The Boson peak in alkali silicate glasses

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Abstract

In an effort to understand the nature of the vibrational modes contributing to the Boson peak in glasses, we have performed a low frequency Raman study of different alkali silicate glasses at 300 K ($X_2O_{(g)} \cdot SiO_{2(1-g)}$ = 25%, 35% by weight; X: Na, K, Rb, Cs). The introduction of alkali ions in silica is known to break Si–O bonds, resulting in non-bridging oxygens and thus reducing the connectivity of the glass. Because of their identical charge, different alkali ions are expected to modify the glass network in the same way. We find that the shape of the Boson peak can be well fitted with a Lorentzian squared function characterized by a single parameter ν_0. Analysis of the dependence of ν_0 on the type and concentration of alkali suggests that the position of the Boson peak is essentially governed by the ratio 'force constant' over 'mass' of localized oscillators and is not determined by the connectivity of the glass. The results also show little difference between quenched and annealed glasses, indicating the absence of a strong relation to the extended structure of the glass. © 1997 Elsevier Science B.V.

1. Introduction

The Boson peak appears to be a universal feature of the glassy state. Still, the origin of the Boson peak is the subject of much debate. The soft potential model is derived from the two-level system model of localized oscillators in anharmonic double potential wells [1]. Others believe that the peak is due to scattering from acoustic modes propagating in a disordered medium [2]. The goal of our study is to answer the question of whether the vibrational modes underlying the Boson peak are localized or extended. In an effort to answer this question, we have measured the low frequency Raman spectra of silicate glasses doped with Na, K, Rb and Cs.

2. Theoretical background

There are two dominant low frequency components in the Raman spectra of v-SiO_2, a broad

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band and a Boson peak. The broad band has been studied by Galeener [3] who has shown that it arises from the bending motion of Si–O–Si bridges. In the present paper, we have considered primarily the Boson peak. The Raman spectrum of pure silica is shown in Fig. 1. The Boson peak is clearly visible in the VH (depolarized) spectrum and is present in the VV (polarized) spectrum as well, albeit overlapped with the broad band. In an amorphous solid, Shuker and Gammon [4] showed that the first order Raman scattered Stokes intensity could be written as

$$I_S(\nu) \propto \frac{c(\nu)g(\nu)}{\nu}(n(\nu,T) + 1), \qquad (1)$$

where $c(\nu)$ is the coupling coefficient, $g(\nu)$ is the density of states and $n(\nu,T)$ is the Bose–Einstein thermal population factor. If the Boson peak was simply due to acoustic phonons, the coupling coefficient would be proportional to ν^2 [5] and the density of states in a Debye model being also proportional to ν^2, the Raman intensity should be proportional to ν^3. This ν^3 dependence is indeed observed experimentally, but only on the low frequency side of the Boson peak [6]. However, the simple ν^2 dependence for $c(\nu)$ and $g(\nu)$ cannot predict the shape of the Boson peak at higher frequencies (20–300 cm^{-1}), indicating that it cannot simply be due to acoustic phonons. Although a Raman experiment cannot by itself determine $c(\nu)$ and $g(\nu)$ separately, a functional form for the product of the two can be assumed and its validity checked through fitting. We find that the entire Boson peak is well fitted by a Lorentzian squared function:

$$I_S(\nu) \propto \frac{\nu^3}{(\nu^2 + \nu_0^2)^2}(n(\nu,T) + 1) \qquad (2)$$

in which ν_0 represents the maximum of $I_S(\nu)$ if the Bose factor is approximated as $kT/h\nu$. The Lorentzian squared function was proposed earlier by Malinovsky and Sokolov [7] and Sommer et al. [8] confirmed the applicability of Eq. (2) above in which the temperature dependence of the Boson peak is given by $(n(\nu,T) + 1)$ indicative of a first order process. The Lorentzian squared function is
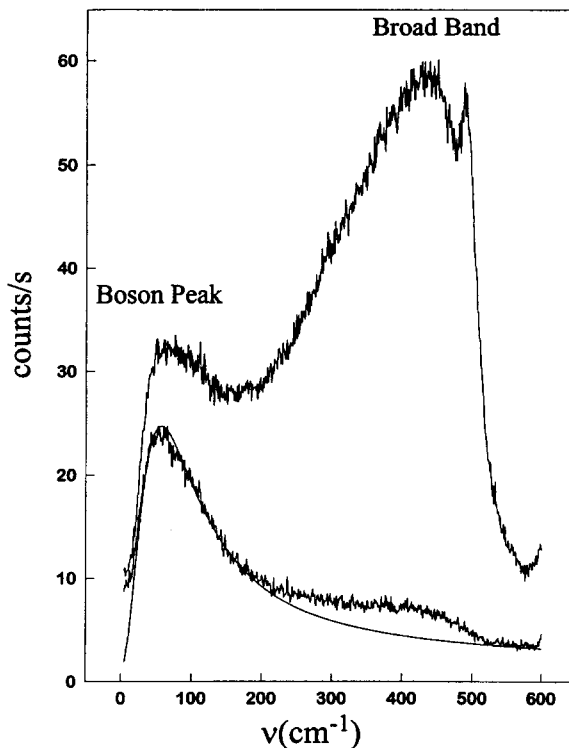

