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IR and Raman spectroscopic studies of sol–gel derived alkaline-earth silicate glasses

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Abstract. IR and Raman spectroscopies have been utilized to study the structure and vibrational modes of sol–gel-derived binary silicate glasses. The present study is motivated by the immense geological significance and focuses on the MO–SiO_2 (M = Ca, Mg) binary systems in an effort to unveil the role of the CaO and MgO modifiers when incorporated to the 3D silica structure. Glasses in the composition range $x = 0, 0·1, 0·2, 0·3$ and $0·4$ prepared by the sol–gel method were compared with the corresponding glasses formed by appropriate mixing of SiO_2 and MO powders through melting and fast cooling. The vibrational spectra of the sol–gel-derived glasses have revealed considerable changes in relative intensities as a function of the MO mole fraction. These changes signify structural modifications on the silica network. The population of the Q^3 species was found to increase for both modified silicate systems. The rate of increase is more pronounced in the CaO–SiO_2 glasses. The extent of network depolymerization in the porous glass is higher at the same content of alkaline earth oxide compared to the bulk glass. The results are indicative of a more 'defective' nature of the sol–gel glasses compared to the corresponding melt-quenched ones.

Keywords. Sol–gel silicate glasses; Raman spectroscopy; IR spectroscopy; structure; silicates.

1. Introduction

The present study is motivated by the immense geological significance of silica based materials since almost all igneous processes are associated with the presence of a silicate melt phase or magma (Heany 1994). However, since the structure of multi-component glasses can be described in a less straightforward way, the choice of binary systems seems advantageous for undertaking systematic studies (McMillan 1984; McMillan and Wolf 1995). The microscopic structure can be vastly different between two glasses of the same composition prepared by different routes. In particular, silicate glasses that are derived by the sol–gel process exhibit extensive differences compared to bulk, melt quenched glasses, at the microstructure as well as at the morphological or textural properties. Silicate glasses that contain calcium and phosphorus are known to exhibit bioactive behaviour (Hench *et al* 2002).

The bioactive silica-based materials present an open structure which enables the accommodation of alkali and/or alkaline earth cations (K^+, Na^+, Li^+, Ca^{2+}, Mg^{2+}, etc). These alkali and/or alkaline earth oxides act as network modifiers provoking the disruption of the continuity of the glassy network due to the breaking of the Si–O–Si bonds leading to the formation of nonbridging oxygen species (Si–O–NBO) (Scholze 1990). Concerning the bioactive processes, this is the key step since the concentration of Si–O–NBO groups monitor the dissolution rate of the silica through the formation of silanol groups at the surface (Kokubo 1990). Thus, the study of the bonding configuration of glasses and the quantitative estimation of the Si–O–NBO species by analytical techniques contribute to improve the ability to design new bioactive glasses. Raman and infrared spectroscopies are sensitive techniques to the local structure of silicate glasses allowing the determination of changes on the Si–O–Si vibrational modes.

The aim of this study is to verify the bonding configuration of silica glasses modified by alkaline earth oxides (MgO, CaO) prepared by the sol–gel method and to identify the presence of nonbridging silicon–oxygen groups by combining the two spectroscopic techniques, viz. Fourier transform Raman and infrared spectroscopies. A complete study of glasses with different silica concentrations and type of alkaline earth is presented.

2. Experimental

2.1 *Sample preparation*

Binary glasses along the joints of $x\text{CaO}·(1-x)\text{SiO}_2$ and $x\text{MgO}·(1-x)\text{SiO}_2$ with $x = 0$, $0·1$, $0·2$, $0·3$ and $0·4$ were prepared by hydrolysis and polycondensation of tetraethyl orthosilicate (TEOS), tetrahydrated calcium ($Ca(NO_3)_2·4H_2O$) and hexahydrated magnesium nitrate

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($Mg(NO_3)_2 \cdot 6H_2O$). Nitric acid (HNO_3, 2 N) was used to catalyze the TEOS hydrolysis, using a molar ratio of ($HNO_3 + H_2O/TEOS = 8$). After the addition of all reactants, the solution was stirred for 1 h. The sol was cast in containers and kept at room temperature to allow the hydrolysis and polycondensation reactions, up until the formation of a viscous gel. For aging, the gel was stored in a sealed container and kept at 60°C for 3 days. The drying of the gel was carried out in three stages by heating the gel at 60°C, 90°C and 130°C for 20, 24 and 40 h, respectively. The stabilization procedure took place in three steps by sintering the samples at 100, 300 and 700°C for 1, 2 and 5 h, respectively. The temperature increase rate was kept constant at 0·1°C/min for all heating procedures.

