

Rigidity transitions in glasses driven by changes in network dimensionality and structural groupings –Supplementary Material

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In this part, we provide the details about synthesis, characterization and Raman analysis of lithium and sodium borates.

I. SYNTHESIS AND CHARACTERIZATION

Synthesis: $(\text{Na}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ (NaB) and $(\text{Li}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$ (LiB) glasses were synthesized in the range, $0\% < x < 44\%$ and $0 < x < 60\%$, respectively, by the usual melt-quenching technique. Stoichiometric amounts of anhydrous Na_2CO_3 (or Li_2CO_3) from Fisher Scientific and B_2O_3 (Puratronic, 200 ppm H_2O , Alfa Aesar) were weighed and thoroughly ground with a mortar and pestle prior to alloying. Due to the hygroscopic nature of base B_2O_3 glass, special precautions were taken in handling the starting materials. All the weight measurements and grinding of the starting materials were done inside a dry N_2 gas filled glove box (Relative humidity $< 10^{-3} \%$) and then immediately transferred to the furnace, which was already kept at 120°C . The mixture was reacted in a platinum or alumina crucible.

Calorimetry: Thermal characterization was performed by using a temperature modulated DSC (Differential Scanning Calorimeter) from TA instruments, model 2920. Aluminum pans and lids were used to hermetically seal the lithium and sodium borate glass samples of approximately 20 mg weight in a platelet configuration. The “thermally reversing heat flow”, which consists of a rounded-step was used to measure T_g from the inflection point of the step, and ΔC_p from the step height. The “non-reversing heat flow” signal is the difference between the “total heat flow” signal and the “reversing heat flow” signal, and was frequency corrected for the finite modulation frequency of 10^{-2} cps. The overshoot observed in a DSC experiment is related to the hysteresis associated with the glass transition and the “non-

reversing heat flow” also comes from this overshoot. The non-reversing enthalpy at T_g , hence forth denoted as $\Delta H_{nr}(x)$, is obtained by integrating the area under the non-reversing heat flow signal. If this area were to be zero, the glass transition would be thermally reversing, which turns out to be the case between 14% to 27% lithia in lithium borates, and between 20% to 40% soda in sodium borates (Fig. 2 of the main manuscript).

Raman scattering: Raman spectra were recorded using a T64000 triple-monochromator dispersive Raman system from Horiba Jobin Yvon Inc., with a charge-coupled device (CCD) camera and a microscope (Olympus BX 41) attachment. The 514.1 nm radiation from an Ar-ion laser was focused to a 2 μm spot size and typically with about 6 mW of incident power used to excite the scattering. Samples were mounted in a dry N_2 gas filled MMR Joule-Thompson refrigerator cold stage (MMR Technologies, Mt.View, CA 94043) held at room temperature to avoid exposing samples to laboratory ambient ($\sim 40\%$ RH).

