Raman Spectroscopy Of Glasses with High And Broad Raman Gain In The Boson Peak Region

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RAMAN SPECTROSCOPY OF GLASSES
WITH HIGH AND BROAD RAMAN GAIN IN THE BOSON PEAK REGION

by

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ABSTRACT

This thesis investigates Raman spectra of novel glasses and their correlation with structure for Raman gain applications. Raman gain for all-optical amplification by fibers depends significantly on the cross section for spontaneous Raman scattering allowing to compare signal strength and spectral coverage. We also investigate the relationship between glass structure and the Boson peak (enhancement of the low-frequency vibrational density of states) and report new inelastic neutron scattering spectra for niobium-phosphate glasses.

Polarization resolved Raman spectra of glasses based on tellurite and phosphate formers have been measured from 6 – 1500 cm⁻¹ using an excitation wavelength of 514 nm. The Tellurite glasses exhibit Raman Spectra at least 10 times more intense, are more spectrally uniform and possess spectral bandwidths more than a factor of two wider than fused silica. Assignments of the vibrational bands are presented and the compositional dependence of the spectra is discussed with respect to the molecular structure. Significantly high Boson peaks were found in the frequency range from 30-100 cm⁻¹.

The Raman gain curves were calculated from the polarized spontaneous Raman spectra. In particular, they show broad and flat band in the low frequency region (50-400 cm⁻¹) suggesting that these glasses may be useful for Raman gain applications extending to very low frequencies.

The inelastic neutron scattering spectra of the niobium-phosphate glasses display a pronounced low-frequency enhancement of the vibrational density of states. By
averaging over the full accessible wavevector range we obtain an approximate spectral
distribution of the vibrational modes. Through direct comparison with the Raman spectra
we determine the Raman coupling function which shows a linear behavior near the Boson
peak maximum. Possible mechanisms contributing to the low frequency Raman band
such as disorder-induced irregular vibrational states are discussed.
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CHAPTER ONE: INTRODUCTION

The history of human society evolution has been a process of integration of the isolated systems (individuals, companies, countries etc.) into a whole system, and the key for the integration of different systems into one is exchange of energy (materials, information etc.). The exchange of large sum of materials, has given birth to the materially prosperous society we are living in right now. Now, in the 21st century, the exchange of information, at the light speed, is setting off to shape this world into a single system in which different regions or countries can share information at light speed and can respond instantaneously as well, it is as if the human race is beginning to evolve into a large organism. The enormous potentially benefits are still hard to determine. The exchange of such large sum of information at light speed, relies greatly on telecommunication technology.

With network load estimates of 40 THz by 2010, the future of telecommunications is bandwidth [1, 2]. The development of broadband optical fiber has made Raman amplifiers attractive. This is attributed to the fact that existing networks operate under Er-doped fiber amplifiers (EDFA) or EDFA/Raman hybrid systems, which possess a rather limited bandwidth. Raman gain occurs through coherent interactions of the pump and signal beams with the vibrational modes of an optical fiber, resulting in the ability to amplify over a broad spectral range. Use of broadband fiber with newly developed Raman amplifiers would enable a large amount of the bandwidth to be
transmitted over long ranges. Schafer and JungJohann [3] limit Raman potential to only short haul applications at 1310 nm, however newer materials could be developed with high enough and broad enough gain profiles to be deployed in the entire telecom window, as illustrated in Figure 1 [1].

Much documentation exists showing how nonlinear processes provide an intriguing means of optical amplification for telecommunication purposes [1]. In the ideal case, amplifying a signal with a large gain over a very broad range would be best. Of the various nonlinear processes such as stimulated Brillouin, stimulated four photon and stimulated Raman scattering (SRS), amplification through SRS has the most potential of achieving ideal conditions. The reason for this is due to well-known Raman amplification characteristics such as inherent phase matching, high-speed response, low noise and broad gain bandwidth [1-3].

![Fiber Transmission Diagram](image)

*Figure 1. Schematic showing the expanded telecommunications window provided by new Lucent technology.*

[1][3]
Nonlinear interactions between an incident EM field (of a pump) and molecular vibrations provide the driving force for the Raman response in Raman gain materials. Raman amplifiers can impact existing networks in two big ways: cost and productivity. By substituting Raman into a network the distance between regeneration sites may be increased from 400-600 km up to 4000 km [4]. These regeneration sites account for a large percentage of the overall network cost, so an order of magnitude increase in distance would save millions if not billions of dollars in network costs. This is possible because SRS can amplify the network signal as it offsets attenuation [5]. Use of WDM (Wavelength Division Multiplexing) and (Dense Wavelength Division Multiplexing) DWDM systems will increase bandwidth as transmission speeds and data rates along each channel increase. This bandwidth increase also requires more amplification. Raman may be used to obtain such amplification without concerns of signal distortion or crosstalk between channels [3]. Raman amplification gains of 45 dB have been reported for a 1.24 µm signal along a GeO2-SiO2 single-mode fiber [4].

The need for Raman in telecommunication networks necessitates materials with broad Raman gain profiles. Silica, though known for its very low loss and the ability to serve as a carrier medium, unfortunately has a relatively low gain as compared to other glasses such as germania. Other multi-component glasses (heavy-metal germanates and arsenates) have been developed exhibiting much higher gains, however they also possessed relatively high losses compared to silica [6].

The spontaneous Raman scattering cross-section is directly proportional to Raman gain coefficient[1]. Experiments have also shown that the Raman gain coefficient curves
mimic the spontaneous Raman spectra curves[7]. The direct and accurate measurement of Raman gain coefficient on bulk glasses, however, is experimentally challenging and time consuming, especially in the low frequency region. Spontaneous Raman spectroscopy thus provides a method to quickly evaluate the Raman gain coefficient performance of bulk glasses over a wide frequency range.

In this study, we use spontaneous Raman spectroscopy to investigate a series of Tellurium oxide glass for application in Raman gain. The study reveals great potential of using these Tellurium oxide glasses for application as Raman gain materials. It is shown that the predicted Raman gain curves show a flat and high gain region in the low frequency range (50-400cm⁻¹). The need for a detailed analysis of the Raman spectroscopic information in the low frequency region, as a result, prompts us to have a deeper understanding of the Boson peak, which is a universal anomaly of the density of states in the low frequency region (<100cm⁻¹).

To this end, a simple binary Niobium Phosphate glass system is studied so that a more complete understanding of the contribution to Raman gain of the Boson peak can be achieved. The study shows a change of intensity in the Boson peak and the low frequency density of states for the binary glasses with varying percentage of components. The density of vibrational states information, however, is hidden in the Raman spectra because of the coupling coefficient’s dependence on frequency. Inelastic Neutron Scattering (INS) experiments were conducted on these binary glasses to extract the one-phonon vibrational density of states. A correlation between glass structure and Boson peak could be established, by a combined analysis of the Raman and the inelastic neutron scattering spectra on these binary glasses.
CHAPTER TWO: BACKGROUND

2.1 SPONTANEOUS RAMAN SCATTERING

When a directed light beam passes through any type of medium except the vacuum, there is always a certain amount of the energy of the incident light beam transferred to the scattered light that may propagate along all other directions. What actually happens during this light scattering process is that when light encounters matter, a polarization is induced in the molecules by the oscillating electric field of the incoming light. This induced dipole then radiates scattered light. Light may be scattered elastically, which is called Rayleigh scattering or it can be scattered inelastically, which is called Raman scattering.

2.1.1 SPONTANEOUS RAMAN SCATTERING

2.1.1.1 Classical Theory of Raman scattering

Basic features of Raman scattering can be illustrated by the classical model. Consider a molecule in an electrical field $\vec{E}$. A dipole moment $\vec{P}'$ will be induced by the electrical field and they are related by: $\vec{P}' = \vec{\alpha} \cdot \vec{E}$, where $\vec{\alpha}$ is the polarizability tensor. The polarizability of a molecule tells us the ability of a molecule to be polarized by the incoming electro-magnetic wave.
In the absence of any excitations in the scattering material. For a single molecule, the induced polarization by an incoming electrical field for one of its normal coordinate (e.g. for the case of one dimension) can be written as

\[ P = \varepsilon_0 \chi E \]  
(2-1)

where the electrical field \( E \) is presented by:

\[ E = E_0 \cos(\omega t) \]  
(2-2)

It is easy to see that the induced dipole moment will also alternate with the same frequency. Thus, the molecule emits electromagnetic radiation of the frequency \( \omega \), Rayleigh scattering is due to this process.

If there are excitations in the scattering material, however, the excitations modulate the electric susceptibility and consequently the induced polarization, through fluctuations in their dynamical variables, \( \xi \). Such dynamical variables include vibrational displacement for phonons, magnetization for spin waves and spin fluctuations, and electron (quasiparticle) density for electronic (superconducting) excitations etc.

The modulation of the susceptibility by \( \xi \) adds an additional term to the polarization in the original polarization, giving:

\[ P = \varepsilon_0 (\chi E + \chi' \xi E) \]  
(2-3)

Where \( \chi' = d\chi / d\xi \) is the susceptibility derivative with respect to the dynamical variable, \( \xi \). The first term in equation (2-3) drives the polarization at the incident field frequency, and therefore contribute to simple elastic scattering. However, since \( \xi \) is itself time dependent, reflecting the characteristic fluctuations of the excitation, the second
term modulates the induced polarization at frequencies different from the incident field. This term therefore contributes inelastic features to the spectral response.

In most cases we deal with, the excitation are vibrations. Thus the dynamical variable is the vibrational displacement $q$. Using $k$ to denote different normal coordinates of the molecule, the polarizability of the molecule can be expanded as a Taylor series:

$$\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial q_k} \right)_0 q_k + \left( \frac{\partial^2 \alpha}{\partial q_k^2} \right)_0 \frac{q_k^2}{2} + \cdots \quad (2-4)$$

Where $q_k$ is the displacement of the kth normal coordinate, it can be represented as:

$$q_k = q_k^0 \cos(\omega_m t) \quad (2-5)$$

for a molecule which is oscillating at frequency $\omega_m$ for kth normal coordinate.

From equations (2-1) (2-2) (2-4) (2-5), and neglecting the high power terms, we can get:

$$P = \alpha_0 E_0 \cos(\omega t) + \left( \frac{\partial \alpha}{\partial q_k} \right)_0 E_0 q_k^0 \cos(\omega t) \cos(\omega_m t) \quad (2-6)$$

or

$$P = \alpha_0 E_0 \cos(\omega t) + \left( \frac{\partial \alpha}{\partial q_k} \right)_0 E_0 q_k^0 \frac{1}{2} \left[ \cos(\omega + \omega_m) t + \cos(\omega - \omega_m) t \right] \quad (2-7)$$

This shows that a Hertzian dipole emits electromagnetic radiation. Its intensity $S$ is proportional to the square of the absolute value of the second time derivative of the induced dipole moment: $S \propto \left\langle \hat{P}_k^{(2)} \right\rangle$. Thus, the first of the terms in Equation (2-9) describes Rayleigh scattering, the second term concerns Stokes, and their anti-Stokes
Raman scattering. Note however, the above classical description does not show the individual intensity difference between of the Stokes and anti-Stokes lines. [8]

2.1.1.2. Quantum Theory of Raman scattering

The quantum mechanical treatment of transition matrix elements between vibrational states involves second-order time-dependent perturbation theory.

For the simplest case, let us consider a hydrogen atom, whose stationary (time-independent) spatial wavefunctions are written for convenience as $\psi_j$, and whose actual (time-dependent) wavefunction is $\psi$. It is always possible to write $\psi$ as a linear sum in terms of the orthonormal stationary state space wavefunctions $\psi_j$, because the time-dependent states are a complete set.

Thus: $\psi = \sum_j a_j \psi_j$ \hspace{1cm} (2-8)

When this atom (whose unperturbed Hamiltonian is $H_0$) interacts with classical radiation $E_0 \cos \omega t$, suppose the electrical field is along the normal coordinate $x$, then the extra electrostatic potential energy of the electron will be simply $eE_0 x \cos \omega t$ for visible and lower frequency light because $E_0$ is constant over all three dimensions of the molecule.

The Hamiltonian of the atom becomes

$H_0 + eE_0 x \cos \omega t \hspace{1cm} (2-9)$

where $eE_0 x \cos \omega t$ is the perturbation term.

From Schödinger’s equation, we have:
\[ i\hbar \frac{\partial \psi}{\partial t} = (H_0 + eE_0 x \cos \omega t)\psi \] \hspace{1cm} (2-10)

By substituting (2-10) into (2-8) and after some calculations we obtain:

\[ i\hbar \frac{da_k}{dt} = a_k \epsilon_k + \sum_j a_j eE_0 \cos \omega \tau_{jk} d\tau \] \hspace{1cm} (2-11)

If we make the approximation that all the \( a_k \) are negligible in comparison with the time-dependent coefficient of the ground state, we get:

\[ a_k^* a_k = \frac{x_{jk}}{\hbar} e^2 E_0^2 \int_0^\infty \cos \omega \tau \cdot e^{i(\omega \tau - \epsilon_j/\hbar)} dt \right|^2 \] \hspace{1cm} (2-12)

From (2-12), we can calculate the approximate values of \( a_k \) and we can then substituting them back into (2-11). After a long and tedious calculation one derives the result that there is a second indirect transition probability between the ground state \( G \) and any excited state \( k \) primarily proportional to the square of the Raman Transition Probability:

\[ \text{Raman Transition Probability} = \sum_k \int \psi_j^* eE_0 r \psi_k d\tau \cdot \int \psi_k^* eE_0 r \psi_G d\tau \] \hspace{1cm} (2-13)

where \( \tau \) is the lifetime of the absorbing system between external disturbances, \( -\omega_{jk} \) is the frequency corresponding to the energy jump from state \( j \) to any other state \( k \) (usually \( k \) is a state of much higher energy, and \( j \) is near to \( G \), the ground state). If \( j \) is simply the first excited vibrational state, the above probability, multiplied by the fraction of vibrators in the ground states, governs the intensity of the Stokes Raman lines.

By reversing \( j \) and \( G \), the reverse process (i.e. the appearance of anti-Stokes lines) is also predicted, although with lower intensity because of the lower initial population of the excited state \( j \) from which transitions occur. Thus the quantum theory is
able to explain the observed differences in intensity between the Stokes and the anti-Stokes lines, whereas the classical theory predicted equal intensities.[9]

The physical meaning of Raman scattering becomes obscure because of the long derivation of (2-13). The quantum mechanical theory, however, can be understood in a clear way using the energy level diagrams, as shown in Fig.2. Raman Stokes scattering consists of a transition from the ground state g to a virtual level v’, followed by a transition from the virtual level to the final state v. Raman anti-Stokes scattering entails a transition from a level v to the virtual level v’ and then a transition from v’ to ground state g. Rayleigh scattering consists of a transition from g to v’, and then from v’ back to g. [10]

![Energy level diagrams of (a) Stokess Raman scattering, (b) Anti-Stokes Raman Scattering (c) Rayleigh Scattering.](image)

 Normally most molecules are in their vibrational ground state. According to Boltzmann’s law, a much smaller number is in the vibrationally excited state. Therefore, the Stokes intensities are higher than the anti-Stokes lines. The quantum mechanical energy level picture can thus clearly explain the intensity difference between the Stokes and anti-Stokes lines.
2.1.2 Raman Scattering Cross-Section

The general Raman scattering differential cross section associated with an elementary excitation can be written as:[11]:

\[
\frac{d^2\sigma}{d\Omega d\omega_S} = \frac{V \omega_I \omega_S^3 2 \epsilon^4 |E_I|^2 \langle \hat{e}_S \cdot P_S^* \hat{e}_S \cdot P_S \rangle_{\omega_S}}{(4\pi \epsilon_o)^2 c^4}
\] (2-14)

where \( \langle \hat{e}_S \cdot P_S^* \hat{e}_S \cdot P_S \rangle_{\omega_S} \) is the spectral density of polarization fluctuations, \( V \) is the light scattering volume, \( c \) is the speed of light, and \( \epsilon_S \) is the polarization of the scattered light.

