

Comparative investigation on the effect of alkaline earth oxides on the intensity of absorption bands due to Cu^{2+} , Mn^{3+} and Cr^{3+} ions in ternary silicate glasses

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Abstract. Absorption characteristics of Cu^{2+} , Mn^{3+} and Cr^{3+} ions in ternary silicate ($20\text{Na}_2\text{O}\cdot 10\text{RO}\cdot 70\text{SiO}_2$, where R=Ca, Sr, Ba) glasses were investigated. The intensities of absorption bands due to Cu^{2+} ion was found to increase with increasing ionic radii of the alkaline earth ions whereas it was found to decrease in case of Mn^{3+} and Cr^{3+} ions with increasing ionic radii of the alkaline earth ions. The results were discussed in the light of relation between linear extinction coefficients of these ions and coulombic force of alkaline earth ions. The change in intensities of Cu^{2+} , Mn^{3+} and Cr^{3+} ion is attributed due to change in silicate glass compositions.

Keywords. Comparison; absorption intensities; copper; manganese; chromium ions; silicate glasses.

1. Introduction

Under normal melting conditions, copper can be present in glasses in the form of Cu^{2+} ions, whereas in strongly reducing conditions, it exists as Cu^0 and Cu_2O in glasses (Ram and Prasad 1962; Johnston and Chelko 1966; Weyl 1967; Banerjee and Paul 1974; Singh *et al* 1978a,b; Dwivedi and Nath 1980). The Cu^{2+} ion produces sky blue to green colour depending upon the base glass compositions. Because cupric ion is a d -state ion with $3d^9$ configuration it produces a single broad absorption band centred at around 786 nm in silicate glasses, 1048 nm in aluminoborophosphate glass as well as 787 and 1390 nm in sodium aluminoborate glasses (Kumar 1959; Bamford 1962; Bates 1962; Weyl 1967; Singh *et al* 1978a). Kumar (1959), Bamford (1962) and Bates (1962) attributed these bands due to electronic transition from ${}^2E_g \rightarrow {}^2T_{2g}$ energy level in an octahedral coordination of Cu^{2+} ion. Lee and Bruckner (1984) reported an increase in the absorption coefficient of cupric ion with increasing alkali oxide concentration according to the general behaviour of intensity of the cupric band with basicity of glasses. Cable and Xiang (1989a,b) studied the $\text{Cu}^+ - \text{Cu}^{2+}$ redox equilibrium at different temperatures in air atmosphere and developed a model for the intensity of Cu^{2+} ion in the glass at its I_{max} at around 780 nm.

Copper oxide is the main constituent of blue and green signal glasses. Their strong absorption of the long wavelength of the visible spectrum at around 800 nm due to Cu^{2+} ion prevents the green signal during the foggy wea-

ther for being mistaken for colourless or even red. Cupric ion absorbs the red region of the spectrum completely due to its broad absorption band.

When a compound of manganese is dissolved in a molten glass, the cation normally distributes itself into two valency states, viz. manganous and manganic as assigned by earlier workers (Bhatnagar 1939; Bhatnagar *et al* 1940; Ram *et al* 1957; Kumar 1959; Kumar and Sen 1960; Paul and Lahiri 1966). Manganese plays an important role in colour formation and decolourization of glasses due to the presence of Mn^{3+} ion with $3d^4$ and Mn^{2+} ion with $3d^5$ electronic configurations, respectively. The trivalent manganese is a d -state ion and it was found to produce a single broad absorption band in glasses (Kumar 1959; Kumar and Sen 1960; Bamford 1962; Bates 1962; Weyl 1967; Haddon *et al* 1969). In soda–lime–silica glass, the manganic band was centred at around 20000 cm^{-1} whereas it was at around 21000 cm^{-1} in its hydrated crystals, suggesting a distorted octahedral symmetry for Mn^{3+} ion in glass. Kumar and Sen (1960) studied the optical absorption spectra of Mn^{3+} ion in normal and solarized alkali–magnesia–silica glasses and discussed the shift of the band from a normal to solarized glass. The influence of the base glass had been referred to as “electropolarization” and the larger the size of alkali ion, the lower the electrical perturbing influence.