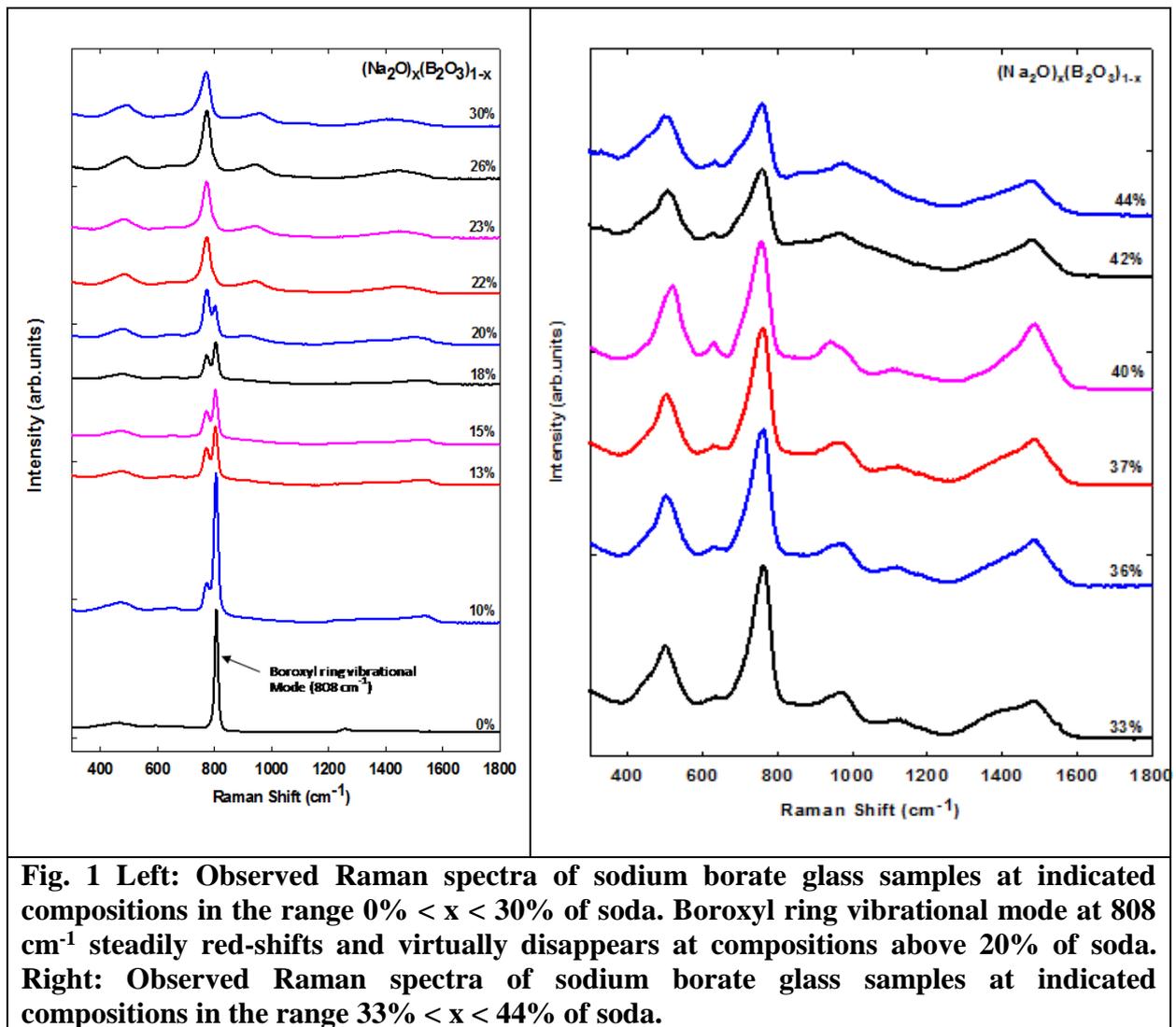
Electrical conductivity : Disc-shaped glass samples with a diameter of about 10 mm and thickness of about 2 mm were synthesized by pouring melts into special troughs machined in a polished stainless sheet. Platelets were thermally relaxed by T_g cycling. Samples were polished, Pt electrodes deposited, and mounted inside a spring-loaded sample holder. AC impedance measurements were performed at different temperatures, using Solartron SI 1260 impedance analyzer in the frequency range 1 Hz to 1 MHz. The ac conductivities and activation energies for conduction were extracted from the impedance data as a function of glass composition.

II. RAMAN SCATTERING DECONVOLUTION

General behavior: Alloying soda (Na_2O) or lithia (Li_2O), acts to modify the B_2O_3 base glass network. Several changes take place as BO_4^- tetrahedral units form; sub- and super-structural units made of base BO_3 triangles and tetrahedral BO_4^- units are observed. Raman

scattering is an effective tool to study evolution of these sub- and super-structural units with the amount of modifier added.

Figs. 1 and 2 show the Raman spectra for samples of soda content, $0\% < x < 44\%$ and Lithia content, $0\% < x < 35\%$ respectively.



A striking observation in the Raman data is that, the Boroxyl ring (BR) vibrational mode at 808 cm^{-1} wave-number virtually disappears when the amount of modifier exceeds 20%. As shown in Fig. 1, with the addition of soda, the intensity of 808 cm^{-1} mode decreases and a new mode starts to emerge at 770 cm^{-1} . The intensity of 770 cm^{-1} mode increases with

the addition of soda and peaks at around 25%. The 770 cm^{-1} mode is due to the tri-borate species in NaB glasses.

