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Optical absorption and fluorescent behaviour of selenium in ternary silicate glasses

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Optical absorption and fluorescent behaviour of selenium in the ternary soda-lime-silica, soda-strontia-silica and soda-baria-silica glasses having molar composition $20Na_2O{\cdot}10RO{\cdot}70SiO_2$ (where R = Ca, Sr and Ba) were studied systematically. Selenium in its elemental form was found to produce a variety of pink colour shades in soda-lime-silica and soda-strontia-silica glasses by optical absorption measurements whereas the infrared transmission studies detected the presence of selenium as selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) ions which did not produce any color in glass. The results of optical measurements in the glass containing $Se \rightleftharpoons SeO_3^{2-} \rightleftharpoons SeO_4^{2-}$ species were discussed in the light of the general principles of spectroscopy. The molar extinction coefficient of selenium was calculated and found to be around 20 and 80 $l \cdot\cdot mol^{-1} \cdot\cdot cm^{-1}$, respectively, in soda-lime-silica and soda-strontia-silica glasses at their wavelength maxima at around 485 and 500 nm, which dictated the intensity of the broad absorption bands marked due to selenium in the glass. However, the selenium was found to produce a golden yellow color in soda-baria-silica glass. This is due to the shift of the valence state of selenium towards the selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) state with increasing basicity of the glass. The values of the emission cross-section obtained for selenium based on the fluorescence spectral studies showed that the soda-lime-silica glass emitted more intense fluorescence than the rest of the silicate glasses.

1. Introduction

Selenium present in its elemental form has always been known as a colourant which imparts pink colour to glass. It is also known as a physico-chemical decolourizer for undesirable blue colour produced by ferrous ion in glasses. Selenium exists in glass in four valence states namely elemental selenium, selenide, selenite as well as selenate.

Selenium is a very volatile material and a part of the total amount added to the batch is lost at high temperature during the melting of glasses. The role of selenium in glass is very much analogous to that of sulphur. Selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}) ions do not produce any colour in glass whereas elemental selenium produces a variety of pink colour shades. The selenide (Se^{2-}) ion has been reported to be present in glass under strongly reducing conditions and to yield brown colour. When selenium was melted with Fe_2O_3, the colour centre is ferric selenide analogous to amber ferric sulphide [1].

The optical absorption characteristics of selenium have been earlier studied by some workers [1 and 2] but a systematic investigation on the optical absorption behavior of selenium has not been done so far.

Weyl [3] reported that selenium imparted a brown shade during annealing of the glass whereas it produced deep red and orange shades due to cadmium sulphoselenide (CdSSe) by using the element in combination with cadmium sulphide (CdS).

The greater polarizability of the large selenium atoms accounts for the fact that the pink colour of selenium doped glass is greatly influenced by the composition of the base glass, specially the nature and the concentration of the alkali. The outer electronic orbits of the selenium atoms are easily deformed by the electric field of the positively charged alkali atoms. That is why selenium brown colour in glass is produced with smaller ions, such as sodium and lithium.

To obtain selenium pink in glass it is essential to attain a mildly oxidizing atmosphere in the furnace at the melting temperature otherwise the reducing condition will spoil the colour due to formation of selenide brown color. It has been recommended earlier to add arsenic oxide as a bodyguard for developing the pink colour due to selenium because any change in the furnace conditions would be first faced by arsenic affecting its valence state [4]. So the presence of elemental selenium is not disturbed due to sudden change in the furnace conditions. In the absence of heavy metals colourless selenide will be formed even under reducing conditions. It indicates that the presence of selenide brown is due to the formation of heavy metal selenides in the glass. In between two extreme states such as strongly reducing and oxidizing conditions the formation of free atomic selenium and its distribution throughout the matrix of the glass imparts an attractive pink color. That is why selenium has found significant commercial applications for producing red

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signal glasses, red glass bangles, containers and patterned window glasses and as physical decolourizer for undesirable ferrous ion blue colour due to complementary selenium pink in the glass.