Chromium ions for coloured glasses were being used since long back. Whenever a compound of chromium is introduced in a molten glass it normally distributes into two valency states viz. the trivalent and the hexavalent chromium. The Cr^{3+} ($3d^3$) produces emerald green colour due to its $d-d$ spin allowed ligand field transition whereas Cr^{6+} ($3d^0$) produces lemon yellow colour due to charge

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transfer in the glass. Nath *et al* (1965) observed four absorption peaks due to Cr^{3+} ion at around 442, 628, 644, and 675 nm in lithium silicate glasses melted with Cr_2O_3 in the visible region. When an appreciable amount of hexavalent chromium was present in the glass, the absorption peak at 442 nm was masked by the strong absorption due to Cr^{6+} ions in this part of spectrum. The other three peaks at 628, 644, and 675 nm were present in all the lithium silicate glasses containing chromium. In sodium silicate glasses containing both Cr^{3+} and Cr^{6+} ions, the absorption peaks due to Cr^{3+} ions were found to be centred at around 635, 650 and 675 nm whereas in potash silicate glasses the sharp visible bands due to Cr^{3+} were found to be centred at around 454, 635, 654, and 680 nm, respectively. Weyl (1967) as well as Nath *et al* (1965) had shown that the absorption spectra of Cr^{6+} ions in glasses were identical with aqueous solution of potassium dichromate.

In the case of glass containing colouring species such as Cu^{2+} , Mn^{3+} and Cr^{3+} ions, many workers had studied the effect of alkali oxides on the optical absorption properties in silicate glasses but the work done previously on the effect of alkaline earth oxides on the optical absorption properties of ternary silicate glasses containing these colourants is not sufficient. Keeping this in view the present investigation was undertaken in order to study the optical absorption behaviour of Cu^{2+} , Mn^{3+} and Cr^{3+} ions both quantitatively and qualitatively as well as to calculate the intensity of their absorption bands in terms of linear extinction coefficients on replacing lime by strontia and strontia by baria in ternary silicate glasses.

2. Experimental

Glasses having molar compositions, $20\text{Na}_2\text{O}\cdot 10\text{RO}\cdot 70\text{SiO}_2$, where R=Ca, Sr, Ba doped with different concentrations of cupric oxide (0.5–1.5 wt%) were melted in a 100 ml capacity Pt-2% Rh crucible kept in an electric globar rod furnace at 1400°C in air atmosphere. Acid washed quartz, analytical reagent grade sodium carbonate, calcium carbonate, strontium carbonate and barium carbonate were used for preparation of glass batches. The concentration of copper was introduced in the glass as an analytical reagent grade cupric oxide. After around 6 h of melting, the glass melts were cast and poured onto an aluminium plate and cooled to room temperature. After crushing the glasses were remelted for another 4 h to ensure homogeneity in the glass. They were taken out of the furnace and poured into a rectangular mould onto an aluminium plate and annealed at 480°C in an annealing furnace for 1 h and then they were cooled to room temperature to remove the stresses from the glass. After grinding and polishing the absorption spectra of glass samples were recorded on a JASCO-7800 recording spectrophotometer in the optical range, 500–1050 nm. Thickness and densities of the glass samples were determined to calculate the intensity of the cupric band at its wavelength maxima in the glass.

In order to prepare ternary silicate glasses containing manganese with analytical reagent grade sodium, calcium, strontium, and barium carbonate along with acid washed quartz were used. Two different concentrations of manganese as 0.5% and 1.0% by wt were introduced in the glass batches as precipitated manganese dioxide. The rest of the procedure for melting, casting, pouring, annealing and cooling were followed as described above. After grinding and polishing, the absorption spectra of polished glass samples were recorded on the above mentioned recording spectrophotometer in the optical range 400–800 nm.

For preparing the ternary silicate glasses of the same composition doped with 0.1–0.3% Cr_2O_3 of analytical reagent grade, the carbonates of sodium, calcium, strontium and barium used were also of the same grade. The rest of the procedures for preparation of the molten glass samples were followed as usual. The glasses were ground and polished. Absorption spectra of the polished glass samples were recorded on a JASCO-7800 recording spectrophotometer in the optical range 400–900 nm.