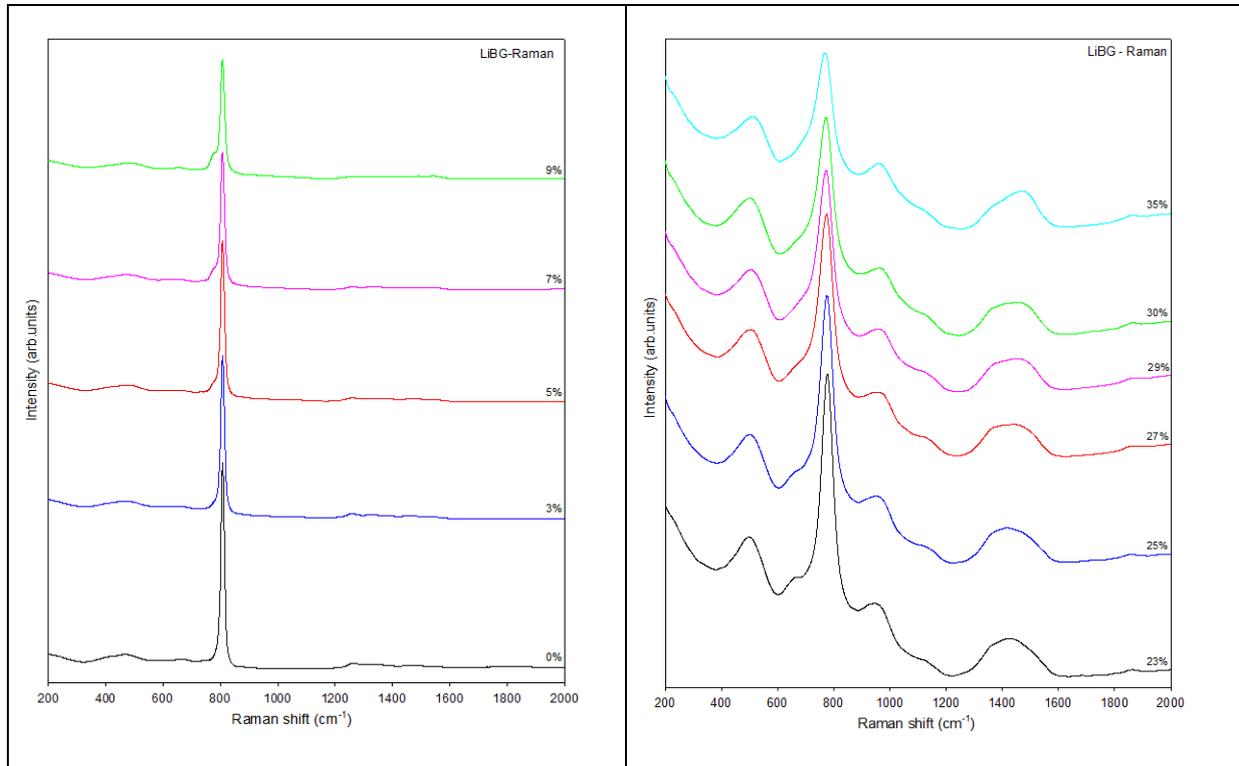


Figure 2: Left: Observed Raman spectra of lithium-borate glasses at indicated compositions in the range $0\% < x < 9\%$ of lithium content. It is very clear that the intensity of Boroxyl ring mode at 808 cm^{-1} steadily goes down with increasing Li_2O content and a companion mode starts to grow at 770 cm^{-1} . Right: Observed Raman spectra of lithium-borate glasses at indicated compositions in the range $23\% < x < 35\%$ of lithium content.

Deconvolution: Peak-fitting the Raman modes and studying the systematic evolution of various modes is very helpful to make the mode assignments and also to learn the evolutionary trends of various modes of interest. Here, we peak-fitted the line shapes in two different wave-number regions of interest. First for the wave-number range 400 cm^{-1} to 1200 cm^{-1} and then for the high frequency range (1200 cm^{-1} to 1650 cm^{-1}). Deconvolution of line shapes for a typical sample is shown in Fig. 3.

