

Optical properties of coloured transparent alumina gel monolith glasses

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Abstract. Optical properties of transparent alumina prepared through gel process at room temperature and coloured with dopants have been studied. The absorption bands, molar absorptivity, effect of concentration and the dependence of oxidation state of copper on the copper content and water content are similar to the random network glasses. The ultra-violet absorption edge at lower energies confirm the disordered nature of the transition phase aluminas γ and δ . The absorption bands in the visible suggest the octahedral symmetry of oxygen around aluminum.

Keywords. Optical properties; transparent alumina; coloured alumina gel; alumina gel; xerogels; transparent ceramic.

1. Introduction

Gel-processed materials have evoked considerable interest in recent years owing to the novel features they exhibit. It has become feasible to prepare transparent ceramics at low temperatures which otherwise could be produced only at high temperatures and pressures. A transparent porous alumina was first prepared by Yoldas (1975) using the gelation process initiated by Roy (1969). A gel-processed silica glass was found to have certain properties different from the melt-quenched conventional silica though both exhibited a random network arrangement of atoms (Yoldas 1982). Alumina prepared from the metal organic alkoxide was found to be polymeric and partially crystalline (Saraswati *et al* 1987). Transition metal ions incorporated in materials show absorption in the visible and have been used as probes for the local structure (Sigel 1977). The alumina gels could be easily coloured at room temperature with iron, copper or organic dyes. The optical properties of these transparent and coloured gel monoliths have been studied for the first time in the ultraviolet, visible and near-infrared regions and are reported in this paper. The colour centres identified due to copper can also help in the study of photochromic silver halide glasses in which copper is added to improve the sensitivity.

2. Experiment and results

2.1 Preparation of the gel monoliths

The gel was prepared by hot hydrolysis and polycondensation of aluminum isopropoxide using a procedure described by Yoldas (1975). The microstructure and properties of the gel depend upon the process parameters such as the amount of water added for hydrolysis, the nature and amount of the acid catalyst. After several

trials for obtaining crack-free clear gel monoliths, we found the best molar ratio for alkoxide:water:acid to be 1:100:0.3. The slow evaporation of the gel in a flat dish produced monolithic glass-like discs. These are called xerogels.

A drop of a dye solution coloured the gel blue or red depending on the dye added. Transition metal ions could be introduced either as salts or metal powders. Pure copper or iron powders were added at room temperature. They took about 48 hr to colour and penetrate into the layers of boehmite (alumina gel). Iron-doped gels were yellow whereas the copper-doped were colourless, blue or green depending on the concentration of copper and the amount of chloride ions in the gel (indicated by the pH value). The dopant concentration was analysed spectrochemically and is given in table 1.

2.2 Transmission and absorption in the xerogels

A double-beam Hitachi spectrophotometer was used for recording the transmission and absorption in the IR, visible and UV region of wavelengths (200–2600 nm). No polishing or surface treatment was done, or required, as the surface was naturally smooth and glossy owing to the fine size of particles and pores. The thickness of samples ranged from 0.1 to 0.5 mm. Scattering losses were found to be negligible as seen from the difference spectra with a similar sample in the reference beam. The doped gels were found to be less transparent as compared to the undoped alumina. Physical properties like density, X-ray diffraction, IR absorption and microhardness remained unaffected within experimental errors and compared well with earlier

Table 1. Molar absorptivity in doped alumina gels.

Dopant colour	Conc. ppm	Thickness (mm)	Abs edge (nm)	Abs max (nm)	ϵ litre mol ⁻¹ cm ⁻¹
Fe, d^5 Yellow	8000	0.36	340	480	3800 46
Cu, d^{10} Colourless	1000	0.24	240		10 ⁴
Cu, d^9 Light blue	5000	0.2	360	730	54.9
Cu, d^9 bluish green	8540	0.2	330	840	480
Cu, d^9 green	8550	0.2	360	880	3900 580
Cu, d^9 acidic	6900	0.5	330	390	2400 78
Cu, d^9 Turquoise	6900	0.5	330	730	110
Cu, d^9 heated 400°C γ phase	6900	0.5	330	720	2400 70
Cu, d^9 heated 950°C δ phase	6900	0.44	240	285 390	2900 280 80
Sample, 2 exposed for 30 min, at 100°C Yellow	1000	0.24		380 880	20 76