Whenever any UV visible radiation interacts with an atom or an element in an ionic state, the transition of electrons takes place from their ground energy level to an excited state as a result of absorption of radiation. If the electronic transition is reversed from excited state to the ground state, radiative photonic transition takes place which exhibits fluorescence as a result of emission of radiation by the system. Several systematic investigations have been carried out in the past on excitation and emission properties of rare earth ions in glasses. Some of the workers [5 and 6] have also studied the optical fluorescent behaviour of 3d-transition metal ions such as Cu^{+}, Ti^{4+}, Ti^{3+}, Cr^{3+} and Mn^{2+} in glasses and they assigned the occurrence of fluorescence phenomena to electronic transition from excited energy state to the ground state. Weyl [3] also reported that fluorescence phenomena in silicate glasses could occur due to the presence of energy of isolated atoms or molecules such as silver and selenium atoms as well as the CdS molecule. The major concentration quenching of selenium vapour in the presence of other gases has been pointed out previously [7], but Löffler [8] observed the disappearance of selenium pink under mildly reducing melting conditions. Further, Löffler [8] concluded that elemental selenium and the selenide both could not remain in the same glass under reducing melting conditions. The fluorescence of selenium as per the clue given by Löffler [8] might be due to the result of a slight distortion of the outermost electronic structure of the shells of selenium atom present in the ground state. The reversal of the same from excited state to ground state causes the fluorescence phenomenon that results in the form of its emission band and might extend to the near infrared region. However, a detailed systematic study of such a fluorescence phenomenon in glasses has not been reported so far.

Glass forming oxides are used as major constituents in glasses because of their network forming structure. The infrared spectroscopic investigations have been done in silicate, borate and phosphate glasses containing modifiers as well as stabilizers present also as major ingredients. Selenium has been used for a longer period as a minor constituent because of its colouring nature and to produce pink colour. The IR spectral studies on glasses for SeO_3^{2-} and SeO_4^{2-} groups of selenium are rare. However, along with the optical absorption and fluorescence characteristic studies on selenium in ternary silicate glasses, it was also planned to check whether SeO_3^{2-} and SeO_4^{2-} impart any IR absorption bond in the glass to ensure the presence of these selenite and selenate groups. Since selenium was known to exist in glass as SeO_3^{2-} and SeO_4^{2-} ions along with selenides and elemental selenium, the IR studies were proposed for structural determination of selenite and selenate groups in soda-lime-silica, soda-strontia-silica and soda-baria-silica glasses melted with selenium.

2. Experimental

Silicate glasses having molar composition $20Na_2O \cdot 10RO \cdot 70SiO_2$ (where R = Ca, Sr, and Ba) were selected as the base glass. Reagent grade BDH is used for preparing the glass batches. Selenium was introduced into the glass batches in form of analytical reagent grade selenium metal powder. Ternary silicate glasses containing selenium were melted in a 100 ml capacity Pt-2% Rh crucible. The crucible containing the glass batch was kept in a Globar rod electric furnace in air atmosphere at 1425 °C. The temperature was controlled within ±10 K with an automatic R-type thermocouple temperature indicator-cum-controller. The glasses were melted for 6 h, then taken out of the furnace and poured onto a steel plate. After cooling they were crushed and remelted in the crucible kept in the electric furnace for another 4 h at 1425 °C to ensure homogeneity. The glasses were taken out of the furnace and poured into a rectangular mould on a steel plate and annealed at 450 °C for 1 h, then cooled to room temperature slowly by controlling the rate of cooling. A portion of the glass samples so obtained was cut, ground and polished and their optical absorption spectra were recorded on a JASCO-7800 UV-visible recording spectrophotometer, Japan Spectroscopic Co. Ltd., in the range of 200 to 800 nm.

The other portion of the glass samples was chemically analyzed by potentiometric method for the concentrations of zero valent selenium conveniently with HBr-Br_2 water mixture using $Na_2S_2O_3$ and I_2 solution according to Close et al. [27]. This method was used for the determination of Se^{0} in the glass keeping in view the presence of Se in other valence states, such as Se^{4+} and Se^{6+}, which were separated before.

