(c) Photograph of Sm$^{3+}$ luminescence in PAgSm glass under violet light irradiation
For PKSm and PAgSm glasses, there is only intensity variations observed in their excitation and emission spectra. This luminescence enhancement for PAgSm glass is due to the energy transfer from silver to Sm$^{3+}$ ions. Some of the literatures have already suggested that the enhancement in the photoluminescence intensity of rare earth ions in glassy materials can be realized by incorporating silver NPs in it [20, 21]. Even if a fraction of silver in the Ag$^+/K^+$ ion exchanged glass had contributed to the formation of NPs, major fraction of silver presumably continued to exist in the form of ions. As a result, the contribution of the silver ions to the intensification of Sm$^{3+}$ photoluminescence cannot be excluded.

![Energy transfer mechanism in PAgSm glass along with partial energy level diagram for Ag$^+$ and Sm$^{3+}$ ions](image)

**Figure 4.10** Energy transfer mechanism in PAgSm glass along with partial energy level diagram for Ag$^+$ and Sm$^{3+}$ ions
The enhancement in photoluminescence of PAgSm glass does not originate from an increment in absorption cross-section in Sm$^{3+}$ ions when the glass is subjected to an intense electromagnetic field originated by the surface plasmon excitation of silver NPs. But it is very likely to be fostered by the energy transfer from silver to Sm$^{3+}$ ions. The schematic representation of viable energy transfer mechanism from silver NPs to Sm$^{3+}$ ions along with the partial energy level diagrams for Ag$^+$ and Sm$^{3+}$ ions is shown in Figure 4.10. The energy transfer mechanism involves the absorption of exciting light by silver and their emitted energy absorbed by the Sm$^{3+}$ ions in the ground state. Thus the additional Sm$^{3+}$ ions are excited to the $^6\text{P}_{3/2}$ level leading to an enhancement in the fluorescence intensity.

4.6.6 Decay analysis

Figure 4.11 shows the decay curves of $^4\text{G}_{5/2}$ level of Sm$^{3+}$ ions in PKSm and PAgSm glasses. It is clearly observed from Figure 4.11 that the decay curves of both glasses have non-exponential nature due to dipole-dipole interactions between Sm$^{3+}$ ions [17]. The lifetime for $^4\text{G}_{5/2}$ level of Sm$^{3+}$ ions in PKSm glass is obtained as 1.493 ms and it slightly decreased to 1.417 ms for Ag$^+$ ions introduced glass via ion exchange. Similar decrements in lifetime were found in silicate and phosphate glasses due to the incorporation of silver in it by thermally diffused ion exchange process [19, 22]. This decrease in lifetime is attributed to the defects due to the silver exchange in the glass substrate. From the diminished lifetime of PAgSm glass, it is obvious that the Sm$^{3+}$-Sm$^{3+}$ electric-dipole interactions and the total transition probability are higher for ion exchanged glass.

It is noted that the K$^+$ ions have low refractive index modifying capacity while Ag$^+$ ions have high refractive index modifying capacity. So the refractive index of Ag$^+/K^+$ ion exchanged glass gradually increases
from the center towards the periphery [23]. Therefore, it is suggested that the high refractive index regions (near to the surfaces) of PAgSm glass can act as planar waveguides. At these waveguide regions, more optical amplification will occur due to the energy transfer from Ag$^+$ to Sm$^{3+}$ ions. It is also noted that the electric-dipole interactions and the transition probability for Sm$^{3+}$ ions will be more at these regions. These planar waveguides can also act as sensors through evanescent coupling when liquid is placed on the surface of the glass.

