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Pressure Induced Metallization in $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ Ternary Mixed Crystals

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Abstract. We use high pressure Raman scattering to investigate the structural stability and the pressure effects on the semiconductor-metal phase transition of $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ ($x = 0.112, 0.16$ and 0.24) mixed crystals up to about 25 GPa. We find that introduction of Be in Zn site results in an increase in the semiconductor-metal phase transition pressure as compared to pure ZnSe. We also determine the mode Grüneisen parameters (γ) and find a decrease in the ratio of the mode Grüneisen parameter ($\gamma_{\text{TO}}/\gamma_{\text{LO}}$) values with increasing Be content suggesting an increased covalency in the system with Be incorporation.

1. Introduction

Wide band gap II–VI compounds are promising for short-wavelength optoelectronic applications in laser diodes and light emitting diodes which display from green to ultraviolet spectral region. They find potential applications in optoelectronics as these lasers could revolutionize areas such as optical information storage and color displays. In this direction, the developments of ZnSe based semiconducting compounds and heterostructures are of particular interest [1, 2]. However, due to defect formation favored by the high ionicity and the smaller bond energies of conventional II-VI materials, devices based on these materials have shorter lifetime compared to III-V based devices. Degradation of devices based on these materials because of shorter lifetimes has been a major challenge. Use of Be in ZnSe based mixed crystals (i.e. $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ ternary alloy) has been suggested [3,4] to improve the device lifetime because of dominant covalent bonding and high cohesive energy of BeSe. The high degree of covalent bonding of Be chalcogenides leads to an increase of their shear modulus [5]. Therefore, mixing of Be chalcogenides with ZnSe would impart rigidity to the lattice and increase the resistance of the structure to defect generation and propagation. The variation of the composition in $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ crystals induces significant changes of the physical properties such as bond polarity, electronic band structure and lattice dynamics. The effect of pressure is of fundamental interest in altering the structural, electrical and optical properties of semiconductors. The pressure dependence of the vibrational modes provides additional insight into the nature of the lattice vibrations. Such information is important in characterizing strained-layer superlattices and heterostructures. High pressure Raman spectroscopy is a very powerful technique to study the lattice dynamics and phase transition of semiconductor materials related to their structural stability. However, the structural stability of $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ with varying Be concentration and the pressure-induced semiconductor (zincblende)-metal(rocksalt) transition as observed in ZnSe [6-9] and related systems [9-11] remained unexplored until a recent x-ray diffraction study [12]. Under pressure, ZnSe transforms to the six-fold coordinated cubic NaCl rocksalt (RS) phase (metallic) whereas BeSe transforms to the six-fold coordinated hexagonal NiAs structure [13,14]. Moreover, the BeSe transition pressure (~ 56 GPa) is much higher than that of ZnSe (~ 13 GPa). In these circumstances, an interesting question to address is that what happens to the nature of the pressure induced semiconductor-metal transition in the ZnBeSe mixed crystals with increased Be content. In this paper,

we use Raman scattering to investigate the pressure effects on the semiconductor-metal phase transition of $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ ($x = 0.112, 0.16$ and 0.24) mixed crystals at high pressures up to about 25 GPa. The effect of Be on the bonding and the semiconductor-metal phase transition is discussed.

2. Experimental Details

$\text{Zn}_{1-x}\text{Be}_x\text{Se}$ ($x = 0.11, 0.16, 0.24$) single crystals were grown by the high-pressure Bridgman method. Samples, mechanically polished to optical quality, were loaded with ruby chips in a Mao/Bell-type diamond anvil cell. Methanol-ethanol-water (16:3:1) was used as the pressure transmitting medium, the pressure being determined via the ruby fluorescence linear scale [15]. Unpolarized Raman spectra were recorded in backscattering geometry by a custom built in Raman spectrometer details of which is described elsewhere [16].