The power spectrum due to polarization fluctuations may be written as:

\[
\frac{d^2\sigma}{d\Omega d\omega_S} = \frac{V \omega_I \omega_S^3 2 \epsilon^4 |E_I|^2 \langle \hat{e}_S \cdot \chi \hat{e}_I \rangle \langle \hat{e}_S \rangle_{\omega_S}}{(4\pi \epsilon_o)^2 c^4}
\] (2-15)

Here \( \epsilon_S \) and \( \epsilon_I \) are the scattered and incident polarization directions, and \( \langle \hat{e}_S \rangle_{\omega_S} \) is the thermally-averaged correlation function for the dynamical variable \( \xi \).

The light scattering cross section is related both to the correlation function of the relevant dynamical variable, \( \xi \), and to the light scattering volume \( V \). Furthermore, the light scattering cross section depends on the symmetry of the susceptibility derivative tensor, \( \chi \), and indeed one can obtain excitation symmetry information by varying the scattering geometry, \( \epsilon_I \) and \( \epsilon_S \). As we shall see, this is an extremely powerful feature of light scattering techniques, since it allows identification of excitation symmetries.[12]

The scattering cross sections is proportional to the correlation function of dielectric fluctuations, which can be represented by \( \langle \hat{e}_S \hat{e}_S^* \rangle_{\omega_S} \) or by:
For normal mode vibrations, we can expand dielectric tensor to first order in atomic displacements:

\[
\Delta \xi_{\alpha \beta}(\vec{r}', t') = \sum_{j=1}^{3N} \frac{\partial \xi_{\alpha \beta}(\vec{r})}{\partial q_j} q_j(t)
\]  

(2-17)

Insert 2-17 into 2-16 and using the statistical independence of normal coordinates of different modes and the properties of harmonic oscillators, scattering cross sections can be written as proportional to:

\[
\sum_j < \frac{\partial \xi_{\alpha \beta}(\vec{r}')}{\partial q_j} \frac{\partial \xi_{\alpha \beta}(\vec{r}+\vec{r})}{\partial q_j} > < Q_j(t')Q_j(t'+t) >
\]  

(2-18)

Where:

\[
< Q_j(t')Q_j(t'+t) >= \frac{\hbar}{2\omega_j} \{ n_j(\omega)e^{i\omega_jt} + [1 + n(\omega)]e^{-i\omega_jt} \}
\]  

(2-19)

Insert 2-18 and 2-19 into 2-15, for scattering at angle \( \phi \), rewriting equation (2-15) in terms of intensity of the scattered light

\[
\frac{I_\beta(\omega_x)}{\Delta \Omega I(\omega_p)} = \frac{N\omega^4}{8e^4(4\pi)^2} \sin^2 \phi \left| \frac{\partial \alpha_\beta}{\partial q_\beta} \right|^2 \frac{\hbar}{m_\beta\omega_\beta} [1 - \exp(-\frac{\hbar\Omega_\beta}{kT})]^{-1}
\]

gives:

\[
\left\{ \frac{\Gamma_\beta/2\pi}{(\omega_p - \omega_x + \Omega_\beta)^2 + \Gamma_\beta^2} + \exp(-\frac{\hbar\Omega_\beta}{kT}) \left( \frac{\Gamma_\beta/2\pi}{(\omega_p - \omega_x - \Omega_\beta)^2 + \Gamma_\beta^2} \right) \right\}
\]  

(2-20)

This involves an incident laser beam and scattered light collected at an angle \( \phi \) from the incident light. Here, in addition to the previous definitions, \( \Delta \Omega \) is the solid angle subtended at the detector, \( \hbar = \) Planck’s constant, \( k = \) Boltzman’s constant and \( T \) is the temperature in degrees Kelvin.
2.2 **STIMULATED RAMAN SCATTERING AND RAMAN GAIN**

Spontaneous Raman scattering normally arises from local modes of vibration and rotation. The molecules vibrate due to thermal fluctuations, and since the noise fluctuations are uncorrelated, the light scattered from each molecular vibrations is uncorrelated to that from any other molecule. As a result, the spontaneous Raman scattering is an incoherent and weak process, and the scattered light goes into all directions.

When the incident laser has very high intensity, however, the strong electric field will cause many initially uncorrelated vibrating molecules to vibrate in phase. The excited optical phonons and the scattered Raman light will then drive each other and the scattered Raman light builds up quickly. This is called Stimulated Raman scattering (SRS)[1].

While the spontaneous Raman scattering process is a very weak process, the scattering cross section per unit volume for Raman Stokes scattering is only about $10^{-6}$ cm$^{-1}$ (1 part in $10^6$ of the incident radiation will be scattered into the Stokes frequency. The SRS is a much more efficient process. In Stimulated Raman scattering, 10% or more of the energy of the incident laser beam is converted into the Stokes frequency. The spontaneous process gives rise to isotopic emission, while the stimulated process leads to emission in a narrow cone in the forward and backward directions.[10]

Raman gain arises when a strong pump beam of frequency $\omega_L$ transfers energy to a co- or counter-propagating signal beam of frequency $\omega_s$ and excites vibrational modes in the medium when $\omega_L - \omega_s \approx \Omega_v$ where $\Omega_v$ is an allowed vibrational frequency of the medium. This geometry is shown in Figure 2-2.[1]
The total electric field in the scattering medium can be represented by:

$$E(r, t) = \frac{1}{2} \varepsilon(\omega_p) e^{i(k_p - \omega_p) t} + \varepsilon(\omega_s) e^{i(k_s - \omega_s) t} + c.c$$ \hspace{1cm} (2-21)

For the normal coordinate $q$ that gives rise to the Raman scattering, from spontaneous Raman scattering theory, we have:

$$q \propto \left. \frac{\partial \alpha}{\partial q} \right|_{q=0} \varepsilon(\omega_L) \cdot \varepsilon^*(\omega_s) e^{-i(\omega_L - \omega_s) t}$$ \hspace{1cm} (2-22)

The nonlinear polarization that arises from the Raman effect can thus be represented as:

$$P_{NL} \propto \alpha_{NL} E = \left. \frac{\partial \alpha}{\partial q} \right|_{q=0} q[\varepsilon(\omega_L) e^{i(k_s - \omega_s) t} + \varepsilon(\omega_s) e^{i(k_s - \omega_s) t} + c.c]$$ \hspace{1cm} (2-23)

The nonlinear Raman polarization of the pump laser and the Stokes beam can be represented separately as:

$$P_{NL}(\omega_p) \propto \left. \frac{\partial \alpha}{\partial q} \right|_{q=0} \varepsilon^2(\omega_L) e^{i(k_s - \omega_s) t} + c.c$$ \hspace{1cm} (2-24)

$$P_{NL}(\omega_s) \propto \left. \frac{\partial \alpha}{\partial q} \right|_{q=0} \varepsilon^2(\omega_s) e^{i(k_s - \omega_s) t} + c.c$$ \hspace{1cm} (2-25)
From which we can see that the Stokes Raman polarization is dependent upon the intensity of the pump laser.

For single isolated mode $\beta$, in the case of $|\varepsilon(\omega_L)| >> |\varepsilon(\omega_S)|$, (e.g. the intensity of the pump laser is far stronger than the Stokes Raman scattering intensity) using the Slowly Varying Envelope Approximation (SVEA), also neglect loss for the moment, we get: [1]

\[
\frac{dI_\beta(\omega_S)}{I_\beta(\omega_S)} = g_\beta^R I_\beta(\omega_L) dz
\]  
(2-26)

From (2-26), it is easy to show that

\[
I_\beta(\omega_S) \propto e^{G_{\beta}(\omega_L)z}
\]  
(2-27)

As we can see, the exponential gain factor is proportional to $I_\beta(\omega_L)$ (the intensity of the pump beam), $z$ (the overlapping distance for the two beams) and $g_\beta^R$, which is called Raman gain coefficient. Equation 2-27 shows that there is an exponential growth in the signal beam intensity: Where $\alpha$ is the polarizability and $q$ is the wavevector of normal modes.

For single, isolated Raman response, $g_\beta^R$ is given by: [10][13]

\[
g_\beta^R = \frac{\omega_S N}{4mn_L c^2 \varepsilon_0^2} \left| \frac{\partial \alpha_\beta}{\partial q} \right|_q^2 \left[ \frac{G_{\beta}(\omega_L - \omega_S)}{[\Omega^2 - (\omega_L - \omega_S)^2]^2 + \Gamma^2 (\omega_L - \omega_S)^2} \right]
\]  
(2-28)

Here $N$ is the number of molecules (vibrators) per unit volume, $m$ is the effective mass associated with the vibrating species for the $\beta$th mode, $n$ is the refractive index at the signal (pump) frequency, $c$ is the speed of light, $\varepsilon_0$ the dielectric constant of free space, $q$ the vibrational displacement of the $\beta$’th mode, $\partial \alpha/\partial q \mid_{q=0} = $ Raman susceptibility of the
The scattering cross-section has been shown by Equation (2-20). Note that essentially the same vibrational constants appear both in the expressions for spontaneous Raman scattering and the Raman gain. Most importantly, a careful measurement and analysis of the Raman spectrum allows the critical parameters $m_\beta$, $N$, $\partial \alpha_q / \partial q \big|_{q=0}$, $\Omega_\beta$ and $\Gamma_\beta^R$ to be evaluated for a single molecular vibration.[1]

From (2-20) and (2-28) we see that Raman gain is proportional to the Raman susceptibility $\langle \hat{\alpha} \hat{\alpha} \rangle$, which also determines the spontaneous Raman spectrum intensity. We can then evaluate the Raman gain of different materials by studying spontaneous Raman spectra.[14]

The ideal Raman gain material should possess a high and broad Raman gain curve, so the spontaneous Raman spectra of a good Raman gain glass should also be high and broad. The flatness of the Raman gain is another important issue which will be discussed in details later.

As predicted by Hellwarth in 1963, there is a relation between spontaneous and stimulated Raman scattering processes. The results of this derivation are presented in
[15], where the Raman gain coefficient \((g \ [\text{cm/W}])\), also known as the gain factor, is given by:

\[
g \ [\text{cm/W}] = \frac{4\pi^3 N c^2}{\hbar \omega_S^2 \omega_p n_s^2} \left( \frac{\partial^2 \sigma}{\partial \omega \partial \Omega} \right) \tag{2-29}
\]

where \(N\) is the number density of molecules, and \(\omega_S\) and \(\omega_p\) are the Stokes (signal) and pump (laser) frequencies respectively, \(n_s\) is the refractive index at the Stokes wavelength, and \(\frac{\partial^2 \sigma}{\partial \omega \partial \Omega}\) is the differential Raman cross-section.[66]
2.3 GLASS & RAMAN SCATTERING OF GLASS

2.3.1 GLASS; GENERAL OVERVIEW

Glass can be defined as ‘an amorphous solid completely lacking in long-range, periodic atomic structure and exhibiting a region of glass transformation behavior.’ This means glasses only exhibit a limited short-range order, and unlike crystal lattices with infinite periodicity, remain completely random in the long-range scale.[16]

Glass is formed through melting of its batch materials, there are four major groups of constituents: glass formers, modifiers, intermediates and fining agents.

The glassformer forms the basic structure of glass, providing the basis of network where other components fit in. Several major glass formers are silica (SiO$_2$), boric oxide (B$_2$O$_3$), phophorous oxide (P$_2$O$_5$) and GeO$_2$. Some other oxides including As$_2$O$_3$, Sb$_2$O$_3$, Al$_2$O$_3$ and V$_2$O$_5$ can be glassformers too, but they don’t form single-component glasses by themselves, they are usually used to together with major glassformers.

Modifiers are used to reduce the melt temperature of the glass so that it can made within the capabilities of any lab or industry. Typical modifiers are alkali oxides.

While decreasing the melt temperature, the modifiers however deteriorate the properties of the glass significantly. To compensate for this property loss, intermediates such as Al$_2$O$_3$ are added in the batch.

Fining agents such as As$_2$O$_3$, Sb$_2$O$_3$ and NaCl are added sometimes to reduce the amount of bubbles in the final glass.

The composition of a glass is most commonly represented in percentage, such as: 15% Na$_2$O-11%CaO-74%SiO$_2$. The percentages normally are assumed to be weight
percentage because it is easy for batch preparation. It can be converted to molecular percentage using the molecular weight of the constituents.

2.3.1.1 A Structural Approach to Glass; Disorder

To understand the properties of glasses, we need to know their structure. The pioneering work on modeling the structure of glass is due to Zachariasen, who based his theory on the following two observations:

1. The interatomic bonding forces in glass and in crystals must be similar because the mechanical properties of such materials are of comparable magnitudes.

2. Like crystals, glasses must be made of an extended three-dimensional “lattice”, but the diffuse character of x-rays scattering shows that this “lattice” is neither symmetric nor periodic, unlike in crystals; in other words, there is no long-range order.

One can assimilate the “glass lattice” to a unique molecule or to a system of a unique giant elementary cell. The disorder in the “lattice” then introduces a distribution of the bonding forces; their progressive breaking, when heating the glass, can thus explain the gradual decrease of viscosity. The disorder equally explains an energetic content higher than the one in crystals.

The structure of oxide glasses can be analyzed in terms of cation coordination polyhedra surrounded by a variable number of oxygens. In the corresponding crystalline oxides, the polyhedra can have common summits, edges or faces.
For example, in its different crystalline forms, silica (quartz, cristobalite, tridymnite, etc.) exhibits a lattice built with SiO$_4$ tetrahedra linked together by their summits. In the case of vitreous (glass) silica, the “glass lattice” is made of the same tetrahedral SiO$_4$ units, linked by their summits, but the mutual orientation of the constitutive tetrahedra is variable. The structure is illustrated in Fig.4.

![Diagram of a (a) single SiO$_2$ tetrahedron followed by a (b) 2D and (c) 3D depiction of the silica network.](image)

By examining systematically the structures of different coordination polyhedra, Zachariasen showed that in oxide glass, the following rules are applied:

1. The number of oxygens surrounding the cation A must be small.
2. No oxygen is bonded to more than two cations A:A$_2$O$_3$
3. The polyhedra can have only common summits (neither edges nor faces): AO$_2$ and A$_2$O$_5$.
4. At least three summits of each polyhedron must be put in common with other polyhedra: AO$_3$ and A$_2$O$_7$ [17]

Under the assumption of a continuous random network distribution, the short-distance order (up to 3 Å) is made of basic structural units determined by the properties of the chemical bonds (coordination number, bond length, bond angles). The medium distance order (up to 5-10 Å) describes the sequence of the basic structural units. [17]
2.3.1.2 Vibrations of Glass Molecular Groups

The molecular groups which form a glass are characterized by a number of vibrational modes determined by the masses of the constituent atoms, the interatomic forces, and the geometry of their arrangement. Even in the case of crystals, the direct determination of the structure by means of vibrational spectroscopy is impossible; the structure must be known in advance by radio-crystallographic or neutron methods. Spectral analysis is based on group theory applied to isolated molecules or to crystal lattices triply periodic. In disordered structures, such an approach is impossible; one must proceed by successive approximations.

1) Isolated Molecular Groups

In the case of a SiO$_4$ tetrahedron, for instance, one may assume that the tetrahedron vibrates independent of the remaining lattice. Under this assumption, group-theoretical considerations allow one to establish that there will be only four modes of vibrations corresponding to the displacements, e.g. 1) a symmetric stretching mode, 2) a bending doubly degenerate, 3) a stretching triply degenerate mode.

