Advanced Glass Science

(4016101)

Instructor: Asst.Prof.Dr. Jakrapong Kaewkhao

Course Outline:

Week 9: Glass composition, structures and applications (1)

- Silica Glass
- Alkali Silicate Glass
- Alkali-Earth Silicate Glass
- *Case studies from international publications*

Book:

A.K., Varshneya. ***Fundamentals of inorganic glasses***
A., Paul A, ***Chemistry of glasses***
J.E. Shelby, ***Introduction to glass science and technology***

Silica Glass

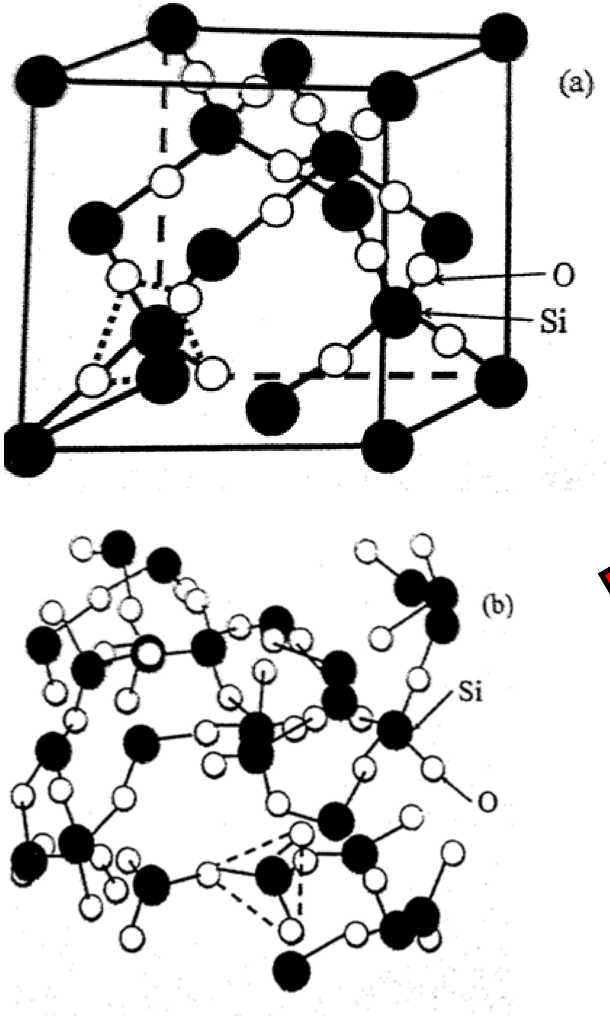


Fig. 1 Dimensional representation of SiO_2: (a) crystal and (b) glass

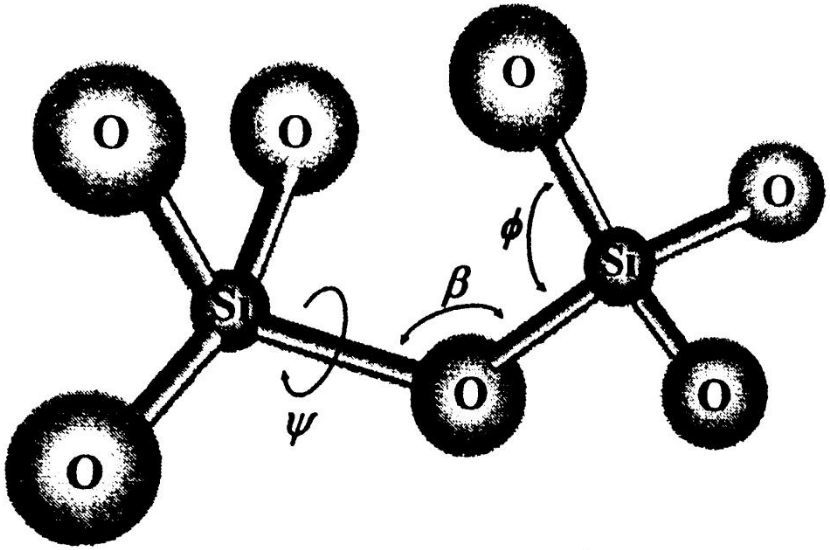


Fig. 2 The structure of pure SiO_2 glass
A band-and-stick model of two SiO_4 tetrahedra, $\phi \sim 109^{o}28^{/}$

