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Molar extinction coefficients of the cupric ion in silicate glasses

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The absorption characteristics of Cu^{2+} ions in binary alkali silicate and ternary silicate glasses were investigated. The molar extinction coefficients of the Cu^{2+} ion were determined in a series of binary alkali silicate and a ternary soda–lime–silica glasses for the actual intensities of the observed bands at their wavelength maxima. The absorption maxima due to Cu^{2+} ions were found to shift towards the longer wavelengths with increasing ionic radii of the alkali ions, in the present series of glasses. The base glass compositions were selected as $30R_2O \cdot 70SiO_2$ and $20Na_2O \cdot 10CaO \cdot 70SiO_2$ where $R^+ = Li^+$, Na^+ and K^+ ions. The results obtained are discussed in the light of a ligand field approach.

1. Introduction

Ionic colours in molten glasses are generated by dissolving transition metal ions in them. The first group of transition metal ions of which copper is a member, is characterized by an incomplete 3d-shell. In the free gaseous state for an ion, all the five d orbitals, denoted d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}, are degenerate and an electron in a 3d-shell may have equal probability of lying anywhere in the five degenerate d-orbitals. In a cubic field of octahedral symmetry where the central metal ion, M^{x+} is surrounded by six ligands, the five d-orbitals are split into two groups – a lower group of three (d_{xy}, d_{xz}, d_{yz}) known as T_{2g} and an upper group of two ($d_{x^2-y^2}$, d_{z^2}) known as E_g orbitals, as a result of which the degeneracy is removed. When the four ligands are placed symmetrically so as to establish a tetrahedral field around the transition metal ion M^{x+}, the above situation is reversed. The electrostatic splitting of d-orbitals is shown in the energy level diagram (Fig. 1). The magnitude of splitting, Δ, between the T_{2g} and E_g levels is taken as a measure of the ligand field strength and Δ_{tet} is less than Δ_{oct}. Both are related as in Equation 1

$$\Delta_{tet} = \tfrac{4}{9}\,\Delta_{oct} \qquad (1)$$

The value of the ligand field strength, Δ, is determined experimentally from the position of the absorption band which is observed as a result of an electronic transition from the ground state to the next higher state having the same spin degeneracy.

Under normal melting conditions, copper can be present in glass in the form of Cu^{2+} ions, whereas in strongly reducing conditions, it exists as Cu° and Cu_2O in glasses [1–7]. The Cu^+ ion does not produce any absorption in the visible region because of its $3d^{10}$ configuration, whereas the Cu^{2+} ion produces a blue to green colour depending upon the base glass compositions. Earlier, it was believed that the Cu^{2+} ion was a weak colourant[2] but later it was shown that an intense blue colour could be obtained by melting glasses containing copper under oxidizing conditions [8].

Because the cupric ion is a D-state ion with $3d^9$ configuration, it produces a single broad absorption band centred around 786 nm in silicate glasses, 1048 nm in aluminoborophosphate glass and 787 and 1390 nm in sodium aluminoborate glasses [2, 7, 9–11]. Kumar [9], Bamford [10] and Bates [11] attributed these bands to the electronic transition from ${}^2E_g \rightarrow {}^2T_g$ energy level in an octahedral coordination of Cu^{2+} ion. The cupric ion band was centred around 800 nm into its hydrated complexes, suggesting a distorted octahedral symmetry for cupric ion in glass [11].

Singh *et al.* [7] attributed the weak band due to the Cu^{2+} ions in borate glass around 1390 nm, to the transition of electrons from ground level ${}^2E_g \rightarrow {}^2A_{1g}$, ${}^2T_{1g}$ levels. The energy level diagram for the Cu^{2+} ion in distorted octahedral symmetry had shown that this transition was taking place at a point where ${}^2A_{1g}$ and ${}^2T_{1g}$ levels crossed each other resulting in only one peak at 1390 nm due to transitions from ground level to these two levels. The values of molar extinction coefficient $\varepsilon_{cu^{2+}}$ in borate glass were reported to be $9.2\ \mathrm{g\,mol\,l^{-1}\,cm}$ and $1.4\ \mathrm{g\,mol\,l^{-1}\,cm}$ at around 787 and 1390 nm, respectively. It has been pointed out that ions with E_g ground state are subjected to a large Jahn–Teller distortion. Bates [11] and Bamford [10] determined the molar extinction coefficient of the Cu^{2+} ion, assuming that all the copper was present in the cupric state in glasses. Even under oxidizing conditions, part of the copper can be present in the cuprous state and thus the values of molar extinction coefficients reported by these authors in glasses are only approximate. Cable and Xiang [12] calculated the molar extinction coefficient of the Cu^{2+} ion as