3. Results and discussion

In case of Cu^{2+} ion results presented in figure 1 show the single broad absorption band due to Cu^{2+} ion at around 796 nm in ternary silicate glasses. This peak has been assigned to spin allowed transition from ${}^2E_g \rightarrow {}^2T_{2g}$ energy levels in distorted octahedral symmetry of Cu^{2+} ions in glasses. It is clear from figure 1 that the absorption peaks due to

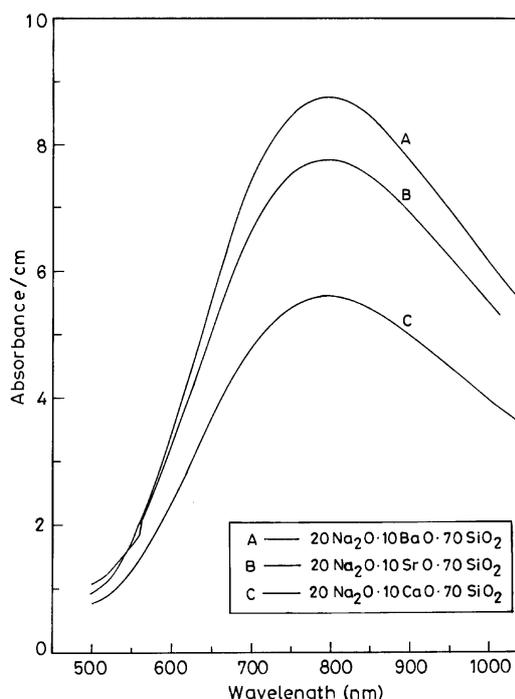


Figure 1. Optical absorption characteristics of Cu^{2+} ion in ternary silicate ($20\text{Na}_2\text{O}\cdot 10\text{RO}\cdot 70\text{SiO}_2$, where R = Ca, Sr, Ba) glasses.

Cu^{2+} ion in (ternary) silicate glasses ($20\text{Na}_2\text{O}\cdot 10\text{RO}\cdot 70\text{SiO}_2$ where, R=Ca, Sr, Ba) are centred at around 796 nm. The absorption intensity calculated was found to increase with increasing ionic radii of alkaline ions in order of $\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$ ions.

The linear extinction coefficients of Cu^{2+} ion, $a_{\text{Cu}^{2+}}$, were calculated in ternary silicate glasses from absorption spectra using the following Lambert–Beer's equation no. (1) and are presented in table 1.

$$a_{\text{Cu}^{2+}} = A/ct, \quad (1)$$

here A is the absorbance due to Cu^{2+} ions at its wavelength maxima in the glass, c the concentration of Cu^{2+} ions (wt%) and t the thickness of the glass sample (cm).

In a particular silicate glass, the linear extinction coefficients ($a_{\text{Cu}^{2+}}$) of the Cu^{2+} ion were found to be nearly constant within an experimental error. The linear extinction coefficient of the Cu^{2+} ion in glass was found to increase considerably with the increase in basicity of the glass as CaO was replaced with SrO and SrO with BaO.

All the experiments done so far on redox equilibrium had reported that the proportion of the redox ion in the higher oxidation state increases with the basicity of the glass. The basicity of the glass increases with replacement of Ca^{2+} by Sr^{2+} and Sr^{2+} by Ba^{2+} ion. As a result of which higher proportion of Cu^{2+} ion was formed in ternary soda–baria–silica glass as compared to other ternary silicate glasses. Similarly concentration of Cu^{2+} ion is more in soda–strontia–silica glass in comparison to soda–lime glass. This leads to higher absorption value in soda–baria–silica than soda–strontia–silica and soda–lime–silica glass. The values of $a_{\text{Cu}^{2+}}$ at its I_{max} in silicate glasses were found to be $5.13\text{--}7.58 \text{ cm}^{-1}$ per wt%.