Figure 4.11  Decay curves for $^4\text{G}_{5/2}$ level of Sm$^{3+}$ ions in PKSm and PAgSm glasses
4.6.7 Dielectric studies

Dielectric properties are complex functions of frequency, shape, dimension and spatial ordering of the constituents [24]. It has been perceived that the addition of silver particles in Sm$^{3+}$-doped K-Mg-Al-Zn fluorophosphate glass through ion exchange causes some variations in the dielectric properties as related to pre-ion exchanged glass (PKSm). Different frequencies of sinusoidal voltages have been applied to the glass of thickness $t$ and area $A$ for the dielectric measurements of PKSm and PAgSm glasses. Figures 4.12 (a) and (b) show the variation of real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of dielectric constant with $\log f$ in PKSm and PAgSm glasses for the entire domain that was investigated.

![Figure 4.12(a) Real part of dielectric constant for PKSm and PAgSm glasses](image.png)
Figure 4.12(b) Imaginary part of dielectric constant for PKSm and PAgSm glasses

It is noted that the dielectric constants of the PKSm and PAgSm glasses decreased with an increase in frequency. The real part of dielectric constants for PKSm and PAgSm glasses at selected frequencies ($f_i$) are summarized in Table 4.1. From the values of dielectric constant, it is obvious that the glasses behave as charge transfer type insulators.

| Table 4.1 Dielectric constant for PKSm and PAgSm glasses at selected frequencies |
|---|---|---|---|---|---|---|
| Glass Code | $f = 0.1$ KHz | $f = 1$ KHz | $f = 10$ KHz | $f = 0.1$ MHz | $f = 1$ MHz | $f = 2$ MHz |
It is discerned from Figure 4.12 that the Ag⁺/K⁺ ion exchanged Sm³⁺-doped K-Mg-Al-Zn fluorophosphate glass have higher dielectric values than PKSm glass. This is how Ag⁺ ions in the PAgSm glass create pathways convenient for the migration of free ions that have developed space charge [25]. It implies that the space charge polarization and so the dielectric constants augment when the glass network becomes weaker due to increase in the degree of disorder. The enhancement of dielectric constants for PAgSm glass suggests an increment in the freedom of dipoles to align in the field direction, triggered by reduction in the rigidity of glass network. It is ascribed that the resistance of Sm³⁺-doped K-Mg-Al-Zn fluorophosphate glass increases owing to the Coulomb blockade effect by the incorporation of silver in it [26]. In microscopic view, the Ag NPs will increase the insulating behavior of the glass by preventing charge carriers from moving according to a particular electric field and they can be regarded as several tunneling knots. Coulomb blockade is one of the significant phenomena caused by NPs, which provides awareness regarding to the scheming of inimitable nanocomposites by means of insulating materials [16].

Figure 4.13 shows the variation of ac conductivity with log f in PKSm and PAgSm glasses. It is noted from Figure 4.13 that the value of ac conductivity changed from 0 to 1.06×10⁻⁷ Ω⁻¹ cm⁻¹ during which the frequency runs from 100 Hz to 2MHz. Above 0.083 MHz, the Ag⁺/K⁺ ion exchanged glass shows lower ac conductivity with respect to that in PKSm glass. While below 0.083 MHz, an inverse effect is remarked because of change in predominance of polarization when the frequency varies [27]. The decrease in conductivity of PAgSm glass at higher frequencies is also attributed to the large surface scattering and intrawell hopping of charge carriers in short range among localized states. Some of the previous
research reported that the conductivity decreased due to the doping of silver, in which the involvement of effective number of charge carriers is reduced [28, 29]. Correlated barrier-hopping (CBH) model proposes the electrons are proficient to hop amid charged defects D- and D+ over the Coulombic barrier. To describe the influence of frequency on the conductivity of a material, Jonscher suggested a suitable formula acknowledged as power-law relation [30].

Table 4.2 shows the power-law parameters ($\sigma_0$, $s$ and $A$) for PKSm and PAgSm glasses. It is observed that the value of $s$ (universal power-law exponent) is slightly enhanced for Ag$^+/K^+$ ion exchanged glass. Generally, the value of $s$ is a gauge having the degree of correlation between conductivity and frequency. The arbitrary hopping of electrons was symbolized by the zero value of $s$ whereas it tends towards unity as the
correlation increases. Consequently, it is obvious that the $\text{Ag}^+/\text{K}^+$ ion exchange process effectuated an increment in correlation among frequency and conductivity of PAgSm glass.

