

# Rigidity Transition in $\text{Si}_x\text{Se}_{1-x}$ Binary Glasses

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An adequate understanding of the structures of amorphous solids must be a basic requirement for progress in the next century--in a way it has not really been so far<sup>1</sup>. It might seem very strange especially once one recalls that it was some four thousand years ago that man discovered glass in the embers of a fire built somewhere in the deserts of the Near East. Right now glass fibers transmit more information than copper wires ever could. Thus glass is at once both one of the oldest and one of the newest materials known to civilization. Yet the science of glass is still in its infancy, and the most basic questions remain largely unanswered. The cause of our ignorance of this valuable material is not want of trying.<sup>2</sup> Over the past few decades there has been an enormous effort to try to understand the properties of non-crystalline materials in terms of their microscopic structure. The problems encountered in such an undertaking are formidable from both the theoretical and experimental standpoints. The loss of translational symmetry renders the potent arsenal of condensed matter theorists useless, while experimentally, many measured properties depend strongly upon the preparation techniques (e.g., quenching rate)<sup>3</sup>. Since the properties of glass depend on its previous history, then, thermodynamically speaking, it is not in equilibrium. This, coupled with nonperiodicity of glass, makes it an assembly of interlocking microcosms whose relaxation and organization has been arrested to varying degrees. We can thus think of a macroscopic glass sample as of the universe of regions at different stages of evolution<sup>2</sup>. Having painted this bleak picture allow me shine some light on this subject.

The primary object of this experiment is  $\text{Si}_x\text{Se}_{1-x}$  binary glass system, which is a covalently bonded chalcogenide glass. Chalcogenide glasses are a recognized group of inorganic glassy materials which always contain one or more of the chalcogen elements: S, Se or Te, but not O, in conjunction with more electropositive elements most commonly As and Ge, but also P, Sb, Bi, Si, Sn, Pb, B, Al, Ga, In, TL, Ag, lanthanides, and Na<sup>4</sup>. The chalcogenide glasses are bandgap semiconductors, and, as such, they were investigated in the past as alternatives for silicon semiconductors<sup>5</sup>. More recently, these glasses have attracted attention for potential application not only in middle infrared transmission<sup>6,7</sup> but also for

acousto-optic devices<sup>8</sup>, non-linear optical devices<sup>9</sup>. In chalcogenide glasses, the coordination number of the covalent atoms is given by the 8-N rule, where N is the number of the outer shell electrons in a given atom. The concept of the average coordination number,  $\langle r \rangle$ , is useful in describing glasses: it is defined as the atom-averaged covalent coordination of the constituents<sup>10</sup>. In particular, for  $\text{Si}_x\text{Se}_{1-x}$ ,  $\langle r \rangle = 4 \cdot x + 2 \cdot (1 - x) = 2 \cdot (1 + x)$ . Let me give you the simplistic description of  $\text{Si}_x\text{Se}_{1-x}$  binary glass system. Se glass is the simplest, stable twofold-coordinated polymer. It is thought to consist mainly of tangled chains with some closing on themselves to form rings of various sizes. The chains are linked by covalent bonds and the forces between chains arise from van der Waals interactions. Each bond imposes mechanical constraints on the motion of the atom to which it is linked. The constraints introduced by van der Waals forces are weak by comparison. Si atoms, with their fourfold-bonding property, provide a means to crosslink the Se chains. Eventually, the dimension of the network will be changed from one-dimensional (as in Se) to three-dimensional (as in Si).

