Structural studies of transition metal doped soda lime silicate glass using deconvolution method

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ABSTRACT

Deconvolution method is applied to infrared (IR) absorption spectra of some prepared undoped and transition metals doped soda-lime-silicate glasses in the region of 400-4000 cm^{-1}. IR spectra were analyzed to determine and differentiate the various vibrational modes by applying the deconvolution method to the IR spectra from which the first sight reveals close similarity between the different transition metals (TM's) -doped samples, but careful inspection indicates some minor differences depending on the type of TM ions. These observed data are correlated with the similarity of the 3d orbitals in the neutral atoms and when the atoms are ionized, the 3d orbitals becomes more stable than the 4s orbitals.   © 2009 Trade Science Inc. - INDIA

KEYWORDS

1. INTRODUCTION

Vibrational spectroscopy has been employed over the last decades to investigate the structure of glasses and specifically the identification of the main structural groups[1-4]. Infrared spectroscopy, in particular, was proven very useful because it provides a means to determine local structure of building units which constitutes the glass network, some of the properties of the sites hosting the modifying metal cations, and the interactions between charge carriers and network segments[5].

Over the full scale, quantitative IR spectroscopy comprises two stages of spectrum treatment implying a reconstruction of the spectra and the description of the spectrum under study in terms of individual band parameters.

Over the last few decades, great importance has been devoted for glass doped with transition metal ions because of the intensive spectroscopic properties of their 3d electrons[6,7]. The physical properties, viz, electrical, optical and mechanical properties[8,9] of various transition-metal ions doped glasses have been under investigation in recent years in view of their technological applications especially in lasers, phosphors, solar energy converter, plasma display panels and in a number of electronic devices.

The local network structure and formation of glass, though being studied for decades, are still puzzling problems[9]. Liquids or melts quenched with different cooling rate, or having different thermal histories, provide glasses with different structures and properties[10]. The local structure of silicate glasses is rather well known, the "building units" are similar to that of the crystalline

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counterparts (SiO_4 tetrahedra), but at intermediate range, the tetrahedra are linked together in a disordered or non-periodic fashion with a bound angle distribution, which has been shown to depend on thermal history in glassy silica[11]. Modifiers induce breaking of inter-tetrahedral bounds. This phenomenon is often referred to as 'depolymerization' of glassy network. Not much information is known about the structure at larger scale[10].

Soda lime silica (SLS) glasses have been known for their high insulating properties[12], good and acceptable mechanical[9,12-14] and chemical properties[8,15,16]. Also, they have been used as radiation-sensitive dosimeter glasses doped with transition metal ions[17,18] or rare earth ions[18]. SLS glasses are attractive materials for the fabrication of low cost integrated optical amplifiers[19] and other commercial tableware and sheet glasses.

ElBatal, F.et al[20,21] measured the IR absorption spectra of undoped and Ni- or Co-doped ternary silicate glasses and concluded that the IR absorption spectra slightly change with the introduction of TMs oxide and the main structural building vibrations dur to main silicate groups are identical. They attributed the slight change to the low doping level content (0.1%) of NiO or CoO to the base soda lime silica glass.

The main objective of this work is to study the infrared absorption spectra of nominally pure undoped and transition metals-doped (3d: Ti→Cu 0.1%) soda lime silicate (SLS) glasses in the range from 400 to 4000 cm^{-1}.

2. EXPERIMENTAL

2.1. Preparation of glasses

Glasses of the soda lime silica system with the basic composition SiO_2 75% - Na_2O 15%, CaO 10% (mol %) undoped and transition metal doped samples of the same nominal composition were prepared from chemically pure raw materials. Pulverized A. R. quality quartz was used as the source of silica while soda and lime were added in the form of their respective anhydrous carbonates. 3d transition metals (Ti→Cu) were added (0.1%) separately to the respective batch in the form of their oxides in each batch, respectively.