2) Coupled Molecular Groups

The different molecular groups in a glass interact with the neighboring ones. If one assumes that the interaction is weak and that the first neighbors of the unit form a group of fixed symmetry, one can define a site group of symmetry which can be know if the space group of the crystal is given as well as the point group of the molecule and the number of molecules in the elementary cell. The site symmetry can be lower than the symmetry of the molecule; in this case, once can observe relaxation of the selection rules and forbidden modes can be observed or degeneracies can be lifted.
3) Limited Lattice Models

One can analyze the vibrational modes of structural units made of longer and longer chains, more and more complex, as, for example, chains or leaflets of SiO$_4$ tetrahedra. The list of predicted modes can then be compared to the experimental observation. This method allowed the determination of the deformations of the SiO$_4$ tetrahedra and the comparison of the force constants of the Si-O, Ge$_2$, and Be-F bonds. [18]

4) Statistic Disorder Lattice

The statistic model of Bell and Dean [19] has often been used as a basis of vibrational spectra calculations. It leads to a distribution of the density of the modes able to be compared to infrared or Raman measurements[20]. It is, however, impossible to assign the observed bands to one vibrational mode or another, the maxima in absorption correspond to additions of several modes in various proportions, depending on the shape of the density of vibrational states.[21]

In the case of silica, Si-O tetrahedra form the network based on a coordination of four. The tetrahedra possess high internal order, thus preserving the short range order (SRO) of the glass [22].
2.3.2 The TeO$_2$-P$_2$O$_5$-PbO-Sb$_2$O$_3$ Family

2.3.2.1 The TeO$_2$-P$_2$O$_5$-PbO-Sb$_2$O$_3$ Family – Constituent Properties

The glasses based on tellurium oxides (TeO$_2$) have recently attracted a lot of attention for Raman gain application because of their large Raman scattering cross-section.[7]

In this study we concentrate on a glass family consisting of tellurium oxide (TeO$_2$), lead oxide (PbO), phosphorous oxide (P$_2$O$_5$) and antimony oxide (Sb$_2$O$_3$). The presence of TeO$_2$ in the glass provides such key characteristics as a large infrared transmission window (4 – 6 µm), large $n_1$ and $n_2$ values (>2) and a $\chi^3$ value two orders of magnitude greater than silica [23]. TeO$_2$ is commonly referred to as a “conditional” network former, meaning it does not readily form glass on its own, therefore making it necessary for a major former (P$_2$O$_5$) or modifier (PbO) to be present.

Addition of P$_2$O$_5$ in the presence of PbO yields transmission in the ultraviolet region (< 350nm). Inherent problems of P$_2$O$_5$ in glass melts are hydroscopicity and volatility during melting. This may be improved with additions of metal oxides such as Al$_2$O$_3$, In$_2$O$_3$ or Sb$_2$O$_3$ [24]. Such additions not only help decrease the effects of hydroscopicity and volatility, but also improve the overall glass stability and optical properties as well.

The presence of PbO increases both nonlinear refractive index and birefringence. This stems from the fact Pb$^{2+}$ is a highly polarizable cation possessing large electron clouds, a small coordination number and low field strength [22].
Ultimately the constituents serve to balance the weaknesses of the others present and aid towards the overall optimization of the glass. The mol % of any given constituent added is equally important to the optimization process as the constituents themselves; that is, the intended effect of any specific constituent may change as more (or less) mol % is found within the composition. Such factors also play a vital role when discussing the structure of a given family.

2.3.2.2 The TeO$_2$-P$_2$O$_5$-PbO-Sb$_2$O$_3$ family – Structure

Studying the glass structure of a given family of glasses is most often the key step in explaining or predicting the properties and performance of that family. Therefore, it is important to study the coordination of the network formers, their interactions with modifier cations, etc.

Amorphous TeO$_2$ consists of a 3D network containing TeO$_4$ trigonal bipyramids (tbp) [23]. The TeO$_4$ tbp possess one unshared electron pair which occupies a single equatorial site; the remainder of the structure is dictated by Te-O-Te linkages [25, 26].

![Diagram](image)

*Figure 5.* a) and b) represent the TeO$_4$ tbp a) two-dimensionally and b) in a 3D network[27].
As mentioned previously, TeO₂ is a conditional network former requiring the presence of either a modifier or major network former to produce a glass. The addition of a modifier or major former gradually changes the TeO₄ tbp into a slightly distorted structural unit known as TeO₃₊₁ units, then further into a TeO₃ tbp with a single non-bridging oxygen. These transformations have been confirmed by data obtained from such techniques as XANES (X-ray Absorption Near Edge Structure) [40] as well as vibrational spectroscopy [28]. The mechanism for such a transformation occurs as the addition of modifier/former begins. For example, the addition of a metal oxide such as PbO occupies certain sites within the network. The presence of PbO in such sites causes disruption or breakage along the axial Te-O bonds [23]. This occurs along the axial Te-O bond because the polarizability of the unshared electron pair is too high for interactions. The greater the addition of PbO, the greater the number of non-bridging oxygens (NBO) Te-O bonds formed and consequently the greater the amount of TeO₃₊₁ to TeO₃ tbp formed [23].
Figures 6 illustrates such mechanisms for monovalent cations introduced into the TeO$_4$ tbp network, thus forming TeO$_{3+1}$ units and consequently TeO$_3$ tps [33]. In the case of PbO, a divalent modifier, the only difference would be that only one “M” would occupy the site between the two given oxygen atoms. Studies of V$_2$O$_5$-TeO$_2$ binary systems showed similar transformation of TeO$_4$ units into TeO$_3$ tbps. [29] With V$_2$O$_5$ and P$_2$O$_5$ identical in structure, it is safe to assume that identical effects will occur with P$_2$O$_5$ additions.

P$_2$O$_5$, in its vitreous state, possesses a tetrahedral structural unit with 3 bridging oxygens (BO) and 1 NBO. This results from the P$^{5+}$ pentavalent ion, whereas a tetrahedron with 4 BO could not be formed due to an excess positive charge. One of the
oxygens must then form a double bond with phosphorous therefore keeping the charge balance [22,30,31,32]. The addition of this single NBO results in a low connectivity for P$_2$O$_5$. Though the tetrahedron are connected at the corners and are in fact three dimensional themselves, only a two dimensional network may be formed due to the presence of NBOs. This is illustrated in Figure 7.

![Image of P$_2$O$_5$ network](image.png)

**Figure 7.** A diagram of a P$_2$O$_5$ network consisting of tetrahedral units with 3 BO and 1 NBO.[33]

The NBO also results in a high volatility and hydroscopicity of P$_2$O$_5$ melts, making them prone to crystallize. The P = O may react with moisture surrounding the melt, therein forming phosphoric acid. This then causes volatility upon heating. The crystalline form of the melt reagent also plays a role in determining the IRO of a given composition [22].

Addition of PbO into a P$_2$O$_5$ may lead to one of two outcomes; it is either incorporated into the structure as a modifier or network former. In the case of the modifier the Pb$^{2+}$ ion occupies an interstitial of octahedral coordination, thus breaking down the network connectivity further.
Sudarsan [24] provided means by which PbO interacts and incorporates itself into the network as a former. PbO is of \( \text{PbO}_4^{2-} \) tetrahedra, requiring extra oxygens must be provided by the host network. This requires breakdown of existing PO\(_4\) double-bonded tetrahedra into single-bonded tetrahedra with an excess positive charge of +1. It follows that two of these newly formed single-bonded tetrahedra combine with a single \( \text{PbO}_4^{2-} \) tetrahedra to compose the new, altered network.

![Figure 8. A 3D representation of a Sb\(_2\)O\(_3\) network. Planar rings are “crumpled” to form the third dimension.](image)

Incorporation of Sb\(_2\)O\(_3\) also leads to interesting results. Figure 8 shows the 3D model of Sb\(_2\)O\(_3\) [25], whereas a similar structure to that of B\(_2\)O\(_3\) can be seen consisting of planar rings “crumpled” into a three-dimensional network. Work of Sudarsan and Nalin et. al. [24] gave insight into interactions between Sb\(_2\)O\(_3\) and P2O5. While Nalin focused primarily on glass formation regions and homogeneity, Sudarsan provided key 31P MAS NMR (Magic Angle Spinning Nuclear Magnetic Resonance) and XRD studies. Conclusions yielded that Sb\(_2\)O\(_3\) may incorporate into the network as either Sb\(^{3+}\) and Sb\(^{5+}\) ions, thus forming P-O-Sb\(^{3+}\) and P-O-Sb\(^{5+}\) linkages. Conversion from either trivalent to pentavalent ions or linkages results in a significant chemical shift in the NMR spectra. This stems from the relatively high electron density of P-O-Sb\(^{3+}\) linkages to that of P-O-
Sb$^{5+}$ linkages. P-O-Sb$^{3+}$ linkages are found to have a lone pair of electrons, creating such a paramagnetic shift. Trends from this data may suggest similar shifts in Raman spectra.[33]

### 2.3.3 Breakdown of the Selection Rule in Glasses

The wavevector $q$ is defined as $q = \frac{2\pi}{\lambda}$. For visible light $\lambda = 400-700$ nm, which corresponds to a wavevector of

$$q = \frac{1}{10^{-6} \text{m}} = \frac{1}{10000 \text{Å}} = 10^{-4} \text{Å}^{-1},$$

which is small compared to the extension of the Brillouin zone. This means that the visible light will only be able to interact with the vibrational modes with wavevector at the center of the Brillouin zone. As a result, Raman spectroscopy of crystals will probe the optical phonon branches.

This selection rule for Raman scattering of light, however, breaks down for amorphous material. This can be explained in a very simple physical model, called the giant molecule model. For amorphous materials, we can think of the structure as starting by a crystal characterized by its elementary cell repeated periodically in the three directions of the real space. Then, as the disorder increases, the size of the elementary cell increases, suggesting reduction of the associated Brillouin zone in the reciprocal space; and so on, until one can assimilate the final vitreous substance to a giant molecule that is to a unique cell of “infinite size”, associated to a Brillouin zone reduced to zero. [34][35]

We can also understand this selection rule from the viewpoint of the law of conservation of energy and momentum. Consider a monochromatic light beam of frequency $\omega_L$. The propagation vector is represented by $\vec{k}_L$, and the scattered vector is represented by...
\( \bar{k}_s \). Due to the scattering, a fraction of the incident photons are annihilated with creation of a scattered field in which the photons have frequency \( \omega_s \). The conservation laws give us:

Scattering frequency: \( \omega = \omega_k - \omega_s \) \hspace{1cm} (2-30)

Scattering wave vector: \( \bar{k} = \bar{k}_k - \bar{k}_s \) \hspace{1cm} (2-31)

Inelastic scattering must satisfy conservation of energy and momentum. In perfect crystals, e.g. in idealized materials that display perfect translation symmetry, the elementary excitations can be labeled by the wave vector \( \bar{q} \), also known as the crystal momentum. In first-order processes, only a single elementary excitation participates. In such situations, momentum conservation translates into the requirement that the scattering wave vector equal the wave vector of the excitation: \( \bar{k} = \bar{q} \). So this is selection rule for the Raman spectroscopy of crystals.

Wave vector conservation as represented by (2-31) breaks down when the medium has no translation symmetry. In the language of quantum mechanics, we say that the Bloch theorem does not apply and, hence, that wave vectors are not good quantum numbers for labeling modes. This applies to amorphous solids (glasses).[36]

This leads to a continuous first-order vibrational spectrum of glasses instead of the discrete Raman spectrum of crystals. Two properties of glass are responsible for this fundamental difference. Firstly, in glass the coupling between the atomic displacement and the fluctuation of the dielectric susceptibility is itself a random quantity because of the irregular atomic bonding. This aspect of the disorder is referred to as “electrical disorder”. Secondly, with the exception of very low frequencies, the vibrational modes of the glass are not plane waves. The disorder which manifests itself by the distortion of the vibrational modes is termed “mechanical disorder”.

30
Even for a perfect plane-wave phonon mode with finite wave vector $\tilde{q}$, the disorder of the atomic coupling allows inelastic scattering of light from this mode. With the $-\tilde{q}$ component of the random spatial distribution of atomic couplings, the phonon $\tilde{q}$ is folded back to yield a $\vec{k} = 0$ component of the fluctuating dielectric polarizability which can be measured by light scattering[37].

The effect of the mechanical disorder on the Raman scattering was first explained by Shuker and Gamon[38]. They define a correlation length $\xi(\omega)$ over which a vibrational mode of frequency $\omega / 2\pi$ represents a plane wave and argue that the wave-vector selection rule is annulled as soon as $\xi(\omega)$ is as short as the mode wavelength[39].
2.4 Low Frequency Vibrational Density of States and Boson peak

2.4.1 Density of States and Debye’s model

The density of states, \( g(\omega) \), is defined as the number of normal modes between \( \omega, \omega + d\omega \); or \( q, q + dq \), it is a concept of great importance in solid-state physics, also for electronic properties.

The specific heat of a lattice can be written either as:

\[
\frac{1}{V} \sum \int \frac{dk}{(2\pi)^3} Q(\omega_s(k))
\]

or using frequency integrals, it can be written as:

\[
\int d\omega Q(\omega)
\]

By comparing equ.2-32 and equ.2-33, it is clear that the density of normal modes can be represented in the form:

\[
g(\omega) = \sum \int \frac{dk}{(2\pi)^3} \delta(\omega - \omega_s(k))
\]

Debye model tells us that if all three branches of the vibrational spectrum have the linear dispersion relation, and if the wave vectors of the normal modes are assumed to lie within a sphere of radius \( k_D \) rather than the first Brillouin zone, then the density of states can be written as:

\[
g(\omega) = 3 \int_{k<k_D} \frac{dk}{(2\pi)^3} \delta(\omega - ck) = \frac{3}{2\pi^2} k_D^2 \int_0^{k_D} dk \delta(\omega - ck) = \begin{cases} 
\frac{3}{2\pi^2} \frac{\omega^2}{c^3}, & \omega < \omega_D = k_D c; \\
0, & \omega > \omega_D
\end{cases}
\]
Thus the density of states for an elastic isotropic medium, and likewise for a crystal lattice at small frequencies and wavevectors, increase quadratically with frequency. [40]
2.4.2 Density of states and Boson peak

The Debye model for an elastic continuum predicts that the vibrational density of states (VDOS) is a quadratic function of frequency, \( g_\nu(\omega) \propto \omega^2 \), and the associated vibrational excitations are acoustic phonons. A sound wave with a wavelength \( \lambda = 50 \text{ Å} \) has a wavevector \( q = 2\pi / \lambda \approx 0.1 \text{ Å}^{-1} \), and a corresponding frequency \( \nu = \nu_s q / 2\pi \) of the order of a few terahertz, where \( \nu_s \) is the appropriate sound velocity (1-6 km/s in glasses).

In this THz frequency region, the VDOS of many crystals is indeed as predicted by the Debye’s law. However, the VDOS of amorphous materials, whose structure is disordered as compared with that of crystals, doesn’t obey the Debye’s law in the terahertz region.

![Figure 9. Density of states of additional modes in vitreous silica compared to the Debye density of states.][57]
As shown in Fig. 9, the density of states predicted by Debye’s law is shown as the dotted line, while the actual density of states is shown to be a peak.

Debye’s law gives the density of states in the crystals, and this density of states can be used to calculate the thermal quantities such as the specific heat and the thermal conductivity. The Debye model for an elastic continuum predicts that the low-temperature specific heat has a cubic temperature dependence, \( C \propto T^3 \), a consequence of the quadratic frequency dependence of the VDOS. [41] The experimental results, however, don’t agree with this prediction. The plot of \( C(T)/T^3 \) as a function of \( T \), show a peak at \( T=10\text{K} \). This suggests that there is extra density of states in the THz region in the amorphous materials as compared with the prediction of Debye’s law.

The Boson peak was first discovered when the thermodynamic properties were investigated. Berman noticed the unexpected deviation from the prediction of Debye’s law in 1949 when he was measuring the thermal conductivity for vitreous silica.[42, 43]. He measured the thermal conductivities of several samples of \( \text{v-SiO}_2 \) and found the plateau behavior of the thermal conductivities at around 10K with a magnitude several orders smaller than those of crystals. This kind of anomaly from the prediction of Debye’s law was also confirmed in low temperature specific heat measurements on other amorphous materials[44]. Recently, W. Schirmacher has presented a theory to explain the plateau in the temperature variation of the thermal conductivity as arise from the enhanced scattering in the boson peak regime and to be essentially a harmonic phenomenon[45].