Rüssel [28] as well as Simon et al. [29] have used voltammetric as well as thermodynamic methods for the investigations of redox behavior of selenium in soda-lime-silica glasses at high temperature. However, square wave voltammetric and the thermodynamic methods could only indicate the proportions of the variable valence states of selenium distributed in the glass melt at high temperatures. Therefore, the wet chemical analysis for the determination of Se^{0} after separation of Se^{4+} and Se^{6+} ions from the glass samples was done by potentiometric method. The atomic absorption spectrometric and photometric as well as spectrophotometric determination of different oxidation states of Se^{0} and total selenium in glasses as developed by earlier workers [30 and 31] are also quite useful, but the present work involved the application of titrimetric method for satisfactory determination of the concentrations of Se^{0} in ternary silicate glasses.

The excitation and emission spectra of the glass samples prepared in the form of window were recorded on the Perkin-Elmer LS-45 fluorescence spectrometer.

The infrared spectra of the powdered glass samples were recorded using KBr technique on the JASCO FTIR-5300 IR-spectrometer (Japan) in the range of 400 to 4000 cm^{-1}. The thicknesses of the glass samples were measured and their densities were also determined by Archimedes principle.

3. Results and discussion

Results presented in tables 1 and 2 as well as figures 1 to 4 show the optical absorption, fluorescence characteristics as well as IR transmission spectra, respectively, of ternary silicate glasses ($20Na_2O \cdot 10RO \cdot 70SiO_2$, R = Ca, Sr and Ba)

Table 1. Molar extinction coefficients of Se in ternary silicate ($20Na_2O \cdot 10RO \cdot 70SiO_2$, R=Ca, Sr, Ba) glasses

sample no.	glass composition in mol%	absorbance in cm^{-1} on JASCO-7800 recording spectrometer	wavelength maxima λ_{max} in nm	thickness t in cm	concentration C_w of zero valent selenium (Se^0) in wt%	molar extinction coefficient ε_{Se^0} x 10^{-2} in $l \cdot mol^{-1} \cdot cm^{-1}$	average ε_{Se^0} x 10^{-2} in $l \cdot mol^{-1} \cdot cm^{-1}$	MEC (% error)
C_1	$20Na_2O \cdot 10CaO \cdot 70SiO_2$	0.220	485	0.586	0.012	0.78		−3.85
C_2	$20Na_2O \cdot 10CaO \cdot 70SiO_2$	0.467	485	0.583	0.028	0.81	0.81	0.00
C_3	$20Na_2O \cdot 10CaO \cdot 70SiO_2$	0.133	485	0.239	0.015	0.83		+2.41
S_1	$20Na_2O \cdot 10SrO \cdot 70SiO_2$	0.067	500	0.542	0.008	0.20		−5.00
S_2	$20Na_2O \cdot 10SrO \cdot 70SiO_2$	0.096	500	0.571	0.014	0.22	0.21	+5.00
S_3	$20Na_2O \cdot 10SrO \cdot 70SiO_2$	0.117	500	0.544	0.021	0.21		0.00
B_1	$20Na_2O \cdot 10BaO \cdot 70SiO_2$	0.168	520	0.566	traces	–	–	—
B_2	$20Na_2O \cdot 10BaO \cdot 70SiO_2$	0.084	520	0.509	traces	–		–

Table 2. Physical properties and the stimulated emission cross section σ_{Se} of Se doped in ternary silicate ($20Na_2O \cdot 10RO \cdot 70SiO_2$, R=Ca, Sr, Ba) glasses

physical properties	$20Na_2O \cdot 10CaO \cdot 70SiO_2$	$20Na_2O \cdot 10SrO \cdot 70SiO_2$	$20Na_2O \cdot 10BaO \cdot 70SiO_2$
concentration of Se in wt%	0.012	0.014	traces
refractive index n	1.523	1.518	1.513
density d in g/cm^3	2.525	2.559	2.593
reflection loss R in %, $R = [(n-1)/(n+1)]^2$	4.30	4.23	4.16
emission peak position λ in nm	643	640	645
emission band width $\Delta\lambda$ in nm	17.50	20.00	18.75
stimulated emission cross section σ_{Se} x 10^{-50} in cm^2	3.81	3.32	3.62