In late 70's, J.C. Phillips<sup>11</sup> introduced and M. F. Thorpe<sup>12</sup> developed the notion of understanding the mechanical and structural properties of glasses in terms of the average number of mechanical constraints per atom. In chalcogenide glasses, covalent central bond-stretching and Keating-type angle-bending forces dominate van der Waals and various other intermediate and long range forces. Hence, only stretching and bending constraints are counted. The number of bond-stretching constraints for atoms having  $r$  bonds is  $r/2$  since each bond is shared by two atoms. The number of bond-bending constraints is  $2r-3$ , since beyond  $r=2$  each new bond introduces two new angles<sup>13</sup>. An under-constrained system admits the displacement of groups of atoms without any elastic response from the system. These displacements are known as "floppy" modes. Actually, the forces ignored in counting the constraints will shift these modes from zero to low frequency. Adding up all the covalent constraints, we get

$\frac{5}{2}r - 3$ , which, after averaging over the network, turns into  $\frac{5}{2}\langle r \rangle - 3$ . Finally, we can calculate the

number of floppy modes to be  $3 \cdot N \left( 2 - \frac{5}{6}\langle r \rangle \right)$ . According to Phillips, the ideal glass-forming

condition occurs when the number derived above is zero. This condition is evidently met at  $\langle r \rangle = 2.4$ .

For  $\langle r \rangle < 2.4$ , the structure is under-constrained, or "floppy", and tends to disintegrate into molecular fragments that can crystallize easily. For  $\langle r \rangle > 2.4$ , the structure is over-constrained, or "rigid", and tends to become too continuous, which might eventually lead to crystallization. This line of reasoning shows that it is of great industrial importance to understand the floppy to rigid transition in glasses.

In 80's, a number of articles by M.F. Thorpe and his collaborators tried to explain the floppy to rigid transition in terms of rigidity percolation concept<sup>11, 13-16</sup>. Let me try to illustrate this concept on  $\text{Si}_x\text{Se}_{1-x}$  binary system. For  $x=0$ , we have elemental amorphous selenium--the most stable known twofold coordinated polymer. The bulk sample consists of long selenium chains. The bonding within the chain is covalent, whereas the bonding between different chains is governed by van der Waals interactions. As we add more and more silicon, silicon atoms start crosslinking selenium chains. Still, for low (less than .2) values of  $x$ , the network is floppy; applying a force to it would elicit no elastic response. At this stage, the network consists of rigid clusters imbedded in a floppy matrix. Then, at  $x=.2$  ( $\langle r \rangle = 2.4$ ), the rigidity clusters percolate throughout the whole network, and it attains nonzero elastic constants. So, for  $x>.2$  ( $\langle r \rangle > 2.4$ ), the network is nothing but a collection of floppy clusters imbedded in a rigid matrix. Rigidity transition should manifest itself directly in elastic properties of the network. In calculations on systems where the average coordination can be varied, it was found that the elastic constants  $c_{ij}$  of the material have the following form:

$$c_{ij} = \begin{cases} 0, \langle r \rangle < 2.4 \\ A \cdot (\langle r \rangle - 2.4)^{1.5}, \langle r \rangle \geq 2.4 \end{cases} .$$

If this model were correct, then the system with  $\langle r \rangle < 2.4$

would be structurally unstable, which is not the case experimentally. The noncovalent interactions that were ignored by Phillips and Thorpe evidently play a significant role in stabilizing a network for low values of the average coordination number.

The other prediction that Phillips and Thorpe make is that of a solitary transition point at  $\langle r \rangle = 2.4$ . Numerical calculations done by Thorpe and coworkers assume a random covalent network model. What it means is that they begin with fully coordinated network and then start randomly deleting bonds, recalculating the elastic constants each time a certain number of deletions has been made. This presupposes that network has no intermediate range order whatsoever. That might not be the case in reality. Previously, I worked on  $\text{Ge}_x\text{Se}_{1-x}$  binary system that is very similar to  $\text{Si}_x\text{Se}_{1-x}$  system. Figure 1 shows two graphs: the upper graph shows the dependence of frequency of acoustic phonon on the concentration of germanium (lower x-axis) or coordination number (upper x-axis), while the lower graph show the dependence of linewidth of longitudinal acoustic phonon on the concentration of germanium (lower x-axis) or coordination number (upper x-axis). The data taken at low powers shows a "normal" behavior: the frequency monotonically grows whereas the linewidth monotonically drops off. In comparison, for higher powers we see the onset of softening/broadening at  $x = .2$  and a distinct minimum/maximum at  $x = .22$  on frequency/linewidth plot. This anomalous behavior leads me to believe that there exists a transition region between floppy and rigid glasses.

