Dielectric and conductivity studies on lead silicate glasses having mixed alkali and alkaline earth metal oxides

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Lead silicate glasses containing different amounts of Na_2O and K_2O along with BaO were prepared by conventional melt and quench method. Dielectric constant and its dispersion were investigated as a function of frequency over the range 10 kHz to 5 MHz at room temperature. Ionic conductivity was studied on three selected mixed alkali glasses $(Na_2O)_{0.069} - (K_2O)_{0.036} - (BaO)_{0.026} - (PbO)_{0.11} - (SiO_2)_{0.76}$ (LS31), $(Na_2O)_{0.066} - (K_2O)_{0.07} - (BaO)_{0.021} - (PbO)_{0.106} - (SiO_2)_{0.736}$ (LS1) and $(Na_2O)_{0.062} - (K_2O)_{0.013} - (BaO)_{0.02} - (PbO)_{0.099} - (SiO_2)_{0.689}$ (LS33) as a function of frequency over the range 100 Hz to 500 kHz in the temperature interval 25–380°C in vacuum of 10^{-2} mbar. Both DC conductivity and the hopping frequency, inferred from the analysis of AC conductivity data, exhibit Arrhenius behaviour with temperature. Unlike the conventional mixed alkali system, in the present glass system, it is found that the activation energies associated with DC conduction (E_σ) and that of hopping process (E_h) for LS1, having nearly equal amounts of Na^+ and K^+ ions, are found to be less compared to those for glasses LS31 and LS33. E_σ (1.14 eV) calculated for LS1 using Anderson–Stuart model agrees well with that obtained experimentally (1.18 eV). The above behaviour observed in E_σ and E_h for the present glass system may be attributed to the complex effect due to both mixed alkali effect and the structural changes introduced by the change in SiO_2 content.

THE PbO–SiO_2 system, among various lead-oxide-containing glasses, has been found to form glass over a wide composition range and has got many applications in making electron multipliers, TV picture tubes, electrical feedthroughs, and glass-to-metal (GM) seals. Various physical properties like electrical and thermal conductivity, micro hardness, dielectric constant, etc. of the above glass system can be modified by changing the PbO–SiO_2 composition or by adding modifiers like Na_2O, K_2O and BaO. For example, glass having the composition (in mol%) $(Na_2O)_{0.066} - (K_2O)_{0.07} - (BaO)_{0.021} - (PbO)_{0.106} - (SiO_2)_{0.736}$ is ideally suitable for compression-type GM seals, as it can withstand high pressures and highly corrosive environment in che-

mical plants. We have prepared a series of PbO–SiO_2 glasses containing alkali and alkaline earth metal oxides with different proportions (Table 1) and studied their mechanical[1] and structural[2] properties in view of their industrial applications. Glasses with high dielectric constant (ε) and low dispersion ($\Delta\varepsilon$) with frequency ($w = 2\pi f$) are desirable for some other technological applications. It is being argued that a large dielectric dispersion with frequency in conducting glasses is mainly due to the interaction among mobile ions[3]. The ionic conductivity in alkali silicate glass arises largely because of mobile alkali ions. Considerable efforts have been made to understand the mechanism of ionic conduction in these mixed alkali glasses[4,5].

This communication deals with dielectric dispersion behaviour and a study of ionic conductivity in alkali silicate glasses having different mobile ions (Na^+ and K^+) in different concentrations, as given in Table 1. Frequency dependence of ionic conductivity has been studied on three glasses, LS31, LS1 and LS33. The activation energy for DC conductivity has been calculated using Anderson–Stuart model and compared with experimental results.

The glass was synthesized using a three-stage heating cycle involving calcination, melting and quenching, as reported earlier[1]. The starting charge was prepared by mixing and grinding of pre-determined amounts of nitrates of Na, K, Ba and precipitated silica. The charge was heated to 1023 K for a period up to 40 h followed by thorough grinding and mixing at room temperature in the planetary ball mill (PM4000, Retsch Germany). The charge was then raised to 1223 K in a controlled manner and maintained there for 24 h. It was again ground in the planetary ball mill at room temperature for homogenization. Appropriate amount of PbO was added to the calcined charge and raised to 1573 K where it was held for 2–3 h followed by normal quenching of molten liquids onto a stainless-steel plate kept at room temperature.