3. Results and Discussion

Unpolarized Raman spectra for $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ mixed crystals at room temperature are shown in Figure 1. The dashed lines are Lorentzian fit to the experimental data. Pages *et al* [17-18] have done a very detailed and systematic room temperature Raman investigations on these systems. Hence the origin of the various Raman modes is briefly discussed here. According to Pages *et al*, in the ZnBeSe ternary alloy, there is formation of a percolating pseudo-continuous chain of Be–Se bonds throughout the alloy which consists of randomly formed hard-like (h) Be-rich bounded clusters embedded in a soft-like (s) Zn-rich matrix. Due to the different mechanical properties of the two host media, the Be–Se bonds from each of them vibrate at two separate frequencies giving rise to a so-called percolation doublet of the transverse optic (TO) modes (i.e. $\text{TO}_{\text{Be-Se}}^{\text{Zn}}$ and $\text{TO}_{\text{Be-Se}}^{\text{Be}}$). In labelling the modes, the subscript and superscript refer to the bond species and to the host region, respectively. A basic rule of the percolation model [18] is that *bonds are longer when they stay in the environment of the short species (thereby vibrating at a lower frequency), and vice versa*. This is because the Be–Se bonds in the h-region undergo a larger internal tensile strain to match the surrounding lattice parameter than those dispersed within the much softer ZnSe-like host matrix. With this, the TO modes from the BeSe-like region vibrate at a lower frequency than those from the ZnSe-like region, in both the Zn–Se and Be–Se spectral ranges and at any alloy composition. This explains the origin of the $\text{TO}_{\text{Be-Se}}^{\text{Zn}} - \text{TO}_{\text{Be-Se}}^{\text{Be}}$ splitting (as shown in Figure 1). A similar splitting has also been evidenced for the Zn–Se bonds, but shows up clearly only at high pressure [19]. Furthermore, in these mixed crystals, the wave vector conservation selection rule is relaxed as a result of the violation of translational invariance, and some of the Raman features correspond to phonons from regions of the Brillouin zone (BZ) where the phonon density of state has a maximum, that is, at the edge of the BZ. Therefore, apart from the zone centre (Γ) modes, a disorder activated LA_L mode assigned as longitudinal acoustic modes at L-point of the BZ is also seen. Combinational overtones ($2\text{TA} + \text{TO}_{\text{Zn-Se}}$) are also seen.

Figure 2 shows the pressure evolution of the Raman spectra at a few representative pressures in the increasing pressure run. It can be seen (marked by arrows in Figure 2) that new modes start appearing at ~ 8 and 9 GPa. Origin of these modes has been explained by a pressure-induced Fano-decoupling of the TO mode from the 2TA_K and $(\text{TA}+\text{LA})_L$ two-phonon continua at the BZ edge [19]. When starting from the pressure-induced TO splitting pattern in pure ZnSe [20], these two new modes can be explained simply by postulating the existence of an extra TO ($\text{TO}_{\text{Zn-Se}}^{\text{Be}}$), which substitutes for the main TO ($\text{TO}_{\text{Zn-Se}}^{\text{Zn}}$) for the anharmonic decay into the 2TA continuum. With this, the 2TA -decoupling occurs at 8 GPa in ZnBeSe, in reference to the first new mode, while the second new mode at ~ 9 GPa is due to the transient appearance of the $\text{TA}+\text{LA}$ continuum just after decoupling from the main TO and just before re-coupling with the additional minor TO ($\text{TO}_{\text{Zn-Se}}^{\text{Be}}$) [19].

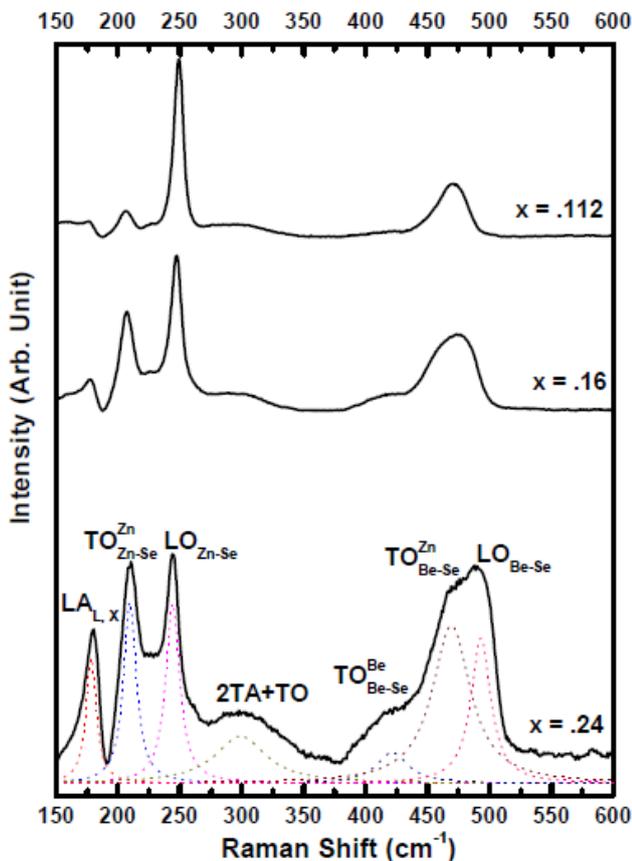


Figure 1. Raman spectra for $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ mixed crystals at ambient conditions

