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# Identification of $I_1^{deep}$ and its LO phonon replicas in $ZnS_xSe_{1-x}$ single crystals

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**Abstract.** The I<sup>deep</sup> line and its LO phonon replicas have been studied for the first time in the photoluminescence of  $ZnS_xSe_{1-x}$  (0.02 $\leq x \leq 0.125$ ) single crystals at 2 K using excitation spectroscopy, selectively excited photoluminescence and by doping and annealing with controlled partial pressures. The Huang–Rhys parameter *S*, defined by the intensity ratio of the one LO phonon and no-phonon luminescence lines, increases non-linearly as the composition parameter *x* increases.

# 1. Introduction

There has recently been great interest in the study of the ternary compound  $ZnS_xSe_{1-x}$ , because it is a direct band-gap semiconductor, and the achievement of every wavelength from the ultraviolet to the blue region of the spectrum may be expected, since the two binary compounds ZnS and ZnSe form solid solutions over the whole composition range  $0 \le x \le 1$ . Extensive investigations concerning the growth and luminescence properties of the ZnS<sub>x</sub>Se<sub>1-x</sub> system have been performed [1–7]. In addition to the S–A luminescence [6, 7], some studies on bound exciton emission spectra have been reported, but not in detail.

In an attempt to identify some peaks on the low energy side of the I<sub>2</sub> line we performed some experiments using photoluminescence excitation, selective photoluminescence, back-doping and thermal treatment under controlled partial pressure of the components. In the excitation spectroscopy technique the intensity of an emission is monitored while the exciting light source is scanned in energy. In the selectivity excited photoluminescence, emission spectra are recorded using different dye-laser wavelengths for excitation. These techniques can detect bound exciton components and their satellites, because excitation spectroscopy allows the preferential isolation of absorption processes for a given luminescent transition, while selective excited photoluminescence allows one to excite certain luminescent transitions resonantly. In order to identify the spectra, we make use of the knowledge of bound excitons in II-VI compounds; for example, the most striking feature of the I<sup>deep</sup> line is that it is always accompanied by a strong series of longitudinal optical (LO) phonon replicas [8,9]. The  $I_1^{deep}$  line is due to excitons bound at neutral acceptors, either at a zinc vacancy ( $V_{Zn}$ ) or at a copper on a zinc site ( $Cu_{Zn}$ ) [10].

# 2. Experiment

The  $ZnS_xSe_{1-x}$  single crystals used in the present work were grown by the sublimation method at  $\sim 1000$  °C. The composition x ( $0 \le x \le 0.125$ ) of the grown crystals was measured with an x-ray microanalyser. The samples for the optical measurements were cut from single crystals along the (110) cleavage planes. The copper back-doping process was as follows. Copper was deposited on both surfaces of the cleaved wafer using a vacuum evaporator. Then the sample was sealed in a quartz ampoule and kept at 300 °C for 12 h under an argon atmosphere in order to produce Cu-doping by diffusion. After that, the ampoule was quenched in water. To remove any remaining copper on the surface, the sample was dipped in 6N HCl for 2 min. Another wafer was only heat treated in molten Zn at 700 °C for 72 h. Finally the samples were etched using a mixed solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and concentrated H<sub>2</sub>SO<sub>4</sub>.

The samples were mounted in a strain-free fashion and immersed in liquid helium which could be pumped to achieve the superfluid state, usually at 2 K. Photoluminescence was excited by a 2 kW Xe lamp. Monochromatic light from a grating monochromator equipped with a 2 kW Xe lamp was utilised as the source for the excitation spectra. A frequency-tunable dye laser pumped by an N<sub>2</sub> laser (AVCO-C950) was used as the excitation source in the selectively excited



Figure 1. Exciton luminescence spectra of as-grown  $ZnS_xSe_{1.x}$  at 2 K. (a) x=0; (b) x=0.02; (c) x=0.045; (d) x=0.125.

photoluminescence. Spectra were measured using a JYU-1000 double monochromator and HTVR-106 UH photomultiplier.