The Boson peak can be defined as an excess contribution to the usual Debye density of states (DOS). The name is give because the temperature dependence of the
intensity of the peak follows that of a harmonic oscillator characterized by the Bose factor. It can be observed with a variety of optical, neutron and thermal measurements, including Raman spectroscopy.

Krishnan observed in 1953 the boson peak with Raman scattering[46] He found for v-SiO$_2$ a broad band in the vicinity of 30-120 cm$^{-1}$ (note that 1THz=33.35 cm$^{-1}$) which markedly differs from the behavior of crystals.

Because the Raman light scattering is an electronically driven process, not all the vibrations will be able to interact with the incoming light. The intensity of Raman scattered light depends not only on the vibrational density of states, but also on the coupling between photons and vibrations. R. Shuker and R.W. Gamon derived a relationship between Raman intensity and density of states [38]:

$$I(\omega) = g(\omega)C(\omega)[n(\omega) + 1]/\omega \quad (2-36)$$

where $C(\omega)$ is the photon-vibration coupling coefficient and $[n(\omega) + 1]$ is the Bose-Einstein thermal occupation factor.

The real Boson peak features can only be revealed if we can exclude the influence of the factor $C(\omega)[n(\omega) + 1]/\omega$. So the Boson peak is evident in plots of the “reduced” Raman intensity. The reduced Raman intensity can be defined as

$$I_R = I(\omega) / [n(\omega) + 1] = C(\omega)g(\omega) / \omega^2 \quad (2-37)$$

The peak of such a reduced Raman intensity is due to a peak in $g(\omega) / \omega^2$, not a peak in $C(\omega)$, which for a number of glasses has been found to depend approximately linearly on frequency in the region of the boson peak[47].
2.4.3 Theoretical models for Boson peak

There are essentially three different scenarios that have been proposed for the origin of the boson peak in glasses. [48] One assumes that vibrational modes additional to sound waves exist, another ascribes the boson peak to localized vibrational modes, perhaps associated with inhomogeneities in the glass structure, while the third ascribes the non-Debye excess of modes to the effect of disorder (strong scattering) on sound wave excitation.[49]

Model 1: Soft Potential Model

The tunneling model postulates the existence in glasses of localized modes, whose character is still disputed, that are responsible for low-temperature anomalies in thermal properties. Such modes are believed to exist at frequencies below 1GHz. [48]

In the so-called soft potential model, it is postulated that such localized modes persist up to much higher frequencies, crossing over to vibrational modes in soft harmonic potential wells at frequencies in the boson peak region. This approach, naturally accounts for both relaxational and vibrational modes. [50] Quasi-localized modes have been identified in simulations of vitreous SiO$_2$. [51] Such modes comprise coupled rotations and bodily translations of SiO$_4$ tetrahedra. [52]

Model 2: Localized Vibration Model

This model assumes that the structure of glasses is inhomogeneous, consisting of an aggregated blobs with different density from the matrix. The boson peak is assumed to be due to vibrational modes spatially localized in such blobs. However, there is no evidence, from computer simulation, that the sort of density fluctuations envisaged exist in the structure of glass network. There is no evidence that true localization of modes exists at low
frequencies of the order of 1THz. Also, Vibrational localization should occur only at the edges of the acoustic and optic bands in the VDOS at much higher frequencies. [53]

Model 3: Medium Range Disorder Model

The third model attributes the extra, non-Debye-like modes in the boson peak region to the result of strong scattering of sound waves by the disorder (in force constants or atomic positions) characteristic of the amorphous states. [54] W. Schirmacher et. al presented compelling evidence that a strongly disordered three-dimensional system of coupled harmonic oscillators with a continuous force constant distribution exhibits an excess low-frequency DOS (Boson Peak) as a generic feature. This was achieved by comparing the results of a CPA (coherent-potential approximation) calculation with those of a numerical diagonalization[55]. The extra states in the boson peak region are supposed to be the high k acoustic or low k optics modes pushed down in frequency by disorder and mixed with the low k acoustic modes.[56]

![Figure 10. Schematic of broadening of a vibration peak by medium range disorder. Red: Vibration peak without medium range disorder broadening Blue: Vibration peak with medium range disorder broadening.][57]
The physical picture of the third model can be illustrated with Figure.10. The medium range disorder will induce the broadening of the vibration lines in the high frequency range, some vibration states will extend to the low frequency range, which gives rise to the excess of density of states in the low frequency range as compared with what is predicted by the Debye’s model.

When the disorder increases, more broadening will cause the vibrational peaks in the high frequency region to broaden more, thus more excess of density of states will extend to the low frequency region, giving rise to a higher Boson peak intensity; while on the other side, more broadening will cause the peaks extend to lower frequency, which means the Boson peak energy will decrease.[57] [58]. According to the theoretical prediction of this model, Boson peak energy decreases and its intensity increases with increasing disorder.

To obtain a better understanding of the density of states in the Boson peak regime more spectral information is needed. This is hard to get merely from Raman spectroscopy because of the coupling coefficient is frequency dependent. In the case of inelastic neutron scattering, the VDOS is obtained more directly, with no strongly frequency-dependent coupling coefficient being involved.
2.5  *Inelastic Neutron Scattering*

2.5.1  **Introduction to INS**

Whenever it is important to know precisely where atoms are or how atoms move one should consider a neutron scattering investigation. Neutron scattering is a very powerful probe of microscopic structure and dynamics. Although neutron scattering requires complex and expensive equipment, it is actually very difficult to conceive a simpler scattering event than that of thermal or cold neutrons. As neutrons carry no electric charge they experience no Coulomb barrier and thus penetrate deeply into matter unless they encounter absorbing nuclei like Li, Cd or Gd.

2.5.2  **Method of Neutron Production**

Free neutrons are produced via the excitation of nuclei. In the case of fission slow neutrons interact with metastable $^{235}U$ nuclei. The excited nucleus decays in a cascade of fission products. In the average 2.5 neutrons are produced by the fission of one $^{235}U$ nucleus. These neutrons possess very elevated energies of about 2MeV and are thus unsuitable for inducing further fission processes. With the help of moderators the fast neutrons are slowed down to meV energies. These slow neutrons sustain the chain reaction in a nuclear reactor. By allowing some of the moderated neutrons to escape from the core region free neutrons for scientific use are obtained.

The energy of a free neutron is related to its classical speed via
\[
E = \frac{1}{2} mv^2 = \frac{\hbar^2 k^2}{2m},
\]

where \( k = \frac{2\pi}{\lambda} \), \( \vec{k} \) is the wavevector of the matter wave associated with the free neutron of well-defined linear momentum \( \vec{p} = \hbar \vec{k} \).

Using standard units we get the useful relation

\[
E[\text{meV}] = 81.796 \cdot \lambda^2 [\AA^{-2}]
\]

This means that neutrons of a few \( \AA \) wavelength possess an energy of a few meV, which corresponds to typical excitations in solids. This perfect match of microscopic length and energy scales with the wavelength and energy of the neutron is one of the many reasons why neutrons are such a well adapted tool for the investigation of microscopic processes.

As shown in Fig 11, the incoming neutrons have a wavevector of \( \vec{k}_i \), where the scattered neutrons have a wavevector of \( \vec{k}_f \), the scattering angle is \( 2\theta \). The scattering wavevector is shown in the figure to be \( \vec{q} \).

Where \( \vec{q} = \vec{k}_f - \vec{k}_i \), it is easy to deduce that:

\[
q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos 2\theta
\]

\[ (2-39) \]

---

**Figure 11.** Wavevector diagram of the neutron scattering.
2.5.3 s-wave scattering

For the neutrons we consider here the nuclei with dimensions of $10^{-4}$ Å are pointlike. As a consequence the scattering from these structure-less objects must be purely isotropic. Mathematically speaking we are dealing with pure s-wave scattering. The strength of this scattering is parametrized by the scattering length $b$ of the nucleus ($b$ is a complex number. The imaginary part of $b$ describes the absorption of neutrons by the nucleus.)

The kinetics of neutron scattering is in many respects not too different from light or X-ray scattering. It is, therefore, possible to apply principles familiar from classical optics. The main difference resides in the fact that the dispersion of a material wave differs from that of light because the Schrodinger equation is first order in time, whereas the Helmholtz equation is second order in time.

Light scattered from a point-like particle can be described as a superposition of spherical waves of the form

$$\varphi(r, \theta, \phi) = A \frac{e^{i(\theta \phi - kr)}}{r}$$  \hspace{1cm} (2-40)

For the observer the scattered light is indistinguishable from that of a point-like light source. Exactly the same holds for neutrons. The whole task of analyzing the data consists in correctly summing these spherical waves as they are scattered by the different constituents of our sample.

Due to the rather weak scattering amplitude of neutrons (the scattering length is very much smaller than the interparticle distances in the sample) the Born approximation holds in most practical cases.
Using Fermi’s Golden Rule we obtain for the cross-section within the Born approximation can be written as [59]:

\[
\frac{d^2 \sigma}{d\Omega dE_f} = \frac{k_f}{k_i} \sum_{\lambda_i, \lambda_f} p_{\lambda_i} \left| \langle \tilde{k}_f \sigma_f, \lambda_f | V | \tilde{k}_i \sigma_i, \lambda_i \rangle \right|^2 \delta (\hbar \omega + E_{\lambda_i} - E_{\lambda_f}) \quad (2-41)
\]

\( \tilde{k}_f \) and \( \sigma_f \) denote the wavevector and spin of the scattered neutron. Summation takes place over all accessible initial and final states of the sample. \( \lambda_i \) and \( \lambda_f \) stand for the ensemble of quantum numbers characterizing these states. The function \( p_{\lambda_i} \) weights the initial states according to the thermodynamic conditions and thus contains e.g. the temperature factor. The prefactor \( k_f/k_i \) originates in the normalization of the cross-section to the incident neutron flux and takes care of the density of scattered neutrons

\[
\rho_{\lambda_f} (E_f) = \frac{mk_f}{\hbar^2} \quad \text{within} \quad d\Omega dE_f.
\]

In the limit where the nuclear dimensions are much smaller than the neutron wavelength, the neutron-nuclear potential can be replaced by Fermi’ pseudopotential,

\[
V(\vec{r}) = \frac{2\pi \hbar^2}{m} \sum_l b_l \delta (\vec{r} - \vec{r}_l) ; l = 1...N, \quad (2-42)
\]

with \( \vec{r}_l \) denoting the position of the nucleus \( l \). The prefactors are chosen such that the total scattering cross-section integrated over all angles for an isolated scatterer is given by

\[
\sigma = 4\pi |b|^2
\]

Inserting eq. 2-42 into eq. 2-41 leads to the so-called master equation of neutron scattering:
\[
\frac{d^2 \sigma}{d\Omega dE_f} = \frac{1}{N} \frac{k_f}{k_i} \sum_{\lambda_i, \delta_i} p_\lambda P_\delta \sum_{\lambda_f, \delta_f} \left| \sigma_f, \lambda_f \left| \sum_{l} b_l e^{i\tilde{Q}l} \right| \sigma, \lambda \right|^2 \delta(h \omega + E_{\lambda_f} - E_{\lambda_i})
\]

\[
= \frac{k_f}{k_i} \frac{1}{N} \sum_{i,j} \int d\omega e^{-i\omega\tau} < e^{i\tilde{Q}R_i(t)} e^{-i\tilde{Q}R_j(0)} > = \frac{k_f}{k_i} S(k, \omega)
\]

\[
\frac{d^2 \sigma}{d\Omega dE_f} = \frac{k_f}{k_i} N \frac{\delta}{4\pi} S(\tilde{Q}, \omega); \quad \text{(2-44)}
\]

\[
S(\tilde{Q}, \omega) = \frac{1}{2\pi\hbar N} \int_{-\infty}^{\infty} dt e^{-i\omega\tau} \sum_{k,l} b_k b_l < e^{-i\tilde{Q}R_i} e^{i\tilde{Q}R_j(0)} > \quad \text{(2-45)}
\]

with \( \tilde{Q} = \tilde{k}_i - \tilde{k}_f \). We assume that neutrons are detected independent of their spin.

This is why we have to sum over \( \sigma_f \). The \( \delta \)-function indicates the conservation of energy.

The energy lost or gained by the neutron is taken up or provided by the sample, respectively. \( S(\tilde{Q}, \omega) \) is called scattering function or dynamic structure factor.

### 2.5.4 Time of flight spectrometers

The principle of a time-of-flight spectrometer relies on the fact that particles with varying speeds separate when travelling. Energies can thus be determined by measuring the time of flight along a known distance \( L \). To do so we have to know the time of departure. As neutrons could be identified only by their spin, this is only possible by imposing the same departure times to all of them, i.e. by working with pulsed beams. The pulsing is achieved by turning devices commonly called choppers. The degree of monochromaticity relies strongly on the opening times of these devices. It is certainly advantageous in terms of efficiency if the neutron source itself is pulsed. Apart from pure time-of-flight spectrometers mixtures of crystal and time-of-flight analysis are possible (see Figure 12). Monochromatization in this
case is obtained via a crystal. The monochromatic beam is then chopped into pulses by a
turning drum with a well-defined opening of a few degrees. The monochromatic neutron
pulses are scattered by the sample into all directions. According to whether they have gained
or lost energy they will arrive earlier or latter in the position sensitive detector. Thus both the
change in energy and momentum can be measured over a wide range simultaneously. The
prize to pay is the reduced intensity at the sample due to the pulsing process.

2.5.6. Coherent and incoherent scattering

If there is no exchange interaction between neighboring nuclei then the
distribution of nuclear spins in the sample may be considered at all temperatures
interesting to the solid state scientist as random. The same randomness is certainly found for the isotope distribution. In this case the double differential cross section separates into two parts:

\[
\frac{d^2\sigma}{d\Omega dE_f} = (\frac{d^2\sigma}{d\Omega dE_f})_{\text{coherent}} + (\frac{d^2\sigma}{d\Omega dE_f})_{\text{incoherent}}
\]

2.5.7. Scattering Function and Density of States

The scattering function \( S(\bar{Q}, \omega) \) has the dimension of an inverse energy and does not contain variables referring to the wavefunctions of the incoming and scattered neutrons. The relevant parameters are the momentum transfer \( \bar{Q} = \bar{k}_i - \bar{k}_f \) and energy transfer \( \hbar\omega = E_i - E_f \), therefore, states the fact that we can decoupled the probe from the system investigated. This is another important feature of neutron scattering that has its origin in the fact that the neutrons, because they are a very weak probe, monitor the unperturbed sample state. In other words, the experiment yields direct information on the spontaneous fluctuations in the sample, and this despite the fact that the neutrons interact with it. This circumstance is mathematically expressed in the fluctuation dissipation theorem.[60]

In 1985, Buchenau derived that it is possible to determine the vibrational density of states and an average dispersion relation from neutron scattering measurements without separating coherent and incoherent contributions. The density of states of glasses can then be calculated directly from the dynamic factor of the incoherent scattering, the relationship between these two was shown to be[59, 61]:

\[
S_{\text{incoh}}(\bar{Q}, \omega) \propto q^2 \frac{1}{\omega} (n(\omega) + 1)g(\omega) \]

(2-46)
CHAPTER THREE: EXPERIMENTAL SETUP AND PROCEDURES

3.1 A General Overview

A typical Raman setup is composed of three important parts: the excitation source which is generally a narrow band laser; the sample stage which includes the focusing optics; and the collection optics and detector.

Over the past fifteen years the development of efficient filters for Rayleigh rejection and the availability of multichannel detectors have considerably simplified the experimental set up with the additional benefits of increased optical throughput and shorter acquisition time. The spectrometer can be reduced to a single spectrograph stage with a notch [62,63] or sharp cut-off filter [64] selected for high extinction at the Rayleigh line. Thus Raman spectroscopy has become even more accessible as a scientific tool.