In case of Mn^{3+} ion, results presented in figure 2 show the single broad absorption band due to Mn^{3+} ion in ternary silicate glasses. This peak has been assigned due to spin allowed transition from ${}^5E_g \rightarrow {}^5T_{2g}$ energy levels in an octahedral symmetry of Mn^{3+} ion in glass. It is clear from the figure that the absorption peaks due to Mn^{3+} in

ternary glasses ($20\text{Na}_2\text{O}\cdot 10\text{RO}\cdot 70\text{SiO}_2$ where, R=Ca, Sr, Ba) are centred at around 494 nm. The value of absorption intensity was found to be higher contrarily with decreasing ionic radii of alkaline earth ions in order of $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+}$ in the glass. The general consensus is that manganese ion is present in glass in the form of Mn^{2+} and Mn^{3+} ions. In the present investigation the absorption intensity due to Mn^{3+} ion which shifts more towards the higher value with decreasing ionic radii of alkaline earth ions in order of $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+}$ dictates that other higher valency states of manganese ions might also be formed in glass in minor amounts to affect the intensity of Mn^{3+} ion.

The linear extinction coefficients of Mn^{3+} ion, $a_{\text{Mn}^{3+}}$ were calculated in ternary silicate glasses from absorption

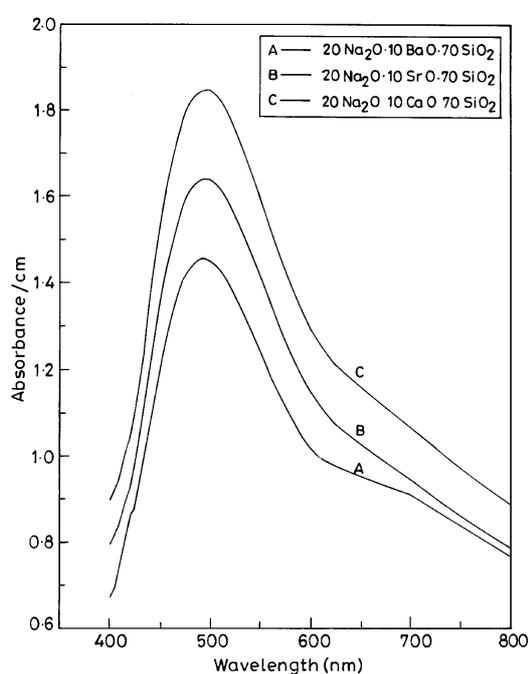


Figure 2. Optical absorption characteristics of Mn^{3+} ion in ternary silicate ($20\text{Na}_2\text{O}\cdot 10\text{RO}\cdot 70\text{SiO}_2$, where R = Ca, Sr, Ba) glasses.

Table 1. Effect of alkaline earth oxide on the intensity of absorption bands due to Cu^{2+} ion in ternary silicate ($20\text{Na}_2\text{O}\cdot 10\text{RO}\cdot 70\text{SiO}_2$, where R=Ca, Sr, Ba) glasses.

Glass composition	Absorbance on Jasco-7800 recording spectrophotometer	Wavelength maxima (nm)	Thickness (cm)	Conc (wt%) ΣCu	Absorbance $(\text{cm})^{-1}$	Linear extinction coefficient
$20\text{Na}_2\text{O}\cdot 10\text{CaO}\cdot 70\text{SiO}_2$	0.452	795	0.227	0.399	1.99	4.98
$20\text{Na}_2\text{O}\cdot 10\text{CaO}\cdot 70\text{SiO}_2$	0.685	795	0.164	0.798	4.18	5.24
$20\text{Na}_2\text{O}\cdot 10\text{CaO}\cdot 70\text{SiO}_2$	1.148	795	0.204	1.197	6.21	5.18
$20\text{Na}_2\text{O}\cdot 10\text{SrO}\cdot 70\text{SiO}_2$	0.589	796	0.234	0.399	2.51	6.3
$20\text{Na}_2\text{O}\cdot 10\text{SrO}\cdot 70\text{SiO}_2$	1.246	796	0.239	0.798	5.29	6.62
$20\text{Na}_2\text{O}\cdot 10\text{SrO}\cdot 70\text{SiO}_2$	1.980	796	0.254	1.197	7.79	6.51
$20\text{Na}_2\text{O}\cdot 10\text{BaO}\cdot 70\text{SiO}_2$	0.654	797	0.216	0.399	3.03	7.59
$20\text{Na}_2\text{O}\cdot 10\text{BaO}\cdot 70\text{SiO}_2$	1.334	797	0.213	0.798	6.26	7.85
$20\text{Na}_2\text{O}\cdot 10\text{BaO}\cdot 70\text{SiO}_2$	1.792	797	0.204	1.197	8.74	7.30