measurements (Saraswati and Rama Rao 1986). The absorption edge, measured at $T \sim 0.1\%$, was found to have shifted to longer wavelengths in the doped xerogels. The absorption edges in the UV, the absorption bands in the visible and the molar absorptivity calculated are all listed in table 1. Figure 1 shows the spectra in the dye doped xerogel. The colourless, copper-doped xerogels showed no absorption in the visible for concentration of copper less than 1000 ppm, whereas the green and blue xerogels (concentration = 6900 ppm) exhibited a broad band centred between 720 and 900 nm depending on the concentration of copper ions and the chloride content. Figure 2 exposes the results. Absorption band shifts towards longer wavelength with increase in copper and chlorine content. The chloride ion comes from the hydrochloric acid, which is added to catalyse the gelation of boehmite. The pH value of the acidic gels were between 2 and 4 and the resultant xerogel was yellowish green, the yellowness increasing with increasing chlorine content. In the visible, one more band at ~ 380 nm appears with increasing chlorine content. Two more weak absorptions at 510 and 470 nm have been observed in some xerogels with copper. The lack of colour and the absence of absorption for ion concentration of copper (< 1000 ppm) was attributed to the monovalent state of copper, which has an electronic configuration d^{10} and hence cannot have a $d-d$ transition in the visible.

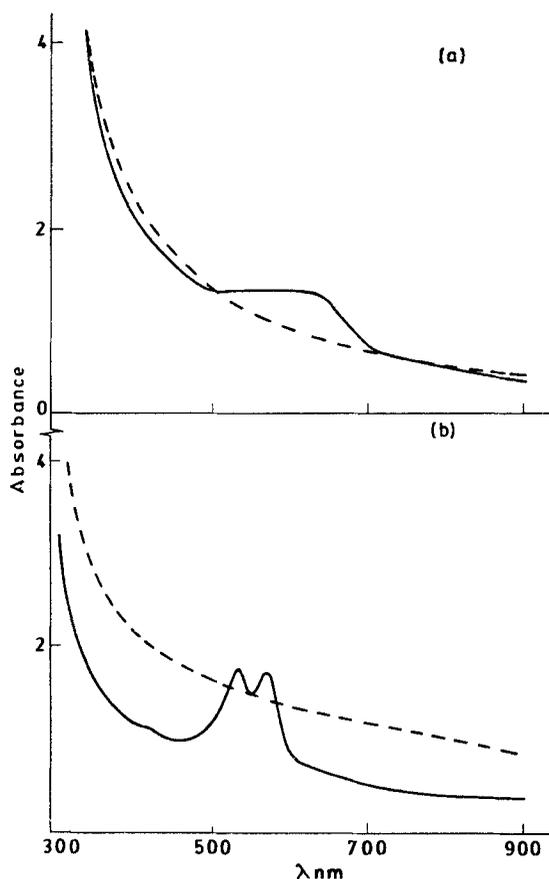


Figure 1. Absorption in boehmite xerogel doped with a. Blue dye. b. Red dye. The dashed curve is for the $\gamma\text{-Al}_2\text{O}_3$ phase in the same, heated to 700°C .