A schematic of a typical Raman setup is shown in Fig. 13. Raman scattering is excited by either an Ar ion or a Ti: sapphire laser. The scattered light is collected with a low f-number lens and focused with a second lens on the entrance slit of a single grating spectrograph (typical dispersion: 1.2 nm / mm in the focal plane). Multichannel detection at the single photon level is achieved with a backthinned charge-coupled device (CCD) detector.
3.2 Experimental Apparatus

3.2.1. Lasers for Raman scattering

Because of the very weak Raman scattering intensity compared with the fluorescence, we don’t want the excitation line to be within the absorption band of the material, otherwise the Raman signal will be blocked by the fluorescence. On the other hand, because of the $\gamma^4$ dependence of the cross section, we want the laser frequency to be as high as possible. Most of the experiments were thus conducted with the argon laser line at 514nm for the above reasons.

The Ar laser is “ion laser” because the lasing species is a singly ionized Ar+. A direct current (DC) electron discharge through low-pressure Ar forms a plasma, which is magnetically confined inside a resonant cavity consisting of one highly reflecting mirror and one partially transmitting mirror. Ion lasers are quite inefficient in terms of converting electrical to optical energy because much of the power is used to create the ions.
rather than exciting the laser transition. This inefficiency leads to the high electrical power and water cooling requirements. [65]

The Ar laser has the advantage of high power output and several lasing lines available, which covers from ultraviolet to visible range.

3.2.2 Spectrometer and filter

Rayleigh scattering is 5-10 orders higher in intensity comparing with the Raman scattering. The Rayleigh scattering can thus obscure most of the Raman scattering signals and must be rejected using appropriate method.

A double monochromator (Figure 14) has the advantage over single monochromators by combining two single-grating monochromators in series, with common “intermediate” slits (S2 and S3), the light is dispersed twice and the bandpass can be quite narrow. More importantly, the stray light becomes the product of the stray light levels of the single stages, leading to excellent rejection of elastic scattering. The double monochromater can reject most of the Rayleigh scattering and let us go down to several wavenumbers, it also increases the resolution of the spectra because two diffracting gratings(G1 and G2) were used. Due to high resolution and effective suppression of Rayleigh line, an U1000 double monochromator (located in E13 of Technical University of Munich) was used for our experiments.

Although a single monochromator together with holographic notch filters can be used for this purpose too because it selectively rejects (through Bragg diffraction) a narrow band of light, while passing light outside of the band rejection region. The Rayleigh can be reduced and the Raman signal can be shown to as low as 150-200 cm$^{-1}$. 
If we want to analyze the spectrum range below 100\,\text{cm}^{-1}, a double monochromater is needed.

![Figure 14: Schematic of a double grating monochromator](image)

3.2.3. Detector

Until recently photomultipliers were the standard detectors used for Raman spectral measurements. The entire UV, visible to near IR spectral region (<900\,\text{nm}) is well covered with an AlGaAs photocathode which has quantum yields $> 10\%$ over this entire spectral range. These detectors are ideal detectors with only a few counts per second of background and a linear dynamic range of $> 10^6$. The resolution of the single monochromator system equipped with CCD is limited by the relative large CCD pixel
size. So PMT (photo multiplied tube) scanning detectors are still used for high resolution Raman measurements because they can be masked by a final slit which be as narrow as a few microns (in contrast to the ~25 microns limits associated with the pixels of CCD).[65]

### 3.3. Experimental Methods and Processures

Briefly, for the measurements of the Raman spectroscopy of both tellurium oxide glasses and niobium-phosphate glasses, the glasses were excited by an argon ion laser at 514nm, and a Jobin Yvon U1000 double monochromator was used to analyze the scattered light, a photomultiplier tube (PMT) with resolution of less than 1cm\(^{-1}\) was used for the detection of the Raman signals.

The backscattering geometry was chosen for our experiments because it gives a reliable intensity comparison of the samples. In most cases, the backscattered light was analyzed by a double monochromator (ISA U1000) and detected with a PMT. The spectral coverage in this case can go down to several wavenumbers. In some experiments, the scattered light was analyzed by single monochromators (ISA HR640) equipped with CCDs. The spectral information below 150cm\(^{-1}\) are normally not visible in such cases because of the cutoff of the notch filter.

During an experiment, the samples were positioned carefully on the sample stage, the position of the sample were adjusted so that it is at the exact focal point of the collection lens. The excitation laser is then turned on, room lights are shut off at this point before the collection of the data, to prevent the stray light from entering the detector. The scattered light signals are detected by PMT, and finally the scattering intensity as a function of frequency were saved in the computer. The ASCII files were loaded into the
Origin scientific plotting program and the resultant Raman spectra are plotted. A schematics of the setup that was used to collect the data is shown in Figure. 15.

![Figure 15. Schematics of an experimental setup for Raman spectroscopy using a double-grating spectrograph.](image)

### 3.3.1 Polarization analysis

![Figure 16. Schematics of depolarized(HV) and polarized(VV) light scattering.](image)

Polarization dependence was also studied by polarization setup, in which a polarization rotator is put in front of the laser to change the incident laser polarization direction and a polarizor is put in before the laser enters the spectrometer to analyze the polarization direction of scattered light.
The depolarization ratio is defined as the ratio of the intensity of the scattered light that changes its polarization direction over the intensity of the scattered light that keeps its polarization direction. (Fig. 16)

$$\rho = \frac{I_{\perp}}{I_{\|}}$$

The depolarization ratio is indicative of the symmetry of the vibrations involved in the scattering process. The more highly symmetric the vibration is, the closer to 0 will the depolarization ratio be.
CHAPTER FOUR. RESULTS AND DISCUSSIONS

4.1 Tellurite glass system

4.1.1 Glass Composition and Preparation Processure

First, some new Tellurite glasses were fabricated by our research collaborators (Clara Rivero, Kathleen Richardson, Thierry Cardinal). Glasses in the system TeO$_2$ – PbO – P$_2$O$_5$ – Sb$_2$O$_3$ were prepared from high purity raw materials: TeO$_2$ (Cerac 99.99%), (NH$_4$)$_2$HPO$_4$ (Merck minimum 98%), PbO (Cerac 99.99%), Sb$_2$O$_3$ (Cerac 99.999%). [3]

Before melting, a pre-heat treatment was conducted at 200°C and 400°C to eliminate the water and ammonia respectively, present in the primary starting materials. The batch mixture was melted in alumina crucibles at a temperature range of 900°C to 1000°C depending on the composition, for 30 min. Following melting, the glasses were quenched on to a pre-heated carbon plate, and annealed at a temperature of 40°C below their glass transition temperature (Tg). Approximately 1 mol% of alumina attributable to the crucible material was detected in the glass using elemental dispersive spectroscopy (EDS). Finally, the glasses were cut and optically polished.[66]

A list of compositions and properties of the Tellurite glasses is shown in the Table 1.
Table 1. Glass compositions and properties of Tellurium oxide glasses.[3,66]

<table>
<thead>
<tr>
<th>Glass Composition (Molar Percent)</th>
<th>Sample Code</th>
<th>ρ (g/cm³)</th>
<th>n 532nm</th>
<th>n 1064nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>76.5 TeO₂ – 9 PbO – 9 P₂O₅ – 5.5 Sb₂O₅</td>
<td>T76</td>
<td>5.38</td>
<td>2.05</td>
<td>1.99</td>
</tr>
<tr>
<td>56 TeO₂ – 20 PbO – 20 P₂O₅ – 4 Sb₂O₅</td>
<td>T56</td>
<td>5.13</td>
<td>1.99</td>
<td>1.94</td>
</tr>
<tr>
<td>48 TeO₂ – 17 PbO – 17 P₂O₅ – 18 Sb₂O₅</td>
<td>T48</td>
<td>5.34</td>
<td>1.98</td>
<td>1.97</td>
</tr>
<tr>
<td>85 TeO₂ – 15 WO₃</td>
<td>T85W</td>
<td>5.89</td>
<td>2.20</td>
<td>2.08</td>
</tr>
<tr>
<td>85 TeO₂ – 10 Nb₂O₅ – 5 MgO</td>
<td>T85NM</td>
<td>5.26</td>
<td>2.15</td>
<td>2.13</td>
</tr>
<tr>
<td>SiO₂</td>
<td>SiO₂</td>
<td>2.205</td>
<td>1.462</td>
<td>(514.5nm)</td>
</tr>
</tbody>
</table>

4.1.2. Raman spectra of the Tellurite glasses

Polarization dependent spontaneous Raman spectra of these novel Tellurium Oxide glasses listed in Table 1 were measured. Both the polarized spectra (vv) and the depolarized spectra (vh) are shown in Fig.17. The frequency of the Raman scattered light covers the range from 6 to 1500 cm⁻¹ or 180 GHz - 45 THz. The Raman spectra were taken using the 514nm excitation line of an Argon ion laser, the scattered signals were collected and then dispersed by an U1000 double monochromator and detected by a PMT. The spectral resolution is 2cm⁻¹. The Raman spectra of fused silica are also included in the figure for comparison of both intensity and bandwidth.

In the polarized Raman spectra, we can see that the Raman scattering intensity is significantly higher than that of fused silica. The intense features in the low frequency region below 100 cm⁻¹ is especially high, corresponding to the so-called Boson peak.
Figure 17. (above). Polarized (vv) spontaneous Raman spectra of Tellurium Oxide glasses and fused silica (below). Depolarized (vh) spontaneous Raman spectra of Tellurium Oxide glasses and fused silica.
Because of the very different physical origin of the Raman scattering in the high and low frequency region, we will analyze the Raman spectra by dividing the spectra into two major spectral regions. The first region, e.g. the high frequency region, is the spectral region above about 100 cm\(^{-1}\), where the Raman scattering originates from the molecular vibrations. The second region, the low frequency region, is the spectra region below 100 cm\(^{-1}\), where the contribution of the Boson peak is prominent. The physical origin of the Raman scattering in this region is much more complex in this region than in the high frequency region, as discussed in Chapter 2.4.

**4.1.2.1 Spectral Deconvolution of the Raman spectra of Tellurium Oxide Glasses**

In the high frequency region, the Raman spectrum is known to originate from the molecular vibrations of the molecular bonds. The continuous curve shaped Raman spectrum of glasses can thus be deconvoluted into several separate peaks, each of which corresponds to the Raman scattering contribution from a vibrational molecular bond. This gives a clear specification on the contributions of different molecular bonds on the Raman scattering profile.

For the deconvolution of the spectra, Voigtian lineshapes were fitted to the various peaks. In a perfect crystal environment, the local environment is exactly the same for each molecular subunit, thus the spectral lineshapes are supposed to be homogeneously broadened Lorentzians. The width of the line is called the homogeneous width. The homogeneous width is determined by excited-state dephasing interactions or lifetime effects that are identical for all centers.
In a glass, however, a distribution of local environments is present. The inhomogeneous environment will give rise to the inhomogeneous broadening, the center of the homogeneous lines being distributed with a Gaussian statistics.

In short, a Voigtian distribution is the Gaussian superposition of Lorentzian lines, which can be represented by:

\[
I(\nu) = \int G(\nu - \nu_o) L(\nu - \nu') dv' = \frac{c\Gamma}{\sigma} \int e^{-(\nu - \nu_o)^2/(2\sigma^2)} \frac{1}{(\nu - \nu')^2 + \Gamma^2} dv'
\]

where \( G(\nu - \nu_o) \) is the Gaussian distribution, and \( L(\nu - \nu') \) is the Lorentzian distribution.

For the deconvolution, the GRAMS software package was used. The Voigt function is represented by:

\[
f(x) = \frac{a_0 \exp(-y^2)}{-a_3^2 + [(\frac{X - a_1}{a_2}) - y]^2}
\]

where

- \( a_0 \) = height or amplitude
- \( a_1 \) = position of center frequency
- \( a_2 \) = Gaussian inhomogeneous width
- \( a_3 \) = Lorentzian homogeneous width

With same Lorentzian width, Gaussian width will determine the disorder of the composition or the peak.

The deconvolution using Voigtian lineshapes allows us to quantify the contribution of the molecular constituents to the Raman spectra in the high frequency
range. The low frequency region (<100 cm\(^{-1}\)) was excluded. All spectra were fitted with the same number of peaks consistent with assignments and literature data as far as available, the same homogeneous width were also used for the same corresponding peaks in different compositions. The compositional dependence is described by differences in intensity and inhomogeneous linewidth of the component bands.

In the following the component bands beyond the boson peak are labeled by #1, #2, #3,.. in order of increasing frequency. The assignments are summarized in Table 2, the deconvoluted spectra are displayed in Fig.18 & Fig.19, and the deconvolution parameters were shown in Table 3 and Table 4.

**Table 2.** Band positions and assignments of the various peaks within the TeO\(_2\)-P\(_2\)O\(_5\)-PbO-Sb\(_2\)O\(_3\) compositions. [33]

<table>
<thead>
<tr>
<th>Band Position (cm(^{-1}))</th>
<th>Assignment</th>
<th>Peak Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>340</td>
<td>P-O bending vibrations in P-O-P linkages</td>
<td>Peak#3</td>
</tr>
<tr>
<td>460</td>
<td>Symmetric stretching(bending) vibrations of Te-O-Te linkages between TeO(<em>4), TeO(</em>{3+1}) and TeO(_3) units</td>
<td>Peak#5</td>
</tr>
<tr>
<td>610</td>
<td>Vibrations of the continuous TeO(_4) tbp network</td>
<td></td>
</tr>
<tr>
<td>610-680</td>
<td>Stretching vibrational mode of Sb-O-P linkages</td>
<td>Peak#6</td>
</tr>
<tr>
<td>660</td>
<td>Asymmetric vibrations of linkages between short and longer Te-O bonds(i.e. Te(<em>{3+1})-O—Te(</em>{3+1}))</td>
<td>Peak#7</td>
</tr>
<tr>
<td>750</td>
<td>Cleavage of Te-O-Te linkages</td>
<td>Peak#8</td>
</tr>
<tr>
<td>950</td>
<td>Vibrational mode of PO(_3)(^-) groups</td>
<td>Peak#9</td>
</tr>
<tr>
<td>980,1020-1100</td>
<td>Symmetric and asymmetric stretching fundamental of PO(_4)(^3-) tetrahedral groups</td>
<td>Peak#10</td>
</tr>
</tbody>
</table>
Peak #3 (292-297 cm\(^{-1}\)) is attributed to the P-O bending vibrations. Peak #4 (393-405 cm\(^{-1}\)) is rather weak, only appearing as a slight shoulder as the intense middle peak took shape. Based on literature data this feature appears as a result of an overlap between bending modes of PO\(_4\) groups and those of Sb-O linkages.

Peak #5 (464-475 cm\(^{-1}\)) corresponds to the symmetric stretching (bending) vibrations of Te-O-Te linkages between the various Te-based structural units previously mentioned.

Peak #6 (604-626 cm\(^{-1}\)) is observed as a combined feature of TeO\(_4\) vibrations and Sb-O-P stretching, however, the shift in the peak is consequently due to the Sb-O-P stretching vibrations. Composition T76 had a significantly lower amount of P\(_2\)O\(_5\) and Sb\(_2\)O\(_3\) than Compositions T56 and T48, therefore its peak is observed at lower frequency than the respective peaks of T56 and T48.

Peak #7 (664-685 cm\(^{-1}\)) is similar to that of #5 in that compositional differences caused a red-shift. This feature was previously mentioned as the asymmetric vibrations of linkages between shorter and longer Te-O bonds (i.e. TeO\(_{3+1}\)-O-TeO\(_{3+1}\)). With Composition T76 being Te-rich, it is expected that its peak agree to the literary value of 660 cm\(^{-1}\). This is clearly not the case in Compositions T56 and T48, as the peak is shifted 20 cm\(^{-1}\) and drastically drops in intensity.