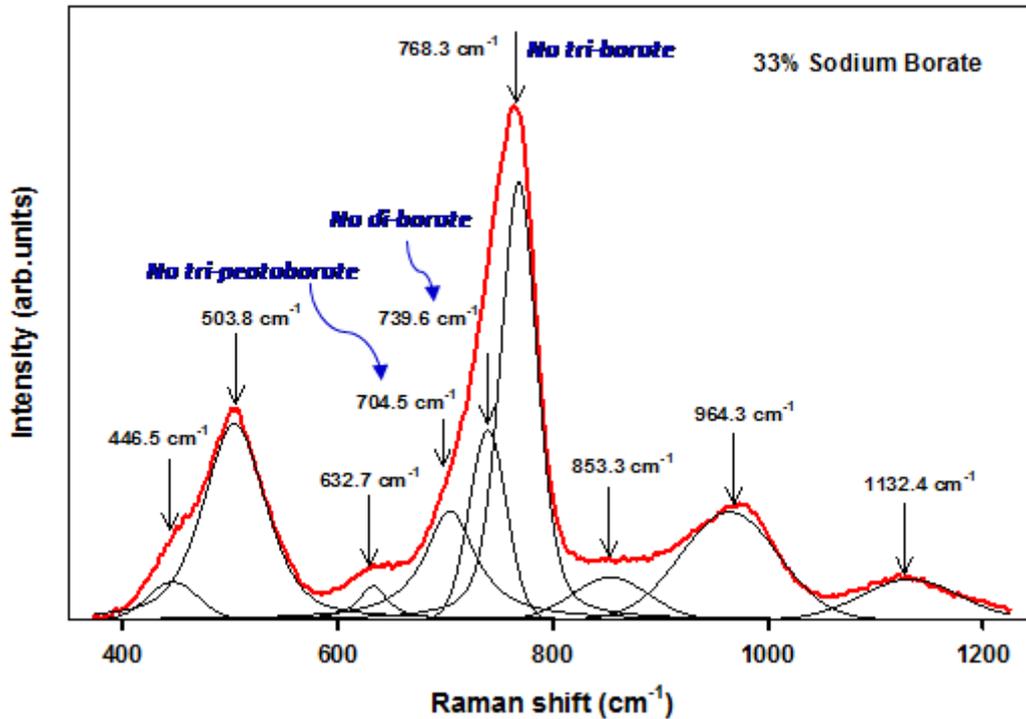


Fig. 3: Typical Raman line shape analysis of 33% sample for the wave-number range 400 cm^{-1} to 1200 cm^{-1} . Combination of Gaussian plus Lorentzian line-shapes have been used to de-convolute the Raman spectrum. Mode assignments are given in Tables 2 and 3.

A combination of Gaussian plus Lorentzian line shapes have been used to de-convolute the Raman spectra. Systematic evolution of mode frequencies and mode scattering strengths are then followed with composition. At $x = 0$ (i.e. pure B_2O_3), the Boroxyl ring vibrational mode at 808 cm^{-1} is the highest intensity mode (Left panels of Fig. 1 and 2). When soda or lithia is added, three new modes 770 cm^{-1} , 740 cm^{-1} and 705 cm^{-1} start to grow respectively one after the other inside a broad envelope as shown in Fig. 3 for a typical sample. These three modes are related to the formation of BO_4^- tetrahedral units at the expense of BO_3 triangular units in 3 membered rings (see below). Mode assignments and their justification are given below.

Mode assignments: In the present work, we have de-convoluted the Raman line-shapes for the first time, and one can extract the mode scattering strengths and mode

frequencies from these line shape analyses. It is then possible to make the mode assignments purely from the variation of Raman mode scattering strength variation with composition.