Amorphous nature of these glasses was confirmed using XRD. Electrical measurements were carried out using an Impedance/Gain Phase Analyzer (HP 4194A). The glass sample, coated using silver paint and sandwiched between two silver electrodes, was mounted in a spring-loaded stainless-steel conductivity cell, as described elsewhere[6]. Four silver wires connected to silver electrodes were used as measuring leads. The capacitance was measured over the frequency range 10 kHz–5 MHz at room temperature. However, the conductance data were collected over the frequency range of 100 Hz–500 kHz, for several temperatures in the range of 339–429°C. The temperature was controlled to an accuracy of ± 0.2°C using an Eurotherm (818 P) PID temperature controlled and a thyristor unit. All measurements were carried out at less than 10^{-2} mbar pressure, in order to avoid stray impedance due to moisture.

Figure 1 presents the variation of dielectric constant (ε) as a function of frequency (w) at room temperature

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Table 1. Composition of different glass samples

	Composition									
	Na$_2$O		K$_2$O		BaO		PbO		SiO$_2$	
Glass	Parts (wt)	Mole	Parts (wt)	Mole	Parts (wt)	Mole	Parts (wt)	Mole	Parts (wt)	Mole
LS31	5	0.069	4	0.036	4	0.026	29	0.11	54	0.76
LS1	5	0.066	8	0.07	4	0.021	29	0.10	54	0.736
LS32	5	0.064	12	0.102	4	0.024	29	0.103	54	0.71
LS30	5	0.063	13	0.11	4	0.020	29	0.102	54	0.705
LS31	5	0.062	16	0.13	4	0.002	29	0.099	54	0.689

Table 2. Dielectric constant of different glasses at some selected frequencies

	Dielectric constant ε				Average ε (over selected frequencies)
Glass	$f = 100$ kHz	500 kHz	1 MHz	5 MHz	
LS31	14.83	14.58	14.57	14.65	14.66
LS1	7.84	7.81	7.80	7.66	7.78
LS32	9.19	9.15	9.14	8.93	9.10
LS30	7.69	7.67	7.65	7.46	7.62
LS33	7.74	7.72	7.71	7.52	7.67
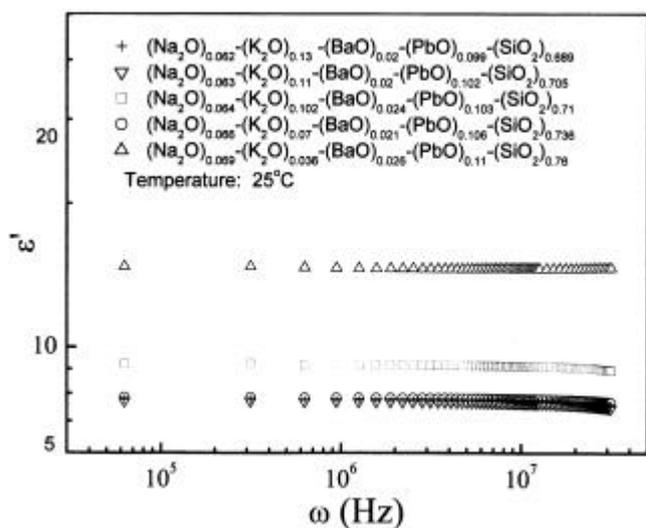
Figure 1. Dielectric constant (ε) as a function of frequency (ω) at room temperature for different glasses.