Peak #8 (749-756 cm\(^{-1}\)) is cleavage of Te-O-Te linkages, again only experiencing a slight shift due to compositional differences.

Peaks #9 (960-968 cm\(^{-1}\)) and #10 (1051-1072 cm\(^{-1}\)) were the expected PO\(_3^-\) vibrational and PO\(_4\) stretching fundamentals, showing a slight shift due varying amounts of PbO.
From the above deconvolution, we can see that in the tellurite system increasing TeO$_2$ and decreasing PbO concentrations are determinants for the peak intensity.

In assigning the bands of the tellurate spectra, the importance of PbO concentration becomes quite evident, as many of the features are significantly altered and/or exist as a result of increasing (decreasing) PbO content. The reduction of TeO$_2$ resulted in a significant reduction in intensity of the 460 cm$^{-1}$ and 660 cm$^{-1}$ bands.
Figure 18. Peak deconvolution for the depolarized Raman spectra (vh) of Sample T48, T56 & T77.

Figure 19. Peak deconvolution for the polarized Raman spectra (vv) of Sample T48, T56 & T77.
### Table 3. Deconvolution of vh spectra of Tellurium Oxide glasses

<table>
<thead>
<tr>
<th></th>
<th>48% TeO2,17% PbO,17% P2O5,18% Sb2O3</th>
<th>56% TeO2,20% PbO,20% P2O5,4% Sb2O3</th>
<th>76.5% TeO2,9% PbO,9% P2O5,5.5% Sb2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Center X (cm⁻¹)</td>
<td>Height (A.U.)</td>
<td>Width (cm⁻¹)</td>
</tr>
<tr>
<td>Peak 1</td>
<td>143</td>
<td>3439</td>
<td>52</td>
</tr>
<tr>
<td>Peak 2</td>
<td>204</td>
<td>2026</td>
<td>83</td>
</tr>
<tr>
<td>Peak 3</td>
<td>291</td>
<td>2196</td>
<td>101</td>
</tr>
<tr>
<td>Peak 4</td>
<td>401</td>
<td>813</td>
<td>61</td>
</tr>
<tr>
<td>Peak 5</td>
<td>468</td>
<td>2132</td>
<td>103</td>
</tr>
<tr>
<td>Peak 6</td>
<td>618</td>
<td>4141</td>
<td>75</td>
</tr>
<tr>
<td>Peak 7</td>
<td>683</td>
<td>3934</td>
<td>68</td>
</tr>
<tr>
<td>Peak 8</td>
<td>757</td>
<td>7261</td>
<td>96</td>
</tr>
<tr>
<td>Peak 9</td>
<td>983</td>
<td>1421</td>
<td>101</td>
</tr>
<tr>
<td>Peak 10</td>
<td>1079</td>
<td>1088</td>
<td>140</td>
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**Table 4.** Deconvolusion of vv spectra of Tellurium Oxide glasses

<table>
<thead>
<tr>
<th>48% TeO$_2$,17% PbO,17% P$_2$O$_5$,18% Sb$_2$O$_3$</th>
<th>Center X (cm$^{-1}$)</th>
<th>Height (A.U.)</th>
<th>Width (cm$^{-1}$)</th>
<th>Lorz. Width (cm$^{-1}$)</th>
<th>Peak Area (A.U.)</th>
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</thead>
<tbody>
<tr>
<td>Peak 1</td>
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<td>12413</td>
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<tr>
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<td>6.31E+05</td>
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<tr>
<td>Peak 3</td>
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<td>7043</td>
<td>44</td>
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<td>Peak 4</td>
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<td>80</td>
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<td>4.10E+05</td>
</tr>
<tr>
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<td>10750</td>
<td>102</td>
<td>20</td>
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<td>618</td>
<td>4141</td>
<td>75</td>
<td>19</td>
<td>3.93E+05</td>
</tr>
<tr>
<td>Peak 7</td>
<td>683</td>
<td>3934</td>
<td>68</td>
<td>20</td>
<td>2.05E+05</td>
</tr>
<tr>
<td>Peak 8</td>
<td>757</td>
<td>7261</td>
<td>96</td>
<td>20</td>
<td>1.62E+05</td>
</tr>
<tr>
<td>Peak 9</td>
<td>983</td>
<td>1421</td>
<td>231</td>
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<td>7.27E+05</td>
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<td>Peak 10</td>
<td>1079</td>
<td>1088</td>
<td>180</td>
<td>5</td>
<td>3.42E+05</td>
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<table>
<thead>
<tr>
<th>56% TeO$_2$,20% PbO,20% P$_2$O$_5$,4% Sb$_2$O$_3$</th>
<th>Center X (cm$^{-1}$)</th>
<th>Height (A.U.)</th>
<th>Width (cm$^{-1}$)</th>
<th>Lorz. Width (cm$^{-1}$)</th>
<th>Peak Area (A.U.)</th>
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<td>11814</td>
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<tr>
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<td>74</td>
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<td>Peak 4</td>
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</tr>
<tr>
<td>Peak 5</td>
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<td>13323</td>
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<td>616</td>
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<td>116</td>
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<td>6856</td>
<td>78</td>
<td>20</td>
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<td>250</td>
<td>5</td>
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<tr>
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<td>1081</td>
<td>1889</td>
<td>171</td>
<td>5</td>
<td>1.62E+05</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>76.5% TeO$_2$,9% PbO,9% P$_2$O$_5$,5.5% Sb$_2$O$_3$</th>
<th>Center X (cm$^{-1}$)</th>
<th>Height (A.U.)</th>
<th>Width (cm$^{-1}$)</th>
<th>Lorz. Width (cm$^{-1}$)</th>
<th>Peak Area (A.U.)</th>
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<tbody>
<tr>
<td>Peak 1</td>
<td>150</td>
<td>8718</td>
<td>40</td>
<td>20</td>
<td>6.09E+05</td>
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<td>Peak 2</td>
<td>215</td>
<td>7957</td>
<td>42</td>
<td>20</td>
<td>6.68E+05</td>
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<tr>
<td>Peak 3</td>
<td>294</td>
<td>6050</td>
<td>45</td>
<td>20</td>
<td>5.50E+05</td>
</tr>
<tr>
<td>Peak 4</td>
<td>398</td>
<td>7448</td>
<td>81</td>
<td>20</td>
<td>7.82E+05</td>
</tr>
<tr>
<td>Peak 5</td>
<td>461</td>
<td>12149</td>
<td>102</td>
<td>20</td>
<td>1.62E+06</td>
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<tr>
<td>Peak 6</td>
<td>624</td>
<td>4726</td>
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<td>Peak 7</td>
<td>693</td>
<td>9171</td>
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<td>9.91E+05</td>
</tr>
<tr>
<td>Peak 8</td>
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<td>6259</td>
<td>99</td>
<td>20</td>
<td>6.11E+05</td>
</tr>
<tr>
<td>Peak 9</td>
<td>987</td>
<td>709</td>
<td>235</td>
<td>5</td>
<td>1.23E+05</td>
</tr>
<tr>
<td>Peak 10</td>
<td>1093</td>
<td>743</td>
<td>196</td>
<td>5</td>
<td>1.21E+05</td>
</tr>
</tbody>
</table>
Figure 20.  Peak area ratio of peak 7 for the polarized spectra of T48, T56, T77.

The ratio of the separate deconvoluted area over the total spectra area can give us some idea about the relative peak bond intensity of the bond that peak corresponds to. In Fig.4.7, the area ratio (ratio of the peak over the whole spectrum area) of peak 7 was plotted as a function of the compositions. The peak ratio shows a consistent raise as the percentage of TeO₂ increases. Peak 7 is attributed to the asymmetric vibrations of linkages between short and longer Te-O bonds (i.e. Te$_{3+1}$-O---Te$_{3+1}$), the increase of this peak suggests a stable rise of ratio of the Te-O network in the total glass network.
4.1.3 Raman Gain of Tellurium Oxide Glasses

4.1.3.1 Raman Gain in the High Frequency Region (>100 cm\(^{-1}\))

From Figure 17, it is obvious that the peak intensities of the polarized Raman spectra in the high frequency region are more than ten times higher than that of the fused silica peak Raman scattering intensity. This suggests that the Raman gain coefficients in the high frequency region are much higher than that of the fused silica as well.

To prove this, direct Raman gain measurements from these glasses are necessary. Raman gain measurement is normally conducted in the optical fiber where the pump and signal lasers can overlap for a very long distance. A direct Raman gain measurement on these millimeter thick bulk glasses is quite experimentally challenging. Our research collaborators (R. Stegeman, G. Stegeman et. al), however, have successfully designed a setup and was able to measure the Raman gain curves of two of these TeO\(_2\) based glasses directly from the bulk samples[7], as shown in Figure 21 and Figure 22. The measured Raman gain coefficient data were represented by the black dots, while the spontaneous Raman scattering spectra are shown as the red curves. The Raman gain coefficients of these two glasses were calibrated with the gain coefficient of the fused silica. So the y axis is scaled by the number of the fused silica peak gain at 440 cm\(^{-1}\). The blue curve gives the spontaneous Raman spectrum of fused silica, already multiplied by a factor of 10.[7]

This proves that in the high frequency region, the Raman gain data follows the spontaneous Raman spectrum, it also shows that these two Tellurium oxide glasses
possess peak Raman gain more than 10 times higher than of the peak fused silica gain, and provides a bandwidth twice as wide. This means that these glasses are very promising Raman gain material in the high frequency region, excluding the consideration of fiber loss and other factors. A real experimental test on the applicability of these glasses as Raman fiber amplifier materials is in process, fibers are being drawn from these materials and Raman gain measurements on the drawn fiber will be measured\[^{67}\].

Although direct Raman gain measurement on these glasses are possible, as have been done by our collaborators, an accurate direct measurement of a lot of samples can be quite time consuming and the error bar of these gain measurements are normally quite large. One way out would be to get the theoretical Raman gain coefficient of these glasses by calculating the Raman gain curves from the spontaneous Raman scattering spectra.
Figure 21. Measured Raman gain and spontaneous Raman spectra of T85N[7]

Figure 22. Measured Raman gain and spontaneous Raman spectra of T85W[7]
The Raman gain curve can be obtained from the polarized spontaneous Raman spectrum (vv), by dividing it by the Bose-Einstein thermal population factor:

\[ [n(\omega) + 1] \cdot [\exp\left(\frac{\hbar \omega}{kT}\right) - 1]^{-1}, \]

where \( n(\omega) + 1 \) is the frequency, \( T \) the temperature, and \( \hbar \) and \( k \) are Planck and Boltzmann constants. The vv polarized spectra divided by \( [n(\omega) + 1] \), e.g. predicted Raman gain of four Tellurite glasses are shown in Fig. 23. The predicted Raman gain curves deviate from the Raman intensity spectra in the low frequency range where the correction from the Bose-Einstein factor dominates.

**Figure 23.** Spontaneous Raman spectra and predicted Raman gain curves of Tellurium oxide glasses [70]
The predicted Raman gain curves show an unusually broad and flat Raman gain region in the low frequency region for these Tellurite glasses, while the gain is not so flat and high for the Borophosphate glass and fused silica.

One of the major issues in Raman amplification for WDM is that its gain variation with respect to wavelength, and a variety of approaches are being made to flatten the Raman gain\cite{71, 72, 73}. Although with the appropriate choice of multiple pump wavelengths and powers, e.g. multi-wave pumping technology, the flattening of the gain over a wide bandwidth is theoretically possible\cite{71,72}. But a more direct and cost efficient way would be to find a material with flat and high Raman gain over a wide bandwidth.

4.1.3.1.1 Perspective in employing the low frequency gain region for optical communication

Glasses are one of the most ideal materials in this search because of its wide bandwidth and ability to be drawn into fibers. However, to manufacture a glass with flat Raman gain region in the high frequency region is quite difficult. The reason resides in that in the high frequency region, the Raman scattering comes from the molecular vibrations. Our attempt to search for a wide bandwidth Raman gain material has been focused on multiple component glass, because different molecular bond vibrations give rise to different vibrational frequency peaks, thus providing a wide Raman gain bandwidth. However, different molecular vibrational bond also tends to give different scattering peak intensity, which makes the whole Raman spectrum uneven. Although changing component percentage of different oxide components of the glass seems to be a possible way to change the intensity of different peaks and making the spectrum flat. The change of percentage of a component,
while decrease the intensity of one Raman peak, normally increasing the intensity of another peak.

Here, we prove the low frequency behavior of the Raman spectra of these novel Tellurium oxide based glasses, and the calculated Raman gain in this region come out to be very flat from about 50 cm$^{-1}$ to around 400 cm$^{-1}$. What is amazing is that other than being flat, the Raman gain coefficient is expected to be pretty high compared with the peak Raman gain of fused silica as well. It is expected to be 10 times higher than that of fused silica as we can see from Figure 23. If multi-wave pumping technology is combined with the application of this broadband Raman gain material, [74] then with several excitation waves, this Raman gain region can satisfy the whole bandwidth demand and also the flatness of the gain request.

In Figure 24, a diagram shows the correspondence relationship between the different unit systems, relative wavenumber, nanometer and Terahertz. 300 cm$^{-1}$ corresponds to wavelength of around 1350 nm with 1300 nm excitation. 300 cm$^{-1}$ also equals about 10 THz. The new transmission window for optical communication has been widened up, as we have mentioned earlier, to from 1300 nm to 1650 nm. From the graph, we can see that, with proper excitation wavelength and multiple excitation technique, utilizing the low flat Raman gain region of the Tellurium oxide glasses, a flat Raman gain region from 1300 nm to 1650 nm can be achieved with about 5 excitations. Theoretically, neglecting the consideration of loss and other factors, this means the new Tellurium oxide glasses are probably one of the most promising materials that can be utilized to solve the present gain flattening problem.
The predicted Raman gain in the high frequency region correlates to the experimental data pretty well as we have shown in Figure 21 and Figure 22. Direct measurements on Raman gain on the bulk glasses in the low frequency peak region, however, are hindered by affect of the pump laser because it is so close to the pump line. Raman gain measurements have been conducted for silica dioxide fibers down to 6 cm⁻¹ before and the result coincide with what is predicted from spontaneous Raman spectroscopy. [75] It means the predicted Raman gain curves are quite accurate as compared with those of the measured Raman gain normalized to fused silica. This suggests that the Raman gain application in this low frequency region is possible for these Tellurite glasses.
4.1.3.2 Raman Spectra of Tellurite Based Glasses in the Boson Peak Region

In the low frequency range of the Raman spectra of these Tellurium oxide glasses, prominently high peaks are observed, as shown in Figure. 17.

Although this peak seems to merely due to the Bose-Einstein thermal population factor, the spectra after correction still show high scattering intensity in the low frequency region (Figure.23).

Raman spectroscopy basically reveals the density of states information, but not all density of states are Raman active, only a certain portion of all the density of states are coupled into Raman scattering. There is a factor to quantify this coupling, \( c(\omega) \), which is called the coupling coefficient.

The relationship between the Raman scattering intensity and the vibrational density of states is:

\[
I(\omega) = c(\omega)g(\omega)[n(\omega) + 1]/\omega
\]

where \( I(\omega) \) is the Raman intensity for the Stokes side of the spectrum and \([n(\omega) + 1]\) is the Bose-Einstein thermal population factor.[38]

Debye’s model predicts that for crystals the density of states is proportional to the square of the frequency, \( g_D(\omega) \propto \omega^2 \), in the low frequency region.

The Raman spectra of several of the Tellurium oxide glasses were redrawn as the reduced Raman scattering intensity, \( I_R = I(\omega)/\omega[n(\omega) + 1] = C(\omega)g(\omega)/\omega^2 \), as in Figure.25. The spectra are only shown in the frequency range below 400cm\(^{-1}\), there is peaks centered at 30-50 cm\(^{-1}\). The coupling coefficient, \( C(\omega) \), as most study shown, is
proportional to the frequency, $\omega$. The peak in these curves, are then due to only $g(\omega)/\omega^2$. The density of states however, according to Debye’s law, are supposed to rise up quadraticly with frequency. So there are obviously some extra density of states that are not explained by the Debye’s law in these glasses.