Thus one of my goals for the current project was to look for the evidence for the transition region in  $\text{Si}_x\text{Se}_{1-x}$  glasses. Another feature that was present in  $\text{Ge}_x\text{Se}_{1-x}$  system and that I hoped to find in  $\text{Si}_x\text{Se}_{1-x}$  was the dependence of the frequency of a phonon on a laser power incident on its surface. For the samples in the transition region, this drop was as big as 7GHz. But perhaps the most exciting part of the project was the possibility of observing the floppy modes for the first time. Their existence was predicted theoretically but they have never been seen in light scattering experiments.

Perhaps the most natural question one might arrive at is why we want to study  $\text{Si}_x\text{Se}_{1-x}$  binary system. The answer is quite simple: unlike the oxide glasses where the coordination number can only be modified by additives, the chalcogenide glasses form over wide range of compositions and the coordination number can be changed in a reproducible manner by changing glass compositions. Perhaps the simplest systems amongst the chalcogenides include the IV-VI binary glasses such as Ge-Se, Si-Se, Si-Te.<sup>17</sup> In particular, for  $\text{Si}_x\text{Se}_{1-x}$  binary system, we have  $\langle r \rangle = 2 \cdot (1 + x)$ . Thus, by tuning the concentration of silicon, we tune the coordination number of the system. Another important fact about IV-VI binary glasses is that they do not form a crystalline compound as long as  $\langle r \rangle$  is between 2.36 and 2.66.

This summer I worked with four representatives of  $\text{Si}_x\text{Se}_{1-x}$  binary glass system --  $\text{Si}_{.265}\text{Se}_{.735}$ ,  $\text{Si}_{.27}\text{Se}_{.73}$ ,  $\text{Si}_{.275}\text{Se}_{.725}$ , and  $\text{Si}_{.285}\text{Se}_{.715}$ . These samples have average coordination numbers of 2.53, 2.54, 2.55, and 2.57 respectively. I should thank Dr. Punit Boolchand and Dr. Wayne Bresser of University of Cincinnati for kindly supplying me with samples. All samples were encapsulated in fused silica ( $\text{SiO}_2$ ) ampoules so as to prevent the reaction of samples with atmospheric oxygen. Of all the samples, only  $\text{Si}_{.27}\text{Se}_{.73}$  had well-defined pieces inside of the ampoule. The rest of samples were stuck to the interior of their corresponding ampoules. This, of course, greatly complicates any light scattering experiment, as it becomes necessary to trace the observed excitations to either the ampoule or the sample.

Before giving the result of my experiment, let me acquaint you with the experimental setup I have been using this summer. In Brillouin Light Scattering (BLS), material properties are studied by analyzing inelastically scattered light from thermal excitations (e.g., phonons, magnons, plasmons). BLS probes extremely low energy excitations in the range  $.1\text{-}15 \text{ cm}^{-1}$ . Figure 2 shows a typical setup. A 514.5 nm Ar ion laser is used as an excitation source. Experiments are performed in back-scattering setup where collimating optics focuses laser light on the sample and collects the scattered radiation for analysis. The scattered light, consisting of elastic and inelastic components is collimated, filtered through a pinhole and then directed normally on the first Fabry-Perot Interferometer (FPI). A multi-pass

(6 passes) arrangement through the tandem is implemented using a large rear mirror, a corner cube, and a cat-eye. A final beam is filtered of elastically scattered radiation; after this, it hits a Silicon detector. A multi-channel scalar card along with data acquisition software collects data during scans and stores them in a computer. The final output of the experiment is intensity versus frequency shift plot (and data file). The FPI and Si detector are enclosed with a light tight box and all lights are turned off during data acquisition. The typical integration time to acquire a Brillouin spectrum is between 5 minutes (for incident laser power  $>5\text{mW}$ ) and 20 minutes (for incident laser power  $<2\text{mW}$ ). Due to the delicate nature of the apparatus, the entire system is placed on a floating air table in order to isolate vibrations.