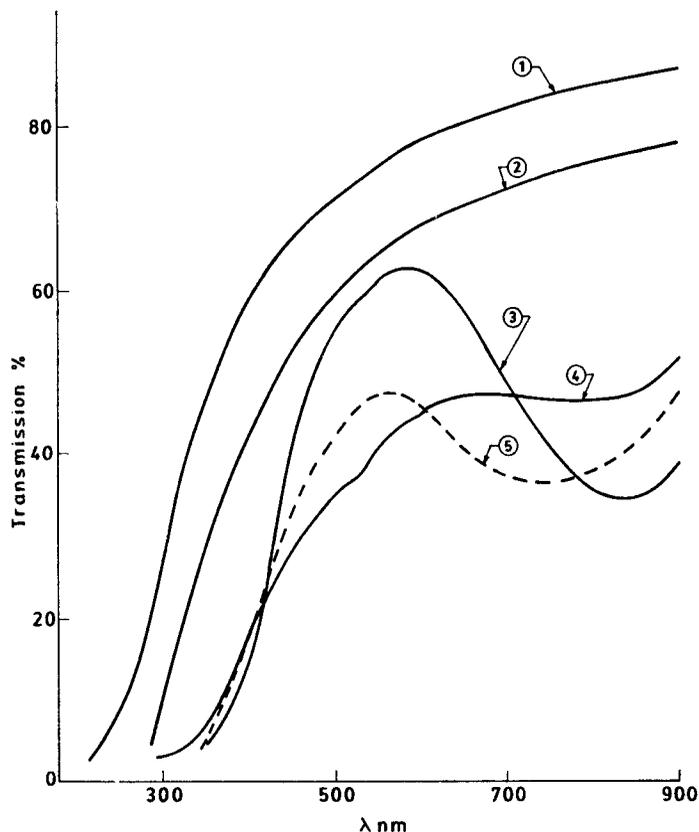


Figure 2. Influence of copper concentration on transmission spectra. Copper content of (1) and (2) < 1000 ppm, (3) 8550 ppm (4) 5000 ppm and (5) sample 3 heated at 500°C for 10 hr.

On slight heating (60–100°C), under an infrared lamp the xerogel turned bright yellow and the glow lasted for a long time after switching off the heating. The spectrum taken in the 'yellow state' of the xerogel for different duration of heating is indicated in figure 3a. The overall transmission improved considerably from 17 to 46% with dehydration and also the oxidation state changed to bivalent copper (d^9) as seen by the absorption maximum at ~ 800 nm. When the chlorine content is greater on dehydration, another peak at 380 nm appears. The dehydration effect can also be seen at room temperature. Light green xerogels turn yellowish in the desiccator.

In the near-infrared region, from 1000 to 2600 nm, all the doped xerogels exhibit similar spectra. The transmission is better and two absorption bands at ~ 1.4 and $1.9 \mu\text{m}$, due to the combinational overtones from OH^- ions of the water molecules are observed.

2.3 Transition phases of the xerogels

The xerogel of alumina is boehmite, AlOOH . On heating in air, the transition phases of alumina were obtained. The γ alumina phase is formed at temperatures between 400–800°C and the δ phase at 900–1000°C. The crystalline, α phase was obtained