Fig. 1. Low frequency Raman spectra of v-SiO$_2$ at 300 K and 514 nm. The upper curve is the VV (polarized) spectrum (scaled down by a factor of two), while the lower curve is the VH (depolarized) spectrum.

applicable over the entire Boson peak and up to the onset of the broad band, as evidenced by the solid line fit on the VH spectrum in Fig. 1. Moreover, at low frequency, where the acoustic phonon contribution is expected to be non-negligible, Eq. (2) can be simplified ($\nu \ll \nu_0$) and does indeed predict the proper ν^3 dependence discussed above.

The physical origin of the Lorentzian squared dependence used in this paper is not known. Inelastic neutron scattering data have suggested that $c(\nu) \propto \nu$ in the Boson peak range [6]. Thus the factor $\nu^3/[(\nu^2 + \nu_0^2)]^2$ may represent the functional form for the density of states in the Boson regime. This functional representation of the Boson peak is convenient as it provides a one-parameter description of both its position and its shape. We can then investigate the effect of alkali dopants in silica by monitoring changes in a single parameter.

When an alkali metal is doped into amorphous silica, it occupies an interstitial site and breaks an Si–O bond, thus causing the formation of a non-bridging oxygen (NBO) [9]. This decreases the connectivity of the glass which should produce a corresponding decrease of the integrated intensity of the broad band. If the Boson peak bears a relation to the connectivity of the glass, we also expect the Boson peak in alkali silicate glasses to exhibit a behavior similar to that of the broad band. In the present paper, we report results on the effect of different alkali dopants and of their concentration on the Boson peak and broad band in silica.

3. Experiment

Raman spectra of the samples were taken at room temperature. The glasses were doped with 25% and 35% by weight X_2O, where $X = $ (Na, K, Rb, Cs) and both quenched and annealed samples were studied. The spectra were taken using an argon ion laser tuned to 514 nm as an exciting wavelength. The spectrometer was a double monochromator (ISA Ramanor U1000) set to 2 cm^{-1} resolution. A photomultiplier tube (PMT) was used to record the counts. A polarizer separated the VV and VH spectra, while a scrambler ensured that the system responded equally to both polarizations. The accuracy of all stated measurements is within ± 2 cm^{-1}.

4. Results

4.1. Boson frequency ν_0

Typical low frequency Raman spectra are shown in Figs. 2 and 3 (VV and VH spectra, respectively) of pure silica, 35% rubidium silicate and 35% cesium silicate samples. The functional form given in Eq. (2) is seen to fit the Boson peak well in all spectra. As in pure silica, the quality of the fit is better appreciated on the VH spectrum in which the broad band is only weakly present. We note that the peak parameter ν_0 is 55.0 cm^{-1} in pure silica but is 34.2 cm^{-1} in rubidium silicate and shifts to a frequency of 25.4 cm^{-1} in cesium silicate. A summary of the Boson peak data is provided in Table 1 along with the molar concentrations of alkalis present in each sample. As the atomic mass of the dopant decreases, the value of ν_0 is seen to increase. The parameter ν_0 also does not appear to be strongly dependent on concentration in this high concentration range. A smooth background is present in all spectra which has been attributed to second order processes [2]. We finally note the appearance of a shoulder on the high frequency side of the Boson peaks in the

Table 1
Boson peak data

Sample	Dopant molar fraction (x)	Number of dopants/Si	ν_0 Annealed (cm^{-1})	ν_0 Quenched (cm^{-1})
Silica	–	–	–	55
Na (molar)	0.14	0.33	–	50
Na-25	0.25	0.65	66	70
Na-35	0.34	1.04	64	64
K-25	0.17	0.42	53	52
K-35	0.26	0.69	49	50
Rb-25	0.10	0.21	33	34
Rb-35	0.15	0.35	33	33
Cs-25	0.07	0.14	25	25
Cs-35	0.10	0.23	25	26