Let me now tell you of the data I have collected so far. For low powers, all the plots showed a presence of a phonon of frequency between 17 and 18 GHz. The peak on the plots was quite narrow ( $\sim 1.5$  GHz) thus forcing us to consider the possibility that it might be coming from the silica container and not from the sample. To erase all the doubt, the following was done.  $\text{Si}_{.265}\text{Se}_{.735}$  was picked for this mini-experiment. Two scans were taken at  $4\text{mW}$ : one from the very tip of the ampoule, and the other one from what I believe to be the sample. Figure 3 show the results. Positions and linewidths of peaks were determined via fitting using Microcal Origin 4.0. The difference in frequency shifts is  $\sim 1.75$  GHz, and this number exceeds experimental error ( $\sim .2$  GHz) significantly. Perhaps the more telling characteristic is the linewidth: that of sample is thrice as big as that of the ampoule. We can now be very sure that the peak does come from the sample. As the power is increased up to  $10\text{mW}$ , the peak softens by 1 to  $1.5$  GHz. Similar power-dependence measurement performed on the ampoule yielded negative results, that is the ampoule peak did not shift down in frequency.

While the 17-18 GHz peak does not shift down by much, the peak that emerges from its shoulder at  $\sim 5\text{mW}$  does. Figure 4 shows that excitations in both  $\text{Ge}_{.26}\text{Se}_{.74}$  and  $\text{Si}_{.27}\text{Se}_{.73}$  respond in a similar way to the increase in incident laser power. In both samples, we see a drop in frequency shift by an amount that is well outside of the experimental error range. Of course, whenever one sees a change in any physical quantity, perhaps the most basic question one has concerns the reversibility of that change.

What we observed in  $\text{Ge}_x\text{Se}_{1-x}$  is that the change in frequency is reversible unless the sample was exposed to powers greater than some  $P_{\text{critical}}$ . The same behavior was observed to be true in  $\text{Si}_x\text{Se}_{1-x}$  binary system, too. Figure 5 show that there is virtually no hysteresis in frequency shift detected in  $\text{Si}_{.27}\text{Se}_{.73}$ . In this figure, black dots denote the data points collected while the incident laser power was increased from 5 mW to 20 mW in steps of  $\sim 2$  mW, whereas the red dots denote the data points accumulated while the incident laser power was decreased from 20 mW to 4 mW in steps of  $\sim 2$  mW.

One of the goals of this project was to collect evidence for the existence of floppy modes. In two of the four samples examined, I have observed an excitation of frequency between 5 and 6 GHz. In the other two samples, the blocking window was set too wide to observe anything at this low of a frequency. (The blocking windows allow us to block some of the light of frequency close to 514.5nm so as to prevent the saturation of a solid state detector) I will most definitely repeat measurements on these two samples and see if the 5-6 GHz peak will be present. Figure 6 shows two half-spectra of  $\text{Si}_{.285}\text{Se}_{.715}$ . Fits obtained with Microcal Origin 4.0 are superimposed on data. Both scans were taken at the same power, 4 mW. The scan on the right was taken on the way up, that is as the power was incrementally increased from 2 mW to 20 mW, whereas the scan on the left was taken on the way down, with power decreasing from 20 mW to 2 mW in increments of  $\sim 2$  mW. Note that since in Brillouin the creation and annihilation are equally likely to occur, the right and left side of the same scan are completely symmetric; this is why, for comparison, I took the liberty of presenting two half-spectra rather than two full spectra. Evidently, assuming the existence of three peaks, we can get exceptionally good fits. Though these spectra were taken at the same power, they differ from each other by quite a bit. The most interesting difference, in my opinion, is the ratio of intensities. On the way up, the outside peak is the most dominant feature in the spectrum, while on the way down the lowest frequency peak dominates. At this point, I have no explanation for that. I will certainly read more articles and try to get to the root of this mysterious behavior.