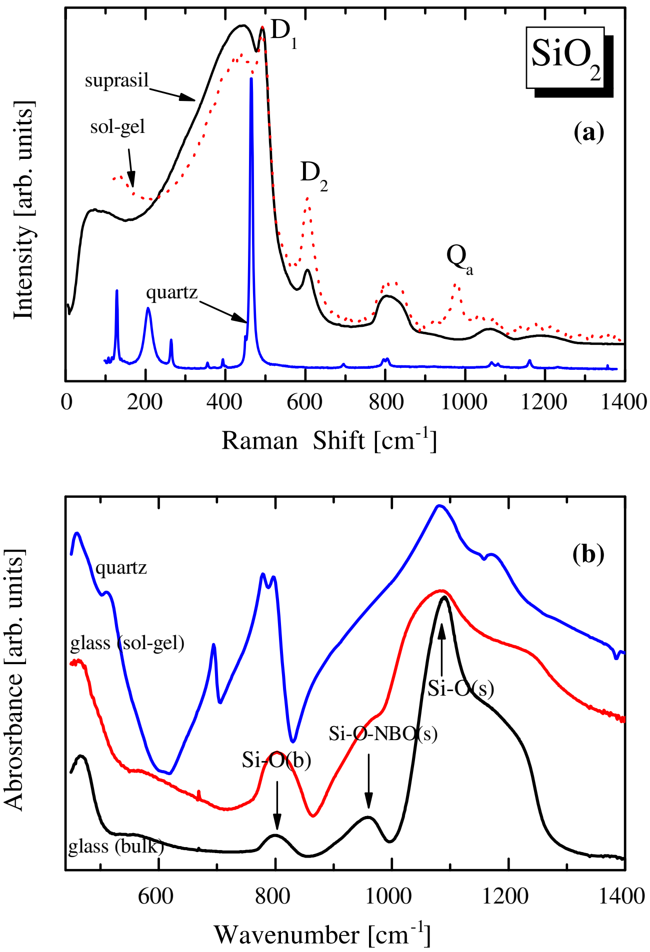

Figure 1. Raman spectra (**a**) and IR absorbance spectra (**b**) of pure melt-quenched and sol–gel derived silica glass. The Raman and IR spectra of quartz crystal are also shown for comparison.

2.2 *Instrumentation—Spectroscopic techniques*

Fourier transform Raman (FT–Raman) measurements were obtained using a Bruker (D) FRA-106/S component attached to an EQUINOX 55 spectrometer. A R510 diode pumped Nd:YAG laser at 1064 nm (with a maximum output power of 500 mW) was used for Raman excitation in a 1808 scattering sample illumination module. An optical filtering reduced the Rayleigh elastic scattering and, in combination with a CaF_2 beamsplitter and a high sensitivity liquid N_2-cooled Ge-detector, allowed the Raman intensities to be recorded from 50–3300 cm^{-1} in Stokes-shifted Raman region, all in one spectrum.

For Fourier transform infrared measurements (FTIR) sol–gel derived glasses were crushed with pestle in an agate mortar. The crushed material was mixed with potassium bromide (Merck IR spectroscopy grade) in 1:100 proportion and dried at 40°C. The mixture was compressed to a 12 mm semitransparent disk by applying a pressure of 10 tonnes for a few min. The FTIR spectra over the wavelength range 4000–400 cm^{-1} were recorded using a FTIR spectrometer (UV–vis-NIR spectrophotometer V-570 Jasco).

3. Results and discussion

3.1 *Bulk and porous silica glass*

In order to facilitate the analysis of the experimental data of the sol–gel-derived glasses, we present in figures 1(a) and 1(b) the Raman and IR spectra of pure bulk (suprasil) and sol–gel silica glass, respectively. The spectra of the corresponding quartz crystal are shown for comparison. In general, the Raman spectra of silica glasses (bulk and sol–gel) seem to be similar and the differences are focused on the relative intensities of several bands and only one new relatively sharp band appears in the spectrum of sol–gel-derived silica. This band is located near ~980 cm^{-1} referred to as Q^a. This band is characteristic of the Si–O stretching vibration of (Si–OH) silanol groups (Stolen and Walrafen 1976; Kamitsos *et al* 1993). The exposure of the glass surface to humidity and the heat-treatment conditions during sample preparation are key factors for the formation of such groups.