Figure 2. Conductivity $\sigma'(\omega)$ for glass LS33 at different temperatures.

for different glasses whose compositions are given in Table 1. We have also tabulated dielectric constants (ε) at four selected frequencies along with their average taken over these frequencies for different glasses (Table 2). Among the glasses studied, LS1 has nearly equal moles of Na$^+$ and K$^+$ ions (Na$^+$: 0.066, K$^+$: 0.067), LS31 is rich in Na$^+$ (Na$^+$: 0.069, K$^+$: 0.036) and LS33 (Na$^+$: 0.062, K$^+$: 0.13), LS30 (Na$^+$: 0.063, K$^+$: 0.11) and LS32 (Na$^+$: 0.064, K$^+$: 0.102) are rich in K$^+$. It is seen that ε for Na-rich glass (LS31) is larger than that for K-rich glasses (LS32, LS30, LS33).
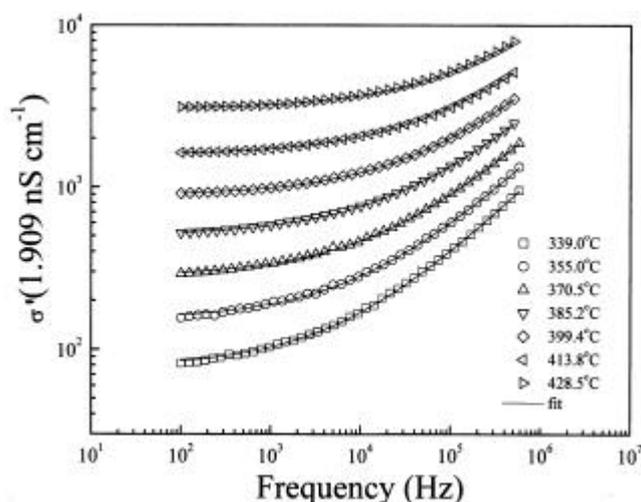
DC conductivity (σ_{dc}) was extracted from the AC conductivity data. Usually, the complex AC conductivity (σ^*) has a real part $\sigma'(\omega)$ and an imaginary part $\sigma''(\omega)$. The following expression has been used to describe the real part of AC conductivity:

$$\sigma'(\omega) = \sigma_{dc}(1 + (\omega \div \omega_h)^n), \tag{1}$$

where ω_h is the hopping frequency of the mobile ions and $n(0 \leq n \leq 1)$ is the dimensionless frequency exponent. AC conductivity has been measured for LS1, LS31 and LS33. All samples showed similar results. Figure 2 presents $\sigma'(\omega)$ for the glass LS33 at different temperatures. It can be seen from Figure 2 that at low frequencies the conductivity is constant, which corresponds to the DC conductivity. However, at higher frequencies it is frequency-dependent. The frequency ω_h which corresponds to the crossover from DC behaviour to dispersive conductivity increases with temperature. AC conductivity data at different temperatures have been fitted to eq. (1) using σ_{dc}, ω_h and n as variable parameters. The solid line in Figure 2 presents such a fit for different temperatures.
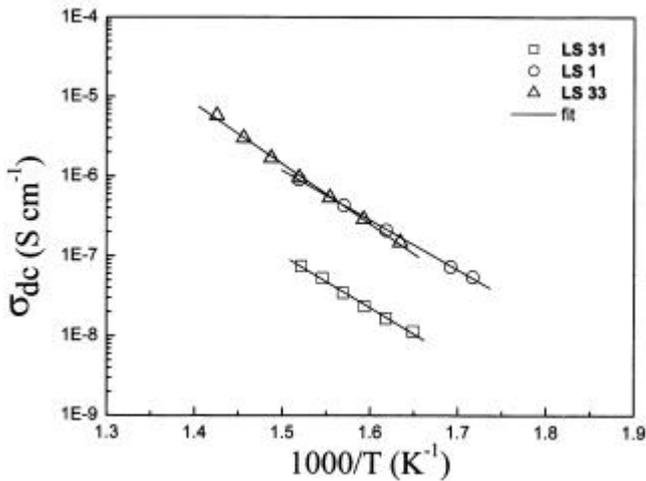
Figure 3. DC conductivity (σ_{dc}) for mobile ions in glass samples LS31, LS1 and LS33 as a function of reciprocal of temperature.
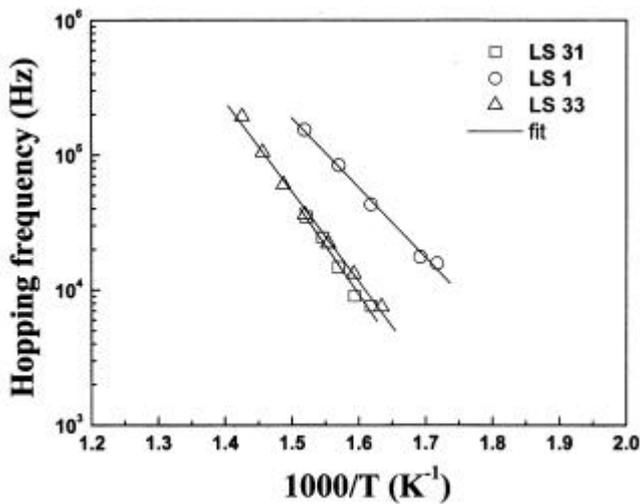