**Table 4.2** Power-law parameters for PKSm and PAgSm glasses

<table>
<thead>
<tr>
<th>Glass Code</th>
<th>$\sigma_0$ ($\times 10^{-11}$)</th>
<th>$s$</th>
<th>$A$ ($\times 10^{-12}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PKSm</td>
<td>6.36</td>
<td>0.55</td>
<td>1.49</td>
</tr>
<tr>
<td>PAgSm</td>
<td>1.60</td>
<td>0.68</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Figures 4.14 (a) and (b) represent the Cole-Cole plots for PKSm and PAgSm glasses and these glasses are modeled by corresponding parallel RC circuits. The contribution of ions in the conductivity was confirmed by the existence of spike at low frequency region in Cole-Cole plot [31].

**Figure 4.14(a)** Complex impedance plot for PKSm glass
Table 4.3 shows the Cole-Cole parameters \((R_b, C_b, \text{ and } \tau)\) for PKSm and PAgSm glasses. It can be inferred that the relaxation time \((\tau)\) is greater than before by the migration of \(\text{Ag}^+\) ions into the glass substrate via \(\text{Ag}^+/\text{K}^+\) ion exchange process. Due to the particular variation of bulk capacitance \((C_b)\), it appears that the value of \(\tau\) is inversely proportional to the bulk resistance \((R_b)\). Since the concentration of silver increased from center towards the periphery, it is expected that the PAgSm glass possesses high dielectric and low conductivity nearer to the glass surfaces. Also, there will be a maximum correlation between frequency and conductivity at the peripherals.

**Table 4.3** Cole-Cole parameters for PKSm and PAgSm glasses

<table>
<thead>
<tr>
<th>Glass Code</th>
<th>(R_b) (MΩ)</th>
<th>(C_b) (×10⁻³ pF)</th>
<th>(\tau) (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PKSm</td>
<td>23.15</td>
<td>9.85</td>
<td>22.80</td>
</tr>
<tr>
<td>PAgSm</td>
<td>10.83</td>
<td>21.88</td>
<td>23.70</td>
</tr>
</tbody>
</table>
4.7 Conclusions

Novel ion exchange unit with a modified dipping mechanism and temperature controller was designed, fabricated and optimized. Silver ions were effectively incorporated in Sm$^{3+}$-doped K-Mg-Al-Zn fluorophosphate glass via Ag$^{+}$/K$^+$ thermally diffused ion exchange process. The crystallite size of the Ag NPs, in the ion exchanged glass was estimated to be 19 nm. The energy transfer mechanism from silver to Sm$^{3+}$ ions causes a slight decrease in the absorption and an enhancement in the photoluminescence intensity of Sm$^{3+}$ ions in PAgSm glass. Lifetime of $^4G_{5/2}$ level of Sm$^{3+}$ ions in PAgSm glass was less than that in PKSm glass. This reduction in the lifetime of PAgSm glass indicates that the total transition probability and Sm$^{3+}$-Sm$^{3+}$ electric-dipole interactions are higher for PAgSm glass. The dielectric constants for silver incorporated glass increased due to the lack of restrictions for dipoles to line up in the field direction whereas the intrawell hopping of charge carriers and large surface scattering resulted in a reduction in conductivity at higher frequencies. It is suggested that regions near to the surface of the Ag$^{+}$/K$^+$ ion exchanged Sm$^{3+}$-doped K-Mg-Al-Zn fluorophosphate glass is suitable for optical communications in the visible region as planar waveguides, optical amplifiers, sensors or optical dielectric polarizers at high optical powers.
References