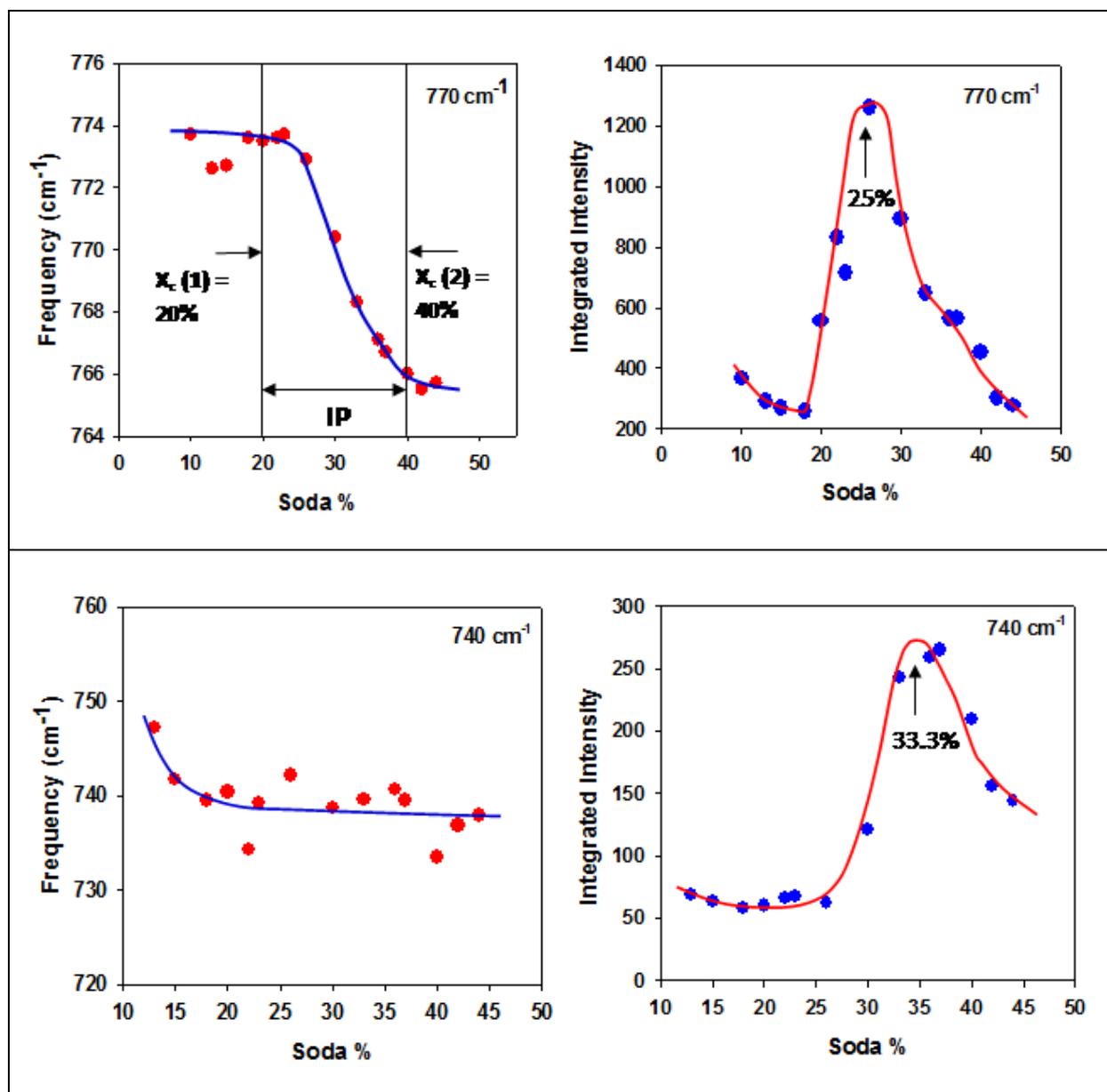
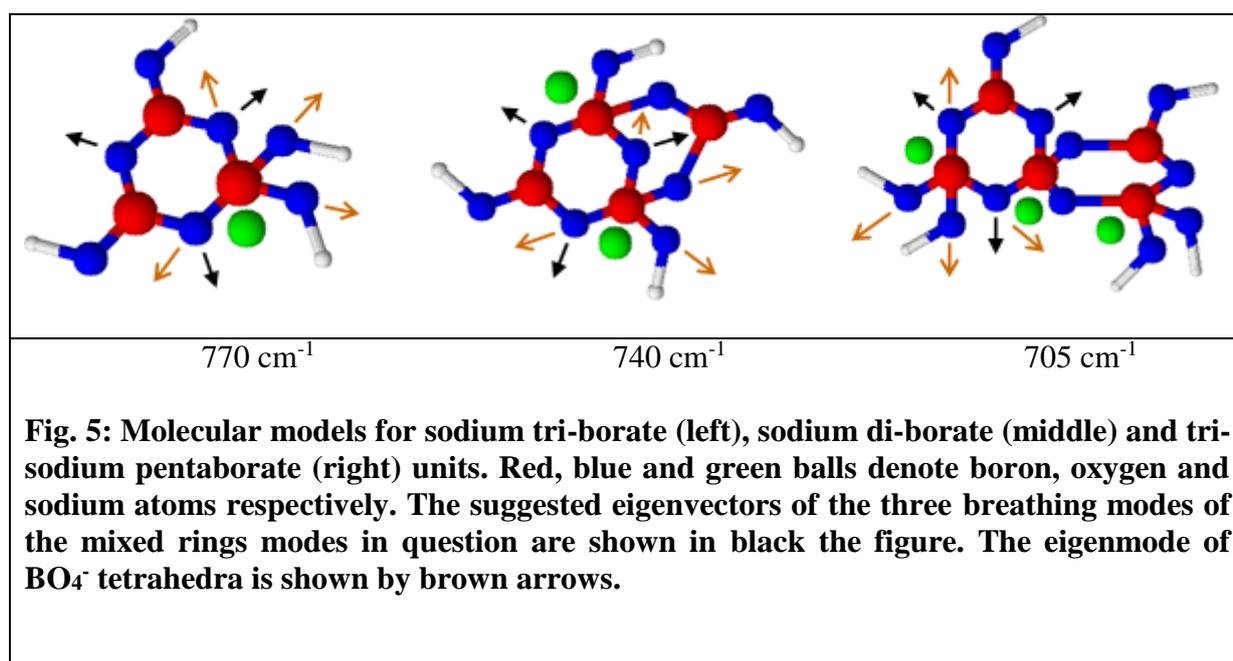