Figure 4. Hopping frequency (ν_h) for mobile ions in glass samples LS31, LS1 and LS33 as a function of reciprocal of temperature.

Figures 3 and 4 show the variation of DC conductivity (σ_{dc}) and hopping frequency (ν_h) for the mobile ions in glass samples LS31, LS1 and LS33 as a function of reciprocal of temperature as extracted for $\sigma'(\omega)$ vs ω data. All the plots are linear, indicating that both DC conductivity and the hopping process exhibit thermally activated behaviour and they obey Arrhenius laws given by the equations:

$$\sigma_c^* T = \sigma_0 \exp(- E_\sigma /kT), \qquad (2)$$

$$\nu_h = \nu_0 \exp(- E_h /kT), \qquad (3)$$

where E_σ is the activation energy for DC conduction and E_h for the hopping process.

These activation energies for the conduction and hopping process obtained from the best fits to the eqs (2) and (3) are presented in Table 3. It is seen that E_σ and E_h have different values, suggesting that the ions have to over-

Table 3. Activation energy for DC conduction and hopping for different glass samples

| Glass | Activation energy (eV) | | | | | | |
| | ΔE_b | | ΔE_s | | E_σ(eV) Calc. | E_σ(eV) Exp. | E_h(eV) Exp. |
	Na^+	K^+	Na^+	K^+			
LS31	–	–	–	–	–	1.31	1.44
LS1	0.82	0.72	0.16	0.49	1.14	1.18	1.03
LS33	–	–	–	–	–	1.51	1.33

come different barriers in the process of DC conduction compared to local hopping.

Ionic conduction in glasses was explained using a structural model by Anderson and Staurt[7] and has since been used by many workers with slight modifications. According to this model, an ion makes a simple hop from one site to another and moves through a 'doorway', which opens as it passes through. Thus the activation energy E_σ for DC conduction is the sum of coulomb binding energy E_b^8 and the strain energy E_s^7 and is given by the equation:

$$E_\sigma = e^2/[4\pi\varepsilon_0\varepsilon_\infty R_{M-O}] + 4\pi Gr_D(r - r_D)^2, \qquad (4)$$

where R_{M-O} is the distance between alkali ion and its neighbouring oxygen ion, r is the radius of the alkali ion, r_D is the radius of the doorway through which the ion must pass, ε_∞ is high frequency dielectric constant and G is the shear modulus of the glass. The average activation energy for LS1 glass for which G is known approximately (2.459×10^{11} dynes/cm^2), was calculated in terms of the above model, from activation energies of individual ions, E_σ was calculated from eq. (4) using r_D (0.62 Å)[8], R_{Na-O} for sodium silicate glass (2.3 Å), R_{K-O} for potassium silicate glass (2.6 Å)[8]; G for sodium silicate glass (3.2×10^{11} dynes/cm^2) and for potassium silicate glass (3.05×10^{11} dynes/cm^2)[7].