Silica Glass

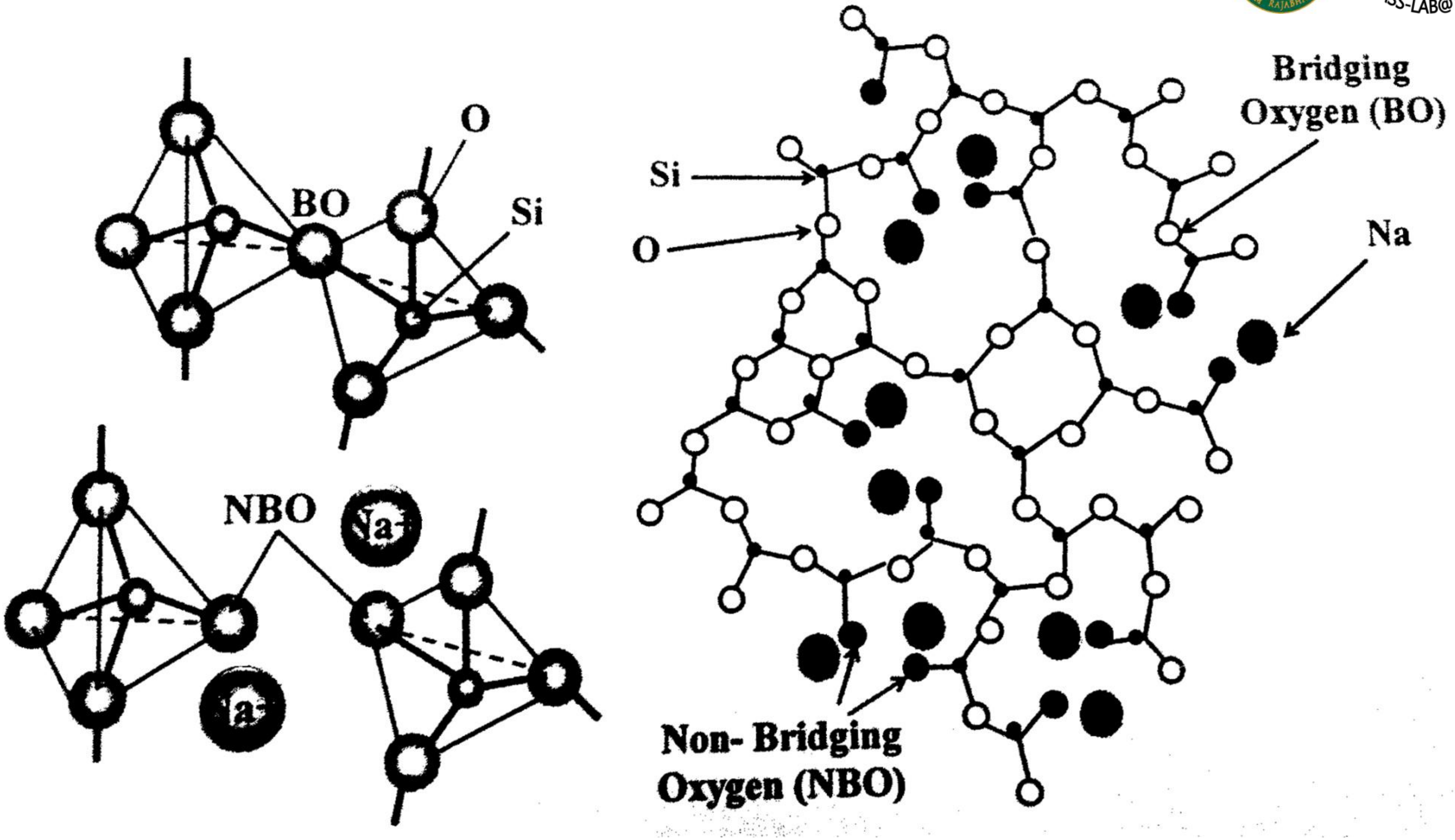


Fig. 3 Dimensional representation of sodium silicate glass

Silica Glass

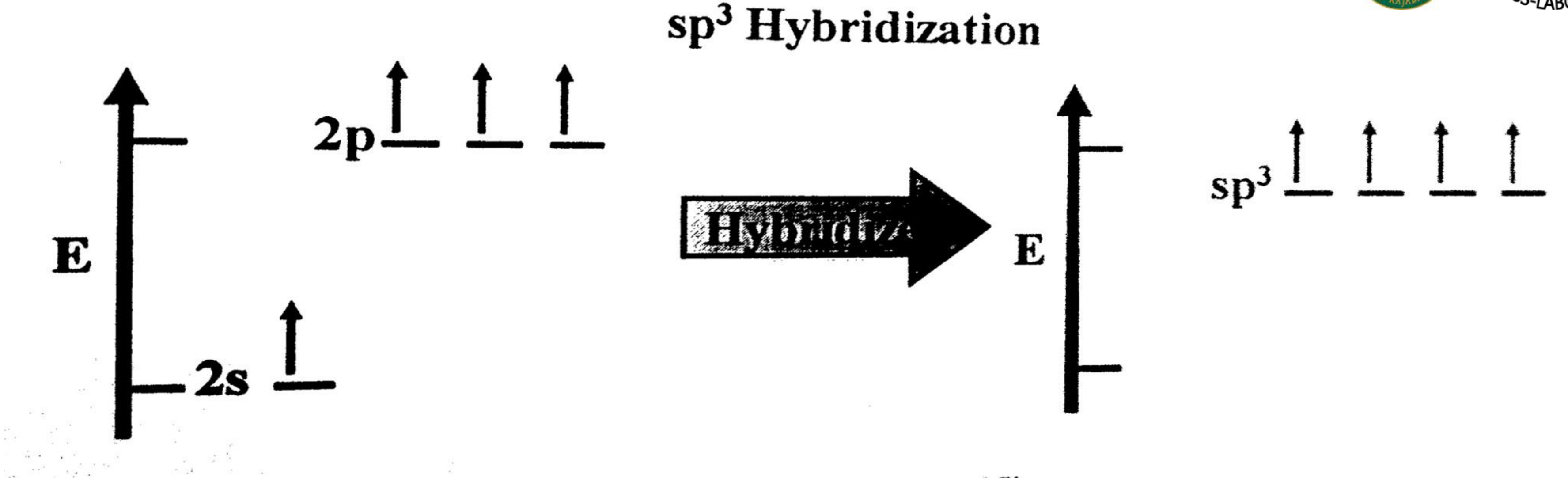


Fig. 4 The sp^3 hybridization

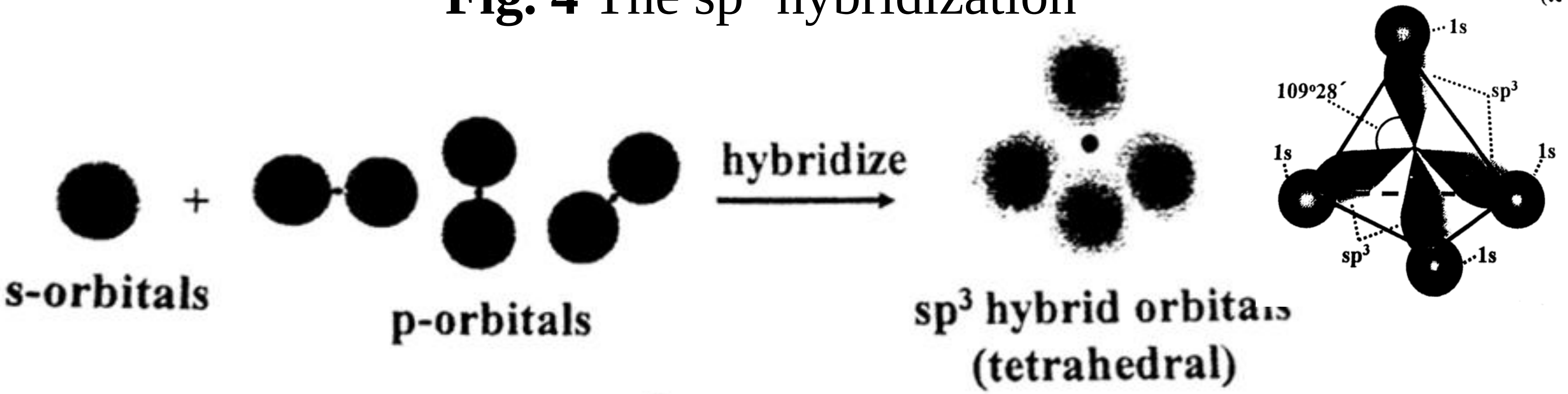


Fig. 5 Three dimensional (3D) hybrid sp^3 orbital

Silicate, Soda-Silicate and Soda-Lime-Silicate Glass

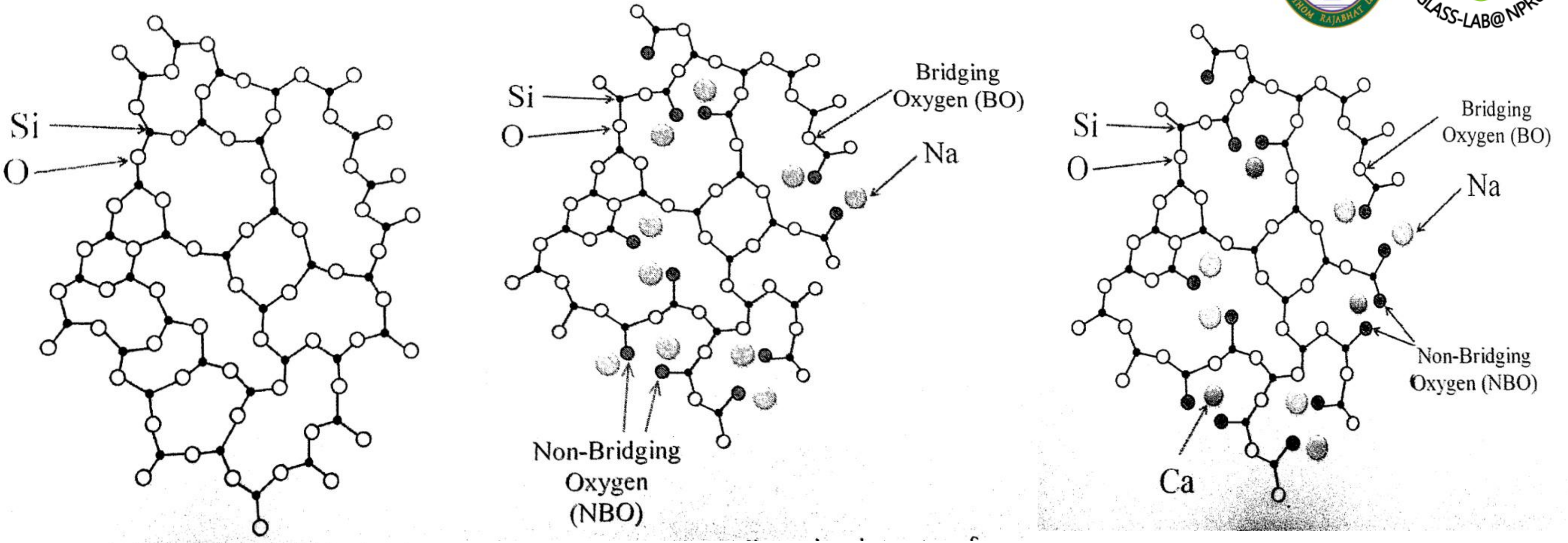
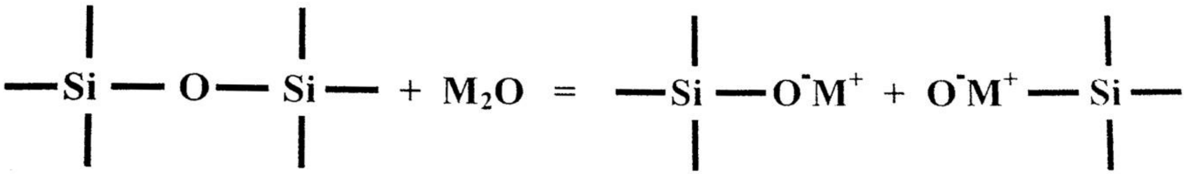