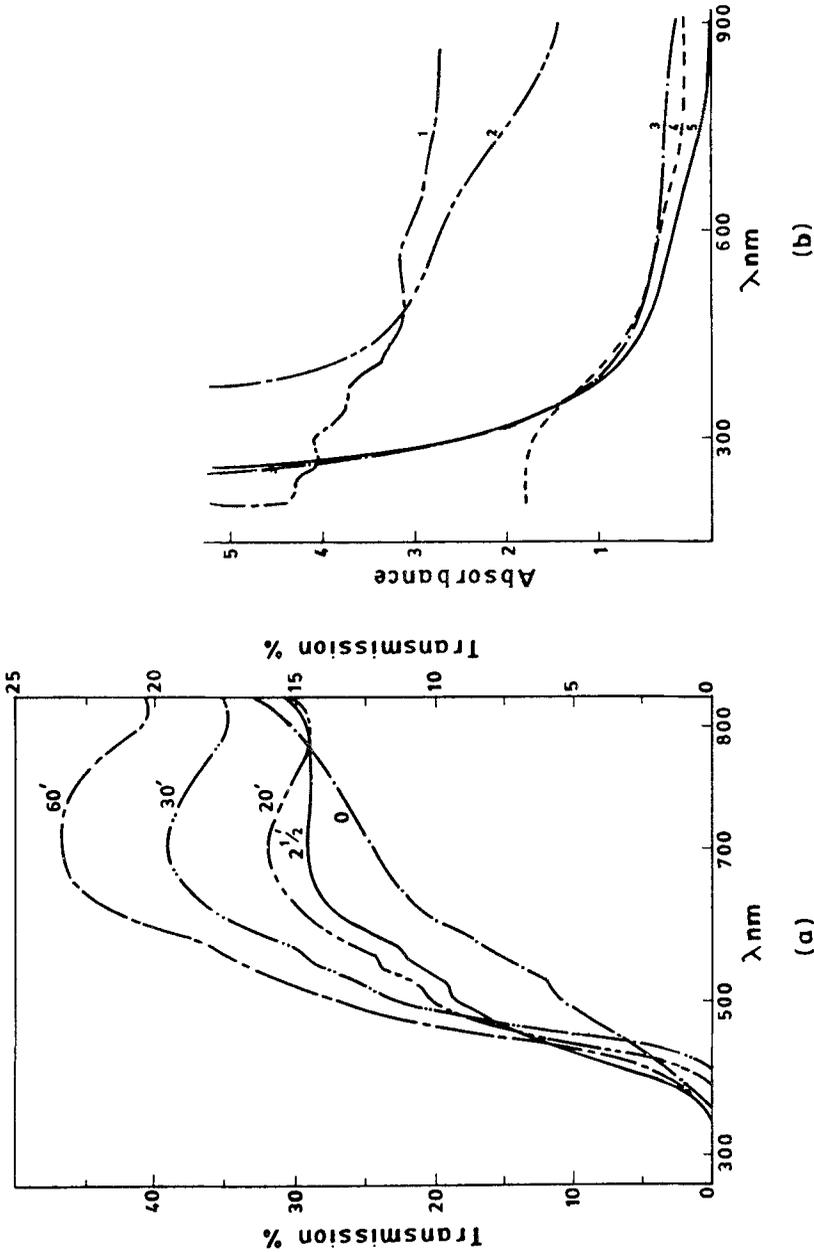


Figure 3. a. Change in transmission spectra on heating a colorless copper doped gel at 100°C. Numbers denote the duration of heating in minutes. b. Absorption in the undoped alumina (1) Sintered pellet, (2) δ -Al₂O₃ (1000°C), (3) γ -Al₂O₃ (600°C), (4) boehmite and (5) γ -Al₂O₃ (800°C).

above 1200°C. The xerogels did not crack when the heating rate was 300° per hour. The xerogels remained transparent upto 950°C and turned opaque above 1000°C. Figure 3b shows the shift in the absorption edge in the UV in the undoped alumina xerogel. For the doped gels, the trend was almost the same. On heating the colours changed. The dyes lost the colour at 700°C, may be due to the decomposition of organic molecules. All the copper gels were pale blue above 900°C. The transmission in the visible is not very different, but considerably improved in the near infra region owing to the absence of absorption due to the water molecules (figure 4). The UV absorption edge in the γ phase did not vary much from the boehmite phase in the doped gels but the δ phase (950°C) was very different. For all the low concentration doped materials the edge was at a longer wavelength, 360 nm and had a kink at \sim 550 nm (figure 3b) which could be due to the mixture of δ and another phase, say θ or α . The microstructure and X-ray diffraction also support the mixture of another phase in these. For a turquoise, Cu doped gel (6900 ppm) in the δ phase, a sharp peak at 285 nm and broad peak at 380 nm also appeared. The 285 nm peak disappeared with time (in a week) and this could be due to the instability of the monovalent copper. The 380 nm peak is due to a Cu-Cl complex (similar to D band of Paul). Figure 5 shows these peaks. Heating at 1300°C for 12 hr, all the doped xerogels became white, thin, more dense and crystalline (α phase). The xerogels became opaque due to the increasing size of the inhomogeneities. In the absorption (the spectra was noisy) weak bands at 585, 420, 290 and 240 nm were observed in all xerogels, irrespective of dopant. The gel also lost its smooth, glossy appearance.

On heating at 1500°C for 90 hr, the gel pieces became \sim 78% dense. The absorption could not be recorded. The microstructure showed the formation of fine grains of micron size. In a sintered pellet weak peaks at 560, 375 and 300 nm were observed. The absorption edge also shifted to higher energies as expected.