As you might have guessed from the coordination numbers of the samples investigated, I was not able to study the rigidity transition per se. In the future, I will procure and study the representatives of the floppy ( $\langle r \rangle < 2.4$ ) and critical ( $\langle r \rangle \approx 2.4$ ) regions in  $\text{Si}_x\text{Se}_{1-x}$  binary system. Power dependence patterns that were observed in  $\text{Ge}_x\text{Se}_{1-x}$  previously were confirmed to occur in  $\text{Si}_x\text{Se}_{1-x}$ , too. As in  $\text{Ge}_x\text{Se}_{1-x}$ , it was established that the changes induced by the laser light are reversible unless the power level exceeds some  $P_{\text{critical}}$ , at which point, most probably, some irreversible phase transition occurs. The most interesting result of this work, however is the observation of very low frequency excitations. It is seems possible that these excitations might be the elusive floppy modes. If it is indeed so, than this would be in direct contradiction with constraint-counting theory which predicts that floppy modes exist in under-constrained glasses only.

In the end, I would like to thank NSF and the Ohio State University for giving me the opportunity to study the fascinating problem of rigidity transition in binary glasses. I should also thank Dr. Sooryakumar, my research advisor, and Dr. Xia Hua, a postdoc in our group, for encouragement and fruitful discussions. I ought to also thank the graduate students in our group, Jared Gump and Relu Chirita, whose friendship made this summer much more pleasurable than it would have been otherwise.

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Figure 1

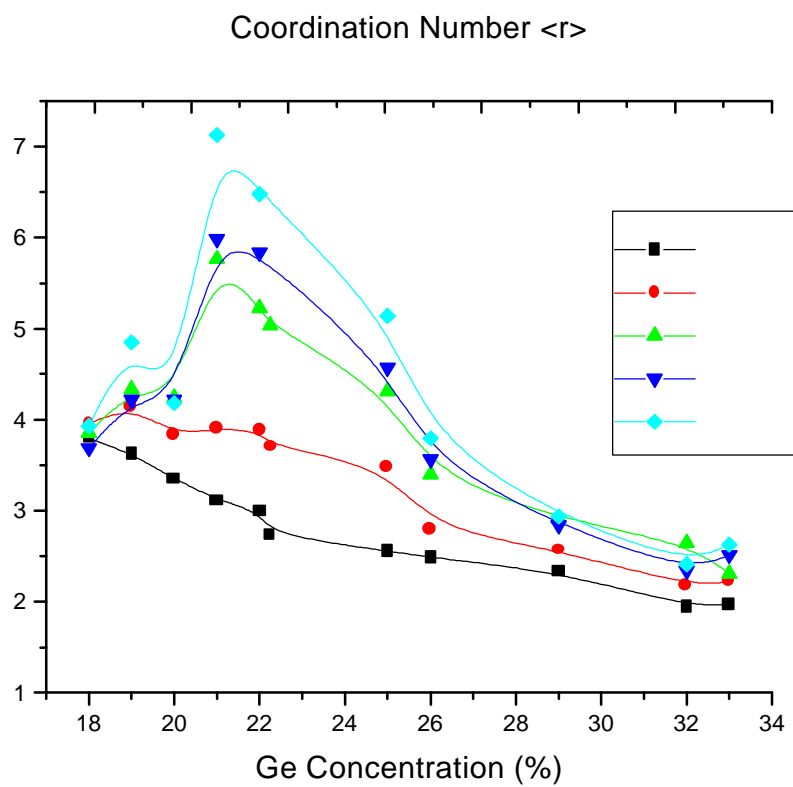
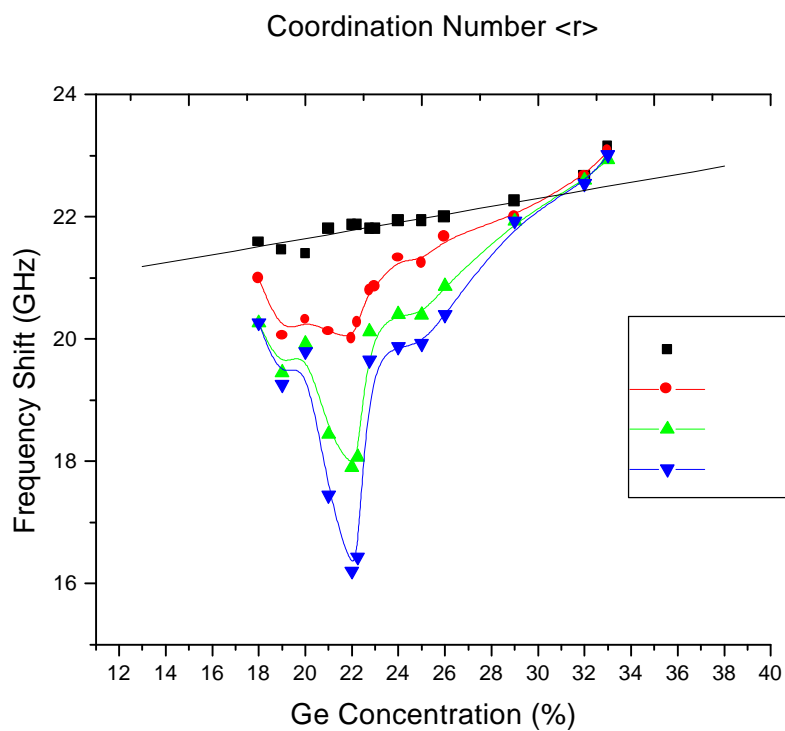
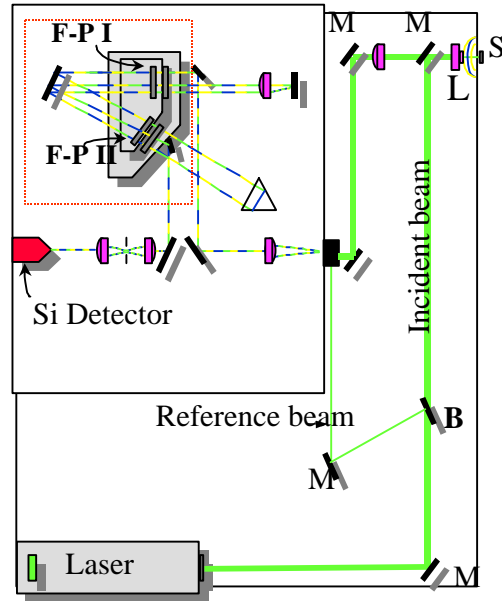