spectra using the Lambert–Beer's equation (1) as usual and are presented in table 2. The rest of the terms in (1) have their usual meanings with respect to manganese in the glass

$$a_{\text{Mn}^{3+}} = A/ct.$$

In a particular ternary silicate glass, the extinction coefficient ($a_{\text{Mn}^{3+}}$) of the Mn^{3+} ion were found to be nearly constant within an experimental error. The value of $a_{\text{Mn}^{3+}}$ in glass varies from 4.02–5.21 ($\text{cm}^{-1}/\text{wt}\%$) considerably from one system to another and was found to decrease with an increase in ionic radii of the alkaline earth ions in order $\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$ in the glass.

It has been mentioned above that the proportion of the redox ions in the higher oxidation states increases with increasing basicity of the glass. The basicity of the glass increases with the replacement of Ca^{2+} by Sr^{2+} and Sr^{2+} by Ba^{2+} ion. The more basic the alkaline earth oxide the more would be the occurrence of the reaction towards forward direction to form more oxidized states of manganese ions. Thus, concentration of Mn^{3+} in the glass is the lowest in case of soda–baria–silica glass and highest in case of soda–lime–silica glass. This leads to the lowest value of linear extinction coefficient ($a_{\text{Mn}^{3+}} = 4.02$) in soda–baria–silica glass for Mn^{3+} ion. The value of $a_{\text{Mn}^{3+}}$ is the highest in soda–lime–silica glass as 5.21 and it was 4.56 in soda–strontia–silica glass but it was the lowest at around 4.0 in soda–baria–silica glass.

In case of Cr^{3+} ion the results presented in figure 3 show two strong absorption bands due to Cr^{3+} ion at around 655 and 685 nm, respectively in ternary silicate glasses. One of the peaks at around 655 nm has been assigned due to the spin allowed transition from ${}^4A_{2g} \rightarrow {}^2T_{2g}$, ground to excited energy levels, other one is due to spin forbidden transition ${}^4A_{2g} \rightarrow {}^2T_{1g}$ energy levels in an octahedral coordination of Cr^{3+} ion (figure 3) in glass. The absorption intensity was found to increase with decreasing ionic radii of alkaline earth ions in order of $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+}$.

The linear extinction coefficients of Cr^{3+} , $a_{\text{Cr}^{3+}}$ were also calculated in ternary silicate glasses from absorption spectra using (1) as usual and are presented in table 3.

The rest of the terms in the Lambert–Beer's equation (1) for chromium have their usual meanings.

In a particular ternary silicate glass, the linear extinction coefficient ($a_{\text{Cr}^{3+}}$) of the Cr^{3+} ion was found to be nearly constant within $\pm 5\%$ experimental error. The linear extinction coefficient of Cr^{3+} ion in the glass varies appreciably from one system to another and was found to increase with decreasing basicity of the glass or decreasing ionic radii of alkaline earth ions in the glass as mentioned above.

As per earlier statement as the alkaline earth oxide is more basic, the formation of higher oxidation states of chromium Cr^{6+} ion would be favoured more which is the most stable state due to its $3d^0$ configuration. Thus, the concentration of Cr^{3+} ion is the lowest in case of soda–baria–silica glass and the highest in case of soda–lime–silica glass. This leads to the lowest value of extinction