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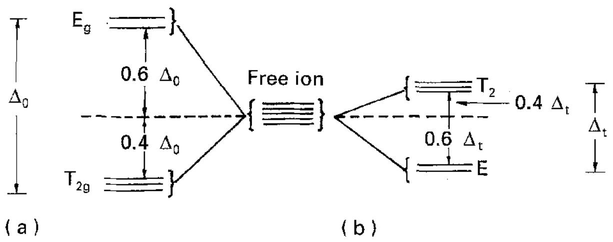

Figure 1 Energy level diagram showing the splitting of a set of d-orbitals by (a) an octahedral field, and (b) a tetrahedral field.

21.7 g mol l^{-1} cm at around 780 nm in soda–lime–silica glass with the help of a useful model assuming that the Cu^+–Cu^{2+} equilibrium in glass studied at different temperatures in an air atmosphere was independent of the total copper concentration over the range 0.1–1.2 mol % as CuO. The value of $\varepsilon_{Cu^{2+}}$ as 21.7 g mol l^{-1} cm for the glass has suffered from some errors in the handling of their own data for the $[Cu^+]/[Cu^{2+}]$ ratio at 1400 °C [12, 13]. Cable and Xiang reported the ratio of cuprous to cupric ($Cu^+:Cu^{2+}$) to be 0.318 in the 17.6 Na_2O–12CaO–70.4SiO_2 glass at 1400 °C in air. They also reported [12, 13] a $[Cu^+]/[Cu^{2+}]$ ratio of 0.400 in the same glass at this temperature, which yielded values of $\varepsilon_{Cu^{2+}}$ of 24.4 and 25.9 g mol l^{-1} cm at 780 nm, respectively, when the molar extinction coefficient of the Cu^{2+} ion was calculated, using Cable and Xiang's data [12, 13], by the Bouger–Beer equation taking surface reflection loss into account.

If similar controversial changes in $[Cu^+]/[Cu^{2+}]$ ratios at 1400 °C are probable in Cable and Xiang's other soda–lime–silica glasses [13], then no claim for reliability of the results on molar extinction coefficients of the cupric ion can be established. However, Cable and Xiang also reported that the extinction coefficient of the cupric ion increases with increasing optical basicity of the soda–lime–silica glass. The other model suggested [13] was a calculation of the value of $\varepsilon_{Cu^{2+}}$ by equilibrating the glass melts at two different oxygen partial pressures but one temperature. A linear increase in molar extinction coefficient of the cupric ion with basicity of the glass was also found by Edwards *et al.* [14] in a series of sodium lead silicate melts where soda was kept constant at 15 mol % and the lead oxide content was increased successively from 15 mol % to 43 mol % after replacing silica. Although Lee and Bruckner [15] as well as Duran and Fernandez Navarro [16] had also determined the values of $\varepsilon_{Cu^{2+}}$ in $25R_2O \cdot 75SiO_2$ glass melts in the range, 19–13 as E/d (in cm^{-1}) and in $30R_2O \cdot 70SiO_2$ melts to be between 37 and 34 g mol l^{-1} cm (where R = Li, Na and K), respectively, nevertheless these authors reported a decrease in molar extinction coefficients of the cupric ion with increasing ionic radii of the alkali ions in the glass. Further, Lee and Bruckner [15] reported an increase in the absorption coefficient of the cupric ion with increasing alkali oxide concentration according to the general behaviour of intensity of the cupric band with basicity of the glasses [13, 14, 17], but the presentation of $\varepsilon_{Cu^{2+}}$ by Duran and Fernandez Navarro [16] was the reverse with increasing alkali oxide content in glasses. The results for $\varepsilon_{Cu^{2+}}$ obtained earlier [15, 16] are open to criticism to some extent in the light of a general increase in the MEC of the Cu^{2+} ion and other d-ions with basicity of the glasses [13–15, 18–20].

