Bose Peak and Vibrational Bands in Raman Spectra of Sodium Borosilicate Glass

Vlasta Mohatch and Krešimir Furšič
Ruder Bošković Institute, P. P. Box 1016, 41000 Zagreb, Croatia

Received July 17, 1991

The existence of an asymmetric broad band called boson (Bose) peak in VV as well as in VH polarized Raman spectra of sodium borosilicate glass with various amounts of $\text{SiO}_2$ is shown and its bandshape fitted according to the formula

$$I_{\text{VV}} = C(\nu)^2 \frac{\alpha(\nu)}{\nu} \left(\frac{\nu}{\nu_0}\right)^{\frac{\alpha(\nu)}{2} + 1},$$

where $\alpha(\nu)$ stands for Bose-Einstein occupation number and $C(\nu)$ is given by

$$C(\nu) = \left(\frac{\nu}{\nu_0}\right)^{\alpha(\nu)/2}.$$ 

Parameter $\nu_0$ seems to depend on the chemical composition and the type of glass. The low frequency band of our sodium borosilicate glass ($1:1:4$ molar ratio of $\text{Na}_2\text{O}:\text{B}_2\text{O}_3: \text{SiO}_2$) obeys this formula well, with $\nu_0 = 82$ cm$^{-1}$, which is approximately the peak position of the band.

On addition of $\text{SiO}_2$ (1.5 to 10 wt %) the shape of boson peak in VH spectra changes on addition of 1.5 wt %, but remains unchanged on further addition of $\text{SiO}_2$. In the VH - $1/3$ VH spectrum, a new peak around 350 cm$^{-1}$ appears, indicating that Si into borate as network formers.

INTRODUCTION

Recently, a number of papers has appeared concerning low frequency Raman spectra of glasses$^{1,2,3}$ and other amorphous solids$^4$ which exhibit the so called boson peak. It became apparent that the excess density of vibrational states (DVS) is responsible for the low frequency maximum common to all glasses.

Shaker and Gammon's expression for intensity of scattered light$^5$

$$I_{\text{VV}} = C(\nu)\nu^\alpha(\nu + 1)$$

served as a starting point for Malinovsky et al.$^6$. They suggested$^6$ that in such an expression for VH polarized Raman intensity and under the assumption of Debye density of states ($\gamma(\nu) - \omega^3$) $C(\nu)$ has $\nu$ - dependence.
\[ C(\omega) = \frac{\alpha^2}{(\omega^2 + \omega_0^2)^2} \]  

(2)

that could reproduce the observed VH spectra of various glasses.

In a more recent article\(^1\) Malinovsky, Novikov et al. report on inelastic neutron scattering measurements that were done on SiO2-As2O3 and an example of metallic glass, all of which show a common pattern of generalized vibrational spectrum \(\frac{\partial^2 V}{\partial \omega^2}\). They conclude that the low lying symmetric band results from excitation of DVS and that \(C(\omega)\) is a monotonous function that increases with \(\omega\) without having any maximum up to the energy of 10 meV (\(\approx 30 \text{ cm}^{-1}\)).

It is worth stressing that, although the boson peak is now considered to be caused by the density of states (as agreed in ref\(^1\)), the product \(C(\omega)\) could still be given by

\[ C(\omega) = \frac{\alpha^2}{(\omega^2 + \omega_0^2)^2}. \]  

(3)

We investigated polarized Raman spectra of sodium borosilicate glass (16.7 wt % \(\text{Na}_2\text{O}, 18.7\) wt % \(\text{B}_2\text{O}_3\) and 64.6 wt % \(\text{SiO}_2\)) into which different amounts of \(\text{SnO}\) were added (1.5 wt %, 2.5 wt %, 5 wt % and 10 wt %). Special attention was paid to VH spectral formula \(1,3\) for the VH intensity were tested.

**EXPERIMENTAL**

Raman spectra were recorded through standard geometry at 90°. An excitation, Coherent Innova-100 laser with \(\lambda = 514.5 \text{ nm}\) was used and the scattered light was analyzed by Dilor X-24 Raman spectrometer. Samples were prepared by Dr. S. Muzii and Z. Bajčík and for Raman measurements, cut in small cubes and optically polished. At the sample, typical laser power was 500 mW. Spectra were recorded in sequential mode with the spectral slits width \(= 2 \text{ cm}^{-1}\) and accumulation time of one second.

**RESULTS AND DISCUSSION**

In Figure 1, VV - 4/3 V H polarized Raman spectra are presented. The chemical composition of samples S-1 to S-5 is given in Table I. Addition of \(\text{SnO}\) causes appearance of a new peak around 500 cm\(^{-1}\), which partly overlaps with the strongest band of vitreous silica. The influence of \(\text{SnO}\) on sodium borosilicate glass is already discussed,\(^1\) where the Moeschbauer spectra are given and the presence of tin in the form of \(\text{Sn}^{+}\) ions confirmed. Tin is, therefore, most likely to replace Si ions in a random network, behaving as network former. Other high frequency bands are also discussed.\(^1\)

| Table I: Chemical composition (in wt %) of samples S-1 to S-5 |
|-----------------|--------|--------|--------|--------|--------|
| Component       | Na2O   | B2O3   | SiO2   | X(%)   | SnO    |
| S-1              | 16.7   | 18.7   | 64.6   | 100    | +3.0   |
| S-2              | 16.7   | 18.7   | 64.6   | 100    | +3.0   |
| S-3              | 16.7   | 18.7   | 64.6   | 100    | +3.0   |
| S-4              | 16.7   | 18.7   | 64.6   | 100    | +10.0  |
| S-5              | 16.7   | 18.7   | 64.6   | 100    | +10.0  |
Various glasses, especially pyrolytic glasses, were studied. The authors report on inelastic neutron scattering and an example of metallic glass. The vibrational spectrum of these glasses results from excess Debye-Waller factor, which is not considered to be caused by fluctuations in local structure.