Fig. 6 Schematic drawing of a 2-dimemsional structure for a silicate, soda-silicate and soda-lime-silicate glass. A fourth oxygen would be located above each silicon in the 3-dimensional structure



$$-\mathrm{Si}-\mathrm{O}-\mathrm{Si}- + \mathrm{M_2O} = -\mathrm{Si}-\mathrm{O^-M^+} + \mathrm{O^-M^+}-\mathrm{Si}-$$

Calculation fraction of NBO

To determine the fraction of NBO, one first converts the glass formula to a mole basis, and proceeds as follows:

Example: For $20Na_2O\text{-}80SiO_2$ (mol%) glass

Since $Na^+ = 40$, hence NBO = 40
Since total oxygen = 180, Silicon atoms = 80,
Hence f_{NBO} = fraction of NBO of the total oxygens = 40/180 = 0.22
f_{BO} = 140/180 = 0.78, and BO/Silicon atom = 140/80 = 1.75

Since Y = corners share / Silicon atoms = 2 x BO / Silicon atoms
Y = 3.5 (because each BO is shared by two silicon atoms)

$$\boxed{Y = 6 - 200/p, \quad \text{where } p = \text{mol\% of } SiO_2}$$

Phase Equilibria of Soda-Lime-Silicate-Glass

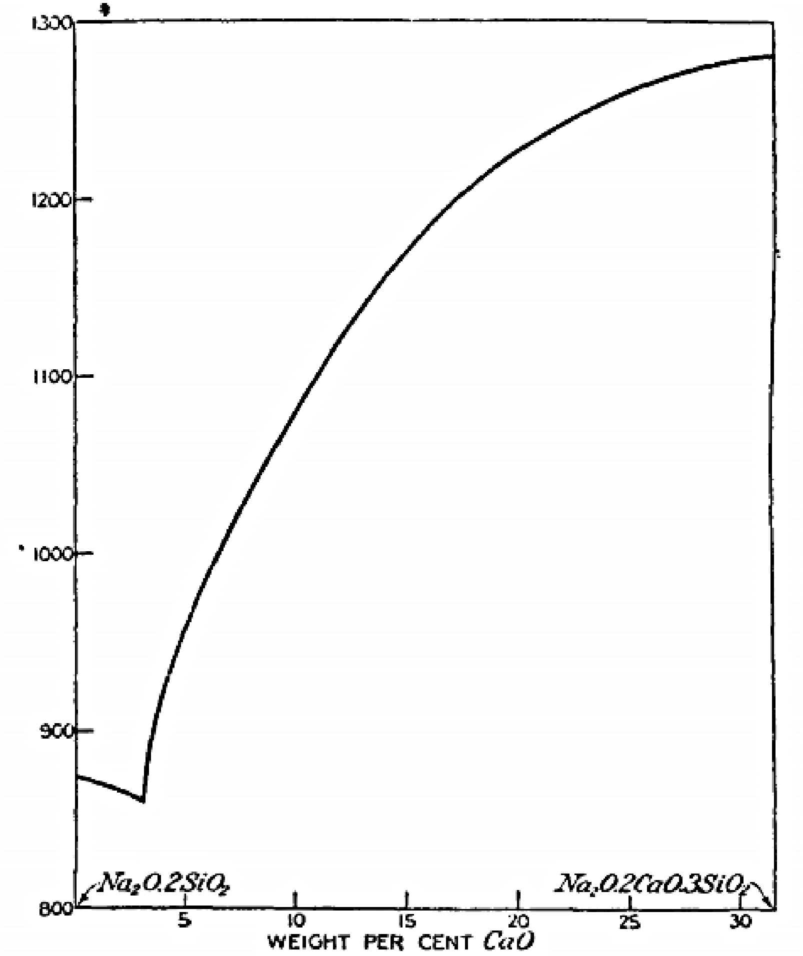


Fig. 7 Melting point diagram of the bunary system Na_2O, $2SiO_2$- Na_2O, 2CaO, $3SiO_2$

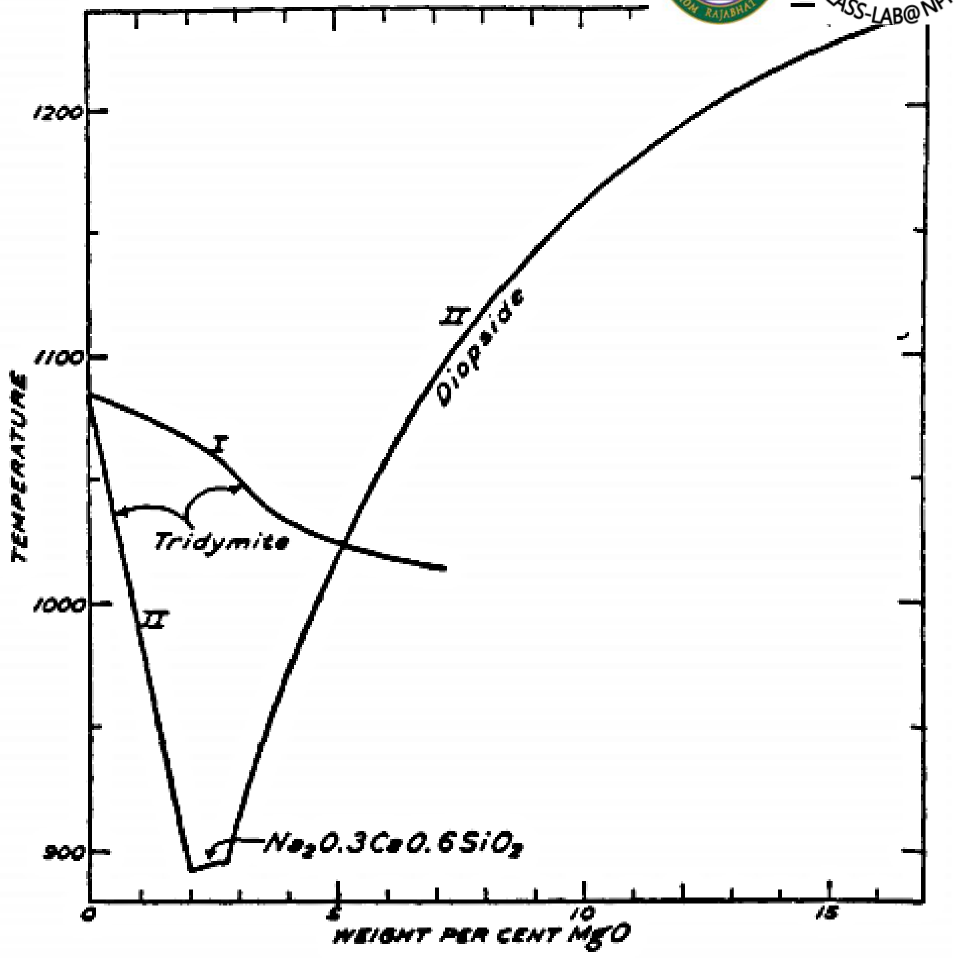


Fig. 8 Effect of Magnesia on the liquids temperature of some glasses in the system Na_2O-CaO-SiO_2