Kumar and Sen [21] studied the optical absorption spectra of the Mn^{3+} ion in normal and solarized alkali–magnesia–silica glasses and discussed the shift of the band from a normal to a solarized glass. Earlier workers [9, 10, 21] suggested that when the size of the alkali ion is large, the screening of the electrostatic field of an alkali ion by an oxygen ion is less effective. As a result of interaction between the positive fields due to the alkali ion and the neighbouring colouring ion, the negative field due to the oxygen ligands influencing splitting of the energy levels is less, causing a lower field energy, Δ.

In the case of glasses containing central metal colouring ions such as the Mn^{3+} ion, it was earlier believed that a decrease in the ligand field energy is due to an increase in the distance between the central metal ion and the oxygen ligands with molar replacement of one alkali ion by another. Keeping this in view, the present investigation was undertaken to determine the molar extinction coefficient of the Cu^{2+} ion in binary alkali silicate and ternary soda–lime–silica glasses, and in order to study the shift of the absorption bands due to Cu^{2+} ions towards longer wavelengths with molar replacement of lithia by soda and soda by potash in the present series of glasses. The studies are expected to throw light on the formation of a variety of colour shades due to the Cu^{2+} ion, ranging from sky blue to greenish blue to bluish green, with molar replacement of one alkali by another as above, in the silicate series of glasses under investigation.

2. Experimental procedure

Glasses of the compositions $30R_2O \cdot 70SiO_2$ ($R^+ = Li^+$, Na^+ and K^+ ions) and $20Na_2O \cdot 10\ CaO \cdot 70SiO_2$ with different concentrations of total copper (0.25–1.5% CuO) were melted in a 100 ml capacity platinum–2% rhodium crucible kept in an electrically heated silicon carbide rod furnace at 1400 °C. For preparing glass batches, acid-washed quartz, analytical reagent grade alkali carbonates and calcium carbonate were used. After approximately 6 h melting, glasses were cast and poured on to an aluminium plate and after crushing they were remelted for another 4 h to ensure homogeneity. They were then removed from the furnace and poured into a rectangular mould on to an aluminium plate and annealed. After grinding and polishing, the absorption spectra of the glass samples were recorded on a Cary-23 recording spectrophotometer in the optical range, 500–1400 nm. Densities, thicknesses and refractive indices of the samples were determined. The glasses were chemically analysed for concentrations of total copper and cuprous ions spectrocolorimetrically. The concentration of cupric ion was found by the difference between the total copper and cuprous ion concentrations in the glass. Sodium

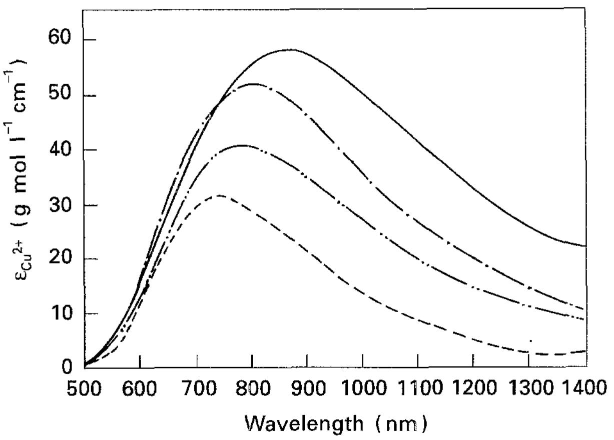

Figure 2 Absorption characteristics of the Cu^{2+} ion in binary alkali silicate and ternary soda–lime–silica glasses. (- - -) $30Li_2O \cdot 70SiO_2$, (—·—) $30Na_2O \cdot 70SiO_2$, (——) $30K_2O \cdot 70SiO_2$, (—··—) $20Na_2O \cdot 10CaO \cdot 70SiO_2$.

diethyldithiocarbamate for estimating total copper as cupric ions, and iodine monochloride for cuprous ions in glasses, were used as spectrocolorimetric reagents [21].