melted with selenium in normal air atmosphere. The silicate glasses melted with selenium show single broad absorption bands centred at around 485 and 500 nm for soda-lime-silica as well as soda-strontia-silica systems in the visible region whereas the soda-baria-silica glass doped with Se does not impart any band in the visible region. However, a plateau was marked in the visible region at around 520 nm for soda-baria-silica glass containing Se as given in figure 1. The visible band imparted due to selenium was found to shift more towards longer wavelengths with increasing ionic radii of alkaline earth ions in the order of $Ca^{2+}<Sr^{2+}<Ba^{2+}$. Selenium was found to produce a brownish pink in soda-lime-silica glass whereas it yielded fascinating pink colour in soda-strontia-silica glass. The soda-baria-silica glass melted with Se was found to be imparted with golden yellow colour. The molar extinction coefficients of selenium ε_{Se^0}, presented in table 1, were calculated in $20Na_2O \cdot 10CaO \cdot 70SiO_2$ and $20Na_2O \cdot 10SrO \cdot 70SiO_2$ glasses from absorption spectra using Bouger-Beer's equation (1), whereas the molar extinction coefficient for Se^0 in $20Na_2O \cdot 10BaO \cdot 70SiO_2$ could not be calculated as its absorption spectra did not show any sign of the selenium absorption band due to presence of elemental Se in the glass. The value of ε_{Se^0} for colouring species Se^0 is solely related to the concentration of zero valent selenium (Se^0) as presented in table 1. However, the appearance of the plateau in the curve for soda-baria-silica glass indicates only the presence of a small trace of Se in the glass that could not be taken for granted to calculate its extinction coefficient in the visible region in the glass.

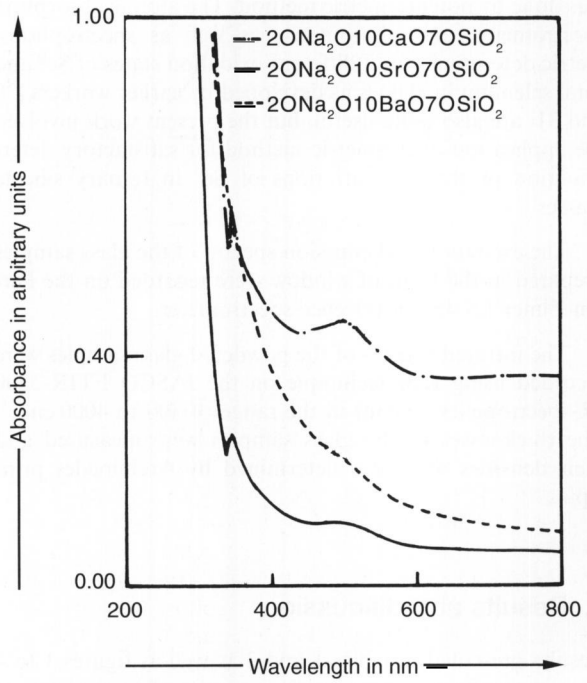

Figure 1. Optical absorption characteristics of selenium in ternary silicate glasses.

$$\varepsilon_{Se^0} = \frac{(2 \lg (1-R) + A) \cdot \text{atomic weight of Se}}{C_w \cdot t \cdot d \cdot 10} \quad (1)$$

where

A = absorbance due to elemental Se at wavelength maximum λ_{max} in the glass,
C_w = concentration of zero valent selenium (Se^0) in wt%,
d = density of the glass in g/cm^3,
R = reflection factor, $R = [(n-1)/(n+1)]^2$,
n = refractive index of glass,
t = thickness of glass sample in cm.