Phase Equilibria of Soda-Lime-Silicate-Glass

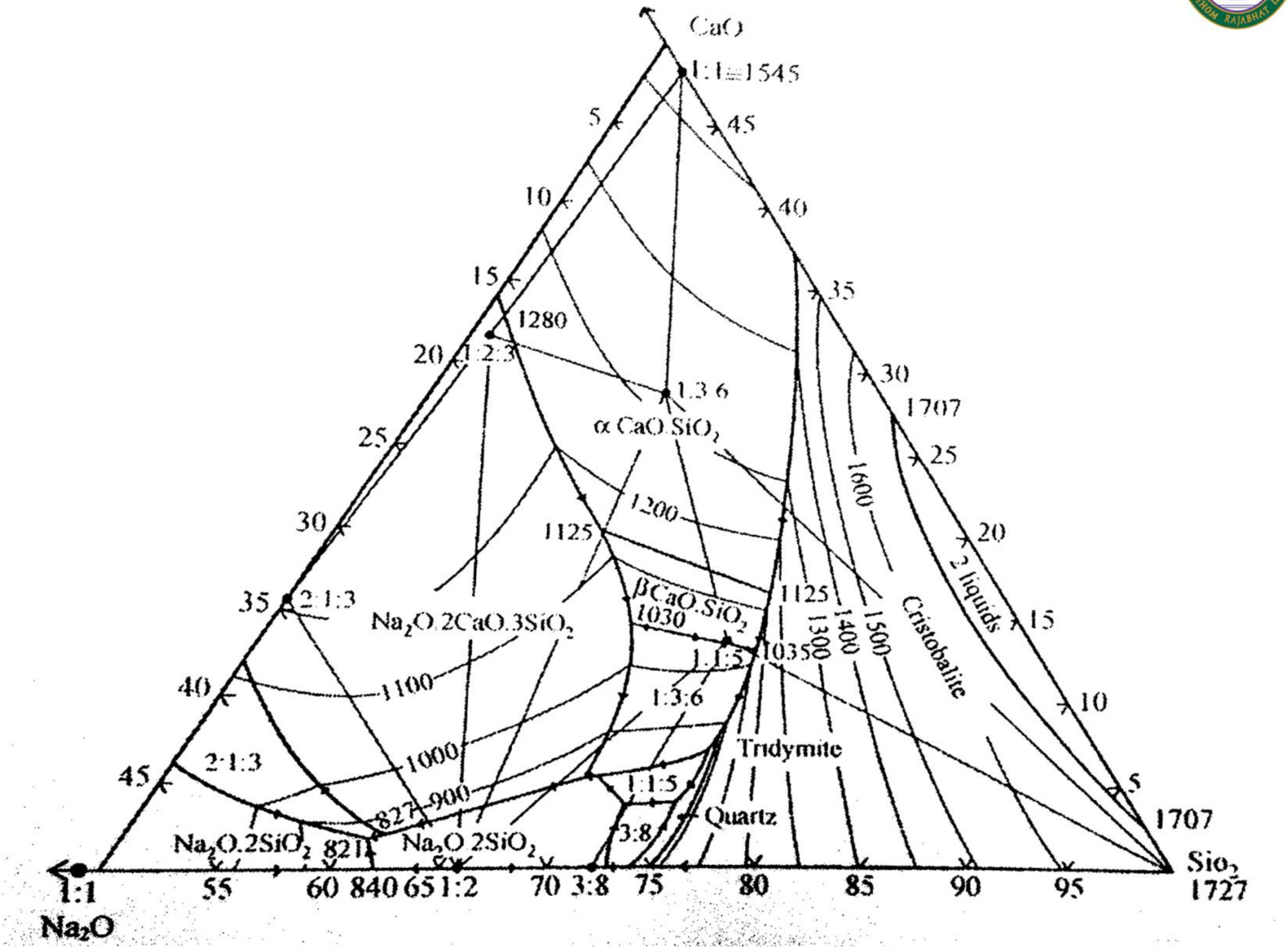


Fig. 9 Phase equilibria and glass formation region in the soda-lime-silicate glass

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Absorption Studies on Some Silicate and Cabal Glasses Containing NiO or Fe_2O_3 or Mixed NiO + Fe_2O_3

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(Received June 5, 2009)

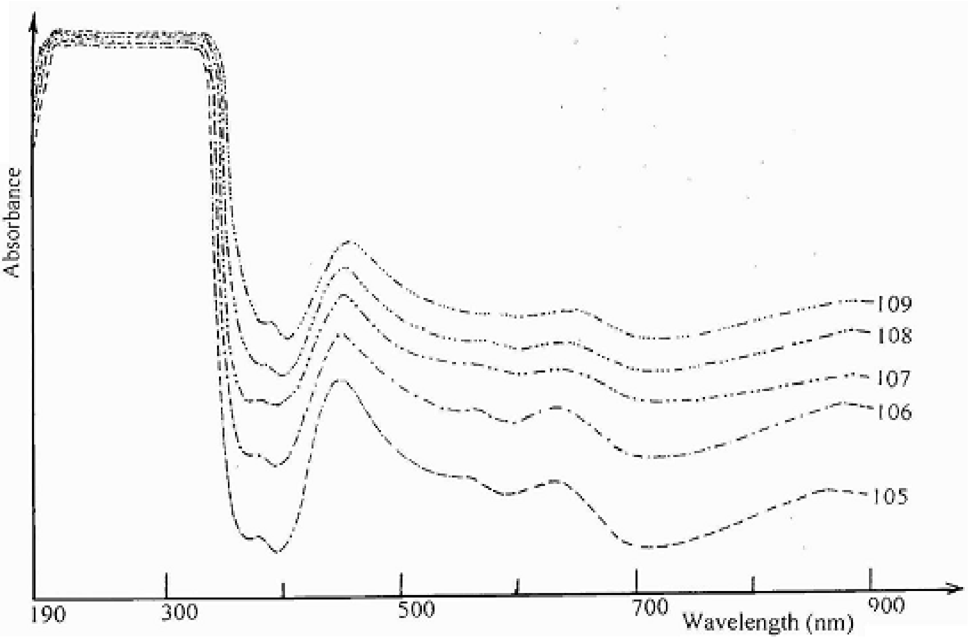


Fig. 10 Absorption curve for a number of sodium silicate glasses containing both 0.2 g NiO and 1.0 g Fe_2O_3 together Na_2O 15% (105), Na_2O 20% (106), Na_2O 25% (107), Na_2O 30% (108), Na_2O 35% (109)