A brief assignment of the Raman spectrum of silica is given below. The sharp bands D_1 and D_2 at ~493 and ~606 cm^{-1}, known as defect modes, have been associated to breathing vibrations of oxygen atoms in four- and three-membered rings, respectively (Barrio *et al* 1993). The insensitivity of the D_1 and D_2 frequencies with increasing temperature imply that the vibrational modes of the rings are decoupled from the rest of the network (McMillan 1984). The number of four-membered rings (D_1) shows no significant change between the two types of silica glass, while the number of three-membered rings (D_2) seems to increase in porous silica. The broad bands located between 100 and 480 cm^{-1}, usually considered as a single asymmetric band centred around ~440 cm^{-1}, have been assigned to symmetric bending vibrations of the Si–O–Si linkage with oxygen motion perpendicular to the Si–Si line and/or to the O–Si–O deformation of the coupled 'tetrahedra' SiO_4 groups. The wide distribution of the intertetrahedral Si–O–Si angles within the structure causes the large full width at half maximum (FWHM). The decrease in intensity of this broad band in the sol–gel-derived silica is indicative of the lowering of network dimensionality by breaking of Si–O–Si bridges within the structure of glass. The asymmetric band situated at ∼800 cm^{-1} consists of two overlapping relatively narrow bands with energies corresponding to Si–O stretching vibrations (Stolen and Walrafen 1976; Kamitsos *et al* 1993). The high frequency bands at ∼1050 and ∼1200 cm^{-1} have controversial origin. From the coincidence of the IR and Raman bands it was proposed that these bands arise from TO–LO splittings. In the case of quartz crystal, the low-lying Raman bands at ∼356, ∼264, ∼207 and ∼128 cm^{-1} are attributed to lattice modes, while the strong peak at ∼465 cm^{-1} is assigned to symmetric stretching vibration. In the high-frequencies, the bands at ∼807 and ∼1083 cm^{-1} are assigned to Si–O–Si bending and SiO_4 asymmetric stretching vibration, respectively (McMillan 1984; Heany 1994).

The IR spectra of silica glasses (bulk and sol–gel) seem to be similar as in the case of Raman spectra. In this case, larger FWHM of the bands are observed in the spectrum of sol–gel-derived silica compared to the corresponding spectrum of bulk glass. In the low-frequencies the spectra of glasses are dominated by a band located at ∼465 cm^{-1}, which is assigned to rocking motion of the bridging oxygen atoms perpendicularly to the Si–O–Si plane. The band at ∼805 cm^{-1} is attributed to bending motion of the oxygen atom along the bisector of the Si–O–Si bridging group. In the high-frequency region of the spectrum, a strong band at ∼1100 cm^{-1} appears which is assigned to antisymmetric stretching mode of Si–O–Si group involving mainly oxygen motion along the Si–Si direction (Lucovsky *et al* 1983). The deformation of pores in the sol–gel material relative to bulk silica leads to longer bridging angles and Si–O–Si bonds causing larger FWHM of the bands observed in the spectrum of porous silica. The IR spectrum of quartz is analogous to the spectra of glasses. In detail, the low-lying bands at ∼462 and ∼512 cm^{-1} are attributed to bending modes of SiO_4 tetrahedra. The bands at ∼789 and ∼780 cm^{-1} are associated with Si–O–Si bending vibrations, while the high-frequency bands located at ∼1084 cm^{-1} are assigned to SiO_4 asymmetric stretching vibrations (Lucovsky *et al* 1983).

3.2 *Bulk and sol–gel-derived xMO–(1–x)SiO₂ glasses*

Figure 2 illustrates representative Raman spectra of the $x\text{CaO}\cdot(1-x)\text{SiO}_2$ binary system for $x = 0$, 0·1, 0·2 and 0·4. Similar results have been obtained for the $x\text{MgO}\cdot(1-x)\text{SiO}_2$ glasses. The Raman spectrum of bulk silica (bottom) as well as the spectrum of the melt-quenched glass of composition $0{\cdot}4\text{CaO}0{\cdot}6\text{SiO}_2$ (top) are also shown for comparison. The incorporation of the CaO modifier into the silica structure entails appreciable changes as evidenced from the generation of new peaks in the high-frequency region. The high-frequency bands above 900 cm^{-1} show changes in their relative intensities with increasing modifier content. These bands correspond to symmetric silicon–oxygen stretching vibrations of silicate tetrahedral units, respectively with four, three, two and one non-bridging oxygen atoms (McMillan 1984). These units are usually termed as the Q^0, Q^1, Q^2 and Q^3 species (Matson *et al* 1983); the notation is borrowed from NMR spectroscopic studies (Engelhardt *et al* 1975). The Q^0, Q^1, Q^2 and Q^3 units appear in the Raman spectrum of alkaline silicate glasses in the ∼850, ∼900, 950–1000 and 1100–1150 cm^{-1} positions, respectively (McMillan 1984).