![Figure 25](image.jpg)

*Figure 25. Boson peaks as revealed in Reduced Raman intensity.*

This extra density of states in these glasses, however, is an universal feature for all glasses, or more generally for all amorphous materials.

This feature corresponds to the Boson peak, as have been discussed in Chapter 2.4.

Although it has been 50 years since the discovery of Boson peak, the physical mechanism that gives rise to the extra density of states in the Boson peak region is still unclear, and the origin of Boson peak remains one of the most debated issues in modern solid state physics.[48]

The main reason resides in the complexity involved by the cross-over of different physics in this frequency region. The Raman scattering in higher frequency (>100 cm$^{-1}$) is
attributed to the interaction between light and optical phonons, or local molecular vibrations. While the lower frequency (<30cm⁻¹) Raman scattering was attributed to the tunelling modes, the relaxation states. The mix of different physical mechanism gives a mixture of different models, the models that are used to describe higher or lower frequency regions actually become not as accurate and valid in this “interface” frequency region, but they are the model people used to explain the Boson peak physics.

There are 3 major models to interpret the origin of Boson peak, as described in Chapter 2.4.

In the first model, the localized modes in the very low frequency (<1GHz), which is called tunneling modes, are postulated to extends to the Boson peak region and gives rise to the Boson peak. This model is called soft potential model, in which both the relaxational and vibrational modes are explained in same physics. The Boson peak is attributed to the existence of anharmonic localized potential wells (and double wells). Simulations have been performed successfully for vitreous silica, suggesting the Boson peak of which arises from coupled rotations and bodily translations of SiO₄ tetrahedrons.

The second model ascribe the Boson peak to localized vibrational modes. It assumes that the structure of the glasses is inhomogeneous, consisting of an aggregate of “blobs” with a different density or elastic constants from the matrix. The Boson peak is assumed to be due to vibrational modes spetially localized in such blobs. No computer simulations, however, have proved such density fluctuations exist, nor is there any evidence that localized mode can occur at such low frequency.
In the third model, it was proposed the Boson peak originates from the medium range disorder of the system. Computer simulations have shown that force constant disorder alone is capable of giving rise to the Boson peak. [86]

The previous two models are actually the utilization of the model that were used to describe the higher and lower frequency regions. We will base our analysis on the third model, which in its simple yet convincing way gives a clear explanation for the Boson peak.

In a simplified language, this model basically states that the disorder leads to a local repulsion of vibrational states, which includes a downward shift of low frequency states as compared to the Debye prediction.

In this model, it is proposed that the more disordered the system is, the higher the Boson peak is.

In these Tellurium oxide glasses, the very high Boson peak indicates high disorder.

Since the Boson peak is caused by the broadening of the high frequency vibrational peaks, the high Boson peak in the low frequency range comes as no surprise because these Tellurium oxide glasses do have high Raman scattering intensity in the high frequency region. Especially, the very high vibrational peak in the low frequency region, just above the Boson peak region, e.g. >100cm⁻¹, might has been a major contribution.

A systematic analytical study of the relationship between Boson peak and the composition or structure, however, requires a glass family with gradual systematic structural change. A binary glass family with one component percentage increases
gradually and the other component decreases gradually would be a good glass system for this study. This leads to the making of the binary phosphate glasses and the study of relationship between Boson peak and medium range disorder in Chapter 4.2.

4.1.4. Depolarization ratio curves in the Boson Peak Region

For the same material, the Boson peak shape of polarized and depolarized Raman spectra are almost the same. As a result, the depolarization ratio, the ratio of intensities of depolarized Raman spectra over polarized Raman spectra, should be a constant. The depolarization ratio curves of different curves are show in Figure.26. A thing that we notice is that in the high frequency range (>100 cm\(^{-1}\)) there are several minima. The two depolarization minima of T56, T48 and T77 are at around 480 cm\(^{-1}\) and 750 cm\(^{-1}\). The deconvolution has shown that the vibrations around 460-480 cm\(^{-1}\) are attributed to symmetric stretching vibrations of Te-O-Te linkages between TeO\(_4\), TeO\(_{3+1}\) and TeO\(_3\) units. The vibration at 750 cm\(^{-1}\) is assigned to cleavage of Te-O-Te linkages (Table.2). Both these minimums correspond to symmetric vibrations. The depolarization ratio is supposed to be at its minimum when the vibrations are symmetric, because when the vibration is symmetric, the scattering tends to be symmetric and the possibility for the incoming light to change polarization is very small. So the depolarization curves further confirmed the accuracy of the assignments of the two peaks.

We found that the vh and vv spectra have the same reduced Raman intensity profile in the Boson peak region(30-100cm\(^{-1}\)) which tells us that the depolarization ratio should be a constant in the Boson peak region.
In Figure 27, the depolarization ratio curves of the Tellurite glasses in the Boson peak alone were shown in enlarged version. The depolarization ratios are almost flat in this region as expected.

The depolarization ratios are larger in the Boson peak region than in the higher frequency range of molecular vibrations. This means that the Raman amplification is less polarization dependent in the Boson peak region compared with that of higher frequency region. This is definitely good for the Raman gain application because less percentage of light will change polarization direction during the time it travels inside the amplification material.

It has been discovered experimentally that the Raman effect is largest when the pump and signal are copolarized or parallel, and is nearly zero when they are orthogonally polarized. [76]

Also, the constant depolarization ratio in this frequency region tells us that for different frequencies in this region, the depolarization effect is the same. In application, that means for different optical communication frequency channel, the depolarization effect is the same, the advantage of which is great.
Figure 26. Depolarization Ratio Curves of Tellurium Oxide Glasses in the whole frequency region.

Figure 27. Depolarization Ratio Curves of Tellurium Oxide Glasses in the low frequency Boson peak region.
4.2.  *Niobium-Phosphate glasses*

In Chapter 4.1, it was shown that there are flat and high Raman gain regions in the low frequency region for multi-component Tellurium Oxide glasses. The Boson peak, which resides at around 30-100cm\(^{-1}\), contributes greatly to the density of states and Raman gain in this low region. A deep understanding of the relationship between Boson peak and glass structure is crucial for further investigation on the Raman gain behavior in the low frequency region or for glasses. Further study of Boson peaks in these specific glasses also can enhance the understanding of this mysterious anomaly which is still being investigated intensely by solid state physicist. In Chapter 4.1, it became apparent that medium range disorder of a glass and the intensity of Boson peak seem to be relate to each other, however, a deeper and clear understanding of this correlation requires the study of a simpler glass system.

4.2.1. Glass Composition and Preparation

A set of niobium phosphate binary glasses were fabricated for this purpose. Binary glasses composed of only two constituents, e.g. two oxides, in this case Nb\(_2\)O\(_5\) and NaPO\(_3\), making the study of structure much simpler than that of the multi-component glasses. The glasses were made by our colleague Thierry Cardinal and coworkers at University of Bordeaux. The composition of these glasses are shown in Table 5.
Table 5. Compositions of the Niobiom Phosphate glasses[3].

<table>
<thead>
<tr>
<th>Glass Composition (Molar Percent)</th>
<th>Glass Transition Temperature (Celsius)</th>
<th>Density (g/cm³)</th>
<th>Linear Refractive Index</th>
</tr>
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<tbody>
<tr>
<td>10% Nb₂O₅ – 90% NaPO₃</td>
<td>380</td>
<td>2.81</td>
<td>1.57</td>
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<tr>
<td>20% Nb₂O₅ – 80% NaPO₃</td>
<td>500</td>
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<tr>
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<tr>
<td>40% Nb₂O₅-60% NaPO₃</td>
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<table>
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<th>Density (g/cm³)</th>
<th>Linear Refractive Index</th>
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</thead>
<tbody>
<tr>
<td>10% Nb₂O₅ – 90% [0.95NaPO₃, 0.05 Na₂B₄O₇]</td>
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<td>20% Nb₂O₅ – 80% [0.95NaPO₃, 0.05 Na₂B₄O₇]</td>
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<tr>
<td>30% Nb₂O₅ – 70% [0.95NaPO₃, 0.05 Na₂B₄O₇]</td>
<td>587</td>
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<td>40% Nb₂O₅ – 60% [0.95NaPO₃, 0.05 Na₂B₄O₇]</td>
<td>630</td>
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</table>

The Niobium Phosphate glasses were elaborated from NaPO₃ and Nb₂O₅ raw material using standard melting methods at 1100 °C in platinum crucibles. After quenching the glass were annealed for 15 hours at 30 °C below their glass transition temperature ranging from 460 °C for the lowest niobium content to 600°C for 45 molar percent of Nb₂O₅. introduced.[77]

An additional family was also made by our colleagues T. Cardinal and coworkers by adding very small amount of Na₂B₄O₇ into the binary system. The small addition of boron strengthens the glass matrix, increases the thermal stability and the glass becomes less hygroscopic as compared to the pure phosphate glasses.[78] The addition also shortens the metaphosphate chains and the borate groups cross-link these chains to build complex borophosphate entities.[81]
4.2.2 Raman spectra of Niobium Phosphate glasses

The polarization dependent Raman spectra of these two glass family were measured using the 514nm excitation line of an Argon ion laser. The scattered signals were collected and then dispersed by an U1000 double monochromator and detected by a PMT.

In Figure. 28, the polarized Raman spectra of these two family of glasses are shown. The frequency range of these spectra extends from 6cm⁻¹ to 1500cm⁻¹. The Raman spectrum of fused silica obtained under the same condition with the same setup is also included for intensity and bandwidth comparison. Although these glasses don’t exhibit high Raman scattering intensities as high as that of the Tellurium Oxide glasses, they still have Raman scattering intensity higher than the 420cm⁻¹ fused silicon peak intensity. These glasses, however, are not for the purpose of high Raman gain, they serve as a model for the study of structure.

We can see from a comparison that the Raman spectra of the glass familie with boron and the glass family without boron are very similar. This is because that the small amount of addition of boron only strengthens the glass matrix, and increases the thermal stability, while gives very little change to glass molecular structure. So the change of Raman spectra of the glass family with the addition of boron is also very small. Therefore, we will only discuss the Niobium Phosphate glasses in later sections.

As before, we will analyze the spectra by dividing them into the high frequency region and low frequency region.
Figure 28. Polarized spontaneous Raman spectra of binary glasses (above) & Polarized spontaneous Raman spectra binary glasses with small addition of boron (below).
4.2.2.1 Spectral Deconvolution in the High Frequency Region

Again, to quantify the contribution of the molecular constituents to the Raman spectra deconvolution using Voigtian lineshapes (GRAMS 32 software) was performed. First, the polarized Raman spectra of the niobium-phosphate glasses were deconvoluted. All spectra were fitted with the same number of peaks consistent with assignments and literature data as far as available. The band below 100cm$^{-1}$, e.g. low frequency vibrations in the Boson peak region, was excluded from the deconvolution.

In order to reveal the underlying physics, we used in the first stage a minimum number of bands corresponding to the number of distinct features observed in the experimental spectrum such as obviously resolved maxima and high intensity shoulders. To improve the deconvolution, in the second stage of the fitting, we added weaker bands obeying the following criteria: 1) they were proved to exist by other experimental investigation such as NMR or IR on other literatures; 2) we take account into the fact that the structural groups present in smaller quantities for a composition but in large quantities for another one.[79, 80]

The spectra of these glasses were deconvoluted into 10 major peaks in the designated frequency region. As shown in Figure 29. The deconvolution parameters are listed in Table 6.

The same deconvolution process were performed on the depolarized Raman spectra as well. The same peaks were used in the deconvolution, however, three extra peaks had to be added in for a perfect fit. As shown in Figure 29. The deconvolution parameters are listed in Table 7.
Figure 29. Polarized (vv) and Depolarized (vh) Raman spectra of the niobium-phosphate glasses. The measured spectra are deconvoluted to vibrational sub-bands. The combinations of all the sub-bands result in the fitted spectra which coincide with the measured spectra perfectly at frequencies above 100 cm⁻¹. Blue curve is the measured Raman spectra, Red curves is the fitted spectra.
Table 6. Deconvolution parameters for VV of Niobium Phosphate glasses

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86
Table 7. Deconvolution parameters for VH of Niobium Phosphate glasses

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</tbody>
</table>

The deconvolution of the polarized Raman spectra shows that in 10% and 20% Nb₂O₅ samples the peak at around 910 cm⁻¹, which is attributed to the isolated Nb-O vibration, is very prominent. The progressive introduction of Nb₂O₅ gives rise to bands around 900 cm⁻¹ at first and then at about 830 cm⁻¹. A band with comparable amplitude occurs at 650 cm⁻¹ for the largest concentration of niobium. The band at 900 cm⁻¹ is typical of isolated NbO₆ octahedra and the band at 830 cm⁻¹ suggests the formation of corner shared NbO₆ octahedra chains. The band at 650 cm⁻¹ is related to the formation of a three-dimensional framework implying less distorted octahedral similar to a tungsten bronze structure [81]. The decrease of the isolated Nb-O vibrational band at 650-680 cm⁻¹ and increase the NbO network vibrational band at 900 cm⁻¹ can be seen very clearly in Fig. We first calculated area ratio of the single peak area of the 650 cm⁻¹ peak over the total spectrum area for each composition, then plotted them as a function of the Nb₂O₅ component percentage. In Fig 30 & 31, we can see a clear decrease of the ratio,
suggesting the decrease of the isolated NbO$_6$ hydratetra unit; on the other hand, the same processure is done for the 900cm$^{-1}$ peak. The ratio of the 900cm$^{-1}$ peak show a very clear decrease with the increase of Nb$_2$O$_5$ percentage, suggesting the formation of the NbO network.

The 266 cm$^{-1}$ peak in the glasses with 10% and 20% Nb$_2$O$_5$ is associated with vibrational modes involving bending and torsional vibrations of the phosphate network [81,82]. In the samples containing 30% and 40% Nb$_2$O$_5$ this peak is shifted to lower frequency. This suggests that when more position of P is taken by Nb, the bond of P-O is replaced by Nb-O. The shifting to lower frequency can be explained if we use a classical simple harmonic oscillator to model the molecular bonds. Suppose the force constant keeps constant, then the vibrational frequency will decrease with increasing mass. Thus the decrease in frequency of the vibrational peak from 266cm$^{-1}$ to lower frequency may be attributed to the larger mass of Nb compared to P.

The peak area ratio of the 917cm$^{-1}$ peak and 650cm$^{-1}$ peak area over the total spectra area of both the polarized and depolarized Raman spectra are show in Fig.30 and Fig.31. The 917cm$^{-1}$ peak is assigned to the vibrational mode of Nb-O in octahedral NbO$_6$. The decrease of this area ratio indicate the decrease of the amount of isolated octahedral NbO$_6$. This suggests the forming of of NbO network with the increase of concentration of Nb$_2$O$_5$ component. This change is again clearly seen in the 650cm$^{-1}$ peak, where the increase of the Nb$_2$O$_5$ gives an increase of that peak ratio, the 650cm$^{-1}$ peak is assigned to the network vibration of three-dimensional network of NbO, which indicates the gradual establishment of the NbO network with the increase of Nb$_2$O$_5$ percentage.
Figure 30.  Peak Area/ Total Area ratio from the polarized Raman spectra of the 917cm⁻¹ peak (above) and 650cm⁻¹ peak (below).
Figure 31. Peak Area/Total Area ratio from the depolarized Raman spectra of 917 cm\(^{-1}\) peak (above) and 650 cm\(^{-1}\) peak (below).
A complete assignment of peaks and vibrational bonds are listed in Table 8.