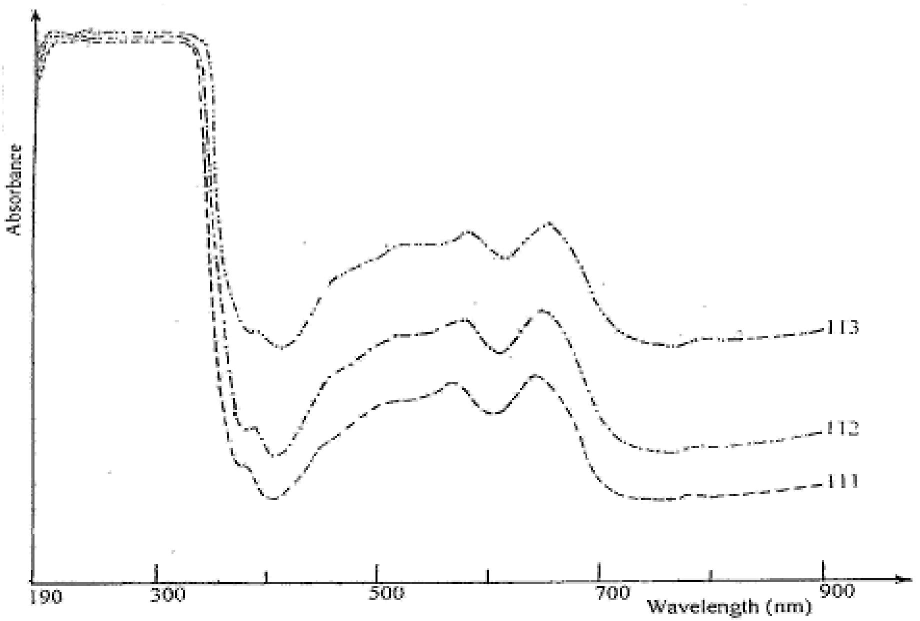


Fig. 11 Absorption curve for a number of potassium silicate glasses containing both 0.2 g NiO and 1.0 g Fe_2O_3 together Na_2O 25% (111), Na_2O 30% (112), Na_2O 35% (113)

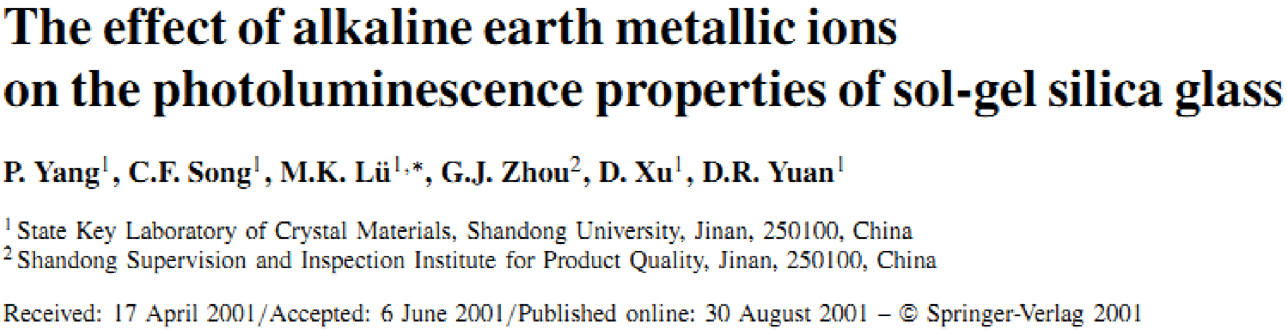
- Eight absorption bands at 205, 230, 330, 380, 450, 565, 630 and 860 nm were observed in the absorption spectrum given by the glass of composition SiO_2 85%, Na_2O 15%, NiO 0.2 g, Fe_2O_3 1.0 g, while nine absorption bands at 205, 230, 335, 380, 450, 510, 570, 640 and 750 nm were observed in the absorption spectrum given by the glass of the composition SiO_2 75%, K_2O 25%, NiO 0.2 g and Fe_2O_3 1.0 g.

-The position of the absorption bands at 205, 230, 330, 380, 450, 565, 630 and 860 nm in the glass of the composition SiO_2 85%, Na_2O 25%, NiO 0.2 g, Fe_2O_3 1.0 g changed to 210, 238, 338, 390, 460, 580, 650 and 890 nm, respectively,

- In the glass of the composition SiO_2 65%, Na_2O 35%, NiO 0.2 g, Fe_2O_3 1.0 g; while the position of the absorption bands at 205, 230, 335, 380, 450, 510, 570, 640 and 750 nm in the glass of the composition SiO_2 75%, K_2O 25%, NiO 0.2 g,Fe_2O_3 1.0 g changed to 210, 240, 360, 390, 460, 520, 580, 647 and 760 nm, respectively, in the glass of the composition SiO_2 65%, K_2O 35%, NiO 0.2 g, Fe_2O_3 1.0 g.

- The intensity of the absorption bands generally increased with the gradual progressive increase in the alkali oxide content.

- The visual color of the glasses studied was pale yellowish brown.



The effect of alkaline earth metallic ions on the photoluminescence properties of sol-gel silica glass

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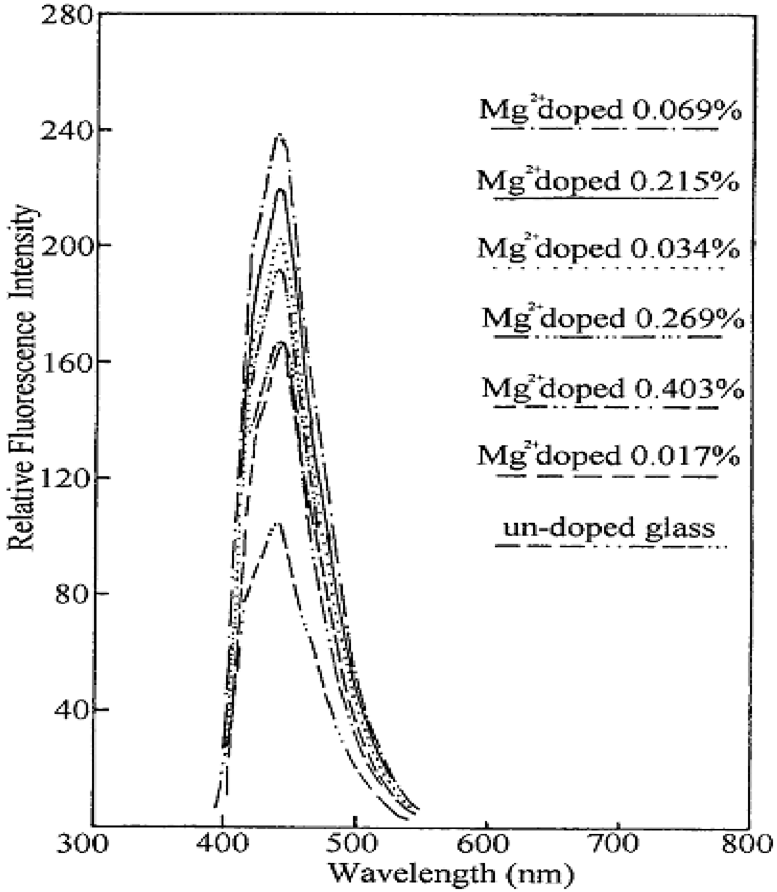


Fig. 12 The emission spectra of Mg^{2+}-doped and undoped samples (λ_{ex} = 380 nm)

- When the impurity mole ratios of Mg^{2+} were less than 0.069%, the relative fluorescence intensity of the Mg^{2+}-doped glass sample increased with increasing impurity mole ratios of Mg^{2+}.

- When the impurity mole ratios of Mg^{2+} were greater than 0.069%, the relative fluorescence intensity of the Mg^{2+}-doped glass samples decreased with increasing impurity mole ratios of Mg^{2+}.

- Relative fluorescence intensity of the Mg^{2+}-doped sample was about 2.5 times that of the pure glass sample. Mg^{2+} ions remarkably enhanced the fluorescence intensity of the sol-gel glass.