All numbers are given in wavenumbers (cm^{-1}). Note that variation of the peak with respect to mass as well as the insensitivity of the Boston peak to doping level and annealation. The conversion from dopant weight to dopant molar fraction is given in the second column (ex. xNa$_2$O·$(1 - x)$SiO$_2$), while the conversion to number of dopants per silicon is provided in the third column.
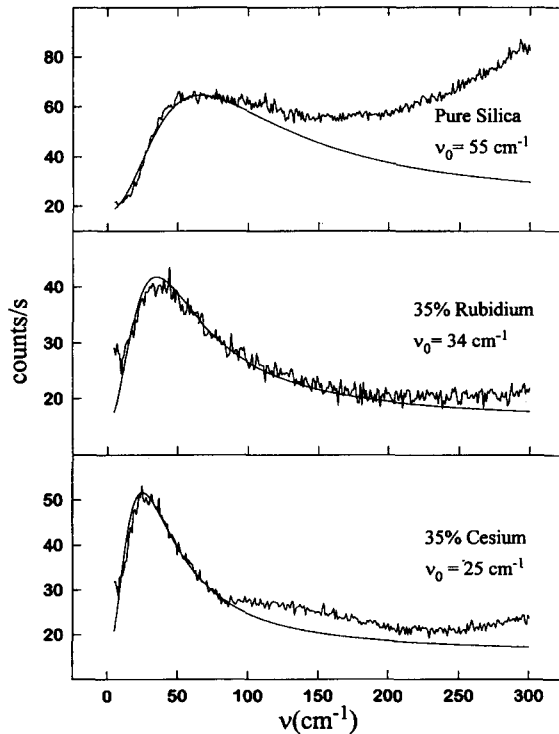
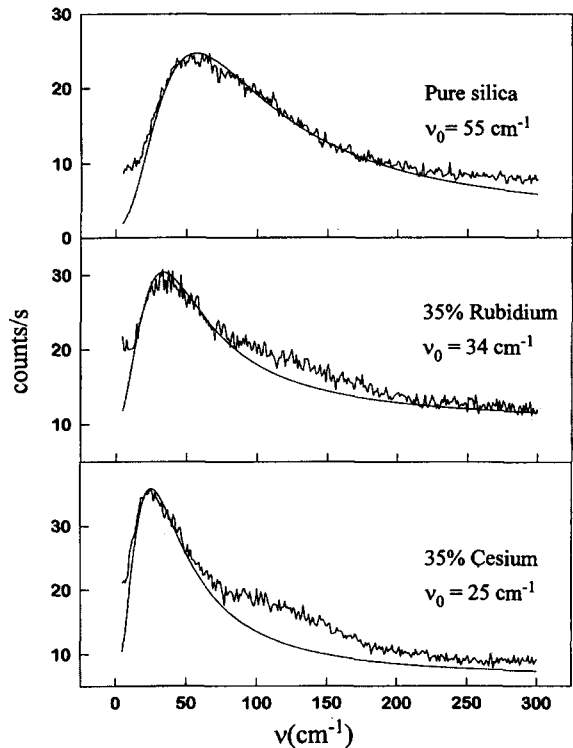Fig. 2. VV spectra of Boson peak in alkali silicate glasses.

Fig. 3. VH spectra of Boson peak in alkali silicate glasses.

rubidium silicate and the cesium silicate spectra that is not present in the pure silica spectrum (Fig. 3).

4.2. Broad band

Data on the broad band peak position is provided in Table 2. In all alkali silicate samples, the broad band decreases in amplitude and shifts to higher frequencies relative to pure SiO_2. This shift increases as the mass (and size) of the alkali decreases. These observations may be due to a decrease in the connectivity of the network and the constraints placed on the Si–O–Si bending mode by the alkalis. Because of this latter effect, it is not surprising to observe a further increase or shift of the broad band frequency with increasing alkali concentration. Finally, the broad band maximum frequency does not appear to be affected by the state of the glass, either quenched or annealed.

4.3. Depolarization ratio

The Boson peak depolarization ratios of the samples are given in Table 3. Although the ratios vary considerably from sample–to–sample, the trend is towards a higher ratio for a larger alkali mass. The depolarization ratio, defined as I_{VV}/I_{VH}, is different for the shoulder than for the Boson peak, as can be seen by comparing the VV and VH spectra (Figs. 2 and 3). Since the depolarization ratio is related to the symmetry of the vibrations, the results suggest that the Boson peak and shoulder do not have the same origin. The shoulder ratio also varies considerably between samples. In the rubidium sample the shoulder depolarization ratio is much greater than one, whereas in cesium it is close to one.