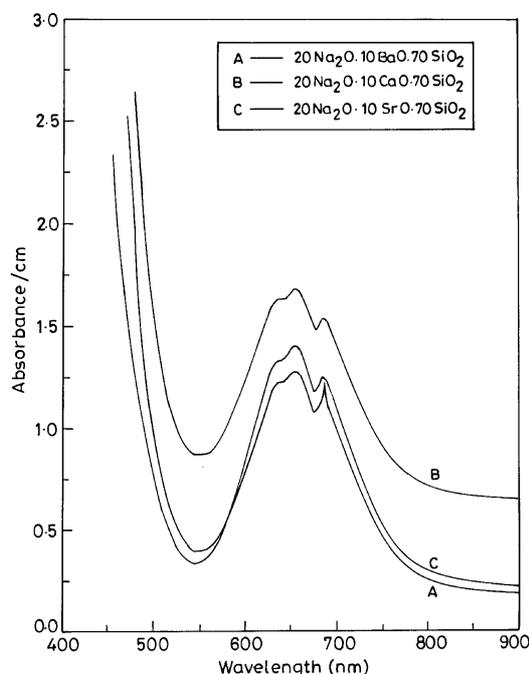


Figure 3. Optical absorption characteristics of Cr^{3+} ion in ternary silicate ($20\text{Na}_2\text{O}\cdot 10\text{RO}\cdot 70\text{SiO}_2$, where R = Ca, Sr, Ba) glasses.

Table 2. Effect of alkaline earth oxide on the intensity of absorption bands due to Mn^{3+} ion in ternary silicate ($20\text{Na}_2\text{O}\cdot 10\text{RO}\cdot 70\text{SiO}_2$, where R = Ca, Sr, Ba) glasses.

Glass composition	Absorbance on Jasco-7800 recording spectrophotometer	Wavelength maxima (nm)	Thickness (cm)	Conc. (wt%) ΣMn	Absorbance (cm^{-1})	Linear extinction coefficient
$20\text{Na}_2\text{O}\cdot 10\text{CaO}\cdot 70\text{SiO}_2$	1.125	494	0.608	0.348	1.85	5.31
$20\text{Na}_2\text{O}\cdot 10\text{CaO}\cdot 70\text{SiO}_2$	2.217	495	0.623	0.696	3.56	5.11
$20\text{Na}_2\text{O}\cdot 10\text{SrO}\cdot 70\text{SiO}_2$	0.091	494	0.604	0.348	1.64	4.71
$20\text{Na}_2\text{O}\cdot 10\text{SrO}\cdot 70\text{SiO}_2$	1.957	495	0.637	0.696	3.07	4.41
$20\text{Na}_2\text{O}\cdot 10\text{BaO}\cdot 70\text{SiO}_2$	1.027	494	0.706	0.348	1.45	4.17
$20\text{Na}_2\text{O}\cdot 10\text{BaO}\cdot 70\text{SiO}_2$	1.489	494	0.553	0.696	2.69	3.86

coefficient, $a_{\text{Cr}^{3+}}$, around 6.25 in soda–baria–silica glass for Cr^{3+} ion. The value of $a_{\text{Cr}^{3+}}$ is the highest in soda–lime–silica glass as 8.82 and the same was 6.98 in soda–strontia–silica glass.

Kumar and Singh (1989) as well as Singh and Kumar (1995) interpreted the shift of the absorption bands due to Mn^{3+} and Cu^{2+} ions in binary alkali silicate glasses towards longer wavelength with an increase in ionic radii of alkali ions on the basis of Ilse and Hartmann (1951) equation in which the ligand field strength, Δ , is inversely proportional to the fifth power of the distance between the central metal ion and ligand (R) as

$$\Delta = 5eqr^4/3R^5, \quad (2)$$

here, the terms have their usual meanings.

The idea of these workers was that an increase in distance between central metal ion and the surrounding oxygen ligands (O^{2-}) with increasing total number of oxygens present per unit volume of glass causes a decrease in the value of ligand field strength (Δ). The decrease in value of ligand field strength (Δ) follows an increase in I_{max} as per the following equation:

$$\Delta = hc/I_{\text{max}}, \quad (3)$$

here, h is the Planck's constant, c the velocity of light and I_{max} the wavelength of maximum absorption.

In the present situation the concentration of Na_2O was kept constant in all the ternary silicate glasses. The molar replacement of CaO was done by SrO and SrO by BaO in these silicate glasses. The results presented in tables 1–3 as well as in figures 1–3 clearly show that the wavelength maxima for Cu^{2+} , Mn^{3+} and Cr^{3+} were nearly 795, 494 and 655 nm, respectively in all the ternary silicate glasses for a particular absorbing species. Although, the band position for a particular colouring ion in the present series of glasses was the same but the intensities of the band in different glasses are different. In the case of Cu^{2+} ion the linear extinction coefficient ($a_{\text{Cu}^{2+}}$) was found to increase with increasing ionic radii of alkaline earth ions but in case of Mn^{3+} and Cr^{3+} the same was the reverse. This may be explained on the basis of the relation obtained on plotting average values of intensities for these ions against the coulombic force of the alkaline earth ions in glasses. The coulombic force calculated as per (4):