# 3. Results and discussion

#### 3.1. Photoluminescence spectra

Figure 1 shows the exciton emission spectra in as-grown  $ZnS_xSe_{1-x}$  single crystals ( $0 \le x \le 0.125$ ). Free exciton and bound exciton emission peaks from an undoped ZnSe single crystal are shown in (a). The peak (Ex) at 2.802 eV is known to be due to the radiative recombination of free excitons [11], and Ex-LO and Ex-2LO are attributed to free exciton recombination with the emission of one and two LO phonons, respectively. The energy separation between these two peaks is  $31.5\pm0.5$  meV, which is in agreement with the energy of a LO phonon is ZnSe [8]. The sharp line at 2.797 eV is considered to be due to the radiative annihilation of excitons bound to neutral donors [12]. The strong sharp line at 2.783 eV is labelled  $I_1^{deep}$  [8], and is attributed to the recombination of excitons bound to neutral acceptors. This line exhibits a strong series of LO phonon replicas, shown as  $I_1^{deep}$ -LO and  $I_1^{deep}$ -2LO lines in figure 1(a). We have examined the chemical origin of the  $I_1^{deep}$ 

line elsewhere [10]. The neutral acceptors which are concerned in the  $I_1^{deep}$  line are composed either of zinc vacancies ( $V_{Zn}$ ) or copper substituted for zinc ( $Cu_{Zn}$ ).

Band-edge spectra in  $ZnS_xSe_{1-x}$  (x = 0.02, 0.045, 0.125) are shown in figures 1(b)-(d). The peaks labelled Ex and  $I_2$  arise from the emission of free excitons and excitons bound to neutral donors, respectively. The energy spacing of these peaks is about 4.6 meV, which agrees with that of ZnSe. These peaks had been detailed elsewhere [13]. The peaks on the low energy side of the  $I_2$  line are temporarily labelled A, B, and C, respectively. The energy separation of each peak is about 32.0 meV, which is equal to the LO phonon energy in  $ZnS_xSe_{1-x}$  (x = 0.125), as measured from Raman scattering experiments. The changes in peaks A, B and C with increasing composition x are as follows: (i) the peaks become broader; (ii) the energy spacing between  $I_2$  and A becomes larger and (iii) peak A becomes weaker and, in contrast, peaks B and C become stronger. Hence the behaviour of these peaks does not correspond completely with that of the I<sup>deep</sup> line and its LO phonon replicas in ZnSe. The origin of these peaks therefore needs to be established.

#### 3.2. Relation between A, B and C

Figure 2(*a*) shows the photoluminescence spectrum of as-grown  $ZnS_xSe_{1-x}$  (x = 0.02) at 2 K. The peaks A, B and C are located at 2.784, 2.752 and 2.720 eV, respectively. The energy separation of each peak from A divided by the number of LO phonons gives the average energy of the LO phonons emitted.

The variation of the intensity of the C emission peak with scanned excitation energy is shown in figure 2(b). The arrow indicates the position of the detection wavelength, which falls just on the peak C. The strongest peak at 2.784 eV is observed when the energy of the exciting radiation differs from peak C by twice the LO phonon energy and corresponds to the position of peak A. This result shows positively that peak C is a two LO phonon replica of peak A, peak A being believed to be a no-phonon emission line.



**Figure 2.** (a) Exciton luminescence spectrum of asgrown  $ZnS_xSe_{1-x}$  (x = 0.02) at 2 K. (b) Excitation spectrum of peak C for as-grown  $ZnS_xSe_{1-x}$  (x = 0.02) at 2 K.



**Figure 3.** (a) Exciton luminescence spectrum of as-grown  $ZnS_xSe_{1-x}$  (x = 0.045) at 2 K. (b)–(d) Selective photoluminescence spectra of as-grown  $ZnS_xSe_{1-x}$ (x = 0.045) at 2 K, with different dye-laser energies.

The photoluminescence spectrum of as-grown  $ZnS_rSe_{1-r}$  (x = 0.045) is shown in figure 3(a). Three broadened peaks (A, B, C) on the low energy side of the  $I_2$  line are observed at 2.794, 2.762 and 2.730 eV, respectively, and have equal energy spacing which corresponds to the LO phonon average energy. Figures 3(b)-(d) show selectively excited photoluminescence spectra obtained with a frequency-tunable dye laser with a spectral width of 0.15 meV as the excitation light source. Arrows indicate the energy of the dye laser, which was adjusted to different positions within peak A. The sharp lines, labelled TO and LO respectively, are considered to be due to resonance phonon Raman scattering and possibly overlapping LO phonon satellites of A. The broadened peaks on the low energy side of the LO line correspond simply to peaks B and C, respectively. The intensities of these peaks decrease with decreasing excitation energy of the A emission centre when the excitation is located in the low energy wing of A. This result reveals that the peaks B and C are LO phonon replicas of peak A.