The prepared batches were melted in platinum crucibles in an electric furnace at $1400° \pm 10^0$C for 2 hours after the last traces of the batches had disappeared.

Each melt was rotated several times every 30 minutes to promote homogeneity. The melts were cast into preheated stainless steel molds in the required dimensions. The prepared glass samples were immediately transferred to an annealing muffle furnace regulated at 450^0C. After 1 hour, the muffle was switched off and the samples were left to cool inside the muffle gradually at a rate of 30^0C/hour to room temperature.

2.2. Infrared absorption measurements

Infrared absorption spectral measurements were carried out on powdered glass samples dispersed in KBr as a matrix material by a fixed ratio 1:100 at the same conditions. IR measurements were performed using a spectrometer (Jasco-Japan) with instrument resolution of about (1 cm^{-1}), in the wave number region from (400-4000 cm^{-1}).

A quantitative analysis for the infrared spectrum has been carried out by a careful deconvolution of the absorption profiles utilizing a computer based program[PeakFit program] which defines a hidden peak as one which is not responsible for a local maximum in the data stream. This does not mean that a hidden peak is not discernible to your perception. (Jandel scientific peakfit, copyright© 1990 AISN Software.)

First IR spectra were corrected for the dark current noises and background using two point base line corrections. Many successive trials have been carried out using different band shapes until best fitted data obtained using spectral Gaussian peaks. The position, full width at half maximum (FWHM) and intensity of each band are adjusted automatically by the program, on the basis of the minimization of the deviations between experimental and simulated spectrum.

Band deconvolution of infrared spectra

A number of studies have used curve-fitting technique to separate unresolved bands into several components[22-24].

In non-periodic or disordered systems, a distribution of individual geometries exists, which results in a distribution of vibrational wavenumbers. At the same time, a vibrational coupling with some degree of coher-

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ence between vibrating units is expected, which also affect the observed band shape.

In order that the fit be as realistic as possible, it is found profitable to use in the first stage a minimum number of bands corresponding to the number of distinct features observed in the experimental spectrum such as resolved maxima and well developed shoulders. To improve the fit, in the second stage, weaker bands are added which obey the following criteria:

a. The IR spectrum revealed an asymmetric mode that could be present in the Raman spectra.

b. To take into account the structural groups present in smaller quantities for a composition but in large quantities for another one.

2.3. Density measurements

The densities of doped and undoped glasses were determined by the Archimedes method using xylene as a buoyancy liquid, the twice reproducibility of the results are $\pm 2\%$.

3. RESULTS AND DISCUSSION

Figure 1 illustrates the full as measured IR absorption spectra before any treatment of the undoped and TM-doped soda lime silicate glasses extending from 400-4000 cm^{-1}. The whole spectrum of all the samples
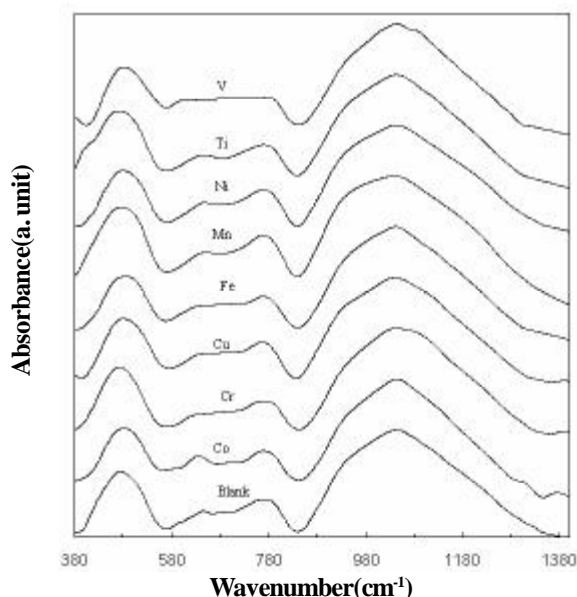

Figure 1 : IR absorption spectra of soda lime silicate glasses undoped and doped with first raw transition metal oxides

seems to be repetitive to that obtained from the base undoped glass. Also, it is obvious that the spectrum as a whole is divided into two sections, the first one comprises the main sharp distinctive and characteristic absorption bands extending in the mid IR region from 400 to about 1400 cm^{-1}, and the second part reveals only small peaks, two peaks at about 1450 and 1640 cm^{-1} and two other small peaks at about 2840 and 2950 cm^{-1} followed by a broad band within the far IR region centered at about 3480 cm^{-1}. Some of the curves show an additional small band around 2400 cm^{-1}.

