Chapter 4

Raman Spectroscopy Investigations on Tin Mixed Chalcogenide Single Crystals
4.1 Introduction

In this chapter, the lattice vibration characteristics of SnS$_{2-X}$Se$_X$ ($0 \leq X \leq 2$) single crystals were studied by Raman scattering measurements. This study was carried out in the temperature range from room temperature to 80 K and pressure variation from ambient pressure to 20 GPa. The pressure and temperature results are combined with reported thermal expansion and compressibility data to evaluate the pure-volume and pure-temperature contribution to the isobaric temperature dependence of the A$_{1g}$ phonon modes. For this work, we have used single crystal of SnS$_{2-X}$Se$_X$ ($0 \leq X \leq 2$) grown by vapor transport technique and their composition as well as crystallinity was verified through energy dispersive analysis of X–rays and powder X–ray diffraction pattern, respectively. The unit cell parameters of SnS$_{2-X}$Se$_X$ ($0 \leq X \leq 2$) crystal matched well with the reported data [1]. Since all SnS$_{2-X}$Se$_X$ ($0 \leq X \leq 2$) crystals were of 2H polytype, therefore we have omitted 2H symbol before composition description throughout the text. The experimental set up for high pressure and low temperature Raman measurements are similar as described in chapter 3.

4.2 Effect on Concentration on Raman Spectra
Figure 4.1 Unpolarized Raman spectra of SnS$_{2-X}$Se$_X$ (0 \leq X \leq 2) mixed crystal at (a) 300 K and (b) 80 K temperatures and ambient pressure

Tin mixed chalcogenide SnS$_{2-X}$Se$_X$ (0 \leq X \leq 2) mixed crystals belongs to space group $D_{3d}$–$P\overline{3}ml$ and has three atoms in the unit cell which extends over only one sandwich layer. The nine normal modes of vibration are represented by the following irreducible representations of the point group $D_{3d}(\overline{3}ml)$ at the center of the Brillouin zone, $\Gamma$:

$$\Gamma = A_{1g} + E_g + 2A_{2u} + 2E_u$$  \hspace{1cm} (4.1)

The six optical modes divide into three Raman-active modes belonging to $A_{1g}$ and $E_g$ and three infrared-active modes belonging to $A_{2u}$ and $E_u$ [2]. Since layered crystals of the member of this series were grown by chemical vapor transport technique and are in the form of thin platelet like shape, they can show only one of the Raman modes the $A_{1g}$ mode ($E_g(\overline{1}c)$) which can be studied.

Figure 4.1 (a) shows the frequency shift and broadening of optical modes with variation in composition of SnS$_{2-X}$Se$_X$, for 0 \leq X \leq 2 from 150 to 350 cm$^{-1}$ at...
room temperature and ambient pressure. The Raman spectrum of SnS$_2$ exhibits one peak at 315 cm$^{-1}$, which correspond to the A$_{1g}$ mode. As $X$ increase the oscillation strength of the A$_{1g}$ modes decrease. At $X = 0.5$ there is a shoulder peak at the lower wavenumber side, which corresponds to the A$_{1g}$ mode of SnSe$_2$. Its intensity increases with $X$, for being dominant mode for the compositional range $0.5 \leq X \leq 1.5$. At $X = 2$ a peak appears at 185 cm$^{-1}$ is assigned to the A$_{1g}$ mode of SnSe$_2$ crystal. The large separation between experimental Raman mode frequencies in SnS$_2$ and SnSe$_2$ comes mostly from the big difference between S and Se atomic masses, $(m_{Se}/m_{S})^{1/2} \approx 1.57$, through the mass dependence $\omega_S \sim (m_{Se}/m_{S})^{1/2}\omega_{Se}$ and this mass difference most probably causes this two-mode behavior of the A$_{1g}$ mode which can be explained on the basis of the atomic displacement. In the case of A$_{1g}$ mode, only chalcogen (S and Se) atoms vibrate together, and the resulting mass difference between the vibrating S and Se anions is a consequence of this two-mode behavior. Figure 4.1 (b) shows the Raman spectra of SnS$_2$, SnSSe and SnSe$_2$ crystals at 80 K. A salient feature of the mixed crystal spectrum is that anharmonicity due to compositional disorder distorts the phonon line-shapes, leading to a tail on the low-energy side. At 80 K, anharmonicity is mainly due to compositional disorder induced anharmonicity. The mixed crystals cannot have an ideal perfect periodic lattice. As the Se composition increases, the disorder effect increases in the layered mixed crystals SnS$_{2-X}$Se$_X$, and the intensities of the modes related to SnS$_2$ decreases, while the SnSe$_2$ associated modes increases. This finite periodicity in the mixed crystals relaxes the $q = 0$ Raman selection rule, thus leading to the broadening and asymmetry of the Raman line shape [3].