The values of ε_{Se^0} in soda-lime-silica glass as well as soda-strontia-silica glass were found to be around 80 and 20 l · mol^{-1} · cm^{-1} of the glass at their wavelengths maxima at around 485 and 500 nm, respectively. The values of ε_{Se^0} in silicate glasses at their wavelengths maxima calculated on the basis of equation (1) keeping in view the reflection loss from the glass surface were found to be constant within ±5 % experimental error. These values of ε_{Se^0} fall in the range of d-d spin allowed electronic transitions for ligand field bands observed in silicate glasses for d-state ions such as Ti^{+3}, Cr^{+3}, Mn^{+3}, Fe^{+2}, Co^{+2}, Ni^{+2} and Cu^{+2} [9 to 15]. Similarly, the present results on the intensity of the bands for Se^0 in silicate glasses at their λ_{max} probably dictate the transition of electrons from ground state ($3d^{10}4p^4$) to excited state ($3d^{10}\ 4p^3\ 4d^1$) as a result of absorption of visible radiation producing broad absorption bands and imparting a variety of pink colour shades to the glass.

It was earlier believed that the red brown colour in glass was mainly due to formation of polyselenide ions (Se_x^{2-}). However, the silicate glasses under present studies were melted with selenium in normal air atmosphere, so that the chances for the association of selenide ions (Se^{2-}) to form polyselenides ($xSe^{2-} \xrightarrow{\triangle} Se_x^{2-}$) were minimum. It was further pointed out by Güldal and Yaraman [16] that the formation of amber colour along with the intense selenium pink can be achieved only under reducing conditions by addition of carbon in soda-magnesia-lime-alumina-silica glass (72.2 SiO_2, 1.35 Al_2O_3, 0.01 Fe_2O_3, 7.4 CaO, 4.0 MgO, 14.5 Na_2O). The same was found to be true by Güldal et al. [17] during their improvement of bronze glass melting conditions with an increase in Se retention. In view of this, it should be mentioned that the pink colouration in our glasses is mainly due to the presence of elemental Se in air as furnace atmosphere. Since the pink colouration is imparted due to absorption of visible radiation by Se atoms in the glass at around 485, 500, 520 nm, the studies were also extended to investigate the fluorescent behaviour of Se^0 in glass.

The fluorescence spectra of silicate glasses containing Se are given in figure 2. The emission bands were observed at around 643, 640 and 645 nm in soda-lime-silica, soda-strontia-silica and soda-baria-silica glasses, respectively, as a result of the excitation in the UV-visible range. The excitation spectrum of a $20Na_2O{\cdot}10CaO{\cdot}70SiO_2$ glass doped with Se is presented in figure 3, where the excitation band is also marked at around 482 nm. The relative intensity of emitted radiation was found to be of the order of around 1.02 to 1.03 x 10^3. The excitation wavelengths are responsible for the energy transfer from ($3d^{10}4p^4$) to ($3d^{10}4p^34d^1$) within the orbital electron that might impart an intense pink fluorescence from excited Se level to its ground level when the emission phenomenon takes place. In reverse, when the photonic energy is released from the excited state of Se ($3d^{10}4p^34d^1$) to the lower energy state ($3d^{10}4p^4$), the fluorescence radiative emissive transition takes place as a result

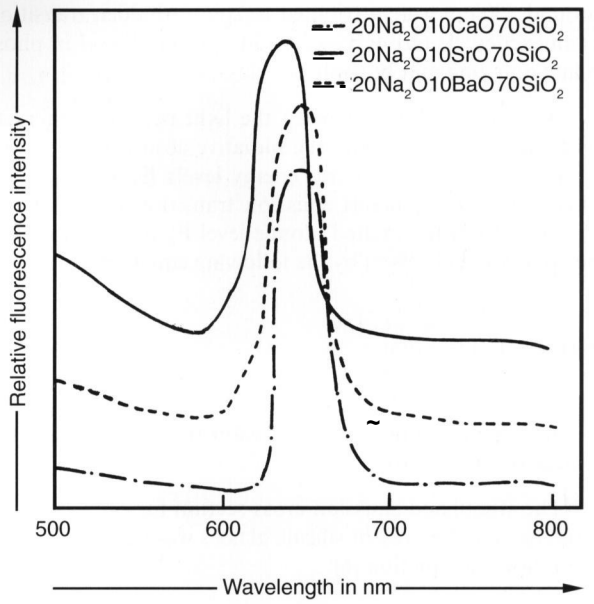

Figure 2. Fluorescence spectra of selenium in ternary silicate glasses.