$$c.f = zz'/(r+r_0)^2, \quad (4)$$

where, z is the charge on alkaline earth ions, z' the charge on oxygen ion, r the radius of alkaline earth ions and r_0 the radius of oxygen ion, has been presented in table 4. The decrease in bond strength might have resulted in some more dissociation of alkaline earth oxides. As the oxygen ion activity or basicity of the glass increases with an in-

Table 3. Effect of alkaline earth oxide on the intensity of absorption bands due to Cr^{3+} ion in ternary silicate ($20\text{Na}_2\text{O}\cdot 10\text{RO}\cdot 70\text{SiO}_2$, where R = Ca, Sr, Ba) glasses.

Glass composition	Absorbance on Jasco-7800 recording spectrophotometer	Wavelength maxima (nm)		Thickness (cm)	Conc (wt%) ΣCr	Absorbance (cm) ⁻¹ at 655 nm	Linear extinction coefficient
		I_1	I_2				
$20\text{Na}_2\text{O}\cdot 10\text{CaO}\cdot 70\text{SiO}_2$	0.491	655	685	0.804	0.068	0.61	8.97
$20\text{Na}_2\text{O}\cdot 10\text{CaO}\cdot 70\text{SiO}_2$	0.885	655	685	0.750	0.137	1.18	8.61
$20\text{Na}_2\text{O}\cdot 10\text{CaO}\cdot 70\text{SiO}_2$	1.374	655	685	0.754	0.205	1.82	8.87
$20\text{Na}_2\text{O}\cdot 10\text{SrO}\cdot 70\text{SiO}_2$	0.387	655	685	0.802	0.068	0.48	7.06
$20\text{Na}_2\text{O}\cdot 10\text{SrO}\cdot 70\text{SiO}_2$	0.800	655	685	0.850	0.137	0.94	6.87
$20\text{Na}_2\text{O}\cdot 10\text{SrO}\cdot 70\text{SiO}_2$	1.020	655	685	0.706	0.205	1.44	7.02
$20\text{Na}_2\text{O}\cdot 10\text{BaO}\cdot 70\text{SiO}_2$	0.409	655	685	0.950	0.068	0.43	6.32
$20\text{Na}_2\text{O}\cdot 10\text{BaO}\cdot 70\text{SiO}_2$	0.544	655	685	0.650	0.137	0.84	6.13
$20\text{Na}_2\text{O}\cdot 10\text{BaO}\cdot 70\text{SiO}_2$	1.033	655	685	0.802	0.205	1.29	6.29

Table 4. Relationship between linear extinction coefficient of Cu^{2+} , Mn^{3+} and Cr^{3+} ions with binding energy of alkaline earth oxides in ternary silicate ($20\text{Na}_2\text{O}\cdot 10\text{RO}\cdot 70\text{SiO}_2$, where R = Ca, Sr, Ba) glasses.

Glass composition	Coulombic force [(e.s.u./Å) ²]	Average linear extinction coefficient at I_{max} (absorbance/cm/wt%)			Ionic radii of ions (Å)
		$a_{\text{Cu}^{2+}}$	$a_{\text{Mn}^{3+}}$	$a_{\text{Cr}^{3+}}$	
$20\text{Na}_2\text{O}\cdot 10\text{CaO}\cdot 70\text{SiO}_2$	0.640	5.13	5.21	8.82	Sr^{2+} (1.40)
$20\text{Na}_2\text{O}\cdot 10\text{SrO}\cdot 70\text{SiO}_2$	0.574	6.48	4.56	6.98	Ba^{2+} (1.56)
$20\text{Na}_2\text{O}\cdot 10\text{BaO}\cdot 70\text{SiO}_2$	0.510	7.58	4.02	6.25	O^{2-} (1.24)