Study on mixed compounds AB$_{1-X}$C$_X$, such as ZnSe$_{1-X}$S$_X$ [4] and CdS$_{1-X}$Se$_X$ [5] shows two types of behavior for long wavelength optical phonons i.e. one-mode and two-mode. The one-mode behavior is characterized by the presence of only one strong transverse optical mode throughout the series of solid solutions, at a frequency which is roughly a weighted average of the frequencies of the end-members. The two-mode behavior is defined by the presence of two dominant modes, the first one at the frequency of the end AC compound with an oscillator strength that decreases as $X$ increases and the second one at the frequency of the phonon of the end AB compound with an oscillator strength that increases with $X$ [6]. Gupta et al. calculated
theoretically and predicted that [7], in the solid solution SnS$_{2-x}$Se$_x$ the substitution is of the higher element and the mass of sulfur is less than the reduced mass of SnSe$_2$. These facts indicate that the two–mode behavior may be expected here.

Figure 4.2 (a) The variation of $A_{1g}$ peaks (b) FWHM as a function of Se composition $X$ of SnS$_{2-x}$Se$_x$ layered mixed crystals
Figure 4.2 (a) shows the evolution of the Raman active $A_{1g}$ mode for SnS$_2$–like and SnSe$_2$–like modes as a function of the composition in SnS$_{2-X}$Se$_X$ mixed crystals and figure 4.2 (b) shows the full width at half the maximum (FWHM) variation with composition and notably modes for SnSe$_2$ crystals were found to be higher than those for SnS$_2$ crystals. This may be due to the following factor: atomic radius of the covalently bonded selenium (0.12 nm) is larger than that of sulfur (0.10 nm) leading to higher probability of defect formation. The broadening of the phonon lines is due to anharmonicity of the lattice vibrations. The presence of anharmonic forces in a crystal leads to interaction between the harmonic normal modes. These interactions produce a temperature and pressure-dependent lifetime of the normal modes. Symmetric phonon line of the $A_{1g}$ mode for pure SnS$_2$ and SnSe$_2$ becomes asymmetric for SnS$_{2-X}$Se$_X$ mixed crystals. As expected, the linewidth dependencies for $A_{1g}$ modes have maximum at the composition of $X = 1$. The low-wavenumber side half-width ($\Gamma_{\text{low}}$) is larger than the high-wavenumber side half-width ($\Gamma_{\text{high}}$). The ratio $\Gamma_{\text{low}}/\Gamma_{\text{high}}$ shows maximum at $X = 1$. Indeed, this composition of SnS$_{2-X}$Se$_X$ mixed crystals corresponds to the maximum in substitutional disorder. This indicates that the mixed crystal disorder effect is the main source for the Raman line shape change as a function of composition. At this point, it is worthwhile to note that similar broadening of the phonon lines were previously observed in the III–V and II–VI mixed crystals (Ga$_{1-X}$Al$_X$As [8], GaAs$_{1-X}$P$_X$ and In$_X$Ga$_{1-X}$As [9], ZnS$_{1-X}$Te$_X$ [10]) and has been explained using a one–dimensional linear chain model and following the spatial correlation model of Parayanthal and Pollak [11]. Unfortunately, due to the lack of necessary parameters in literature for SnS$_2$ and SnSe$_2$ crystals, we could not apply this model for the explanation of broadening of phonon lines in SnS$_{2-X}$Se$_X$ mixed crystals.
4.3 Effect of Pressure on Raman Spectra