3. Results and discussion

Results presented in Table 1 and Fig. 2 show the single broad absorption bands in the visible region due to the Cu^{2+} ion, which were found to shift towards longer wavelengths with increasing ionic radii of alkali ions in the order $Li^+ < Na^+ < K^+$ in the present series of glasses. The ionic radii of Li^+, Na^+ and K^+ ions are 0.060, 0.095 and 0.133 nm, respectively [23]. The molar extinction coefficients of Cu^{2+} ions, $\varepsilon_{Cu^{2+}}$ defined below were calculated in alkali silicate and soda–lime–silica glasses from absorption spectra using the following Bouger-Beer's equation and are presented in Table I and Fig. 2

$$\varepsilon_{Cu^{2+}} = \frac{[2 \log (1 - R) + A] \text{ (atomic weight of Cu)}}{10\, C_w\, td} \tag{2}$$

where A is the absorbance due to Cu^{2+} ions at λ_{max} in the glass, C_w the concentration of Cu^{2+} ions (wt %), d the density of glass (g cm^{-3}), R the reflection factor, i.e. $R = [n - 1)/(n + 1)]^2$, n the refractive index of glass, and t the thickness of the glass sample (cm). In a particular silicate glass, the molar extinction coefficients of the Cu^{2+} ion were found to be nearly constant within ± 5% experimental error, as given in Table I, which indicates that the Cu^+: Cu^{2+} ratio in glass is not disturbed during its decomposition with 48% HF + dilute HCl. The molar extinction coefficient of the Cu^{2+} ion in glass varies considerably from one system to another. The visible absorption due to a Cu^{2+} ion in glass normally extends into the near infrared region and is found to obey the Urbach Rule in the present series of glasses as in Equations 3 and 4.

$$\varepsilon_{Cu^{2+}} = K_0\, e^{-\sigma(h\nu_0 - h\nu)/kT} \tag{3}$$

where K_0, σ and ν_0 are the material constants and T is the temperature.

$$\log \varepsilon_{Cu^{2+}} = A + B\nu \tag{4}$$

where A and B are constants and ν is the frequency of visible and near infrared radiations. The logarithm of $\varepsilon_{Cu^{2+}}$ was plotted against frequency of visible – infrared radiations, as shown in Fig. 3. The low-energy tail of the cupric band justifies the applicability of the Urbach rule in experimental glasses over the region of near infrared radiation (Fig. 3). The deviation of the curve from linearity indicates that the absorption peak due to the Cu^{2+} ion is being approached in the glass. This suggests that only the Cu^{2+} ion has absorption in glasses in this region.

It can be mentioned here that the Urbach Rule is not only applicable to charge transfer bands extending into the visible region but also to an intense ligand field band extending into the near infrared region. The variation in molar extinction coefficient, $\varepsilon_{Cu^{2+}}$ with glass composition dictates that the intensity of the cupric ion band increases considerably with increasing basicity of the glass. The value of $\varepsilon_{Cu^{2+}}$ can be used to predict the concentration of Cu^{2+} ions optically in a particular glass in accordance with Equation 2 provided the remaining other parameters are known.

The first set of experiments conducted by Lee and Bruckner [15] has resulted in the intensity of the cupric band as the absorption coefficients of Cu^{2+} ion (absorption cm^{-1}) at its wavelength maxima in $25R_2O \cdot 75\ SiO_2$ melts, whereas Duran and Fernandez Navarro [16] have reported it in terms of its molar extinction coefficients at λ_{max} in $30R_2O \cdot 70SiO_2$ glasses. It is suspected that there is some discrepancy between both their sets of results on intensities of cupric bands at λ_{max} in alkali silicate glasses [15, 16]. In the case of alkali silicate glasses containing 0.5 mol % CuO, an increase in absorption of the Cu^{2+} ion, E/d (cm^{-1}), with increasing alkali oxide concentration from 20 mol % to 35 mol % R_2O (R = Li, Na and K) was reported by Lee and Bruckner [15] but we have found a contrary decrease in the cupric absorption coefficient in $25R_2O \cdot 75SiO_2$ (R = Li, Na and K) glass with increasing ionic radii of alkali ions, where the basicity of the glasses increases in the same direction with increase of both the ionic radii as well as the concentration of alkali ions. The discussion of the results on absorption coefficients by these authors [15], suggests that the glasses investigated with Cu^{2+} ions form tetragonally distorted octahedral cupric complexes, the elongation of which increases with increasing basicity. This should be true not only for an increase in ionic radii of the alkali ions but also for alkali oxide concentrations. Duran and Fernandez Navarro's report that the extinction coefficient, $\varepsilon_{Cu^{2+}}$, depends upon the structure of the base glass and an increase in molar extinction coefficient in the order $Li_2O > Na_2O > K_2O$ for a fixed quantity of alkali oxide in a $30R_2O \cdot 70SiO_2$ glass, reflects a more rigid, strengthened and stable network, which may be in accordance with the observations made by Lee and Bruckner in $25R_2O \cdot 75SiO_2$ glasses, but an increase in $\varepsilon_{Cu^{2+}}$, as mentioned earlier [16], with increasing alkali