Equation (2):

\[ V(VH)^{1/3} \]

Equation (3):

A boric oxide-glass (16.7 wt % B2O3) with different amounts of SnO were examined. Special attention was paid to the VH spectrum at 90°. An excitation, Coherent Extended X-rays were applied by BILOR. A buildup of X-rays and X-rays for Raman scattering in the sample. Typical laser power was 100 mW and the spectral slit width was 2 cm⁻¹.

The following table presents the results of the study for samples S-1 to S-5:

<table>
<thead>
<tr>
<th>Sample</th>
<th>SnO (wt %)</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>S-2</td>
<td>1.5</td>
<td>100 + 1.5</td>
</tr>
<tr>
<td>S-3</td>
<td>2.5</td>
<td>100 + 2.5</td>
</tr>
<tr>
<td>S-4</td>
<td>5.0</td>
<td>100 + 5.0</td>
</tr>
<tr>
<td>S-5</td>
<td>10.0</td>
<td>100 + 10.0</td>
</tr>
</tbody>
</table>

Figure 1. \( VV = 4/3 \) V-polarized Raman spectra of samples S-1, S-2, S-3, S-4 and S-5.
All the recorded VH spectra of samples S-2 to S-5 look similar; Figure 2 presents spectra of samples S-1 and S-2 for comparison. The change in boson peak is clearly visible – its maximum shifts to higher wavenumbers and its "width" is greater. Using formulas 1 and 3, a numerical fit was made to find \( \omega_0 \) for samples S-1 and S-3 (which was chosen because of the slightly better signal to noise ratio) and values of \( \sim 52 \text{ cm}^{-1} \) and \( \sim 63 \text{ cm}^{-1} \) were found. These values approximate peak positions of boson peaks.

In the case where boson peak overlaps with the neighbouring bands and on the basis of the fact that \( \omega_0 \) in the approximate peak position of the band, we expect to be able to eliminate boson peaks from VH spectrum by spectra subtraction, once we can simulate its shape. This would enable a more clear observation of other bands in its vicinity more clearly.

As seen in Figure 2, the observed maximum of the Bose peak shifts from 54 cm\(^{-1}\) to 66 cm\(^{-1}\) on addition of 1.5 wt % of SnO. Since the Bose peak is generally accepted as the measure of the amorphousness of the material inspected, the shift could be attributed to the change in glass network produced by replacement of Si\(^+4\) by Sn\(^+4\) ions. For the explanation of the fact that on further addition of SnO no change in VH Raman spectra is observed, additional data are required.

![Figure 2. VH polarized Raman spectra of samples S-1 and S-2.](image)

Acknowledgement. – We are grateful to Dr. V. Balian for his samples and help during the work.


**Bosov v.h.**

Ramanovej spektroskópicoj
SnO. Univerzalne je postojný zvyk o plastosporovom

\[ C_{\text{Ho}}(n) = \text{proporčný.} \]

Parameter \( n \) ovladá súčasné maximálnu intenzitú. Sn
vysoce mene hlavne ak je odlišné
lakové schémy.
5-5 look similar; Figure 2 presents a change in boson peak is clearly
and its width is greater. Using this, for samples S-1 and S-3 (which
have the ratio) and values of ≈ 12 cm⁻¹, the peak positions of boson peaks,
the neighboring bands and on the hand, we expect to
in a by spectra subtraction, once we
see observation of other bands in
the boson peak shifts from 54 cm⁻¹
the boson peak is generally accepted
and observed, the shift could be as
replacement of Sr⁺⁺ by Sr⁺⁺ ion. A
of SrO no change in VH Ra

Acknowledgement. We would like to thank Dr. S. Mesić and Z. Baja for preparation of the samples and help during the work.

REFERENCES

SAŽETAK
Ressonav vrh i vibrationske vrpce u Ramanovim spektrometrima

sastiju hromosilikatnih stakala
Vesna Mohadek i Kraljevic Furidić

Ramanov spektroskopiom izuvana su silikatska stakla u ovisnosti o uželju dobivog SrO. Ustanovljeno je postojanje širokog asimetričnog vrpca (zv. bosonske vrprce) čiji je VH intensitet opisan formulom

I_vH = C(Ο,0)(Ο,0) m(0) x 1,5

gde je m(0) Bose-Einsteinov faktor napravnosti, a g(0o) gustoća stanja. Proučeni C(Ο,0)(Ο,0) je proporcionalan izrazu

C(Ο,0)(Ο,0) = g(0o) e⁻^(-hν/kt).

Parametar m(0), ovisi o kemijskom sastavu i tipu stakla, te se približne poklapa s podacima maksimalnog intenziteta bosonske vrpce. Ugaonim reprodukcijom spektrografske slike Bosonske vrpce mogu bi se ona ukloniti iz VH ramanovih spetra, čime bi se postigli ostalih bliskih vrpca lakše odrediti.