![Graph showing Raman spectra of SnS₂ and SnSe₂ under varying pressures.](image)
Figure 4.3 (a), (b) and (c) Raman spectra at various pressures of SnS$_2$, SnSe$_2$ and SnS$_2$Se respectively while (d) Variation of Raman shift as function of pressure for $A_{1g}$ phonon mode. The solid lines are least squares fits to data in 0-20 GPa pressure range.
Raman spectra of SnS\(_2\), SnSe\(_2\) and SnSSe at different pressure are shown in figure 4.3 (a), (b) and (c) respectively, while figure 4.3 (d) displays the pressure dependence of the Raman shift of the A\(_{1g}\) mode whose frequencies were obtained by a Lorentzian line–fitting procedure. Upon increasing pressure, we could observe that all the Raman peaks shifted to high frequencies with increasing pressure from 0 GPa to 20 GPa. The hardness of the A\(_{1g}\) modes indicated that the pressure reduced the distance between chalcogen–chalcogen bonds. Figure 4.3 (d) exhibit the pressure dependence of the A\(_{1g}\) Raman active mode, which can be well described using a linear function: \(\omega(P) = \omega_i + \alpha P\), where \(\omega_i\) is the Raman frequency of the \(i^{th}\) vibrational mode at ambient pressure, \(\alpha\) is the linear pressure coefficient and their values obtained are shown in the table 4.1. The larger pressure coefficients of the A\(_{1g}\) mode in SnS\(_2\) than in SnSe\(_2\) is mainly related to intralayer vibration which suggest that the intralayer bonds are more covalent in SnS\(_2\) than in SnSe\(_2\). The higher pressure coefficient of the A\(_{1g}\) mode can be understood by comparing the atomic motions of the two vibrations. The A\(_{1g}\) mode is compressional in the direction of the c-axis which is known to decrease with pressure at a much faster rate than the a-axis. As reported X–ray study of bulk 2H–SnS\(_2\) the a-axis decreased by 0.9% and the c-axis decreased by 7.1% at 3 GPa. It clearly indicates that the c-direction is much more compressible than the a-direction. The larger compression rate in c-direction can be ascribed to the distance reduction between adjacent chalcogen–chalcogen planes, which are weakly bonded by the van der Waals force along c-direction [12].

It is well known that the Grüneisen parameter \(\gamma\) plays a crucial role in understanding the thermodynamic and thermoelastic behavior of condensed matter at high pressure and temperatures. The dependence of the phonon mode frequency on pressure can be conveniently expressed through the isothermal mode Grüneisen parameter defined as [13]: \(\gamma_{iT} = - \left( \frac{d \ln \omega_i}{d \ln V} \right)_T = \frac{B_T}{\omega_i} \left( \frac{d \omega_i}{d P} \right)_T\) where, \(\omega_i\) is the frequency of the \(i^{th}\) phonon mode and is evaluated from figure 4.3 (d) by intercept on y–axis., \(V\) is the volume, \(B_T\) is the bulk modulus at a given pressure and is taken from the reported data for SnS\(_2\), SnSe\(_2\) [14], and \(d \omega_i/dP\) is pressure coefficient. These values are displayed in table 4.1.
Table 4.1 Bulk modulus [14], thermal expansion coefficient [14], Phonon energies with their pressure and temperature coefficient, Grüneisen parameter, of Tin dichalcogenide single crystals.

<table>
<thead>
<tr>
<th>Single Crystal</th>
<th>SnS₂</th>
<th>SnSSe</th>
<th>SnSe₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Modulus (GPa)</td>
<td>41.3</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Thermal expansion coefficient ($\times 10^{-3}K^{-1}$)</td>
<td>10.5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$A_{1g}$ phonon mode $\omega_0$ (cm$^{-1}$)</td>
<td>314.7</td>
<td>302.3</td>
<td>202.2</td>
</tr>
<tr>
<td>Pressure coefficient $d\omega/dP$ (cm$^{-1}$ GPa$^{-1}$)</td>
<td>3.4</td>
<td>2.5</td>
<td>1.9</td>
</tr>
<tr>
<td>Isothermal Grüneisen Parameter ($\gamma_T$)</td>
<td>0.45</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Temperature coefficient $d\omega/dT$ ($\times 10^{-2}$ cm$^{-1}$ K$^{-1}$)</td>
<td>−1.579</td>
<td>−2.723</td>
<td>−2.342</td>
</tr>
<tr>
<td>Isobaric Grüneisen parameter ($\gamma_P$)</td>
<td>0.47</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Isochoric Grüneisen parameter ($\gamma_V$)</td>
<td>0.02</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
4.4 Effect of Temperature on Raman Spectra