It is evident that the spectrum existing from 400 to 1400 cm^{-1} comprises the absorption due to main silicate network groups vibrations with different bonding arrangements and the rest of the spectrum from 1400-4000 cm^{-1} is obviously (pertaining) consisting of vibrations due to water, hydroxyl, SiOH or similar groups.

Basic characteristics of silicate glasses structure have generally been agreed upon[1,2 22]. Earlier IR spectroscopic studies on alkali silicate glasses have revealed that the structure of such glasses is generally independent upon the content of the alkali oxide and the constitution retains the tetravalent valence for the main silicon ion[1,2,22]. The fundamental building block is the SiO_4 tetrahedral unit, all the oxygens are shared between two tetrahedra, forming a fully polymerized network[22]. Alkali (Na^+) or alkaline earth (Ca^{2+}) cations act as network modifiers, breaking bridging oxygen bonds to form non-bridging oxygens (NBOs) and residing in sites interstitial to tetrahedral network in the vicinity of the negatively charged NBOs.

The principle absorption frequencies usually observed in soda lime silicate glasses are identified as follows;[1,2,18,22-25]

1. Bands at 400-505 and 600 cm^{-1}, are generally correlated with Si-O-Si and O-Si-O bending modes.

2. Bands around 770-820 cm^{-1}, are attributed to Si-O-Si symmetric stretching of bridging oxygen between tetrahedra.

3. Bands around 970-1095 cm^{-1}, are related to Si-O-Si antisymmetric stretching of bridging oxygen within the tetrahedra.

Regarding the other absorption bands in the region 1400-4000 cm^{-1}, different authors have correlated the observed bands as follows;[25-28]

1. Band at 1460 cm^{-1}, is related to carbonate groups.

2. Band at 1640 cm⁻¹, can be related to molecular water or hydroxyl related band.
3. Bands around 2800-2980 cm⁻¹, are attributed to asymmetric and symmetric stretching modes of interstitial H_2O molecules.
4. Bands around 3400-3500 cm⁻¹, are due to molecular water.
5. Bands around 3600-3950 cm⁻¹, are attributed to different stretching modes of silanol Si(OH) groups.

Experimental IR data indicate that only very small variations are observed when transition metal oxides are separately introduced into the composition of the glasses. These small changes are not in a systematic order in correspondence to the number of unpaired electrons ($3d^n$ level) or to the atomic number of the respective transition metal cation as shown in TABLE 1 and the experimental IR spectra are realized and interpreted in the following points:

1. The main absorption bands of doped transition metals are almost the same indicating that structural silicate units are persistent without any indication of variation with the addition of any transition metal at low doping level (0.1 %).
2. Eight peaks could be identified by the use of the deconvolution process taking into consideration the first derivative of the spectrum and literature survey for previous work in silicate glasses and using average position and minimum number of bands determined.

Eight peaks could be identified at the wavenumbers (cm⁻¹).

Peak (1)	Peak (2)	Peak (3)	Peak (4)	Peak (5)	Peak (6)	Peak (7)	Peak (8)
449-468	488-512	640-668	725-758	779-793	924-936	1023-1040	1153-1174

3. The area under the peaks mostly decreases from peak 1 to 5 then increases in both 6 and 7 followed by a decrease in peak 8.
4. The difference in the position of each of the eight peaks with the neighboring peak ranges between 50 cm⁻¹ - 150 cm⁻¹ without constant or continuous variation.
5. The maximum difference for each specific peak with the transition metals ranges from 16 cm⁻¹ - 21 cm⁻¹ except the peak 3 and 4 which reaches 33 cm⁻¹.