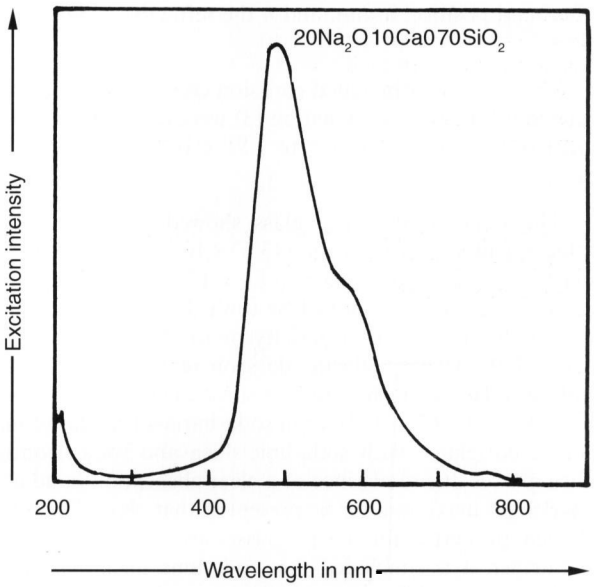

Figure 3. Excitation spectrum of soda-lime-silica glass containing selenium at room temperature.

of which emission bands are observed in the glass as given in the fluorescence spectrum in figure 3. This is caused due to a change in electronic state of Se within the orbital electron resulting in emission spectra. This kind of mechanism may be attributed due to charge transfer in Se that is responsible for the pinkish violet emission in the glass. Similar results were also observed due to charge transfer in the form of $Ti^{4+}-F^-Ti^{3+}$ in reduced fluorophosphate glass containing Ti^{3+} and Ti^{4+} ions [6]. Parle and Webb [18] as well as Annapurna et al. [5] studied the UV excitation in silicate glasses of Cu^+ ions from $3d^{10}$ to $3d^94s^1$ configuration and reported the fluorescent transition as the phonon assisted greenish blue emission the broader visible bands, which at

around 500 nm were attributed to spin forbidden transition from excited $^3E_g(3d^94s^1) \rightarrow {}^1A_g(3d^{10})$ ground level in phosphate and zinc and borosilicate glasses.

As mentioned earlier when the light radiation interacts with an electronic system, the radiative absorption or emission transition between two energy levels E_a and E_b is induced. The spontaneous emission transition probability A ($E_b \rightarrow E_a$) from the excited atomic level E_b to a level E_a can be approximately given by the following equation [6 and 19]:

$$A\,(E_b \rightarrow E_a) = \frac{8 \cdot \upsilon^2 \cdot 10^6}{e^2} \qquad (2)$$

where υ is the frequency of emission transition, and e the charge of the electron.

The stimulated emission cross-section for each emission band (σ_{Se}) in the present silicate glasses was calculated using the following equation [6]:

$$\sigma_{Se} = \left(\frac{\lambda^4}{8\,\pi\,c\,n^2\,\Delta\lambda}\right) A\,(E_b \rightarrow E_a) \qquad (3)$$

where $\Delta\lambda$ is the effective half band width in nm, λ the emission band position in nm, and n the refractive index of the glass.

The values of stimulated emission cross-section, σ_{Se}, calculated on the basis of equation (3) were found to be of the order of around 3.32 x 10^{50} to 3.81 x 10^{50} as presented in the glasses in table 2.

The soda-strontia-silica glass showed a slightly lower value of emission cross-section (3.32 x 10^{50} cm^2) in comparison to soda-lime-silica glass (3.81 x 10^{50} cm^2), which may be attributed to oxidation of Se towards its higher valency state with an increase in basicity or to the oxygen ion activity of the ternary silicate glass on replacement of CaO with SrO. However, the value of stimulated emission cross-section (σ) of 3.62 x 10^{50} cm^2 in soda-baria-silica glass could not be correlated with soda-lime-silica and soda-strontia-silica glasses due to absence of a clear absorption band at a wavelength maximum for Se present in that glass. The other physical properties for silicate glasses are also given in table 2. Further, it is concluded that soda-lime-silica glass containing elemental Se with a higher σ_{Se} value might emit a better radiative fluorescence than the corresponding soda-strontia-silica glass. The presence of Se in traces as evident from optical absorption spectra in soda-baria-silica glass must have been due to its oxidation towards its higher valency state because of high basicity or oxygen ion activity of the glass.