**Table 8. Band positions and assignments of the various peaks within the Nb$_2$O$_5$ NaPO$_3$ compositions.**

<table>
<thead>
<tr>
<th>Peak Position (cm$^{-1}$)</th>
<th>Assigned Vibration</th>
<th>Peak Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>230-270</td>
<td>Bending and torsional vibrations of phosphate network</td>
<td>1</td>
</tr>
<tr>
<td>284</td>
<td>Bending and torsional vibrations of phosphate network</td>
<td></td>
</tr>
<tr>
<td>Below 390, 350</td>
<td>O-P-O bending vibrations</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>684-689</td>
<td>Symmetric P-O-P</td>
<td></td>
</tr>
<tr>
<td>640-680</td>
<td>Network vibration of three-dimensional network of NbO.</td>
<td>4</td>
</tr>
<tr>
<td>760</td>
<td></td>
<td></td>
</tr>
<tr>
<td>830</td>
<td>Corner shared NbO$_6$ octahedra chains</td>
<td>6</td>
</tr>
<tr>
<td>900-905</td>
<td>Vibrational mode of Nb-O in octahedral NbO$_6$, isolated NbO$_6$ octahedra</td>
<td>7</td>
</tr>
<tr>
<td>1047</td>
<td>Asymmetric (PO$_3$)$_2^-$ vibrations</td>
<td>8</td>
</tr>
<tr>
<td>1150</td>
<td>Symmetric vibrations of (PO$_2$)$^-$</td>
<td>9</td>
</tr>
<tr>
<td>1249</td>
<td>(P-O) asymmetric vibrations</td>
<td>10</td>
</tr>
</tbody>
</table>
4.2.3. Predicted Raman gain and Measured Raman gain

From the spontaneous Raman spectra, we can deduce the predicted Raman gain by division of the thermal population factor, \([n(\omega) + 1]\) where \(n(\omega) = \exp(h\omega/kT) - 1\).

So we calculated the predicted Raman gain from the spontaneous Raman spectra of these binary glasses (Figure 28), and plotted them in Figure 32 as the blue lines.

*Figure 32. Measured Raman gain (full symbols) of (100-x) NaPO₃-xNb₂O₅ glasses with varying Nb₂O₅ concentrations and the predicted Raman curves (full lines) after correcting for the thermal population factor. The pump wavelength is 1064 nm.*[83]
The predicted Raman gain, however, are deduced from the theory and has not been verified by experiments. So a set of Raman gain measurements on these bulk binary glasses were performed.

Direct Raman gain measurements on the bulk glasses were successfully conducted on these glasses, as presented by black dots in Fig 32.

The Raman gain data points basically follow the predicted Raman curves pretty well. The calibration with fused silica for these Raman gain curves, have shown that the Raman gain of these niobium-phosphate glasses have a peak Raman gain 3 times higher that of peak gain of fused silica.

4.2.4. Boson peak of Niobium Phosphate Glasses and Disorder

With our simple binary glass system, the study of a correlation between the structural change and those of the Boson peak becomes possible.

In Figure 33, both the polarized and depolarized Raman spectra of the niobium phosphate glasses are shown in the Boson peak region. One feature that can be noted immediately is that with the increase of percentage of Nb$_2$O$_5$ from 10% to 40%, the Boson peak intensity seem to increase as well. This in turn would suggest that there is a linear relationship between the percentage of Nb$_2$O$_5$ and the density of states.

As outlined in Chapter 2, the relationship between intensity of the Raman scattering light and density of states can be written as:

$$I(\omega) = g(\omega)C(\omega)[n(\omega) + 1]/\omega$$
The intensity of Raman scattering equals the product of the density of states \( g(\omega) \) multiplied with the thermal population factor \([n(\omega) + 1]\) and the frequency dependent coupling coefficient \( C(\omega) \) over frequency \( \omega \).

In order to eliminate the temperature dependence of \( I(\omega) \), it is conventional to use reduced intensity:

\[
I_R = I(\omega) / \omega \{ n(\omega) + 1 \} = C(\omega) g(\omega) / \omega^2
\]
Figure 33. Boson peak of the Niobium Phosphate glasses as shown in the original scattering intensity.
In Figure 34, the low frequency peaks are plotted in reduced intensity $I_R$. In this figure, the density of states information of these glasses are still not shown directly, but hidden under the coupling coefficients $C(\omega)$. On the other hand, the density of states can be directly obtained from inelastic Neutron scattering (INS) spectra. The INS spectra of these glasses will be discussed in 4.2.5 and compared with the Raman spectra Fig 4.23. Combining Raman and INS measurements, information on the coupling coefficient can be extracted.

*Figure 34.* Boson Peaks of Niobium Phosphate glasses in reduced intensity.
In a very recent study on binary alloy films by Nuclear Resonant Inelastic X-ray scattering, it was found that \( g(\omega)/\omega^2 \), which represents the extra density of states excluding the Debye modes, increases linearly with the percentage of one component. [84] For a number of glasses, it has been observed that the coupling coefficient \( c(\omega) \) demonstrates a universal linear frequency behavior near the Boson peak maximum.[47]

If we assume \( c(\omega) \propto \omega \), the density of states information can be directly represented by a revised reduced Raman intensity:

\[
I'_r = I(\omega)/\omega^2[n(\omega)+1] = [C(\omega)/\omega] \cdot [g(\omega)/\omega^3] = g(\omega)/\omega^2
\]

We thus calculate the reduced intensity of the Boson peak, which represents the density of states, and then plotted them as a function of the percentage of Nb2O5, as shown in Figure.35. The Boson peak intensity of different glasses displays a linear increase with the percentage of Nb2O5. A possible mechanism is an increase in medium range disorder[85,86,45]. When the percentage of Nb2O5 is low, the network is still a phosphate network which has a low medium range order. As the concentration of Nb2O5 increases, isolated NbO6 octahedra begin to form, which gradually creates more medium range disorder. More Nb2O5 component gives rise to the formation of corner shared NbO6 octahedra chains, which increases the disorder more.
A recent experiment conducted by Chumakov et al. using probe molecules with resonant nuclei and nuclear inelastic scattering showed that the nature of the modes that constituting the boson peak are collective motions. It was also demonstrated that the reduced density of states of the collective motions universally exhibits an exponential decrease. [87]

To test this theory, the revised reduced intensity $I_{R}'$ of Raman data are plotted on semilogarithmic axis accordingly in Figure 36. Indeed, the reduced intensity decreases approximately exponentially above the Boson peak frequency (around 60 cm$^{-1}$), supporting the probable collective nature of the extra density of states. [88]
4.2.5 Inelastic Neutron scattering on Niobium Phosphate Glasses

As stated in the last chapter, from Raman spectra alone, it is not possible to obtain directly the density of states, because the expression of the Raman intensity, $I_R$, contains a frequency dependent unknown function $C(\omega)$. $C(\omega)$ measures the average scattering efficiency of the vibrational modes with frequency lying between $\omega$ and $\omega + d\omega$. For Stokes scattering, we have:

$$I_r(\omega, T) \propto \frac{n(\omega, T) + 1}{\omega} g(\omega)C(\omega)$$

In principle, not even neutron scattering does supply the true $g(\omega)$, because of the different scattering amplitudes of the atomic components; however, it has been
demonstrated that in glasses[89,90], using the incoherent approximation, the inelastic neutron scattering intensity, \( I_N \), is connected to the vibrational density of states by an similar equation, but which does not contain the factor \( C(\omega) \):

\[
I_N(\omega,T) \propto \frac{n(\omega,T) + 1}{\omega} g(\omega)
\]

Very recently, we carried out an inelastic neutron scattering investigation of these glasses using the time-of-flight spectrometer (TOF-TOF) of the FRM II in Munich to obtain information on the vibrational dynamics of the material (energy transfer \( \sim 1 - 45 \) meV). The constituents of our material are all coherent scatterers of similar cross section. By averaging over the full accessible scattering angle (wavevector) range we obtain an approximate spectral distribution of the vibrational modes.

The time-of-flight data had to undergo a series of corrections before the correct density of states information can be obtained. First, the detector efficiency correction has to be made, after that the subtraction of the empty cell absorption is made. The density of states information was obtained by an iterative procedure after correction of Debye-Waller factor and multiphonon contributions.

The standard procedure for obtaining the density of states \( g(\omega) \) is the following. In the incoherent approximation, one writes the neutron differential scattering cross-section as

\[
\frac{d^2\sigma}{d\Omega d\omega} = \frac{k}{k_0} b^2 \exp\left(-\frac{\hbar\omega}{2k_B T}\right) S_s(q,\omega)
\]

It is determined after the usual data correction procedure, such as the subtraction of the empty cell contribution and normalization to a vanadium scan. In the formula, \( k_0 \)
and $k$ are the incident and scattered neutron wavevectors, $b$ is the scattering length, and $S_S(q, \omega)$ is the dynamic factor, which is directly related to $g(\omega)$. Using the reduced variables $\alpha = \hbar^2 Q^2 / 2Mk_b T$ and $\beta = \hbar \omega / k_b T$, the scattering law may be written:

$$S_S(\alpha, \beta) = \exp(-q^2 <u^2>)[\alpha / 2\beta \sinh(\beta / 2)]g(\omega)$$

The elastic contribution was identified and subtracted, and the generalized frequency distribution $P(\alpha, \beta)$ was then calculated:

$$P(\alpha, \beta) = 2\beta \sinh(\beta / 2)S_S(\alpha, \beta) / \alpha = g(\omega)\exp(-q^2 <u^2>)$$

The multiphonon contribution and background were estimated and subtracted from the experimental $P(\alpha, \beta)$. Finally, $g(\omega)$ was extracted from the corrected $P(\alpha, \beta)$, by dividing by the calculated Debye-Waller factor. [91, 92]

The resultant curves of density of states $g(\omega)$ and the curves of reduced density of states are shown in Figure 37 and Figure 38, where Figure 37 are derived from the neutron scattering with incoming neutrons wavelength at $2.8 \text{ Å}$ and Figure 38 are derived from the neutron scattering with incoming neutrons wavelength at $4.7 \text{ Å}$.

The density of states curves derived from both wavelengths have almost the exact shapes and intensities, providing a confirmation of the accuracy of the neutron scattering data.
Figure 37. **Above:** Density of States as derived from the inelastic neutron scattering with neutron source wavelength at 2.8 Å. **Bottom:** The same density of states over the square of energy.
Figure 38.  Above: Density of States as derived from the inelastic neutron scattering with neutron source wavelength at 2.8 Å. Bottom: The same density of states over the square of energy.
In Figure 34, we have plotted the Raman scattering spectra in reduced intensity, which is \( I_R = I(\omega) / \omega^n (\omega + 1) = C(\omega) g(\omega) / \omega^2 \), while the \( g(\omega) / \omega^2 \) deduced from the inelastic neutron scattering experiment was plotted in Figure 37 and Figure 38. So the coupling coefficient can be deduced by dividing the above two curves, the resultant curves of \( C(\omega) \), are shown in Figure 39.

The linear increase of the coupling coefficients as a function of frequency is clearly seen in the plots. This linear increase has been reported in other recent literatures.[47, 92] All coupling coefficient functions tend to be a constant at frequency higher than the Boson peak, as shown in Figure 40 and Figure 41.

There are many models that assume two different kinds of vibrations coexisting at frequencies around the boson peak: propagating (collective) and localized. For example, in the framework of the soft potential model, it is assumed that propagating waves have a Debye-like density of states and do not contribute to the Raman spectra, while excess vibrations are localized and have constant coupling coefficient as a function of the frequency; e.g. \( C(\omega) = \text{Constant} \).[47] The linear increase of the coupling coefficient as a function of frequency suggests that the origin of Boson peak is not purely localized vibrations. The constant part of the coupling coefficient also appears to be very small compared with the linear increase part, this suggests that major part of the vibration might comes from collective vibrations. This result agrees with our conclusion derived from the linear decrease of reduced density of states (Fig. 36), this also agrees with the experiment conducted by Chumakov et al. using probe molecules with resonant nuclei and nuclear inelastic scattering.[87]
Some knowledge of $c(\omega)$ and an understanding of its frequency dependence have significant importance for the topic of the low-frequency vibration. First of all, a knowledge of $c(\omega)$ provides a relatively simple method to extract the vibrational density of states from a Raman experiment. Secondly, the light-vibration coupling coefficient contains information on the vibrational wavefunction, and therefore, can be used as a test of different models. [48]
Figure 39. Coupling coefficient curves as a function of frequency as derived from Raman spectra and the inelastic neutron scattering of wavelength 2.8 Å and 4.7 Å.
**Figure 40.** Coupling coefficient curve as a function of frequency as derived from Raman spectra and the inelastic neutron scattering of wavelength 2.8 Å of the glass (10%Nb$_2$O$_5$, 90%NaPO$_3$).

**Figure 41.** Coupling coefficient curve as a function of frequency as derived from Raman spectra and the inelastic neutron scattering of wavelength 2.8 Å of the glass (20%Nb$_2$O$_5$, 80%NaPO$_3$).
CONCLUSION

Spontaneous Raman scattering measurements were conducted on a series of Tellurium oxide glasses. Raman gain curves of these glasses were calculated from the spontaneous Raman spectra. Predicted Raman gain curves of these glasses are extraordinarily broad, extending to very low frequencies range. The flat and broad Raman gain region in the low frequency region suggests possibility of using these glasses for Raman gain application. It is also discovered that Boson peak vibrations contribute to the Raman gain in the low frequency region for these glasses. Spontaneous Raman scattering were conducted on a series of Niobium Phosphate binary glasses. Increase of spontaneous Raman scattering intensity in the Boson peak region as a function of increase of Niobium suggests a possible correlation between disorder and Boson peak intensity. Inelastic neutron scattering spectra were measured for these binary glasses. The density of states curves were derived for these glasses from the inelastic neutron scattering data. Light-vibration coupling coefficient curves were derived from the combination of Raman scattering data and inelastic neutron scattering data. The coupling coefficient curves show a linear increase in the Boson peak region. The linear increase behavior of the coupling coefficient curve suggests that the origin of boson peak is not due to pure localized vibrations. The relatively small amount of the constant part of the coupling coefficient also suggests that the major part of the Raman scattering on these glasses is from collective vibrations, confirming the same conclusion derived from the
linear decrease of reduced density of states on a linear-logarithmic scale from the spontaneous Raman data.
Raman spectra of several other glass families were measured, although the Raman scattering intensity of these glasses are not as high as Tellurium oxide glasses, they can be served as alternative structural models for future study.

The compositions that we studied includes:

1. Borophosphate glasses, with borophosphate as the glass former and different other composition were added in, the composition of this glass family is: \((1-X)[95\%NaPO_3-5\%Na_2B_4O_7]-X\), with X being four combinations:

   A. \(20\text{Nb}_2\text{O}_5, 20\text{TiO}_2\)
   B. \(20\text{TiO}_2, 20\text{WO}_3\)
   C. \(20\text{Nb}_2\text{O}_5, 20\text{WO}_3\)
   D. \(40\text{WO}_3\)

   The spectra of the borophosphate glasses are shown in Figure.42.

2. Phospho-Germano-Niobate glasses,

   A. \(3\text{P}_4\text{G}_3\text{N} (30\%\text{P}_2\text{O}_5, 40\%\text{GeO}_2, 30\%\text{Nb}_2\text{O}_5)\)
   B. \(3\text{P}_3\text{G}_4\text{N} (30\%\text{P}_2\text{O}_5, 30\%\text{GeO}_2, 40\%\text{Nb}_2\text{O}_5)\)
   C. \(5\text{P}_2\text{G}_3\text{N} (50\%\text{P}_2\text{O}_5, 20\%\text{GeO}_2, 30\%\text{Nb}_2\text{O}_5)\)
   D. \(4\text{P}_3\text{G}_3\text{N} (40\%\text{P}_2\text{O}_5, 30\%\text{GeO}_2, 30\%\text{Nb}_2\text{O}_5)\)

   The spectra of the borophosphate glasses are shown in Figure.43.
Figure 42. Raman spectra of Boro-Phosphate glasses.

Figure 43. Raman spectra of Phospho-Germano-Niobate glasses.
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