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ISSN 0011-1643
UDC 543.42
CCA-2046

Original Scientific Paper

Bose Peak and Vibrational Bands in Raman Spectra of Sodium Borosilicate Glass*Vlasta Mohaček and Krešimir Furić**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 SnO is shown and its bandshape fitted according to the formula

$$I_{\text{VH}} \sim C(\omega)g(\omega) \frac{n(\omega)+1}{\omega},$$

where $n(\omega)$ stands for Bose-Einstein occupation number and $C(\omega)g(\omega)$ is given by

$$C(\omega)g(\omega) = \frac{\omega\omega_0^4}{(\omega^2 + \omega_0^2)^2}.$$

Parameter ω_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 $\omega_0 \approx 52 \text{ cm}^{-1}$, which is approximately the peak position of the band.

On addition of SnO (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 SnO. In the VV - 4/3 VH spectrum, a new peak around 530 cm^{-1} appears, indicating that tin ions behave as network formers.

INTRODUCTION

Recently, a number of papers has appeared concerning low frequency Raman spectra of glasses^{1,2,3} and other amorphous solids⁴ which exhibit the so called boson peak. It became apparent¹ that the excess density of vibrational states (DVS) is responsible for the low frequency maximum common to all glasses.

Shuker and Gammon's expression for intensity of scattered light⁵

$$I_{\text{VH}} \sim C(\omega)g(\omega) \frac{n(\omega)+1}{\omega} \quad (1)$$

served as a starting point for Malinovsky *et al.* They suggested⁵ that in such an expression for VH polarized Raman intensity and under the assumption of Debye density of states ($g(\omega) \sim \omega^2$) $C(\omega)$ has ω - dependence

$$C(\omega) \sim \frac{\omega^2}{(\omega^2 + \omega_0^2)^2} \quad (2)$$

that could reproduce the observed VH spectra of various glasses.

In a more recent article¹ Malinovsky, Novikov *et al.* report on inelastic neutron scattering measurements that were done on $\text{SiO}_2\text{As}_2\text{S}_3$ and an example of metallic glass, all of which show a common pattern of generalized vibrational spectrum $\theta(E)/E^2$. They conclude that the low lying asymmetric band results from excess DVS and that $C(\omega)$ is a monotonous function that increases with ω without having any maximum up to the energy of 10 meV ($\sim 80 \text{ cm}^{-1}$).

It is worth stressing that, although the boson peak is now considered to be caused by the density of states (as agreed in ref.[2]), the product $C(\omega)g(\omega)$ could still be given by

$$C(\omega)g(\omega) = \frac{\omega^4}{(\omega^2 + \omega_0^2)^2} \quad (3)$$

We investigated polarized Raman spectra of sodium borosilicate glass (16.7 wt % Na_2O , 18.7 wt % B_2O_3 and 64.6 wt % SiO_2) into which different amounts of 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° . As excitation, Coherent Innova-100 laser with $\lambda_0 = 514.5 \text{ nm}$ was used and the scattered light was analyzed by DILOR Z-24 Raman spectrometer. Specimens were prepared by Dr. S. Musić and Z. Bajs⁷ 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 slitwidth $\approx 2 \text{ cm}^{-1}$ 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 SnO causes appearance of a new peak around 530 cm^{-1} , which partly overlaps with the strongest band of vitreous silica. The influence of SnO on sodium borosilicate glass is already discussed,⁷ where the Mössbauer spectra are given and the presence of tin in the form of Sn^{4+} 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.^{7,8}

TABLE I

Chemical composition (in wt %) of samples S-1 to S-5

Component	Na_2O	B_2O_3	SiO_2	$\Sigma(\%)$	SnO
S-1	16.7	18.7	64.6	100	
S-2	16.7	18.7	64.6	100	+1.5
S-3	16.7	18.7	64.6	100	+2.5
S-4	16.7	18.7	64.6	100	+5.0
S-5	16.7	18.7	64.6	100	+10.0

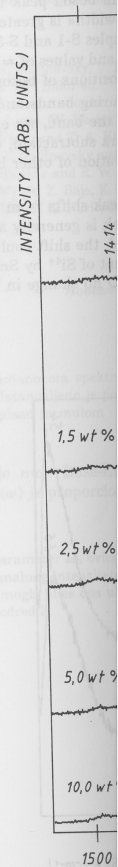


Figure 1. VV - 4/3

(2)

rious glasses.

et al. report on inelastic neutron scattering in As_2S_3 and an example of metallic glasses. Generalized vibrational spectrum results from excess DVS with ω without having any maximum.

is now considered to be caused by $C(\omega)g(\omega)$ could still be given by

(3)

um borosilicate glass (16.7 wt % SnO) with different amounts of SnO were studied. Special attention was paid to VH polarization.

ity at 90° . As excitation, Coherent anti-Stokes Raman light was analyzed by DILOR 3. Mušić and Z. Bajsić and, for Raman scattering, typical laser power was 100 mW, the spectral slitwidth = 2 cm^{-1} and

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tra are presented. The chemical composition of the samples. Addition of SnO causes appearance of new bands which overlaps with the strongest band of borosilicate glass is already disappeared. In the presence of tin in the form of SnO ions to replace Si ions in a random network, frequency bands are also displaced.