Güldal and Yaraman [16] also observed the fading pink colour towards yellowish light pink tint on addition of sulphates (SO_4^{2-}) to the glass while studying the role of sulphur in the colouring mechanism of Se in soda-lime-silica glasses. This agreed with the present observation regarding the change of pink colour towards golden yellow on replacement of CaO with SrO and SrO with BaO in silicate glasses. The findings on fluorescent behaviour of Se in glasses were also in accordance with results obtained by Sreenivasulu and Rao [20] in fluoroboro-phosphate glass containing Pr^{3+} ions at room temperature.

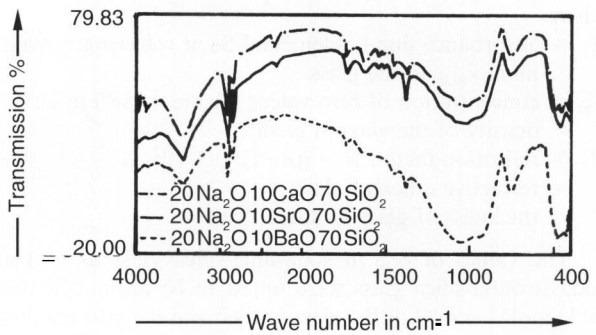

Figure 4. Infrared transmission spectra of ternary silicate glasses melted with selenium.

In the oxide glasses under study the emission band positions marked at three different wavelengths were almost the same for Se present in the glass. In the case of glasses particularly at room temperature the coupling between the active sites of Se and phonons becomes stronger for a cross relaxation and the interaction between them would result in emission by energy transfer. The nature and intensity of the fluorescent centre of Se in glass are its specific characteristics, which depends upon the band position and will not be influenced by the presence of any other minor species unless and until it is overlapped.

As lime was replaced with strontia and strontia with baria, the nature of the optical absorption characteristics of Se clearly showed its oxidation towards selenite and selenate ions. Further, the fading of the pink colour due to the formation of SeO_3^{2-} and SeO_4^{2-} ions also took place as follows in reaction (4) with increasing basicity of the glass. Therefore, infrared transmission characteristics of the glasses were also investigated.

$$Se \rightleftharpoons SeO_3^{2-} \rightleftharpoons SeO_4^{2-}. \qquad (4)$$

Studying the role of Se in colouring mechanisms in soda-lime-silica glasses melted under different atmospheric conditions Güldal and Yaraman [16] reported the possibilities for replacement of Si^{4+} with Se^{6+} ions in the glass structure under oxidizing conditions. The optical transmission measurement of glasses containing Se has been made by them in the UV/visible region (300 to 800 nm) but not in the IR region. Even though having regards to any observations like that IR bands have been assigned earlier at 470 cm^{-1} due to Si–O–Si and 770 cm^{-1} to –O–Si–O– bond vibrations in silicate systems, it should be mentioned here that such an effect in a selenium doped glass could be overcome against a blank glass during IR spectral measurements. However, the authors have recorded the IR spectra of the present glasses with reference to the blank glasses against KBr pellets.

The infrared transmission spectra of the present ternary silicate glasses containing Se with the same thickness have been recorded in the range of 400 to 4000 cm^{-1} and are presented in figure 4. In silicate glasses because of the random structure of SiO_4 (tetrahedra), the Se^{6+} ion having similar ionic radius to the Si^{4+} ion may enter into the glass structure as pointed out earlier by Güldal and Yaraman [16]. In silicate systems the vibration of bonds in SiO_4 tetrahedra have already been reported in the frequency range of