5. Discussion

As reported above, the Boson peak frequency

Table 2
The broad band in alkali silicate glasses (all numbers are given in wavenumbers, i.e. cm^{-1})

Sample	Annealed broad band peak (cm^{-1})	Quenched broad bank peak (cm^{-1})
Silica	–	430
Na-25	539	539
Na-35	584	579
K-25	514	506
K-35	534	530
Rb-25	492	495
Rb-35	501	504
Cs-25	450	453
Cs-35	486	495

Table 3
Boson peak depolarization ratios ($\rho = (I_{VH}/I_{VV})$)

Sample	Annealed depolarization ratio	Quenched deplorization ratio
Silica	–	0.35 ± 0.05
Na-25	0.25 ± 0.05	0.20 ± 0.05
Na-35	0.25 ± 0.05	0.15 ± 0.05
K-25	0.60 ± 0.05	1.00 ± 0.05
K-35	0.25 ± 0.05	0.25 ± 0.05
Rb-25	1.10 ± 0.05	0.50 ± 0.05
Rb-35	1.00 ± 0.05	0.60 ± 0.05
Cs-25	0.65 ± 0.05	1.25 ± 0.05
Cs-35	1.00 ± 0.05	0.50 ± 0.05

Note that ρ tends to increase with alkali mass. Also, there exist major differences between annealed and quenched samples.

decreases with increasing alkali mass while the broad band frequency increases. Moreover, while the broad band amplitude decreases with alkali doping, the Boson peak is unchanged in all the glasses studied, be they pure or doped with different alkalis. As mentioned in the background section, the broad band is due to bending modes of the Si–O–Si bridges and is therefore closely tied to the connectivity of the glass network. Since it is well known that the addition of alkalis breaks Si–O–Si bonds and reduces the connectivity of the network, our results imply that the Boson mode is not affected by the connectivity of the glass but, rather, that the Boson modes are localized. Therefore, a correlation should exist between the Boson frequency, ν_0 and the mass and/or size of the alkali. The simplest possible model being that of a harmonic oscillator, we have attempted to quantitatively relate the frequency, ν_0, to the mass (m) of the alkali, according to the simple formula

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \tag{3}$$

in which k is a constant.

The components of the local oscillator can be identified with several different structural units in the glass. The alkali dopants could vibrate alone or against the nearest SiO_4 tetrahedron, or the motion could involve several alkalis and SiO_4 molecules. Fig. 4 is based on the first possibility, in which ν_0 is plotted simply vs. the inverse square root of the mass of the dopant. The graph is approximately linear and the slope of the line is the square root of the spring constant. The spring constant is expected to be approximately the same for all the alkali metal dopants as they all have one valence electron. The spring constant found from the slope is 4.9 N/m, which is close to the typical value of 5 N/m given for the long wavelength vibrations of atomic planes [10]. However, this agreement may be coincidental due to the simplified assumptions about the vibration upon which the linearity is based. In particular, it is rather surprising that the datum point for pure SiO_2, obtained by taking the mass of Si, also falls on the line. This model of an alkali ion vibrating in the potential of neighboring SiO_4 units may be an oversimplification and may not be applicable. Consequently, we fit our data with another more physically meaningful model in which we considered the coupled vibrations of one dopant with one SiO_4 molecule (Fig. 5). This frequency dependence is also approximately linear and yields a slightly smaller spring constant of 3.55 N/m. The two models tested above are only presented to provide some physical references to what the localized oscillators giving rise to the Boson peak might be and show that even such simple models yield force constants that are reasonable. One
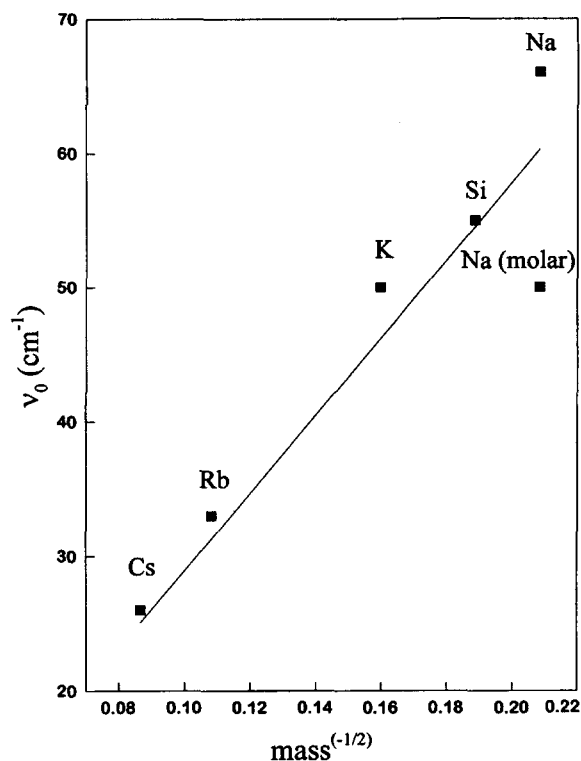
Fig. 4. First harmonic oscillator model for Boson peak. Masses are those of the individual alkalis and silicon. The solid line on this graph and the next are constrained to pass through the origin. The higher sodium silicate data point on this graph and the next two is the 25% doped by weight sample while the lower is the molar sodium sample.