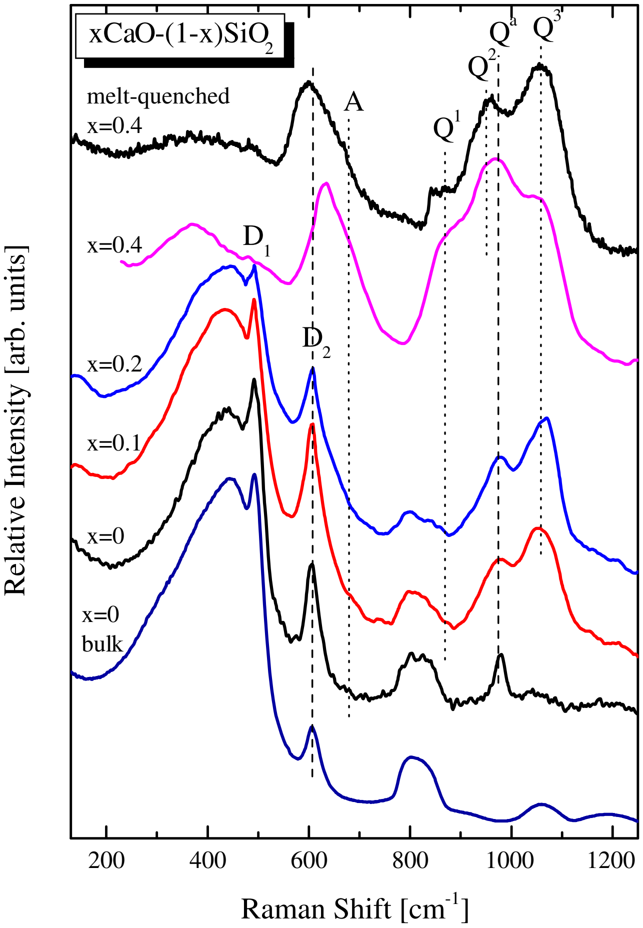

Figure 2. Representative Stokes-side Raman spectra of $x\text{CaO}\cdot(1-x)\text{SiO}_2$ ($x = 0$, 0·1, 0·2 and 0·4) glasses prepared by sol–gel technique at room temperature. The Raman spectra of the bulk, melt-quenched SiO_2 and the $0{\cdot}4\text{CaO}0{\cdot}6\text{SiO}_2$ glasses are also shown at the bottom and top of this figure, respectively.

In figure 2 it is shown that with increasing modifier content the spectra of the sol–gel glasses reveal several changes. The low energy broad band at ∼440 cm^{-1} associated with the bending motion of the oxygen bridges substantially decreased in intensity, while its width remained almost the same. The decrease of intensity is probably related with the lowering of the network dimensionality caused by the addition of alkaline earth oxide. The