Table 3 shows the calculated values of E_b and E_s for Na^+ and K^+ ions and average E_σ for LS1 glass. It is seen that E_s for K^+ ion is higher than that for Na^+ ion. This is borne out from the fact that the energy required for dilating the structure elastically, for K^+ ion ($r = 1.33$ Å) is higher than that required for Na^+ ion ($r = 0.95$ Å). The calculated value of E_σ (1.14 eV) agrees well with that obtained experimentally (1.18 eV). E_σ could not be calculated for other samples, as their shear modulus values were not available.

Figure 1 shows that the dielectric constant for different glasses varies from 7.6 to 14.0 and remains nearly constant over a wide range of frequency. Glass containing larger alkali content exhibits lower dielectric constant. It is likely that as the concentration of total mobile ions increases the alkali–alkali distance is reduced, thereby increasing the interaction between them[3,9]. Such an increase in interaction among mobile ions along with a reduction in

SiO_2 content (in mol%) could possibly reduce the dipole–dipole interaction, leading to a reduction in the dielectric constant. Further, it is seen that the dielectric dispersion ($\Delta \varepsilon$) which is the variation of dielectric constant (ε) over the measured frequency range (10 kHz–5 MHz; $\omega = 2\pi f$), is less than 3% at room temperature. It is interesting to note from Figure 1 and Table 1 that although an increase in total alkali content from 0.105 (LS31) to 0.192 mol% (LS33) could decrease ε_s from 14.73 to 7.76, the dielectric dispersion in the glasses studied remained within ± 3%. The present glass system with a low dielectric dispersion could be considered as a possible candidate for high-frequency applications.

It is seen from Figures 3 and 4 that the LS31 glass has less conductivity, while those for LS1 and LS33 are nearly the same. Table 3 presents the activation energies for the DC conduction (E_σ) and hopping processes (E_h) for the said glasses. The calculated value of E_σ (1.14 eV) using Anderson–Stuart structural model for the glass LS1, agrees well with that obtained experimentally (1.18 eV).

Dielectric constant BaO–PbO–SiO_2 glasses containing different amounts of Na^+ and K^+ ions varies between 7.0 and 14.5 with $\Delta \varepsilon < 3\%$. σ_{dc} and ω_h, and their activation energies (E_σ and E_h) were derived from the conductivity studies on three selected glasses, LS31, LS1 and LS33. E_σ (1.18 eV) calculated using Anderson–Stuart model for LS1 agrees well with that obtained experimentally (1.14 eV). Unlike the conventional mixed-alkali system which exhibits higher activation energy, in the present glass system it is found that E_σ and E_h for LS1 having nearly equal amounts of Na^+ and K^+ ions, are less compared to those for extreme glasses LS31 and LS33. The reason for this unusual behaviour observed in E_σ and E_h for the present glass system is thought to be due to complex effect of both the mixed-alkali effect and some structural changes occurring in the glass network by change in SiO_2 content.

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Sniffing a single molecule through SERS using Au$_{core}$–Ag$_{shell}$ bimetallic nanoparticles

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In this communication we have described the preparation of a new class of core–shell type, i.e. Au$_{core}$–Ag$_{shell}$ bimetallic nanoparticles by seed-mediated technique to examine the surface-enhanced Raman scattering (SERS) involving these particles. It has been demonstrated how the thickness of the Ag-shell could be tuned with the variation of gold seed to Ag-ion ratio with a view to examine the impact of the size and field effects of these bimetallics on SERS spectra. The sensitivity of the SERS detection limit has been improved down to the single molecular level through the formation of hot-particles due to aggregation of core–shell type particles in the presence of NaCl.

DETECTION and quantification of molecules has always been a challenge to a chemist. The greatest challenge is the state-of-the-art detection of a single molecule. Selective single-molecule detection using nanomaterials by surface enhanced Raman scattering (SERS) spectroscopy has currently shown new promise[1,2]. SERS spectroscopy was an accidental discovery by Fleischmann *et al.*[3]. SERS is a phenomenon by which Raman signals of nonresonant molecules adsorbed on noble metal particles are enhanced by 5 to 6 orders of magnitude[4,5]. In certain cases the enhancement is so enormous that it enables detection of a

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