TABLE I Molar extinction coefficients of Cu^{2+} ion in binary and ternary silicate glasses

Sample	Glass composition	Absorbance on Cary-2390 recording spectrophotometer	Wavelength maxima (mm)	Thickness (cm)	Concentration (wt %)			Molar extinction coefficient of Cu^{2+} ion (g mol l^{-1} cm^{-1})	Average $\varepsilon_{Cu^{2+}}$ (g mol l^{-1} cm^{-1})	Error (%)
					ΣCu	Cu^+ ion	Cu^{2+} ion $= \Sigma Cu - Cu^+$ ion			
L_1	$30Li_2O \cdot 70SiO_2$	0.662	740	0.273	0.398	0.224	0.174	34.0	32.6	4.1
L_2	$30Li_2O \cdot 70SiO_2$	0.540	740	0.133	0.815	0.501	0.314	31.1		− 4.8
L_3	$30Li_2O \cdot 70SiO_2$	0.894	740	0.142	1.070	0.591	0.479	32.6		0.0
N_1	$30Na_2O \cdot 70SiO_2$	0.428	800	0.258	0.210	0.134	0.076	50.0	49.5	+ 1.0
N_2	$30Na_2O \cdot 70SiO_2$	0.625	800	0.210	0.385	0.238	0.147	47.1		− 3.8
N_3	$30Na_2O \cdot 70SiO_2$	0.900	800	0.233	0.555	0.366	0.189	49.1		− 0.8
N_4	$30Na_2O \cdot 70SiO_2$	0.590	800	0.107	0.770	0.520	0.250	51.8		+ 4.4
N_5	$30Na_2O \cdot 70SiO_2$	0.880	800	0.112	1.040	0.655	0.385	48.9		− 1.2
K_1	$30K_2O \cdot 70SiO_2$	0.694	860	0.205	0.448	0.303	0.145	56.8	57.5	− 1.2
K_2	$30K_2O \cdot 70SiO_2$	0.942	860	0.176	0.895	0.666	0.229	57.7		+ 0.3
K_3	$30K_2O \cdot 70SiO_2$	0.570	860	0.200	1.230	1.112	0.118	58.0		+ 0.8
C_1	$20Na_2O \cdot 10CaO \cdot 70SiO_2$	0.685	790	0.146	0.745	0.496	0.249	44.6	42.8	+ 4.0
C_2	$20Na_2O \cdot 10CaO \cdot 70SiO_2$	0.600	790	0.150	0.585	0.355	0.230	40.9		− 4.6
C_3	$20Na_2O \cdot 10CaO \cdot 70SiO_2$	0.452	790	0.238	0.238	0.296	0.102	42.8		0.0
C_4	$20Na_2O \cdot 10CaO \cdot 70SiO_2$			0.400	0.303	0.120	0.183			