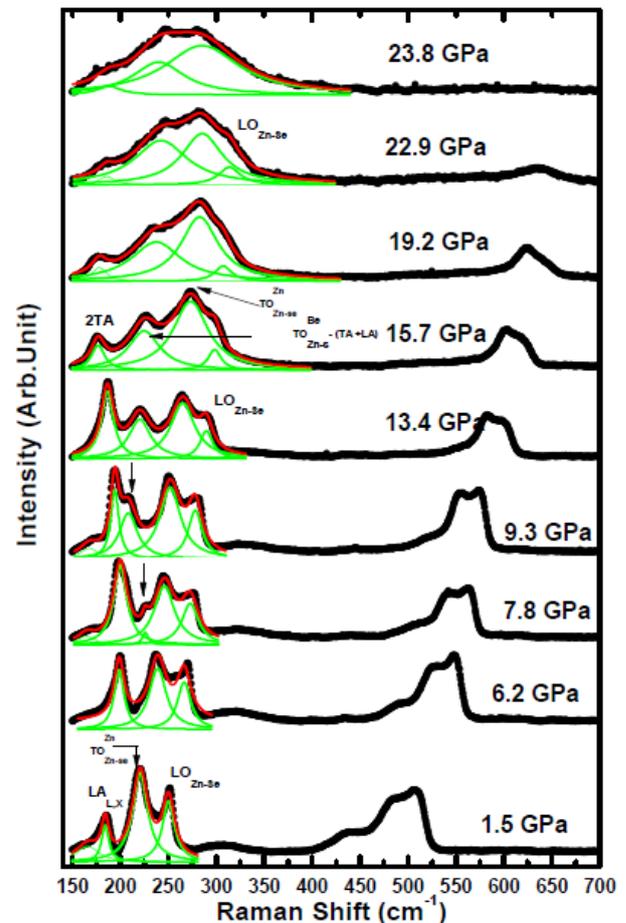


Figure 2. Pressure evolution of the Raman spectra of $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ ($x = 24\%$).

With increasing pressure, the intensity of the Raman modes decreases gradually. For the 24% Be sample, at ~ 23.8 GPa, the sample turned opaque (black) with a sudden decrease in Raman intensity. Therefore, at this pressure the spectra was recorded for 45 minutes and the disappearance of LO_{ZnSe} , LO_{BeSe} , and TO_{BeSe} modes was observed. For both $\text{Zn}_{0.84}\text{Be}_{0.16}\text{Se}$ and $\text{Zn}_{0.888}\text{Be}_{0.112}\text{Se}$, similar behavior was observed but at a lower pressure. Both the sample became opaque along with the disappearance of the LO_{ZnSe} , LO_{BeSe} and TO_{BeSe} modes at 21.1 and 19.5 GPa, respectively for $\text{Zn}_{0.84}\text{Be}_{0.16}\text{Se}$ and $\text{Zn}_{0.888}\text{Be}_{0.112}\text{Se}$, respectively. We attribute these changes to the semiconductor (zinc blende) \rightarrow metal (rock salt) phase transition as observed in ZnSe [6-9] and $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ [9-10] but at different pressure values. It can be recalled that ZnSe also exhibits similar optical behavior [6] (i.e. transparent to opaque transformation) at 13.5 GPa and turns metallic when the structure changes from zinc blende to rocksalt structure [7-9]. From the temperature dependence of resistivity, Galit Itkin *et al* [8] have suggested that in the pressure range of 13.5–17 GPa, the semiconducting and the metallic rock salt phase of ZnSe coexist. Beyond that, there is a complete metallization due to gap closure. In contrast, the semiconductor to metal transition pressure of $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ is lowered with increased Fe concentration [10]. However, the TO modes remain visible till the highest experimental pressure of 35 GPa is reached. Furthermore, it has been calculated [10] that the skin depth to be only about several tens of an Å. If it is to be a skin depth issue then the LO modes will be of extremely weak intensity. This is because of the transverse nature of the incident light which can couple rather strongly to the TO modes. In our experiments, the TO modes were found till the highest achieved pressure of about ~ 25 GPa and the LO_{ZnSe} , TO_{BeSe} , LO_{BeSe} modes disappear at 23.8, 21.1 and 19.5 GPa for $\text{Zn}_{0.76}\text{Be}_{0.24}\text{Se}$,

$\text{Zn}_{0.84}\text{Be}_{0.16}\text{Se}$ and $\text{Zn}_{0.888}\text{Be}_{0.112}\text{Se}$, respectively, marking the onset of the semiconductor to metallic transition.