2.4 Calculation of the molar absorptivity

The light beam incident on a specimen can be reflected, scattered, absorbed and transmitted. As mentioned earlier, the scattering as seen from the difference spectra was negligible. Spectrophotometers record the absorption as percentage transmission or optical density, OD. The attenuation of light on passing through a thickness X of the material is given by $a = 2.303 \text{ OD } X^{-1}$ where a is the absorptivity. The

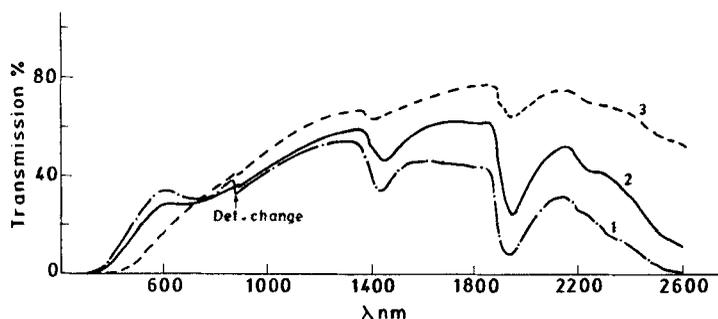


Figure 4. Transmission spectra in a turquoise, Cu-doped alumina; (1) boehmite phase, (2) γ phase and (3) δ phase.

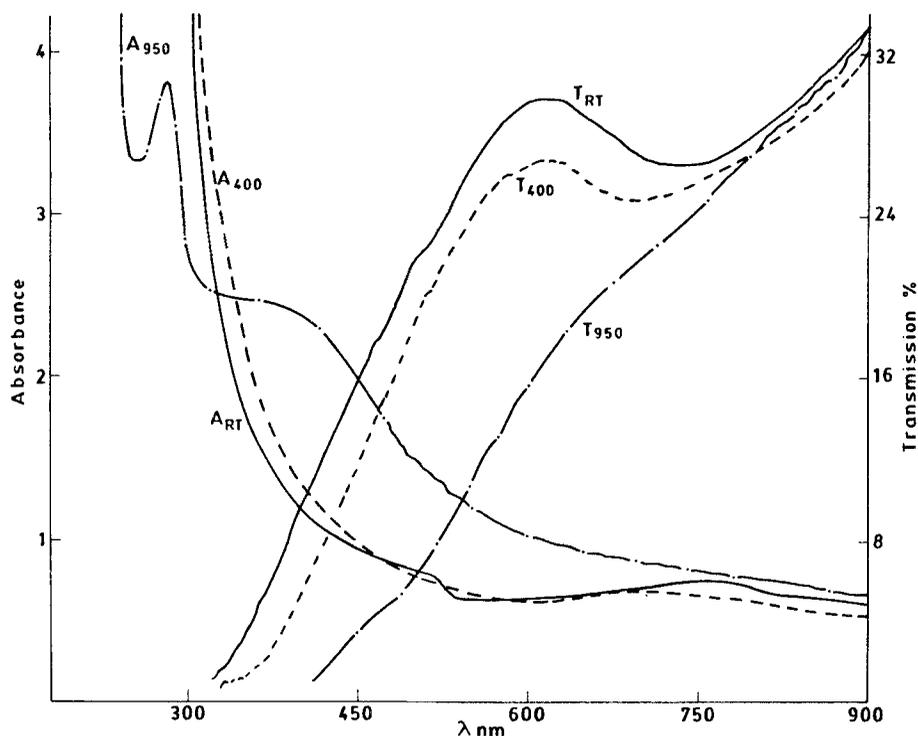


Figure 5. Absorption in the turquoise sample showing the peaks at 285 and 380 nm.

optical absorption produced by a given concentration of dissolved impurities is expressed (Wong and Angell 1976) in terms of molar absorptivity ϵ as,

$$\epsilon = 2.303 \text{ OD } C^{-1} X^{-1},$$

where C is the concentration of the absorbing ion in g moles per litre. Hence the unit of ϵ is litres $\text{mol}^{-1} \text{cm}^{-1}$ throughout.