Fig. 4: Raman deconvolution of sodium borates. The 770 cm^{-1} mode red shifts with soda content, and mode scattering strength is maximized at around 25% indicating that this mode is related to the tri-borate unit. Similarly, the 740 cm^{-1} mode mildly red shifts with soda, and the mode scattering strength is maximized at around 33.3% indicating that this mode is related to the diborate unit.

For example, the scattering strength and frequency variation with soda content for 770 cm^{-1} mode is shown in Fig. 4. Notice that the mode scattering strength is maximized at around 25%. This 25% Na_2O means, Na: B = 1:3, i.e. 1 sodium atom is associated with 3 boron atoms. Therefore, undoubtedly, this mode could be assigned to the tri-borate unit (See Fig. 5

for molecular units). In a similar way, the 740 cm^{-1} mode could be assigned to di-borate unit. Because, 740 cm^{-1} mode shows maximum scattering strength at around 33.3 % soda content (Fig. 22), this means, $\text{Na}:\text{B} = 1:2$, i.e. 1 sodium atom is associated with 2 boron atoms. Without a doubt, it is due to the di-borate species. In a similar fashion, many other mode assignments could be made and a summary of these mode assignments are given in Tables 1 of the manuscript for LiB and NaB.



Low frequency behavior: Observed low frequency Raman spectra for three typical samples are shown in Fig. 6 below. Notice that, there are some sharp modes in all the samples and the very prominent sharp modes are denoted as 1, 2, 3 and 4. These sharp modes appear at the same frequency for all the samples having different soda contents. There is also a broad feature (red line) in all the samples and this broad feature is connected to the intrinsic nature of the sample composition.

The origin of these sharp modes is due to the scattering of the green laser light from oxygen in air, because the green laser travels through roughly a 4 meter long path from the laser to the glass sample positioned on the XY stage of the microscope in the T 64000 dispersive Raman system.

A simple way to proceed to analyze the spectra without these extraneous peaks which are not from the glass sample is to either remove them from the line shapes directly by the software or to signal average the observed line shapes using the software.

We used the second way, i.e., signal averaged the observed line shape using LABSPEC software and used around 10 smoothing cycles. In the smoothed-out spectra (Fig.7), the narrow modes due to oxygen have been removed leaving the broad feature identified with the Boson mode of our glass specimen intact.