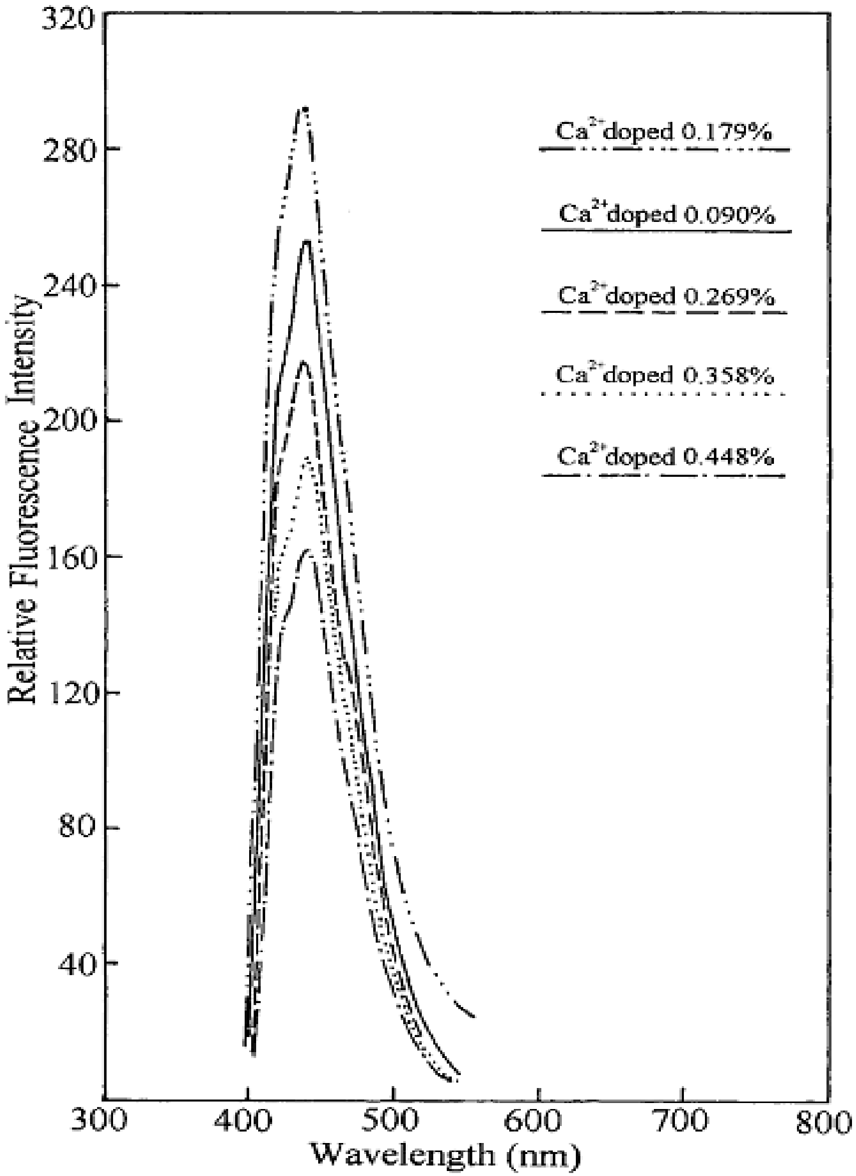


Fig. 12 The emission spectra of Ca^{2+}-doped and undoped samples (λ_{ex} = 380 nm)

-When the impurity mole ratio of Ca^{2+} was 0.179%, the relative fluorescence intensity of the Ca^{2+}-doped sample was about 3 times that of the pure glass sample.

- When the impurity mole ratios of Ca^{2+} were less than 0.179%, the relative fluorescence intensity of the Ca^{2+}-doped glass samples increased with increasing impurity mole ratios of Ca^{2+}.

- When the impurity mole ratios of Ca^{2+} were greater than 0.179%, the relative fluorescence intensity of the Ca^{2+}-doped glass samples decreased with increasing impurity mole ratios of Ca^{2+}.

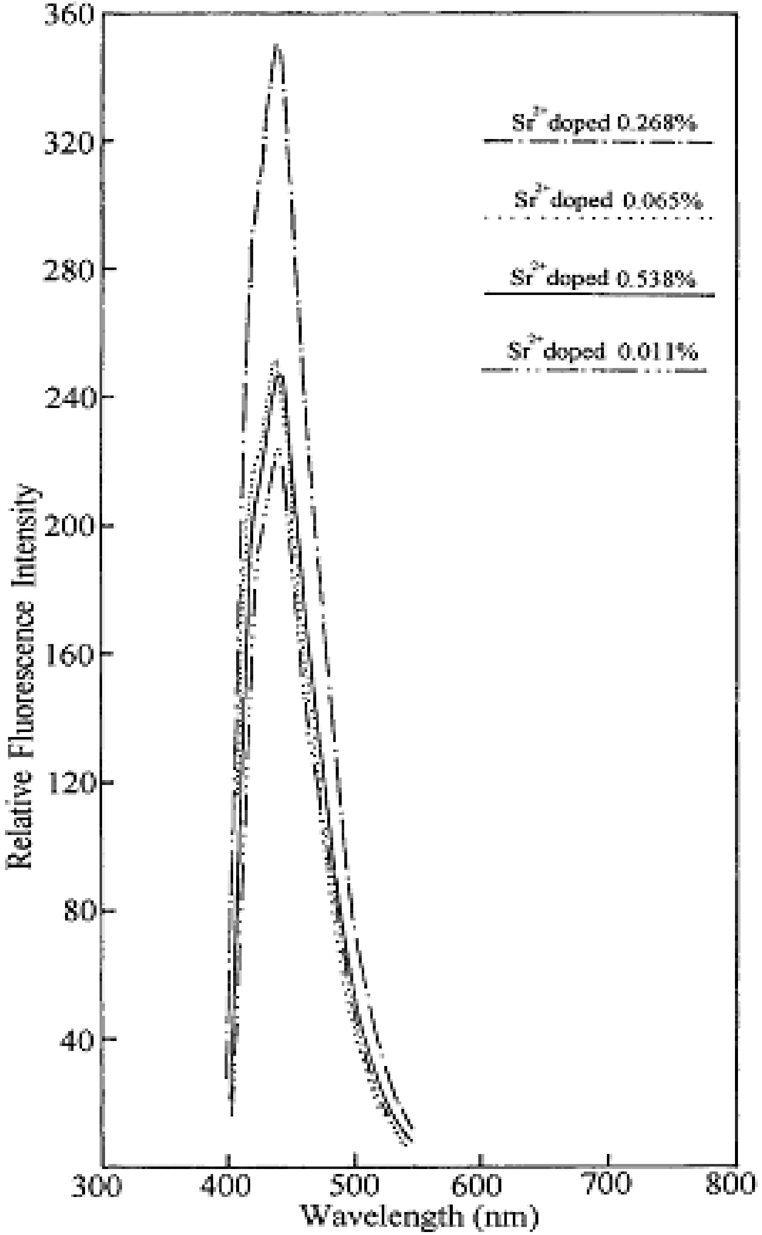


Fig. 13 The emission spectra of Sr^{2+}-doped and undoped samples (λ_{ex} = 380 nm)

-The effects of Sr^{2+} and Ba^{2+} ions on the luminescent properties of sol-gel silica glasses were almost the same as those of Mg^{2+} and Ca^{2+} ions.

- However, the relative fluorescence intensities of Sr^{2+}-and Ba^{2+}- doped samples were higher than those of the Mg^{2+}-and Ca^{2+}-doped samples.

- When the impurity mole ratio of Sr^{2+} was 0.268%, the relative fluorescence intensity of the Sr^{2+}-doped sample was about 4 times that of the pure glass sample.

- When the impurity mole ratio of Ba^{2+} was at 0.448%, the relative fluorescence intensity of the Ba^{2+}-doped sample was about 4 times that of the pure glass sample.