Figure 2

## Brillouin Light Scattering Experimental Setup



S-sample, L-lens, FPI and FPII-Fabry-Perot interferometers, M-mirror.

Figure 3

Spectra of the ampoule and the sample of Si(.265)Se(.735)  
taken at incident laser power of 4mW

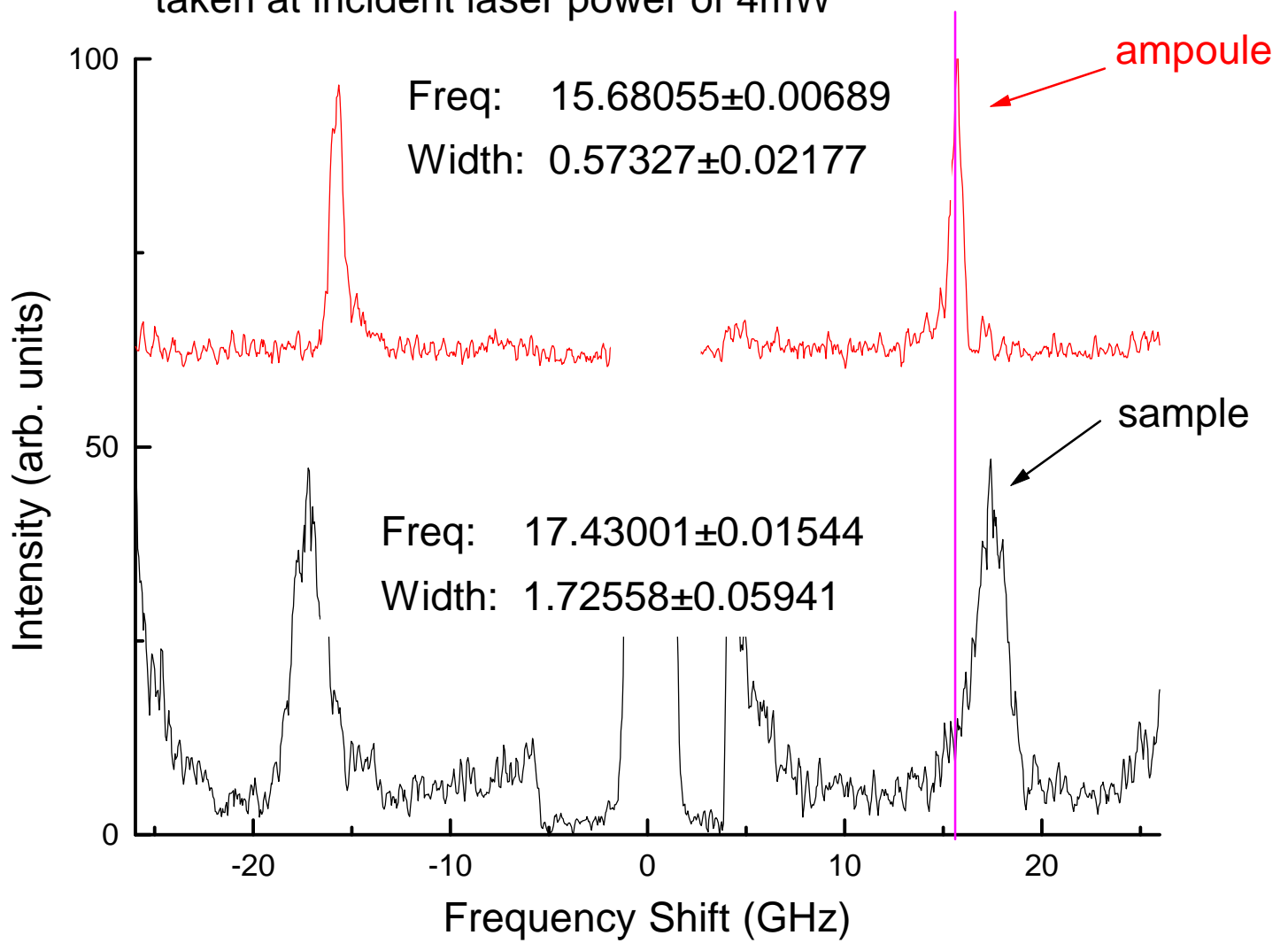
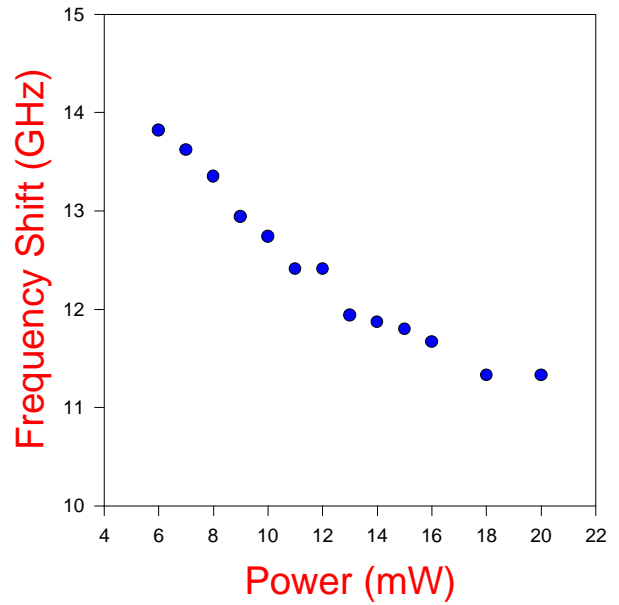