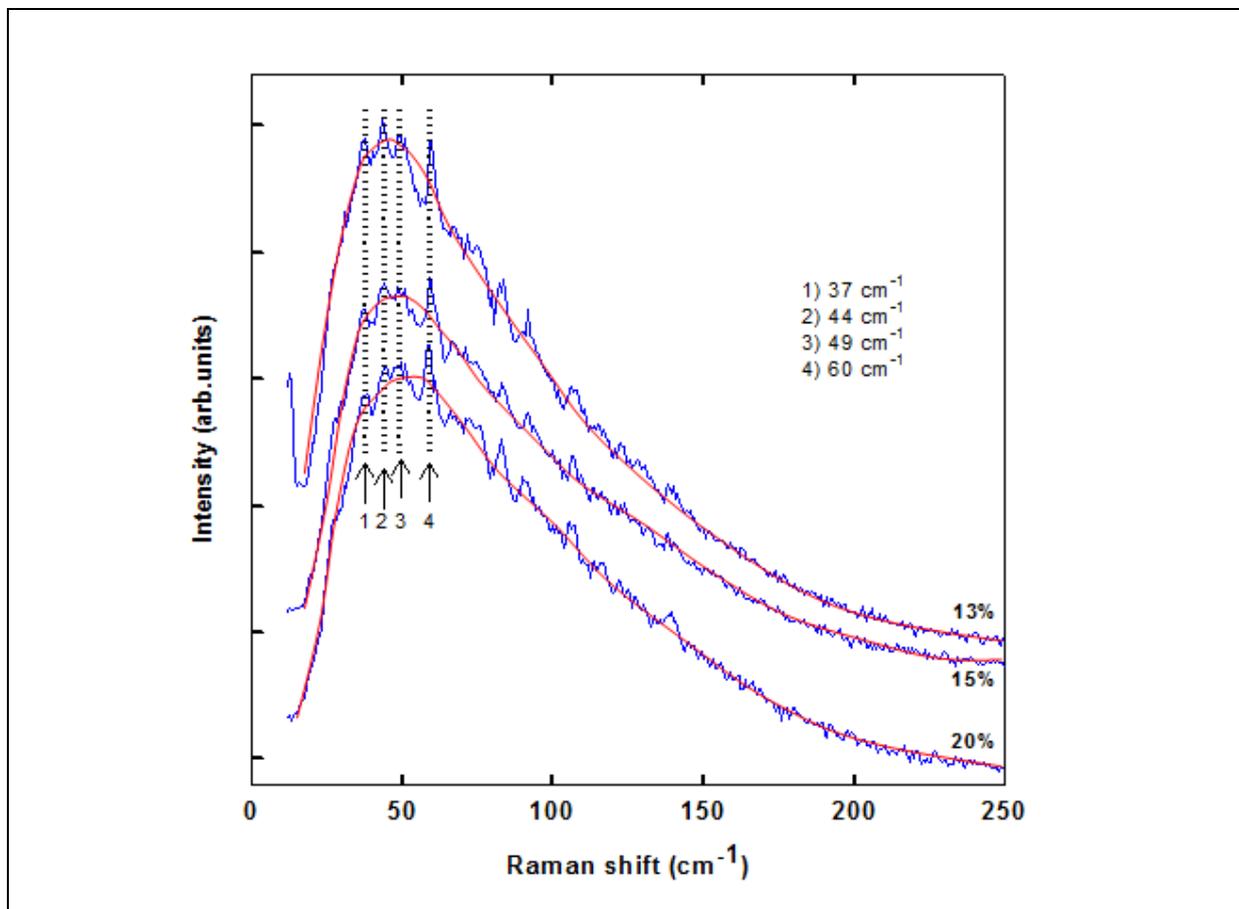


Fig. 6: Observed low frequency Raman spectra for three sodium borate glass samples. There are some sharp features embedded in the broad (red line) feature. These sharp features denoted by 1, 2, 3 and 4 are Oxygen lines due to the long laser path through the atmosphere.

In our experiments, Raman spectra for different compositions were acquired at the same laser power, thus permitting us to normalized the spectra. In general, Raman scattering is given by

$$I_{\text{exp}} = C(\omega)g(\omega)[n_B+1]/\omega$$

where $C(\omega)$ represents the photon-vibration coupling constant, $g(\omega)$ the vibrational density of states (VDOS) and n_B is the Bose occupation number.

In order to analyze the low frequency modes, we obtained the reduced Raman scattering (I_{red}) from I_{exp} ;

$$I_{\text{red}} = I_{\text{exp}}/(n_B+1) \propto [C(\omega)g(\omega)/\omega]$$

A summary of reduced Raman scattering is shown in Fig. 7 for all the sodium borate glasses.