![Raman Spectra Graphs](image-url)
Figure 4.4 (a), (b) and (c) Raman spectra at various temperatures of SnS$_2$, SnSe$_2$ and SnSSe respectively while, (d) shows variation of Raman shift as function of temperature for phonon modes. The solid lines are least squares fits to data in the temperature range 80-300 K.
Figure 4.4 (a), (b) and (c) shows the Raman spectra of SnS$_2$, SnSe$_2$ and SnSSe single crystal obtained from room temperature $T = 300$ K to low temperature $T = 80$ K. Raman mode $A_{1g}$ are found to increase with decrease in temperature; furthermore, the changes in the line width are gradual. The changes in the Raman spectra in this temperature range were caused by the strength change of chalcogen–chalcogen bond due to the temperature induced lattice volume expansion. The extracted Lorentzian peak position of the $A_{1g}$ phonon peak for SnS$_2$, SnSSe and SnSe$_2$ crystals are displayed as a function of temperature in figure 4.4 (d). The symbols are the present experimental data, and the solid curves represent the data are fitted by using a linear function as shown above. The temperature dependence of Raman-peak-shifts reflects the thermal expansion of the lattice and anharmonic interaction between the phonon modes. The isobaric mode Grüneisen parameter [13] is calculated from the equation: $\gamma_{ip} = -\left(\frac{d \ln \omega_i}{d \ln V}\right)_p = -\frac{1}{\alpha \omega_i} \left(\frac{d \omega_i}{dT}\right)_p$. The values of thermal expansion coefficient ($\alpha$) are taken from the reported data for SnS$_2$ and SnSe$_2$ [14]. The calculated value of $\left(\frac{d \omega_i}{dT}\right)_p$ and isobaric mode Grüneisen parameter are presented in table 4.1.

We have used expression (3.6), (3.7), (3.8), (3.9), (3.10) and (3.11) described already in chapter 3 for determining various parameter viz. total anharmonicity, implicit anharmonicity, explicit anharmonicity, anharmonicity constant and adjustable parameter which are shown table 4.2 for SnS$_2$ and SnSe$_2$ single crystal respectively.

The ratio of the volume term to the total variation
\[ \eta = \frac{\left(\frac{d \omega_i}{dp}\right)_T}{\left(\frac{d \omega_i}{dT}\right)_p} \left[ \frac{\alpha}{\beta} \right] = \frac{\gamma_{TT}}{\gamma_{IP}} \]

is a dimensionless parameter introduced by Weinstein and Zallen [15] in order to determine the relative importance of the two effects. This parameter, known as the quasiharmonic fraction, may assume values between 0 and $\infty$ and largely indicates the type of crystal bonding associated with the particular mode. For $\eta$ approaching zero, the explicit effect is almost entirely responsible for the frequency shift observed in Raman measurements under variable temperature, implying that the crystal bonding is essentially covalent or, in the case of molecular crystals, the internal binding of molecular groups is strong; in either case, thermal expansion does not affect the forces involved. For $\eta = 1$, thermal expansion is exclusively responsible for the observed frequency shifts, indicating that the crystal bonding is of ionic character. For $\eta = 0.5$, ...
the contributions of the two effects to the total observed shift are comparable and have the same (opposite) sign. When the volume effect is dominant with a small explicit contribution of the opposite sign, the parameter $\eta$ takes finite values above unity [16].

**Phonon linewidths $\Gamma$ and decay anharmonicity**

In a real crystal, phonons do not propagate infinitely but interact with each other and decay into other phonons with lower energies. In Raman scattering process, optical phonons are created as a result of scattering of light by the sample. Due to anharmonicity of lattice forces, these phonons have finite lifetimes and decay into other phonons thereby attaining thermal equilibrium. The reason to study phonon lifetimes in materials is because finite phonon lifetimes play an important role in the thermal conductance of a material. Hence, the knowledge of phonon lifetimes within a material could be useful in tailoring the thermal properties of materials. One of the first models applied to phonon decay in a Raman process was put forward by Klemens [17]. According to his model, the principal anharmonic interaction is due to the cubic term in the phonon potential, resulting in a splitting of an optical phonon into two acoustic phonons having equal energy but opposite momentum. Klemens’ method has been used to explain thermal conductivity in a variety of materials [18].

Based on perturbation theory, Klemens formulated a simple mechanism which involves the linewidth of a Raman peak. The Raman peak width, or the linewidth, is directly related to the phonon lifetime. Since the Raman peak is plotted as intensity versus wavenumber (or energy) the width of a peak is related to the lifetime through the energy-time uncertainty principle: $\Delta E \Delta t \geq \frac{\hbar}{2}$

In the above expression, $\Delta E$, the uncertainty in energy corresponds to the linewidth of the Raman peak, and the uncertainty in time, $\Delta t$ is taken as the lifetime $\tau$ of the phonon. In other words, the formula can be re-written as $\Gamma \tau \geq \frac{\hbar}{2}$