- The luminescent properties of these materials are very sensitive to impurities. As impurities can lead to non-radiative combination during the luminescent process, the relative fluorescence intensity decreased with increasing doped mole ratios of alkaline earth metallic ions when mole ratios of doped alkaline earth metallic ions exceed certain values (e.g. Mg^{2+}, 0.069%; Ca^{2+}, 0.179%; Sr^{2+}, 0.268%; and Ba^{2+}, 0.448%).

- To date, mechanisms have been proposed to explain the luminescent mechanism of doped sol-gel silica glasses: a luminescent center model and a structure defect model. The luminescent center model explains that the emission change is due to the formation of a luminescent center in glass doped with other metal ions.

- The structure defect model proposes that the PL of sol-gel glass comes mainly from the Si dangling bonds, oxygen vacancies and surface defects etc.

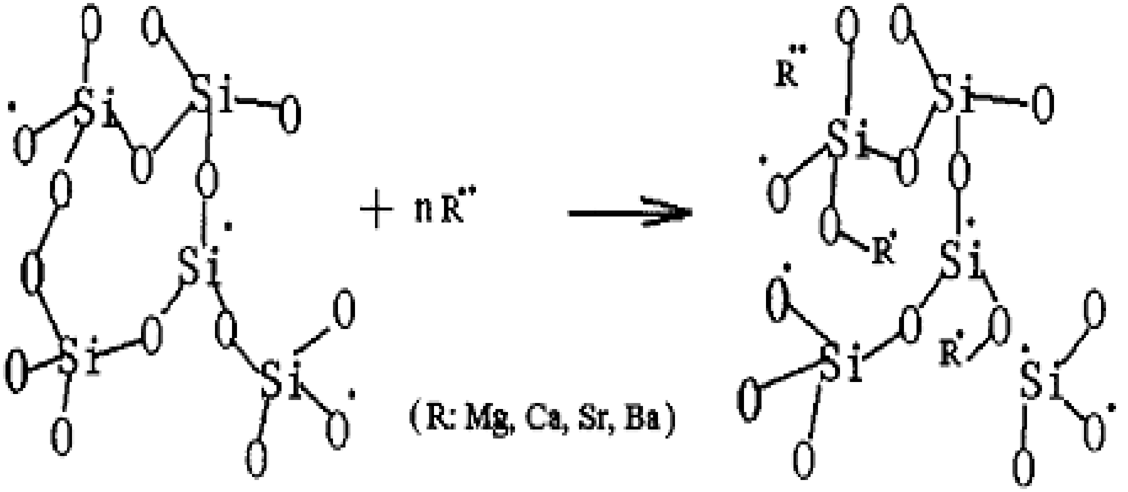
- The structure defects are formed because the hydrolysis condensation polymerization reaction does not go to completion. Therefore, there are a large number of defects in sol-gel silica glasses. The doped metal ions affect the concentration of the defects.

- They can considered be as interstitial ions in the sol-gel SiO_2 glass network. They reside on the surface of nanometer-scale holes in the porous sol-gel silica glass. They can change the formation and conversion of defects in the silica network.

- In the case of the Mg^{2+}-, Ca^{2+}-, Sr^{2+}-and Ba^{2+}-doped sol-gel silica glasses, some Si–O bonds are broken during the process of forming the silica network. Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} may be associated by non-bridging oxygen.

- Therefore, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions lead to an increase in Si dangling bonds and oxygen vacancies in the sol-gel silica glass structure.

- Therefore, these ions can increase the concentration of the structural defects in sol-gel silica glasses (for example, Si dangling bonds, oxygen vacancies):



- Increasing the concentration of composite structural defects in sol-gel silica glasses doped with alkaline earth metallic ions increases the radiative combination in luminescent processes.

- Thus, the relative fluorescence efficiencies of the samples doped with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} are remarkably increased compared with that of the undoped sample.

- Since there are more outer electrons in Sr and Ba atoms than in Ca and Mg atoms, and the energy of these outer electrons is high, the properties of the composite defects of Sr^{2+}-and Ba^{2+}-doped samples are more active than those of Mg^{2+}-and Ba^{2+}-doped samples.

- More electrons and holes are easily excited in the composite defects of Sr^{2+}-and Ba^{2+}-doped samples. The radiative combinations of luminescent processes in Sr^{2+}-and Ba^{2+}-doped samples are increased.

- Therefore, the relative fluorescence intensities of Sr^{2+}-and Ba^{2+}-doped samples are higher than those of Mg^{2+}-and Ba^{2+}-doped samples.

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

S P SINGH*, AMAN and ANAL TARAFDER

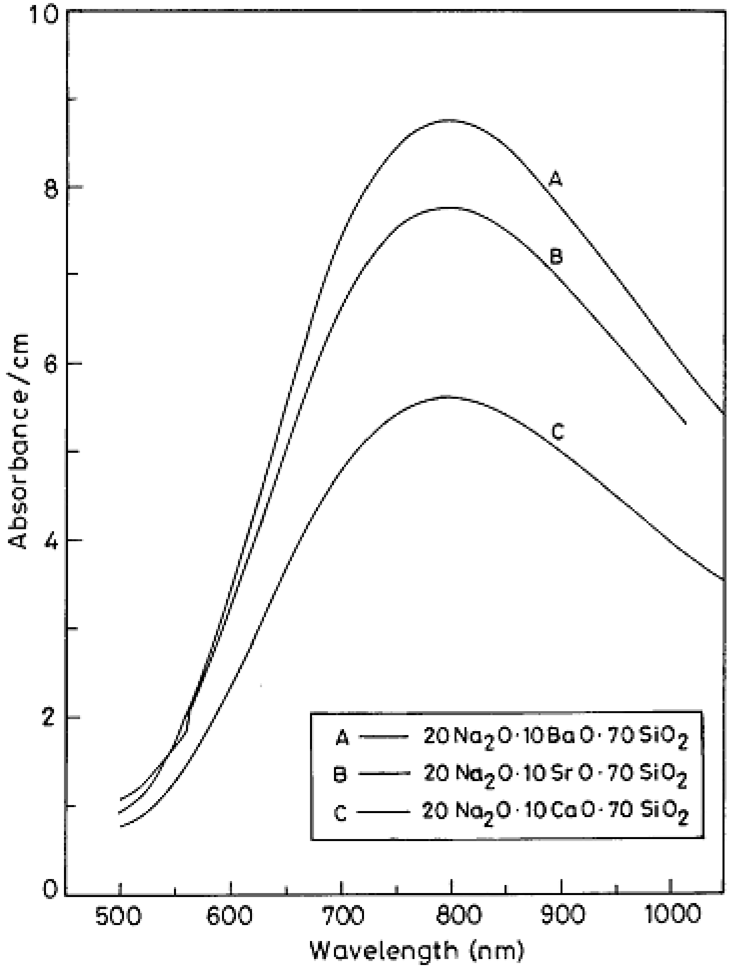


Fig. 14 Optical absorption characteristic of Cu^{2+} ion in ternary silicate ($20Na_2O$-$10RO$-$70SiO_2$, where R = Ca, Sr, Ba) glasses.

- 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 Cu^{2+} ion in silicate glasses are centred at around 796 nm.

- The absorption intensity calculated was found to increase with increasing ionic radii of alkaline ions in order of $Ca^{2+} < Sr^{2+} < Ba^{2+}$ ions.

- Glass basicity: $Ca^{2+} < Sr^{2+} < Ba^{2+}$ ions.