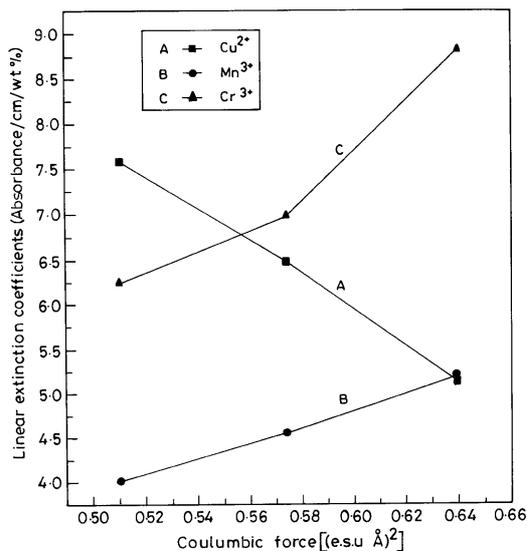


Figure 4. Variation of linear extinction coefficients of Cu^{2+} , Mn^{3+} and Cr^{3+} ions with binding energy of alkaline earth oxides in ternary silicate ($20\text{Na}_2\text{O}\cdot 10\text{RO}\cdot 70\text{SiO}_2$, where $\text{R} = \text{Ca}, \text{Sr}, \text{Ba}$) glasses.

crease in ionic radii of alkaline earth ions the oxidized state of the metal ion is favoured more. Since Cu^{2+} ion is the most common usual oxidation state of copper in the glass so, its formation with increasing O^{2-} ion activity was maximum in the glass. That is why the linear extinction coefficient ($a_{\text{Cu}^{2+}}$) increases with decreasing coulombic force of the alkaline earth ions. In case of glasses containing Mn^{3+} and Cr^{3+} the behaviour of the curves in figure 4 for extinction coefficients plotted against coulombic force was opposite. Therefore, the formation of Cr^{6+} ion is favoured more in soda–baria–silica glass than the corresponding soda–strontia–silica and soda–lime–silica glasses. Apart from Mn^{3+} ion, the metastable state of manganese as Mn^{4+} might have formed at the cost of Mn^{3+} ion with increasing basicity or O^{2-} ion activity of the glass.

Spectrophotometry is ideally an useful method in view of the aim of the present work on quantitative measurements of the intensities of absorption bands for Cu^{2+} , Mn^{3+} and Cr^{3+} ions at I_{max} in glasses. So, the application of ligand field theory for qualitative interpretation of the results in glasses is quite relevant for ions of copper, manganese and chromium.

In the light of these discussions, it is concluded that the reason for the change in intensity of the bands for these ions is due to change in concentration of these ions per unit path length of the glass with increasing oxygen ion activity of the glass which is due to decrease in binding energy of alkaline earth ions and oxygen ions. The variation in the intensities of these $3d$ -transition metal ions at their wavelength maxima in the present series of silicate glasses is also attributed to the change in their coordinations and symmetries in glasses on molar replacement of

CaO by SrO and SrO by BaO which results in a change in availability of oxygen ligands around the central metal ions. Similar results obtained in binary alkali silicate glasses due to Ni^{2+} ion for absorption bands by Singh and Singh (1998) as well as for Ti^{4+} ion for emission bands in TiO_2 sols by Seok *et al* (2002) at their I_{max} , respectively also support the above arguments in the present silicate glasses.

4. Conclusions

On the basis of the present investigations, the conclusions drawn are as follows

- (I) The change in intensities of these colouring ions viz. Cu^{2+} , Mn^{3+} , and Cr^{3+} at their I_{max} in ternary silicate glasses is attributed due to change in their tetrahedral and octahedral coordination balance with replacement of lime by strontia and strontia by baria in ternary silicate glasses. That is why these colouring species produce a variety of colour shades in silicate glasses, respectively.
- (II) The relation between the intensities of absorption for the ions of Cu^{2+} , Mn^{3+} , and Cr^{3+} with coulombic force between alkaline earth ions, Ca^{2+} , Sr^{2+} and Ba^{2+} and oxygen anion was established in the silicate glasses.
- (III) The intensities of absorption bands for Cu^{2+} ions were found to increase with an increasing ionic radii of alkaline earth ions. Whereas in the case of Mn^{3+} and Cr^{3+} the opposite results were observed as their intensities decreased with increasing size of the alkaline earth ions.

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