To get a correct idea of ϵ , very thin samples must be used. As ceramic samples are brittle we used samples $\sim 0.15\text{--}0.5$ mm thick. Thin films of the gel solution coated on glass showed that the variation due to thickness was negligible. The calculated molar absorptivity are in table 1. As it is proportional to the concentration, one should expect a linear variation. This is found to be exactly so. With the presence of chloride ions, the absorptivity will be greater as ascertained from observations.

3. Discussion

Our X-ray diffraction results in the xerogels showed broad diffuse bands and a partially crystalline structure as in a polymer.

3.1 Absorption in the UV region

The ultraviolet absorption in the alumina xerogel arise from (i) absorption intrinsic to the electronic excitation of the Al-O network and (ii) absorption from dopants,

especially the charge transfer spectra of transition metal ions. Xerogel of boehmite consists of molecules that form long chain polymers with the hydroxyl group at the ends of chain. Aluminum atom is in the octahedral environment of oxygen (Saraswati *et al* 1987). As the gel is porous ($\sim 60\%$ porosity) with large surface area, the unsaturated bonds give rise to tail states in the valence and conduction band and lower the energy gap. Impurities, especially transition metal ions, lower it further. Hence, on both accounts, the absorption edge in the ultraviolet will be at longer wavelengths and is observed to be so (table 1). The absorption edge results from the excitation of valence band electrons to unoccupied high energy states such as exciton or conduction band levels. For crystalline corundum, the main absorption edge was found to be 8.55 eV (Arakawa and Williams 1968) and 6.8 eV for the anodized film (amorphous). Our results also show that in the crystalline phase the edge moves to higher energies whereas in the γ and δ phases they are at 5.16 eV and 3.75 eV. Thus we have evidence that the γ and δ phases are disordered. In the δ alumina phase mixture of other phases had been inferred from microstructure. Furthermore, the coarsening of the crystallites and the increased covalency with change in the oxygen network rearrangement, can shift the edge to longer wavelengths. The transition metal ions like Fe and Cu also shift the edge lower to 3.65 eV due to the tail end defect states near the bands. In the δ alumina phase in one of the copper-doped samples the absorption bands at 285 nm and 380 nm could both be due to the charge transfer transitions. The 380 nm band is dependent on the presence of chlorine and can be attributed to π - d charge transfer, the transfer of an electron from filled ligand orbital. The molar absorptivity was higher for the 285 nm band, which, because of its instability could be attributed to Cu^+ charge transfer absorption. From these, again the octahedral coordination of oxygen around aluminum becomes evident.

3.2 Visible absorption

When transition metal ions are introduced in a material, the energy levels of the free ions are split and shifted by the electrostatic fields of the nearest neighbour anions, the ligands. As the field of the metal ion falls off rapidly with distance (r^{-5}) only adjacent interactions need to be considered (Sigel 1977). Hence broad features of crystalline and noncrystalline materials would be similar as long as the short range interactions are similar. Generally, octahedral or tetrahedral coordination by the ligands are noticed with probable distortions of symmetry configuration. When the transition metal ion has an incomplete d shell, as for Fe^{3+} (d^5) and Cu^{2+} (d^9) transition between the crystal field split d levels are possible and these are responsible for the optical absorption band. All the d - d transitions are forbidden by Laporte rule. However, the transitions are weakly allowed if mixing of the $3d$ band with metal $4p$ or ligand p orbitals can take place. The topological disorder in a noncrystalline network can make this possible. The forbidden transitions have weak extinction coefficients (or molar absorptivity). In the tetrahedral coordination, more of mixing is possible compared to octahedral resulting in an increased intensity of absorption. The energy of the absorption band is also dependent on the charge state of the metal ion, coordination and nature of ligand atoms. Thus, local structural information can be gathered from absorption spectra, which normally occurs in the visible for internal transitions between d electron levels. Boehmite gel with iron showed an

absorption maximum at 480 nm ($\epsilon = 46$) comparing with the value of Bamford (1961) for trivalent Fe in the octahedral environment of oxygen atoms.