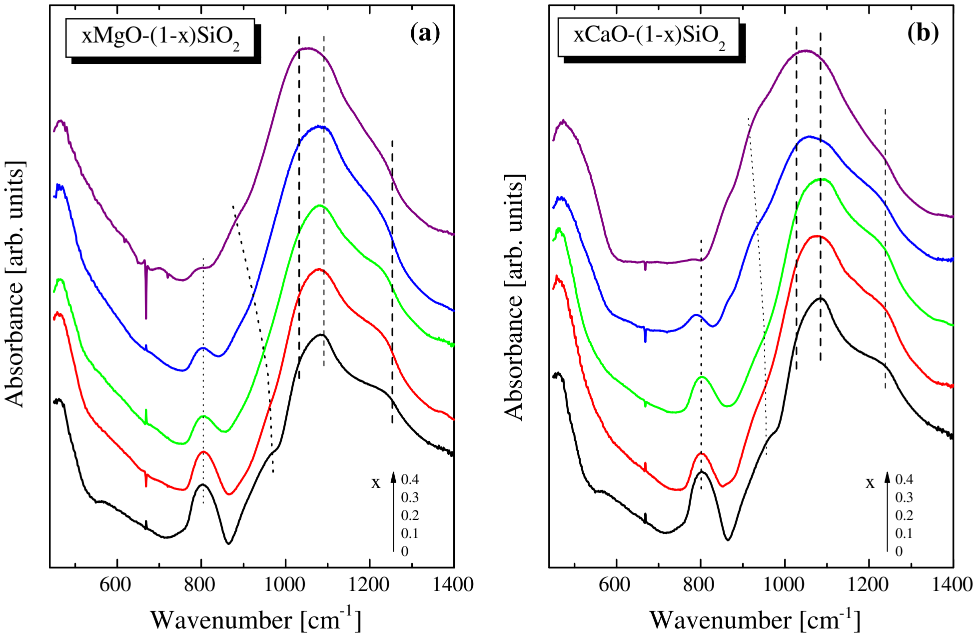

Figure 3. IR absorbance spectra of the binary glassy systems: (**a**) xMgO·$(1-x)$SiO$_2$ and (**b**) xCaO·$(1-x)$SiO$_2$ ($x = 0$, 0·1, 0·2, 0·3 and 0·4) prepared by sol–gel technique at room temperature.

energies of defect bands D_1 and D_2 remain constant up to $x = 0{\cdot}2$, while for higher alkaline earth oxide content, D_1 seems to appreciably blue-shift, while D_2 exhibits slightly the opposite effect. The doublet at ~800 cm^{-1} reveal a gradual decrease with increasing modifier content, while a new band appears as a shoulder band near ~680 cm^{-1} which is attributed to bending motion of oxygen bonds participating in 'defective' structures. These defects are formed by breaking Si–O bridging bonds in the continuous three-dimensional network (Lucovsky 1979). The above reported changes occur for both CaO- and MgO-modified silicate glasses.

In the high-frequency region, two bands at ~980 cm^{-1} and ~1050 cm^{-1} dominate the spectra for both alkaline earth silicate systems studied. These peaks are absent from bulk silica, while Q^a appears in the spectrum of the pure sol–gel-derived SiO$_2$. As mentioned above, this band is characteristic of the Si–O stretching vibration of (Si–OH) silanol groups marked as Q^a. In addition, bands appearing near 980 cm^{-1} are known to correspond to Q^2 units with two bridging oxygen atoms. The band at 1050 cm^{-1} is a manifestation of Q^3 species. The intensity of Q^3 band increases systematically when the modifier content is increased, while its frequency remains unaffected. It is not possible to estimate the relative ratio between Q^3 and Q^2 units in the sol–gel glasses as a function of x; because of the existence of the vibrational mode related to the silanol group, which is situated at the energy of the Q^2 species. The resolution of the peaks in the Q-species neighbourhood for the xMgO·$(1-x)$SiO$_2$ system is lower as expected (McMillan 1984). By comparing the Raman spectrum of the melt-quenched 0·4CaO·0·6SiO$_2$ glass with the corresponding sol–gel-derived glass, it is evident that the extent of network depolymerization in the porous glass is higher with lower content of alkaline earth oxide relative to the bulk glass. This fact is probably related with the presence of OH groups in the porous glass, which is responsible for the connectivity of the network.

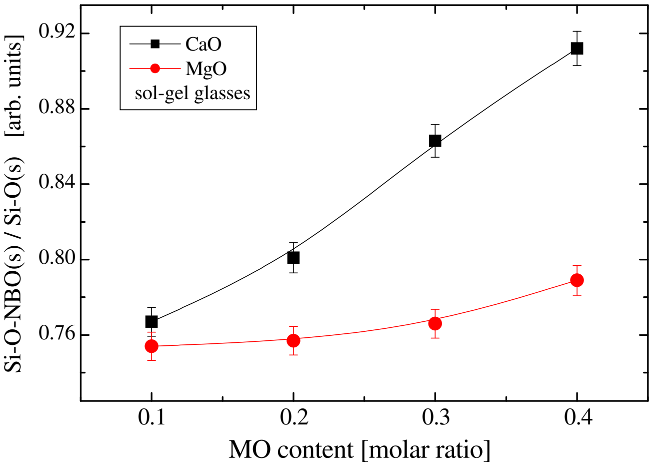

Figure 4. Si–O–NBO(s)/Si–O(s) absorbance intensity ratio versus modifier composition for the xMO·$(1-x)$SiO$_2$ (M = Ca, Mg) glasses. Lines are drawn as guide to the eye.