Fig. 5. Second harmonic oscillator model for Boson peak. Masses are the reduced mass of one alkali plus one SiO_4 molecule.

could obviously consider more sophisticated models yet and consider two alkalis and several SiO_4 molecules, but the normal modes of such a complex oscillator would be more difficult to calculate. Such a model has been proposed by Buchenau et al. [11] in SiO_2 to explain his neutron results. In his model, the Boson peak is attributed to the collective vibrations of five nearest neighbor and corner sharing SiO_4 tetrahedra.

We now address the concentration dependence of ν_0 or, rather, the lack thereof, in the light of the localized oscillator picture presented above. Following the model of Buchenau, we note that an alkali will affect at least five SiO_4 tetrahedra. This number is likely higher, as each of the two tetrahedra connected by the alkali-modified
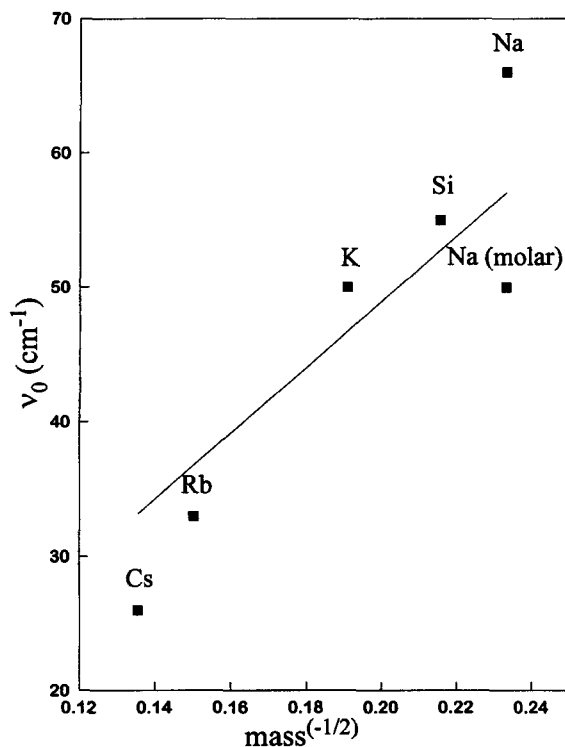
Si–O–Si bridge is itself sharing corners with three others, giving a total of eight tetrahedra which may be affected by a single alkali. Thus, one would predict two distinct concentration ranges for the alkali dopant, a small concentration range, up to approximately one alkali for eight silicon atoms and a large concentration range above that. We expect to see a definite concentration dependence of ν_0 in the small concentration range and a much weaker one in the large concentration range. To second order, we should also expect that the size of the alkali will also have an effect, with fewer tetrahedra being affected for smaller alkalis. We shall argue that all the alkali silicate glasses studied actually fell in the large concentration range (see third column in Table 1). Even the Cs-25 samples, with the smallest molar concentration, correspond to one alkali for seven silicon atoms. Being in a large concentra-

tion regime, we do not expect and indeed do not observe a concentration dependence of ν_0 within experimental uncertainty.

6. Conclusions

The decrease in the amplitude of the broad band and the shift to higher frequency is attributed to a reduction of network connectivity with increasing alkali concentration. The Boson peak remains equally strong in all the glasses investigated in this study, apparently unaffected by the decrease in connectivity of the glass and based on this effect we suggest that the Boson peak is due to localized vibrations. These vibrations can be described reasonably well by a harmonic oscillator model in which the vibrational frequency is primarily determined by the reduced mass of the oscillator.

Acknowledgements

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