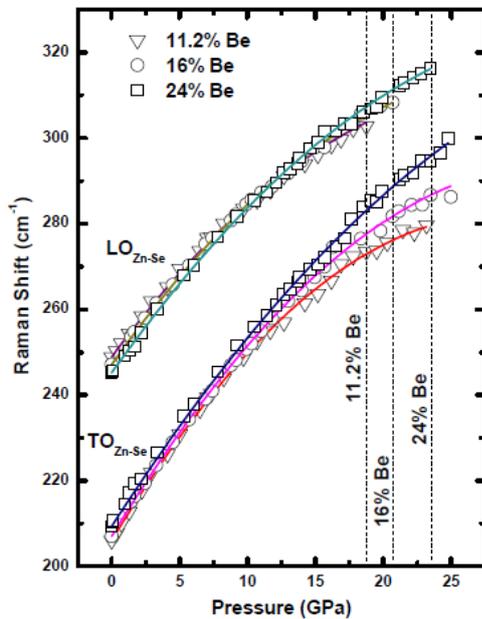


Figure 3. The frequency~pressure variations of the TO and LO modes in the Zn-Se region. The dashed vertical lines indicate transition pressure.

Table 1. Fitting parameter for various modes and calculated mode Gruneisen parameters for different Be concentration.

Be content (x)	Phonon Modes	$d\omega/dP$	γ_i	Transition Pressure
.112	$TO_{\text{Zn-Se}}^{\text{Zn}}$	5.3	1.6	19.5
	$LO_{\text{Zn-Se}}^{\text{Zn}}$	4.3	1	
.16	$TO_{\text{Zn-Se}}^{\text{Zn}}$	5.2	1.5	21.1
	$LO_{\text{Zn-Se}}^{\text{Zn}}$	4.5	1.1	
.24	$TO_{\text{Zn-Se}}^{\text{Zn}}$	4.9	1.4	23.8
	$LO_{\text{Zn-Se}}^{\text{Zn}}$	4.5	1.1	

The pressure dependencies of all the mode frequencies can be obtained by a quadratic ($\omega_p = \omega_i + AP + BP^2$) fitting equation, where ω_p is the mode frequency at pressure P , ω_i is the mode frequency at ambient pressure, A and B are constants. The frequency versus pressure variations of the TO and LO modes in the Zn-Se region are shown in Figure 3. The dotted vertical lines in Figure 3 indicate the semiconductor-metal transition for each sample. Solid lines are quadratic fit to the experimental data (open symbols). Table 1 lists all the fitting parameters, mode Gruneisen parameter (γ_i) and the metallic transition pressure values for each Be concentration. γ_i is calculated using the equation $\gamma_i = (B_0/\omega_i)(d\omega/dP)$, where B_0 is the bulk modulus of ZnSe, and was taken as 62.4 GPa [7]. We have used the same B_0 value for all values of x in $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ system. From table I, the $\gamma_{\text{TO}}/\gamma_{\text{LO}}$ values for the ZnSe-like modes are found to be 1.2, 1.3, and 1.6 for $\text{Zn}_{0.76}\text{Be}_{0.24}\text{Se}$, $\text{Zn}_{0.84}\text{Be}_{0.16}\text{Se}$ and $\text{Zn}_{0.888}\text{Be}_{0.112}\text{Zn}_{0.84}$ respectively whereas the same for ZnSe is 2.082 [9]. One observes a decrease of $\gamma_{\text{TO}}/\gamma_{\text{LO}}$ for the ZnSe-like modes with increase in Be concentration implying an increasing covalency [21]. This again shows that incorporation of Be indeed change the bonding properties by increasing the covalency (reducing the ionicity) thus imparting strength to the mixed crystal lattice. This increased covalency because of Be incorporation increases the transition pressure. It is worth mentioning that in case of $\text{Zn}_{1-x}\text{Fe}_x\text{Se}$ an opposite behavior is seen because of the increased ionicity due to Fe incorporation.

4. Conclusion

High-pressure Raman scattering measurements were performed on $\text{Zn}_{0.76}\text{Be}_{0.24}\text{Se}$, $\text{Zn}_{0.84}\text{Be}_{0.16}\text{Se}$ and $\text{Zn}_{0.888}\text{Be}_{0.112}$ mixed crystals up to about 25 GPa. The semiconductor-metal phase transition pressure was found to be 23.8, 21.1 and 19.5 GPa respectively. Our studies reveal that introduction of Be in Zn

site results in an increase in the semiconductor-metal phase transition pressure as compared to pure ZnSe. The disappearance of most of the phonon modes along with the sample turning opaque marks the onset of this transition. Decrease in γ_{TO}/γ_{LO} values with increasing Be content proves the increased covalency in the system with Be incorporation.

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