# 3.3. Origin of peak A

We have examined the origin of the  $I_1^{deep}$  line in ZnSe [10]. It is associated with two possible kinds of neutral acceptor, namely  $V_{Zn}$  and  $Cu_{Zn}$ . To prove the origin of peak A, both cleaved wafers were back-doped by copper and heat treated in molten Zn, respectively. The band-edge photoluminescence spectrum in ZnS<sub>x</sub>Se<sub>1-x</sub> (x = 0.125) at 2 K is shown in figure 4(a). A number of peaks are observed on the low energy side of

the I<sub>2</sub> line and are labelled Ex-LO and A, B, C. The energy separation between A and B or C is about 32 meV, which is equal to the energy of a LO phonon in  $ZnS_rSe_{1-r}$  (x = 0.125). Cu-doping of the specimen intensified A, B and C only, as seen in figure 4(b). The Ex-LO peak is hardly observed, being hidden by the intensified peak A. The concentration of substitutional defects  $Cu_{Zn}$  is considered to be high in the Cu-doped specimen. Figure 4(c) shows the band-edge photoluminescence spectrum of an undoped specimen subjected to previous heat treatment. No peaks A, B or C are observed, but Ex-LO, I<sub>2</sub>-LO, Ex-2LO and I<sub>2</sub>-2LO clearly occur. We believe that the concentration of  $V_{Zn}$  was decreased, possibly to zero, by being heat treated in molten Zn. This indicates that the behaviour of peak A is similar to that of the  $I_1^{deep}$  line in ZnSe. We therefore conclude that peak A is the  $I_1^{deep}$  line, and peaks B and C are its LO phonon replicas.

# 3.4. The Huang-Rhys parameter S

The  $I_1^{deep}$  line exhibits a strong series of LO phonon replicas, showing that the bound exciton states couple with the lattice through the electron-phonon interaction, which is dominated by LO phonon modes in polar semiconductors. The Huang-Rhys parameter, S, is often used to express the average number of emitted phonons in the relaxation process. The integrated



**Figure 4.** Exciton luminescence spectra of  $ZnS_xSe_{1-x}$  at 2 K. (a) as-grown, undoped, (b) Cu-doped, (c) treated in molten Zn.



**Figure 5.** Composition (*x*) dependence of the Huang–Rhys parameter *S* in  $ZnS_xSe_{1-x}$  ( $0 \le x \le 0.125$ ) single crystals.

intensities of the zero phonon line,  $I_0$ , and *n*th phonon line,  $I_n$ , are expressed by Poisson functions [14]:

$$I_0 = \mathrm{e}^{-S} \tag{1}$$

$$I_n = \mathrm{e}^{-S} \, S^n / n! \tag{2}$$

S is obtained from equations (1) and (2) by the intensity ratio of the one LO phonon and no-phonon lines. The change of S with composition ( $0 \le x \le 0.125$ ) is shown in figure 5, which is divided into two regions. In the first region (x < 0.05), S is smaller than 1, since phonon coupling is weak. The spectral linewidth is increased slightly as shown in figure 1(a) and (b). In the second region ( $x \ge 0.05$ ), S is larger than 1, and strong phonon coupling causes an increase in the linewidth because of an increase in both the rate of the dissipation process and in general background due to direct coupling to a greater range of vibrational modes. A typical spectrum is given in figure 1(d).

### 4. Conclusions

We have used excitation spectroscopy, selectively excited photoluminescence, doping and heat treatment with controlled partial pressures to identify the phonon sidebands and the origin of the  $I_1^{deep}$  emission line in ZnS<sub>x</sub>Se<sub>1-x</sub> single crystals. The behaviour differs from that of the  $I_1^{deep}$  line and its phonon satellites in the binary compound, because in the ternary compound the Huang–Rhys parameter increases with increasing composition parameter x.

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