Figure 4

# Laser Power Dependence in



and

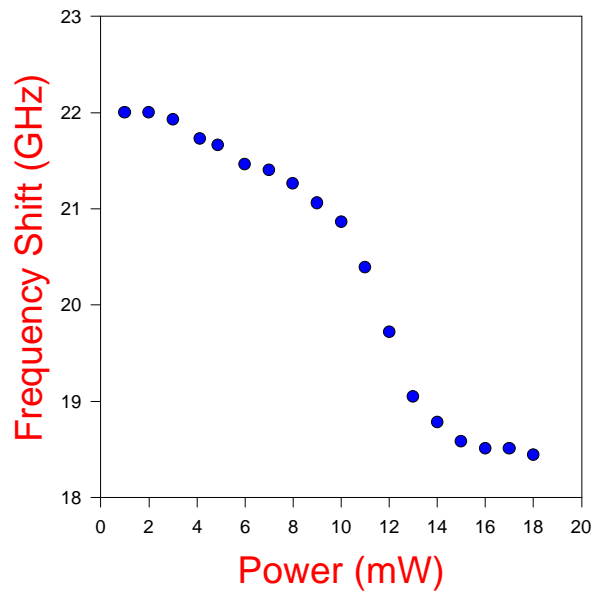


Figure 5

## Power dependence of Brillouin Shift in Si(.27)Se(.63) binary compound

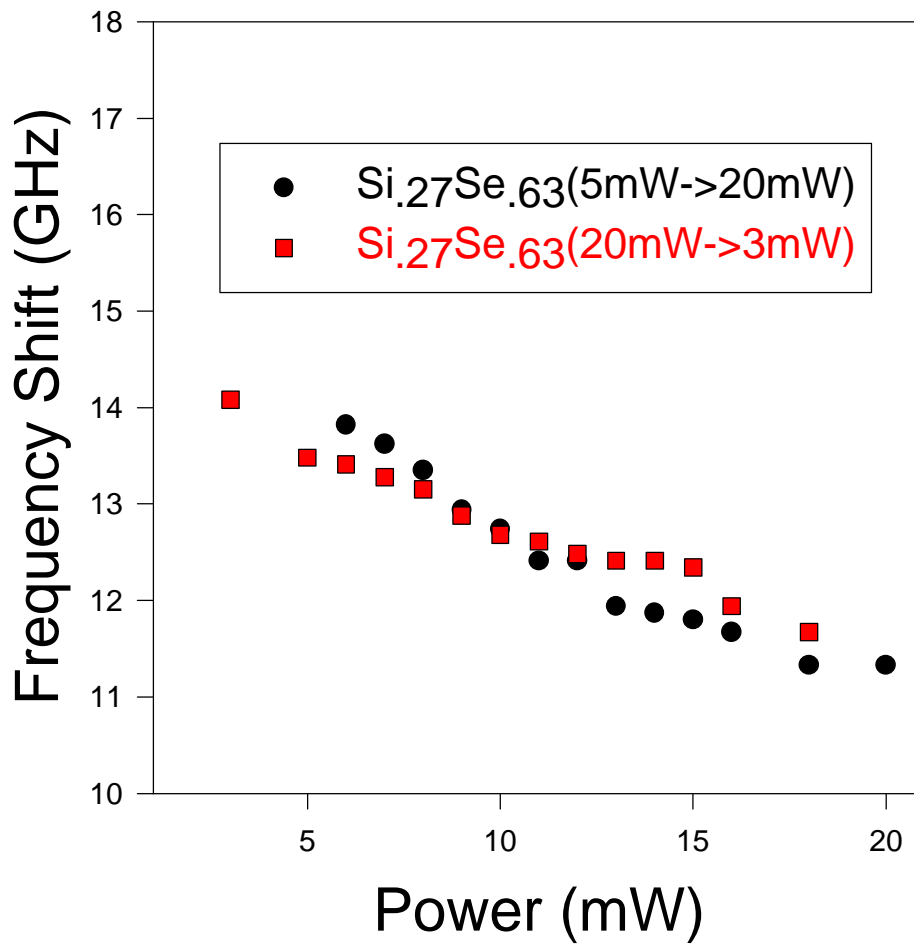


Figure 6

Sample:  $\text{Si}_{.285}\text{Se}_{.715}$

Power: left - 4mW (on the way down)

right - 4 mW (on the way up)