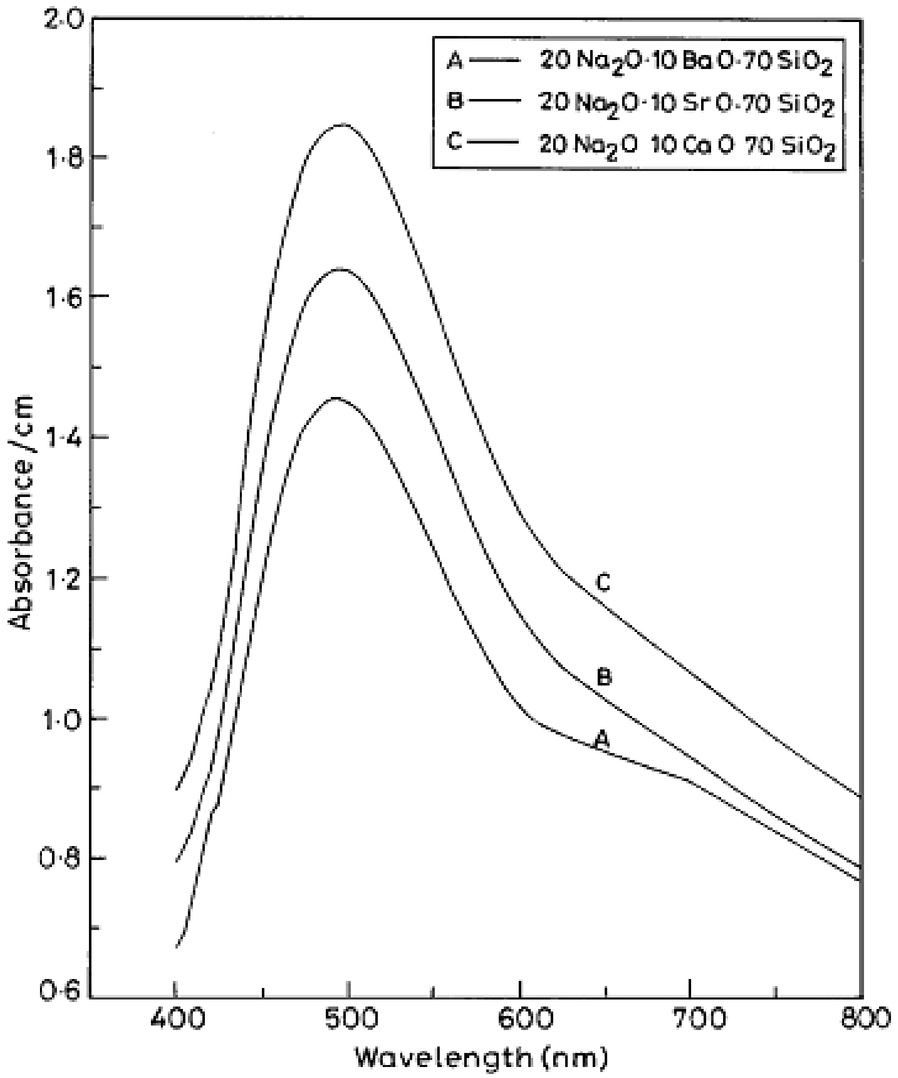


Fig. 15 Optical absorption characteristic of Cu^{2+} ion in ternary silicate ($20Na_2O$-$10RO$-$70SiO_2$, where R = Ca, Sr, Ba) glasses.

-Show the single broad absorption band due to Mn^{3+} ion in silicate glasses. This peak has been assigned due to spin allowed transition from $^5E_g \rightarrow {}^5T_{2g}$ energy levels (494 nm) in an octahedral symmetry of Mn^{3+} ion in glass.

-The value of absorption intensity was found to be higher contrarily with decreasing ionic radii of alkaline earth ions in order of $Ba^{2+} > Sr^{2+} > Ca^{2+}$ in the glass.

- 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 $Ba^{2+} > Sr^{2+} > Ca^{2+}$ 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.

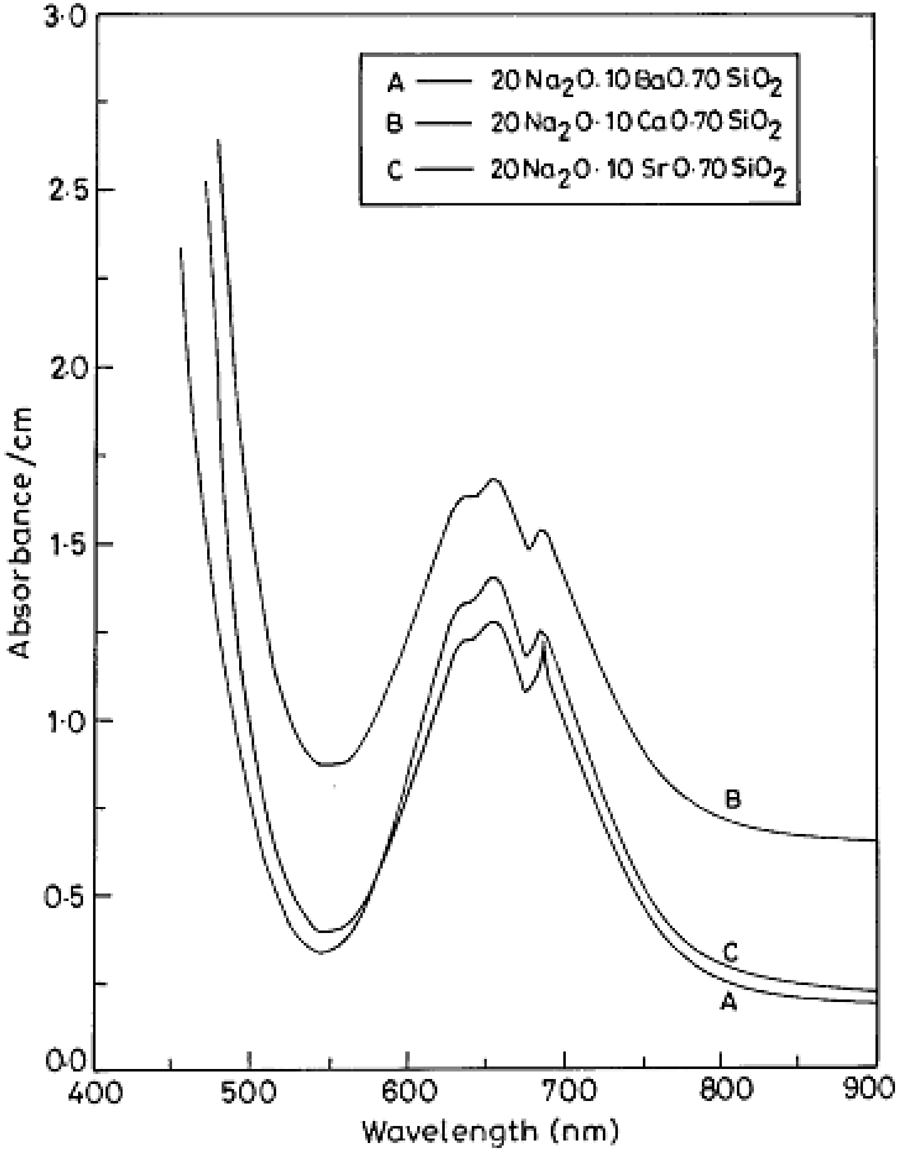


Fig. 16 Optical absorption characteristic of Cr^{2+} ion in ternary silicate ($20Na_2O$-$10RO$-$70SiO_2$, where R = Ca, Sr, Ba) glasses.

- Show two strong absorption bands due to Cr^{3+} ion at around 655 and 685 nm in 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 co-ordination of Cr^{3+} ion in glass.

- The absorption intensity was found to increase with decreasing ionic radii of alkaline earth ions in order of $Ba^{2+} > Sr^{2+} > Ca^{2+}$

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Next week

Course Outine:

Week 10: Glass composition, structures and applications (2)

- Boric Glass
- Alkali-and Alkali-Earth Boric Glass
- *Case studies from international publications*