Table 3. IR band positions (wave number in cm^{-1}) for different bond vibrations in ternary silicate ($20Na_2O{\cdot}10RO{\cdot}70SiO_2$, R=Ca, Sr, Ba) glasses

bond	$20Na_2O{\cdot}10CaO{\cdot}70SiO_2$	$20Na_2O{\cdot}10SrO{\cdot}70SiO_2$	$20Na_2O{\cdot}10BaO{\cdot}70SiO_2$
Se	425 to 440	415 to 460	430 to 480
Se	766	766	766
SeO_3^{2-}	930 to 980	930 to 980	930 to 980
SeO_4^{2-}	900 to 1080	900 to 1080	900 to 1080
SiO_4^{2-}	900 to 1100	900 to 1100	900 to 1100
CO_3^{2-}	1380 to 1730	1380 to 1730	1380 to 1730
OH^-	2330	2330	2330
O–H	2800 to 3460	2800 to 3460	2800 to 3460

900 to 1100 cm^{-1}. Since the Se^{6+} ion also enters the random structure of silica tetrahedra because of its similar ionic radius to form the selenate (SeO_4^{2-}) group, the IR bands observed in the frequency range of 900 to 1080 cm^{-1} must be due to the presence of selenate ions in the present ternary silicate glasses, as given in figure 4. When the elemental Se is oxidized to form selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) ions in glasses having higher basicity, then it is possible that Se^{4+} and Se^{6+} ions both might have entered into the glass structure and there vibrational modes might be overlapping in between 900 to 1100 cm^{-1} with SiO_4 tetrahedra in the glass.

Further, since both the selenite and selenate ions are expected to remain in equilibrium at high temperatures in glasses, it may be mentioned that the IR band at around 900 cm^{-1} could be due to the selenite group (SeO_3^{2-}). Therefore, the IR bands in the observed frequency range of 900 to 1080 cm^{-1} are definitely due to the presence of selenite, selenate and silicate together in glass. It is well known that crystalline forms of Se possess ring or chain structure and the bonding within their structures is covalent. Siemsen and Riccius [21] have already pointed out from the temperature dependence of the IR spectra of glassy state of Se that the transmission bands at 490, 743 and 983 cm^{-1} could be due to the multiphonon modes of vibration of bonds. The present observations for IR bands at frequencies at around 430 and 480 cm^{-1}, 415 and 460 cm^{-1}, 425 and 440 cm^{-1} as well as at 766 cm^{-1} depict the presence of Se in glassy state in soda-lime-silica, soda-strontia-silica as well as soda-baria-silica glass, respectively, as presented in figure 4 and table 3.

The sharp and the broad composite bands in the range of 2800 to 3460 cm^{-1} as presented in table 3 and figure 4 are attributed to the presence of OH group in the glass in accordance with the earlier findings. The peak position in the frequency range of 2800 to 3460 cm^{-1} results due to the hydrogen bonding and it is attributed to O–H stretching vibration as also mentioned by Bray [22]. The hydroxyl group (OH) results in the formation of nonbridging oxygen ($-O^-$) in the glass. The IR spectra in ternary silicate glasses start indicating the effect of the hydroxyl group as also evident from its peak at around 2330 cm^{-1} in the glass.

The IR transmission bands appearing in the form of dips in the frequency range of 1380 to 1730 cm^{-1} seem to be mainly due to the presence of the CO_3^{2-} ion in silicate glasses (figure 4). From the solubility of gases such as CO_2, H_2O and SO_2, previous workers [23 to 26] have shown that there is a definite solubility of gases at high temperature in glasses. Therefore, a part of CO_2 released during dissociation of carbonates during melting at high temperature might have dissolved to form the CO_3^{2-} ion due to oxygen ion activity of the glass according to the following reaction

$$CO_2 + O_2 \rightleftharpoons CO_3^{2-}. \quad (5)$$

The same was also observed earlier during dissolution of water vapour and sulphur dioxide in glasses at high temperature as follows

$$O^{2-} + H_2O \rightleftharpoons 2OH^-, \quad (6)$$

$$O^{2-} + 1/2O_2 + SO_2 \rightleftharpoons SO_4^{2-}. \quad (7)$$

Based on this fact the assignment of the IR bands has been given to carbon oxygen bonds (C=O) vibration in the frequency range of 1380 to 1730 cm^{-1} in the glass.

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