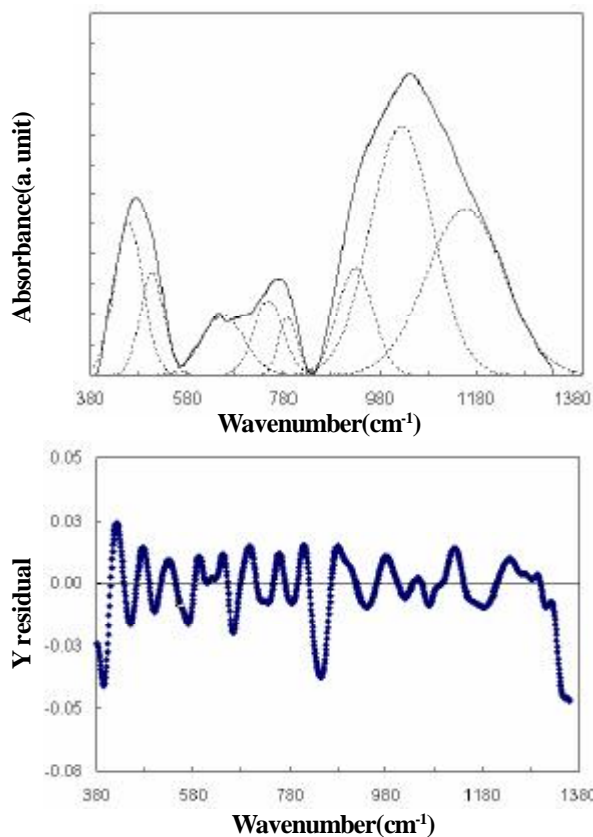The IR absorption spectra of the studied glasses

Figure 2: (a) A typical deconvolution of IR spectra of undoped SLS glass; (b) Residual of IR deconvolution of data of undoped SLS glass

TABLE 1: Transition metal ions and 3dⁿ levels

Transition level (d^n) configuration	Transition metal	Transition level (d^n) configuration	Transition metal
$3d^1$	Titanium (III), Ti^{+3} Vanadium (IV), V^{+4}	$3d^5$	Manganese (II), Ti^{+2} Iron (III), Fe^{+3}
$3d^2$	Titanium (III), Ti^{+3}	$3d^6$	Iron (II), Fe^{+2}
$3d^3$	Chromium (III), Cr^{+3}	$3d^7$	Cobalt (II), Co^{+2}
$3d^4$	Manganese(III), Mn^{+3}	$3d^8$	Nickel (II), Ni^{+2}
		$3d^9$	Copper (II), Cu^{+2}