In figure 3 the IR absorbance spectra of both binary systems studied are shown. The IR spectrum can be divided into three main regions, viz. the low-frequency rocking, the medium frequency bending and the high-frequency antisymmetric stretching bands. Several spectral changes take

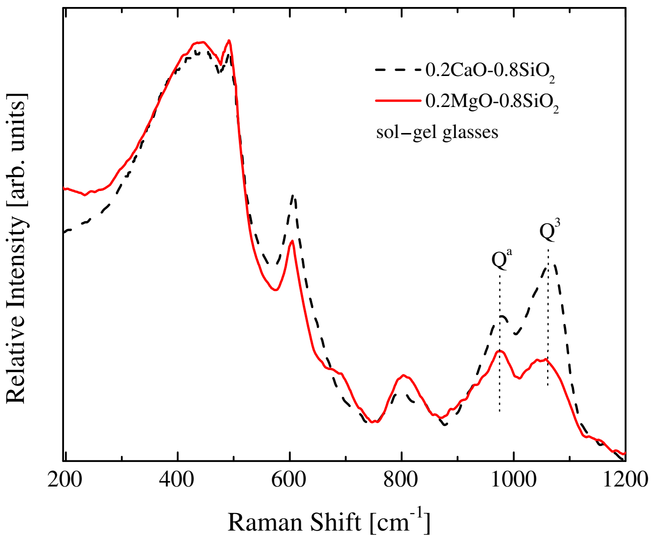

Figure 5. Stokes-side Raman spectra of $0{\cdot}2MO{\cdot}0{\cdot}8SiO_2$ (M = CaO, MgO) sol–gel derived glasses at room temperature for comparison.

place in the spectra with increasing modifier content. In brief, a new band attributed to the vibrational motion of ring structures appears at $\sim$530 cm^{-1} which fall within 500–800 cm^{-1}. In addition, the vibrations of four-membered rings have been located at $\sim$560 cm^{-1} (Kamiya *et al* 1990). The bending mode at $\sim$805 cm^{-1} shifts slightly to lower wavenumbers and its intensity decreases. Furthermore, upon increasing alkaline earth oxide content there is a parallel increase of the intensity of the $\sim$1220 cm^{-1} band compared to the $\sim$1100 cm^{-1} band. The Q^0, Q^1, Q^2 and Q^3 units appear in the IR spectrum of alkaline silicate glasses in the $\sim$860, $\sim$900, 950 and 1070 cm^{-1} positions, respectively (Merzbacher and White 1988). The spectroscopic results indicate that the addition of alkaline earth oxide modifier causes a gradual depolymerization of the silicate network. In order to quantitatively follow the observed spectral changes, the Si–O–NBO(s)/Si–O(s) absorbance intensity ratio has been estimated directly from the IR spectra for both $x\mathrm{MO}{\cdot}(1-x)\mathrm{SiO}_2$ (M = Ca, Mg) glassy systems. This ratio is a measure of the population of the Q^3 species. Figure 4 shows the calculated ratio, where a monotonous increase is exhibited for the one modified by alkaline earth oxides (MgO, CaO) prepared by the sol–gel method. Furthermore, the depolymerization of the silicate network is more enhanced in the CaO-modified silicate glasses. The Raman spectra for the $0{\cdot}2MO{\cdot}0{\cdot}8SiO_2$ (M = Ca, Mg) glasses are shown in figure 5 for comparison. Comparing the two series of sol–gel-derived glasses for the same composition of the modifier, it is clear that the CaO addition causes more significant changes in the structure than MgO as is evident from the increased intensity of the Q^3 species in $0{\cdot}2CaO{\cdot}0{\cdot}8SiO_2$ glass. This fact is in agreement with the above reported IR results.

4. Conclusions

IR and Raman spectroscopies have been used to investigate the structure and vibrational modes of the $x\mathrm{MO}{\cdot}(1-x)\mathrm{SiO}_2$ (M = Ca, Mg) binary silicate glasses prepared by the sol–gel method. Glasses in the composition range $x = 0, 0{\cdot}1, 0{\cdot}2, 0{\cdot}3$ and $0{\cdot}4$ when compared with the corresponding glasses were formed by the conventional melting and fast cooling technique. The vibrational spectra of the sol–gel-derived glasses have revealed significant changes in relative intensities as a function of the alkaline earth oxide mole fraction implying structural modifications of the silica network. The population of the Q^3 species was directly calculated from the spectroscopic results and found to increase for both the modified silicate systems. The rate of increase is more pronounced in the CaO–SiO$_2$ system. The depolymerization in the network of the porous material is higher compared to the corresponding bulk for a given content of alkaline earth oxide signifying a more 'defective' nature of the sol–gel glasses.

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