Samples S-1 to S-5

S	$\Sigma(\%)$	SnO
1	100	
2	100	+1.5
3	100	+2.5
4	100	+5.0
5	100	+10.0

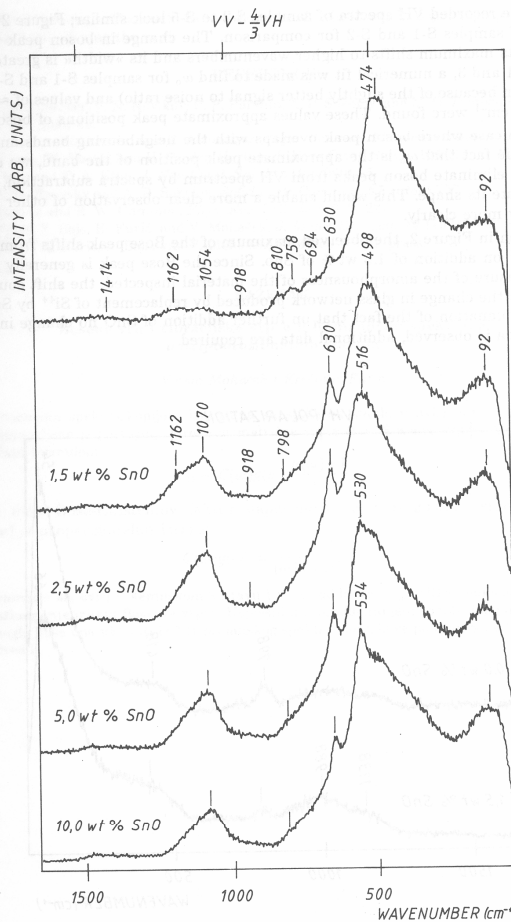


Figure 1. VV - 4/3 VH polarized Raman spectra of samples S-1, S-2, S-3, S-4 and S-5.

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 ω_0 for samples S-1 and S-3 (which was chosen because of the slightly better signal to noise ratio) and values of $\approx 52 \text{ cm}^{-1}$ and $\approx 63 \text{ cm}^{-1}$ 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 ω_0 is 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+} ion⁷. For the explanation of the fact that on further addition of SnO no change in VH Raman spectra is observed, additional data are required.

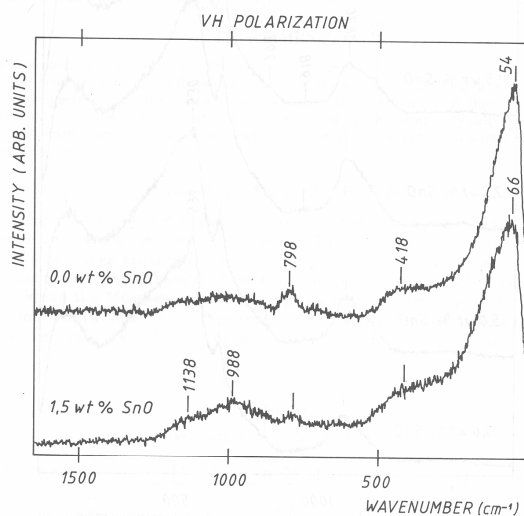


Figure 2. VH polarized Raman spectra of samples S-1 and S-2.

Acknowledgement. – We thank the authors for samples and help during the

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4. F. Viras and T. A. King,
5. V. K. Malinovsky and A.
6. R. Shuker and R. W. Gar
7. S. Musić, Z. Bajsi, K. Fur
8. S. Musić, K. Furić, Z. Ba

Boseov vrh

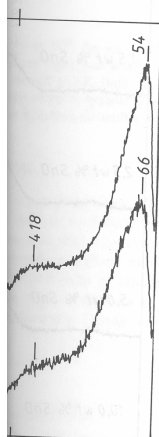
Ramanovom spektroskopi
SnO. Ustanovljeno je postoj
zitet opisan formulom

gdje je $n(\omega)$ Bose-Einst
 $C(\omega)g(\omega)$ je proporcional

Parametar ω_0 ovisi o k
maksimalnog intenziteta Bose
vrpce mogla bi se ona uklon
lakše odrediti.

S-5 look similar; Figure 2 presents the change in boson peak is clearly seen and its «width» is greater. Using ω_0 for samples S-1 and S-3 (which have the same ratio) and values of $\approx 52 \text{ cm}^{-1}$ for the peak positions of boson peaks. The positions of neighbouring bands and on the position of the band, we expect to be confirmed by spectra subtraction, once we have clear observation of other bands in the Raman spectrum.

The Bose peak shifts from 54 cm^{-1} for sample S-1 to 66 cm^{-1} for sample S-2. The Bose peak is generally accepted to be due to the replacement of Si^{4+} by Sn^{4+} ion⁷. The shift of the Bose peak in the Raman spectrum of SnO no change in VH Raman spectrum.



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WAVENUMBER (cm^{-1})

samples S-1 and S-2.

Acknowledgement. – We would like to thank Dr. S. Musić and Z. Bajs for preparation of the samples and help during the work.

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SAŽETAK

Boseov vrh i vibracijske vrpce u Ramanovim spektrima natrij-borosilikatnih stakala

Vlasta Mohaček i Krešimir Furić

Ramanovom spektroskopijom izučavana su silikatna stakla u ovisnosti o udjelu dodanog SnO . Ustanovljeno je postojanje široke asimetrične vrpce (tzv. Boseove vrpce) čiji je VH intenzitet opisan formulom

$$I_{\text{VH}} \sim C(\omega)g(\omega) \frac{n(\omega)+1}{\omega},$$

gdje je $n(\omega)$ Bose-Einsteinov faktor napučenosti, a $g(\omega)$ gustoća stanja. Produkt $C(\omega)g(\omega)$ je proporcionalan izrazu:

$$C(\omega)g(\omega) = \frac{\omega^4}{(\omega^2 + \omega_0^2)^2}.$$

Parametar ω_0 ovisi o kemijskom sastavu i tipu stakla, te se približno poklapa s položajem maksimalnog intenziteta Boseove vrpce. Uspješnim reproduciranjem spektralnog oblika Boseove vrpce mogla bi se ona ukloniti iz VH ramanskog spektra, čime bi se položaji ostalih bliskih vrpca lakše odredili.