appear to be somewhat complicated due to their overlapping bands or nearby positions and, from first sight, appear to be generally more or less similar for all studied samples. To realize and confirm that the network structure is somewhat affected by the type of TMO added, a quantitative analysis is carried out by deconvolution of the infrared absorption profile utilizing
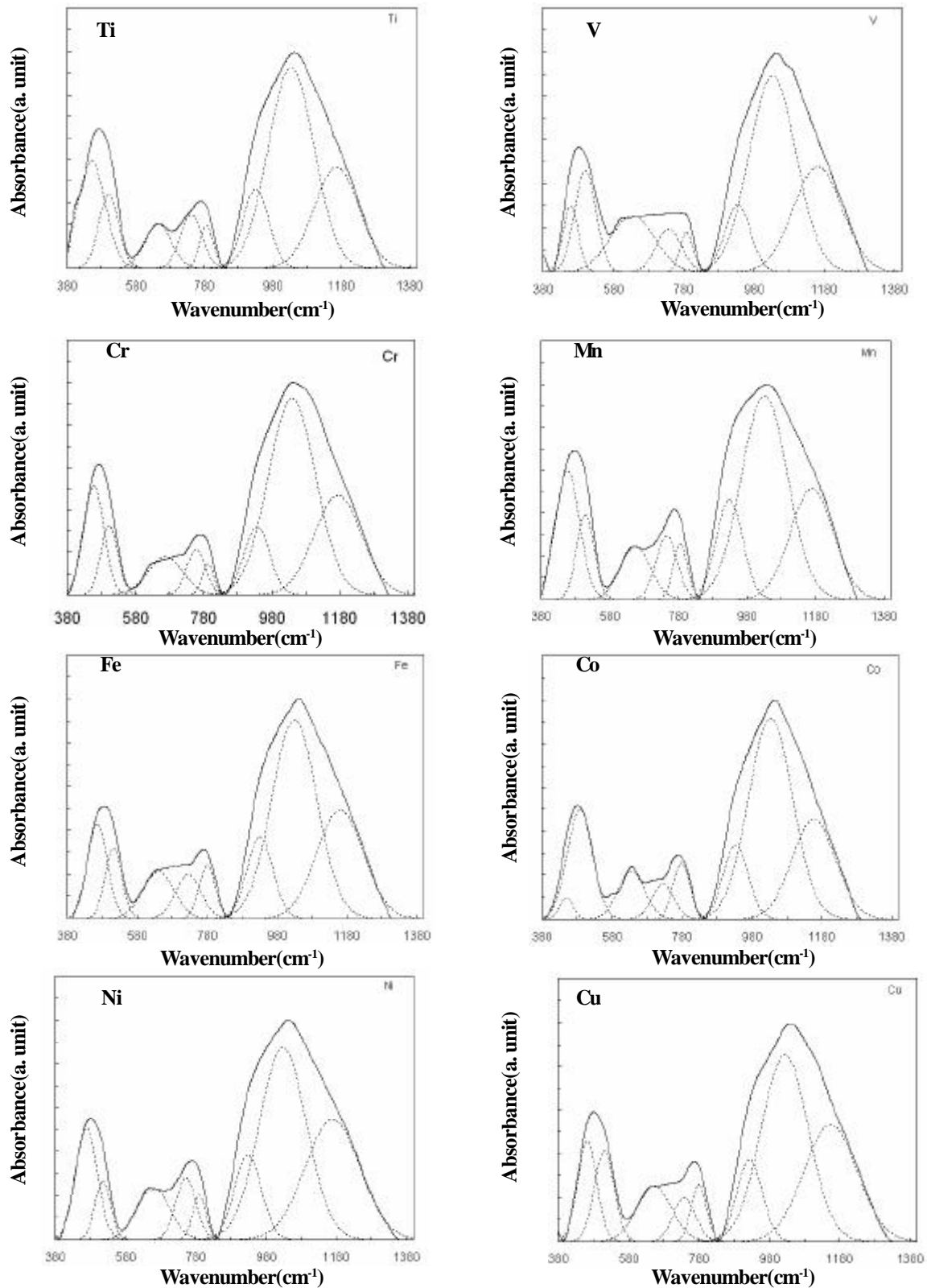
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Figure 3: A typical deconvolution of IR spectra of TM-doped SLS glass

the "Peak Fit" program. A typical deconvolution, in Gaussian bands, of an IR spectrum of the base SLS sample is illustrated in figure (2-a) to reveal the quality of fitted data. It is found that the difference between

TABLE 2 : Density data of the soda lime silica glass (gm/cm³)

Blank	Fe_2O_3	Co_2O_3	Ni_2O_3	Cr_2O_3	MnO_2	V_2O_5	CuO	Ti_2O_3
2.4948	2.5100	2.5016	2.5065	2.5082	2.5104	2.5091	2.5083	2.5084

experimental and simulated curves is less than 0.05 % as can be seen in figure (2-b). It is found to be fruitful to restrict the deconvolution treatment to the spectrum part in the range 400-1400 cm⁻¹ which is due to the main building silicate network and omitting the rest spectrum comprising the bands due mainly to water, OH groups.