The molar absorptivity of copper widely varied depending on the concentration of copper and chloride ion. Paul (1970) had studied in detail the absorption of Cu^{++} and Cu^+ in aqueous solutions containing HCl and borate glasses containing NaCl. We have observed that (i) with an increase in the copper concentration the bivalent state of copper is preferred. The absorption maximum shifts to longer wavelengths from 720 to 840 nm. The molar absorptivity increase is linear with concentration; (ii) with dehydration, monovalent copper ion becomes unstable and the oxidation state changes to bivalent and (iii) with an increase in the chloride content the color of the gel changes, absorption is more intense and shifts to near infra at 900 nm. Another peak at 380 nm also appears.

Interestingly enough most of these observations were noted for copper in glasses by Paul (1970). The influence of chloride ion is very strong and was attributed to the formation of chlorocomplexes. The layered structure of boehmite and the porosity of material with large surface area have enabled the xerogel to form complexes with H_2O , Cl^- and O^{--} ligands. These could also be responsible for the other weak absorptions seen at 510 and 470 nm. The complexes suggested were $[\text{Cu}(\text{OH})(\text{H}_2\text{O})_5]^{1+}$, $[\text{CuCl}(\text{H}_2\text{O})_5]^{1+}$, $[\text{CuCl}_2(\text{H}_2\text{O})_4]$, etc. The shift of the absorption maximum to higher wavelengths was suggested as due to a reduction in copper-halide distances. The enhanced intensity is attributed to a larger distortion of the octahedron. Cu^{++} is a d^9 ion and experiences a strong Jahn-Teller distortion. Hence the coordination polyhedra is usually a tetragonally-distorted octahedron. The transition ${}^2\Gamma_3(D) \rightarrow {}^2\Gamma_5(D)$, results in an asymmetric band around 800 nm and usually consists of 2 or 3 overlapping symmetrical bands. This absorption is more or less a signature to the presence of bivalent copper. Cu^+ being a d^{10} ion is not expected to have ligand field band in the visible and no absorption due to this in the range 300–1400 nm was observed. Cu^+ has charge transfer (oxide-copper) spectrum at ~ 240 nm, similar to Cu^{++} and it is not possible to identify them separately.

In the $\gamma\text{Al}_2\text{O}_3$ phase, the absorption band was centred around 720 nm and in the $\delta\text{Al}_2\text{O}_3$ phase, the ultraviolet range peaks at 285 nm, 390 nm and the edge at 240 nm could be observed. These indicate the penetration of copper into the matrix, possibly at the Al sites, leading to the conclusion that Al is octahedrally surrounded by O ions atleast upto the γ phase. The structural investigations had also shown (Saraswati *et al* 1987) that the $\gamma\text{Al}_2\text{O}_3$ was cubic and octahedral arrangement was evident from IR.

3.3 Infrared region of absorption

The optical absorption of oxide glasses in the near and middle region is determined by collective vibration of molecules and atoms in the network. Absorption correspond to transition in the vibrational energy levels. The absorptions at 1.44 and 1.94 μm are vibrational overtones and combinations linked to the OH^- ion of the absorbed water mols at the surface. In the $\gamma\text{Al}_2\text{O}_3$ and $\delta\text{Al}_2\text{O}_3$ these bands were again observed, slightly shifted and with a shoulder at 1.42, 1.38, 1.93 and 1.88 μm . As the shift is also to lower wavelengths (higher energies) a possibility is that these are bonded and intrinsic to the $\delta\text{Al}_2\text{O}_3$ phase as had been suggested earlier by Leonard *et al* (1967).

4. Conclusions

From our results on the optical transmission and absorption in the doped gel monolith glasses, we arrive at the conclusions that (i) the transition phase aluminas $\gamma\text{Al}_2\text{O}_3$ and $\delta\text{Al}_2\text{O}_3$ are disordered, (ii) γ and δ aluminas could have water associated with them intrinsically and (iii) the optical behaviour of copper doped gels are identical to those of the random network glasses. The concentration of copper affects the oxidation state, absorption wavelengths and intensity. The chloride ions influence the wavelength and intensity of absorption of copper. Desorption of water affects the stability and oxidation state of copper.

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