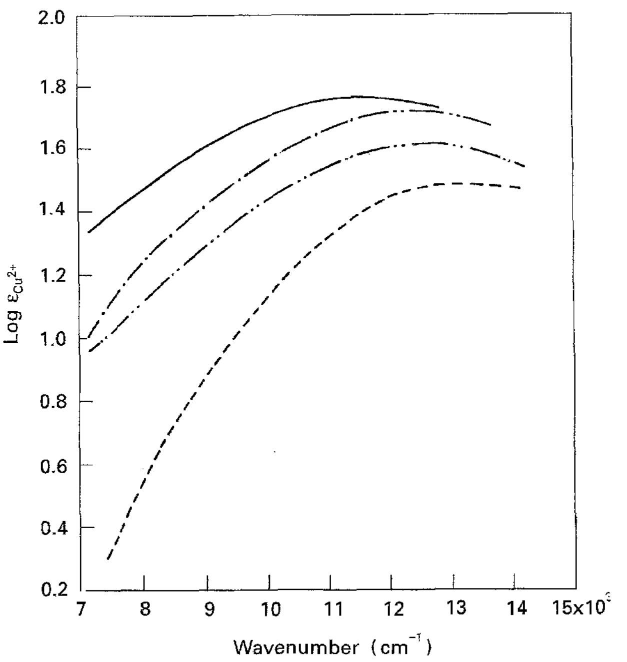

Figure 3 Relation between logarithm of molar extinction coefficient of Cu^{2+} ions in glass and the frequency of radiation. (– – –) $30Li_2O \cdot 70SiO_2$, (—·—) $30Na_2O \cdot 70SiO_2$, (——) $30K_2O \cdot 70SiO_2$, (—··—) $20Na_2O \cdot 10CaO \cdot 70SiO_2$.

oxide concentration was quite the opposite of Lee and Bruckner's [15] for their glasses with 20–35 mol % R_2O. Thus none of these experimental results gives a firm conclusion for the dependence of molar extinction coefficients of the cupric ion with increasing basicity of the silicate glass melts.

Because the coulombic force between the non-bridging oxygen ions and alkali ions decreases with increasing ionic radii of the alkali ions in glass, the O^{2-} ion activity increases. This makes the transition metal ion–ligand bonds more covalent and it is concluded that an increase in covalent bonding is the cause of the increase in $\varepsilon_{Cu^{2+}}$ with basicity of the glass. Similar increases in the intensity of the cupric band were also observed by earlier workers [13, 14, 20] as other evidence in soda–lead–silicate, soda–lime–silicate and sodium borate glasses with increasing basicity of glasses.

The peaks observed for Cu^{2+} ions, respectively, in glasses have been assigned earlier to the spin-allowed transitions from $^2E_g \rightarrow {}^2T_{2g}$ energy levels in distorted octahedral coordination of Cu^{2+} ions in the glass. The changes in colour due to the presence of Cu^{2+} ions, as lithia was completely removed by soda and soda by potash in silicate glass, dictate the shift of their absorption maxima towards longer wavelengths.

Ilse and Hartmann [24] pointed out that the ligand field strength, for an octahedral arrangement around the central metal ion could be approximately expressed as

$$\Delta = \frac{5}{3}\frac{eqr^4}{R^5} \qquad (5)$$

where e is the charge of an electron, r the average distance between nucleus and 3d electrons, R the distance between the central metal ion and ligand, $q = q_1 + q_2$, q_1 is the electrostatic charge or dipole moment due to each ligand, and q_2 the induced charge or induced charge dipole moment due to polarization of the ligand by the surrounding cations.

The ligand field strength was found to be inversely proportional to the fifth power of the distance between the central metal ion and the ligand ($\Delta \alpha R^{-5}$) as in Equation 5, where all the remaining factors were constant. Nath and Douglas [19] calculated the total number of oxygens per litre of glass in a series of lithium, sodium and potassium silicate glasses using the density data of glasses at 1400 °C given by Bockris *et al.* [25]. They found that the total number of oxygens per litre of glass for the same mole per cent of alkali oxide decreased in the order $K_2O < Na_2O < Li_2O$. Similar results for the total number of oxygens per litre of glass were also obtained when it was calculated by the present workers in a series of sodium and potassium silicate glasses utilizing the density data of glasses at room temperature given by Morey and Merwin [26]. It indicates that the oxygens are accommodated more spaciously in the structure of a potash–silica glass than in a soda–silica glass for the same mole per cent of alkali oxides. When the total number of oxygens in the same volume of glass decreases with an increase in ionic radius of alkali ions, the distribution of oxygens in the glass matrix becomes thinner. As a result of this the distance between the central metal ion and O^{2-} ligands in an alkali silicate glass increases with an increase in ionic radius of alkali ions, causing a decrease in ligand field strength. The separation between two groups of d-levels in an octahedral field decreases with an increase in ionic radius of the alkali ions. This decrease in the value of field strength ($\Delta = hc/\lambda_{max}$) can take place only when the wavelength of light absorbed, λ_{max}, will increase. Hence, the absorption peaks for the Cu^{2+} ions are found to shift towards the longer wavelengths with increasing ionic radius of alkali ions in the present series of alkali silicate glasses. The shift of the absorption band with molar replacement of one alkali oxide by another reported earlier in alkali silicate glasses for the Fe^{2+} ion, can be interpreted in the light of the above argument [20].

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