It is obvious that O-Si-O and Si-O-Si bending modes, exhibiting position lower than 500 cm⁻¹ appears in the fitted spectra at 460 cm⁻¹ as previously reported by Efimov[29,30].

The presence of interstitial oxygen is seen to be characterized by a band at 515 cm⁻¹ which is known to be due to vibrational modes of a non-linear molecular unit of Si-O-Si vibrations[31-33].

The relative intensity of the deconvoluted band at 660 cm⁻¹ is strong in this glass and can be attributed to Si-O-Ca asymmetric bending mode that exists in the glass which is in agreement with the expected increase in non-bridging concentration in the silica network which is believed to be depolymerized by calcium. The three shoulders within this close range are due to the asymmetry in the Si-O-Ca bond distribution as a range of environments which can also exist in the glassy materials[22].

Semi-empirical calculations of the spectra of alkali di-silicate crystals point out that the range of the Si-O-Si asymmetric stretches can extend down to 900 cm⁻¹, whereas the range of Si-O⁻ stretches never extends to frequencies less than 1000 cm⁻¹. Therefore, based on the work of Mirogrodskii et al[34], the above assignment of the components should be reversed.

The fundamental Si-O stretching band at ~1100 cm⁻¹ is the predominant structural band in IR absorption spectrum of silica glass. After the pioneering computational work of Bell et al.[35], structural models were developed by various researchers which showed that the position of the Si-O stretching band depends primarily on the average Si-O-Si bond angle in the glass structure.

The somewhat complicated absorption between (800-1400 cm⁻¹) with one maximum and two shoulders, which may be resolved into three Gaussian peaks at nearly 930, 1020 and 1160 cm⁻¹, where the last two peaks are attributed to asymmetric Si-O stretching transverse optical mode and asymmetric Si-O stretching longitudinal optical mode[36].

A change in the fictive temperature and all other physical properties is assumed and observed to be correlated with the structural changes in silicate glasses[37] which are detected by a shift in the Si-O stretching infrared band located at 1150~1170 cm⁻¹ by addition of transition metal oxides.

The quite somewhat similarity of the IR absorption spectra of the different 3d transition metal-doped glasses can be correlated with:

1. The energies of the 3d orbitals in the neutral atoms are quite similar[38] so that while the configurations are of the $3d^{10} 4s^1$ type, the exchange-energy stabilization of filled and half-filled shells gives $3d^5 4s^1$ for Cr and $3d^{10} 4s^1$ for Cu, when the atoms are ionized, the 3d orbitals becomes appreciably more stable than the 4s orbitals and the ions all have $3d^n$ configurations.

2. The presence of 3d TMs in low doping percent (0.1%) which is virtually not expected to cause any obvious change regarding the number of the main structural silicate building units or their arrangement. The transition metal ions are not expected to form separate structural units. It can be assumed that the transition metal ions as this low level behave as network modifier and as such their vibrational modes are located in the range 100-400 cm⁻¹ as other network modifier (Na^+, Ca^{2+})[39].

Density data

TABLE 2 depicts the density data for undoped and TM-doped samples. It is obvious that introducing any of TM ions to the base glass composition increases the density but the tabulated data did not show any specific tendency or relation to the atomic number of the transition metal or to the number of unpaired electrons in the 3d subshells. This behavior can be related to the following factors:

a. The percent of transition metal added (0.1%) is seemingly low in the doping level and cannot be expected to cause obvious change in the network

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structure.

b. The 3d transition metals possess varying possible valencies within the host studied base soda lime silica glass. Most or even all of these TMs exhibit two coordination states with different surrounding oxygen's which virtually affect the packing or compactness of the structure.

c. The density values represent the masses for each volume unit for each glass which cannot be easily compared or represented especially when dealing with doping level content of TMs.

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