Thus according to the above formula, $1 \text{ cm}^{-1} = 5.3 \text{ ps}$. Using time dependent perturbation theory, Klemens derived an expression for the temperature dependent anharmonic linewidth of a Raman peak. The variation of the phonon linewidth of
Raman modes due to changes in temperature is analyzed using formalism with cubic anharmonicities representing three phonon processes, respectively.

$$\Gamma (T) = \Gamma_0 + B \left\{ \exp \left( \frac{\hbar \omega_0}{2k_B T} \right) - 1 \right\}^{-1} + \frac{1}{2}$$

(4.4)

where $\Gamma_0$ is the temperature independent broadening due to the disorder of crystal, $B$ is the coefficient of cubic anharmonicity. $\omega_0$ is the Raman frequency as temperature approaches 0 K. Figure 4.5 (a), (b) represents FWHM (linewidth broadening) and Raman shift as a function of temperature for $A_{1g}$ phonon in SnS$_2$ and SnSe$_2$ crystals respectively. The experimental data of phonon linewidth were fitted by means of equation (4.4) with $\Gamma_0$ and $B$ as fitting parameters. The value of $\Gamma_0$ and $B$ obtained for $A_{1g}$ modes of SnS$_2$ and SnSe$_2$ crystal are shown in Table 4.2 which indicates that the effect of crystal disorder on the line broadening is lower.

Table 4.2 The measured isobaric temperature derivatives are separated into the pure volume and pure temperature contributions of $A_{1g}$ phonon modes in SnS$_2$ and SnSe$_2$ single crystal.

<table>
<thead>
<tr>
<th></th>
<th>$\frac{1}{\omega_i} \left( \frac{d\omega_i}{dT} \right)_P$</th>
<th>$-\gamma_{iT} \alpha$</th>
<th>$\frac{1}{\omega_i} \left( \frac{d\omega_i}{dT} \right)_V$</th>
<th>$\eta$</th>
<th>$\omega(0)$</th>
<th>$\omega_0$</th>
<th>$A$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(\times 10^{-5})$</td>
<td>$(\times 10^{-5})$</td>
<td>$(\times 10^{-5})$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
<td>cm$^{-1}$</td>
</tr>
<tr>
<td>SnS$_2$</td>
<td>-5.02</td>
<td>-4.73</td>
<td>-0.29</td>
<td>0.96</td>
<td>320.68</td>
<td>320.71</td>
<td>-0.024</td>
<td>2.68</td>
</tr>
<tr>
<td>SnSe$_2$</td>
<td>-13.17</td>
<td>-4.6</td>
<td>-8.57</td>
<td>0.35</td>
<td>191.45</td>
<td>191.42</td>
<td>0.029</td>
<td>1.78</td>
</tr>
</tbody>
</table>
Figure 4.5 (a) and (b) Shows temperature dependence of FWHM and Raman shift of $A_{1g}$ phonon in SnS$_2$ and SnSe$_2$ crystals respectively. The solid lines are fits to the symmetrical three-phonon coupling model including thermal expansion contribution.

As was mentioned above, the theory leading to equations (3.7) are valid only for isotropic crystals of cubic symmetry for which the phonon frequency is a function of two variables: volume and temperature: $\omega = \omega(V,T)$. In a uniaxial crystal, such as MCh$_2$, the phonon frequency is a function of three variables, namely the crystal lattice parameters $a$ and $c$ and temperature $\omega = \omega(a,c,T)$ (the ratio $c/a$ of the lattice...
parameters varies with temperature). Certain corrections to isotropic approximation were introduced by Peercy [19] in the case of tetragonal TiO$_2$ by considering uniaxial stress Raman data and repeated later by Cerdeira et al. [20] and Liarokapis et al. [21] in other uniaxial crystals. In a recent work, a complete analysis has been carried out in order to derive the correct expression for a uniaxial crystal and calculate the percentage deviation of the isotropic approximation from the accurate uniaxial approach. For such an accurate analysis, it is necessary to have uniaxial stress Raman data available, but in the absence of such data for SnS$_2$, SnSSe and SnSe$_2$, all calculations have been performed using the isotropic approximation.

4.5 Conclusion

In the case of the A$_{1g}$ mode, only chalcogen (S and Se) atoms vibrate together, and the resulting mass difference between the vibrating S and Se anions consequences in the two-mode behavior. The present study indicates absence of any phase transition in a low temperature and high pressure range which makes tin dichalcogenides a technologically important and useful compound. From measurements of temperature and pressure dependence of Raman mode frequencies of tin dichalcogenides single crystal, anharmonic parameters calculated for the Raman active modes can be useful in modeling of thermodynamic entities.
4.6 References


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