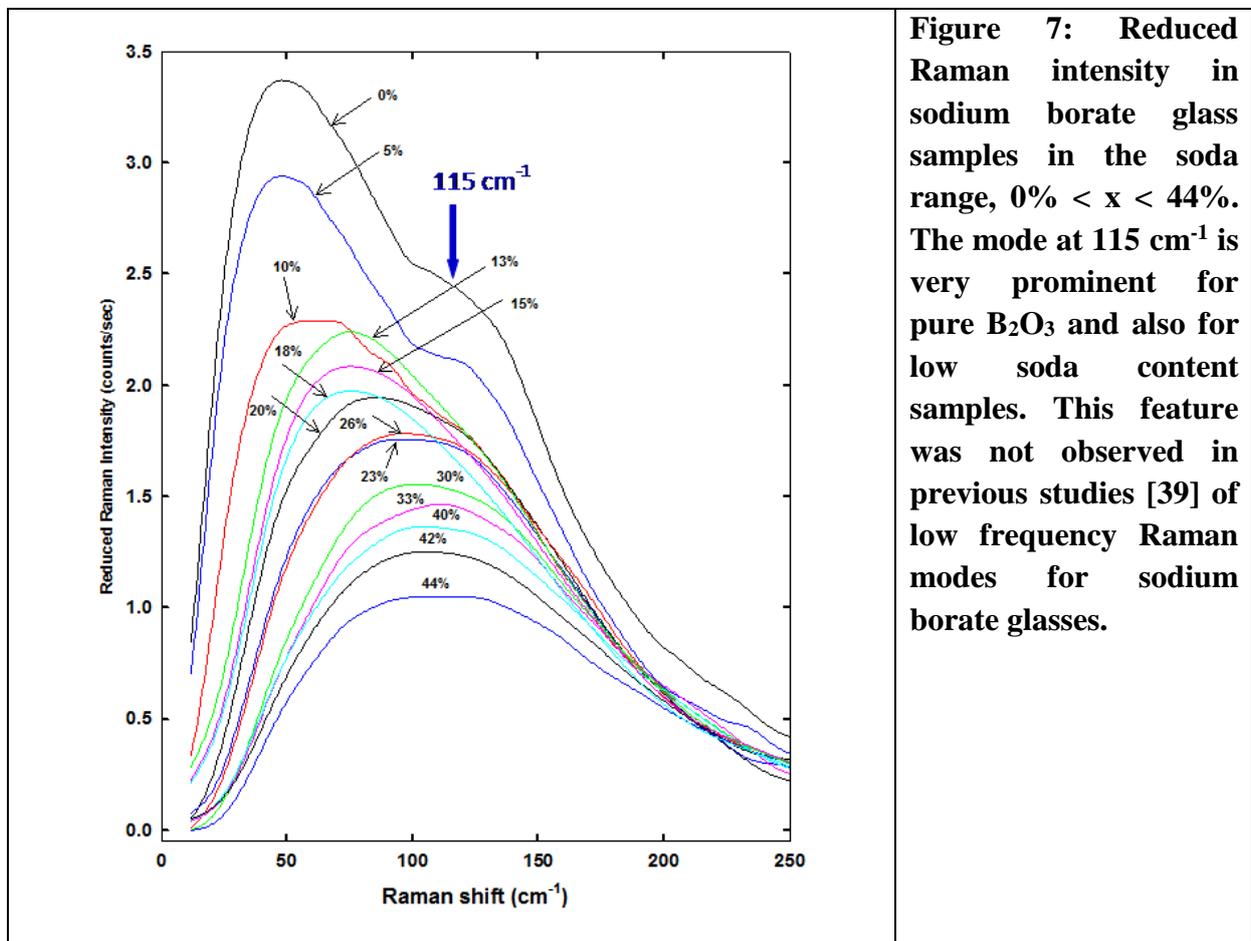


Figure 7: Reduced Raman intensity in sodium borate glass samples in the soda range, $0\% < x < 44\%$. The mode at 115 cm^{-1} is very prominent for pure B_2O_3 and also for low soda content samples. This feature was not observed in previous studies [39] of low frequency Raman modes for sodium borate glasses.