

OPTICAL CHARACTERIZATION OF QUATERNARY $\text{Zn}_{1-x-y}\text{Be}_x\text{Mg}_y\text{Se}$ MIXED CRYSTALS

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Abstract

We present an optical characterization of three Bridgman-grown $\text{Zn}_{1-x-y}\text{Be}_x\text{Mg}_y\text{Se}$ mixed crystals in the near-band-edge interband transitions using temperature-dependent photoluminescence (PL), contactless electorelectance (CER), and photorelectance (PR) in the temperature range of 15–400 K and surface photovoltage spectroscopy (SPS) at room temperature. PL spectra at low temperature are characterized by the presence of clearly distinguished features, such as an excitonic line, an edge emission due to radiative recombination of shallow donor-acceptor pairs, and a broad band related to recombination through deep level defects. The peak positions of the excitonic emission lines in PL spectra correspond quite well to the energies of the fundamental transitions determined from CER, PR, and SPS measurements.

1. Introduction

Wide gap II-VI ternary and quaternary solid solutions are currently under intensive investigation for their possible applications in constructing different electrooptical devices operating in wide spectral region from deep ultraviolet (UV) to near-infrared [1–5]. Be-chalcogenide semiconductor alloys have been recently proposed for improving the performance of ZnSe-based blue-green lasers [1, 2]. According to theoretical calculation [6], it is known that due to the large amount of covalent bonding and high cohesive energy, the beryllium-based bonding can be used to enhance the crystal elastic rigidity in II-VI alloys. It is expected that the incorporation of beryllium will lead to bond strengthening within the II-VI lattice [7], and also will increase the energy of stacking-fault formation, thus reducing defect propagation that has been seriously limiting the lifetimes of ZnSe-based devices. Among the Be-based II-VI compound semiconductors, $\text{Zn}_{1-x-y}\text{Be}_x\text{Mg}_y\text{Se}$ solid solutions are of particular interest for their potential application in photodetectors operating in the blue-violet and UV spectral range [3, 8], in constructing blue laser [4] and long-lived white light emitting diodes (LEDs) [5, 9, 10]. Up-to-date, in spite of the potential applications, very little work has been done on the basic optical and luminescence properties of this quaternary compound.

In this paper, we report a detailed study of near band-edge transitions in three $\text{Zn}_{1-x-y}\text{Be}_x\text{Mg}_y\text{Se}$ mixed crystals grown by the modified high pressure Bridgman method with different content of Be and Mg, using temperature-dependent photoluminescence (PL), contactless electorelectance (CER), photorelectance (PR) and room temperature surface photovoltage spectroscopy (SPS). The PL spectra at low temperature consist of a band-edge exciton line and defect related emission bands. The data of PL measurements correspond quite well to results of the near-band-edge transitions determined from CER, PR, and SPS measurements.

2. Experimental

The $\text{Zn}_{1-x-y}\text{Be}_x\text{Mg}_y\text{Se}$ mixed crystals were grown from the melt by the high-pressure Bridgman method [11]. The obtained crystals were cut into several 1–1.5 mm thick plates. X-ray investigations showed that the samples were uniform in composition and exhibited a single sphalerite (zinc-blende (ZB)) phase for $\text{Zn}_{0.88}\text{Be}_{0.06}\text{Mg}_{0.06}\text{Se}$ (sample A) and some trace of a wurtzite phase in $\text{Zn}_{0.80}\text{Be}_{0.14}\text{Mg}_{0.06}\text{Se}$ (sample B) and $\text{Zn}_{0.72}\text{Be}_{0.14}\text{Mg}_{0.14}\text{Se}$ (sample C) mixed crystals. For optical measurements, the samples were mechanically polished using 0.05 μm aluminum-oxide (Al_2O_3) powder and additionally etched in a mixture of $\text{K}_2\text{Cr}_2\text{O}_7\text{:H}_2\text{SO}_4\text{:H}_2\text{O}$ followed by a treatment in CS_2 and 50% NaOH solution [12].

PL spectra were excited using the 325 nm line (~ 50 mW) of a He-Cd laser. The luminescence signals were analyzed by using a Jobin-Yvon “TRIAx 550” spectrometer equipped with a “SIMPHONY” charge coupled device (CCD) camera. An RMC model 22 close-cycle cryogenic refrigerator equipped with a digital thermometer controller was used to control the measurement temperature between 10 and 300 K with a temperature stability of 0.5 K or better. The CER/PR apparatus is described in Ref. 13. In the CER measurements, the ac modulating voltage was 1000 V peak to peak with a frequency of 200 Hz. The mechanically chopped 325-nm radiation (~ 1 mW) of a He-Cd laser at 200 Hz was used as a pumping source for the PR measurements. The temperature-dependent measurements were made between 15 and 300 K for CER and from 300 to 400 K for PR. In the room-temperature SPS measurement, the contact potential difference between the sample and a reference grid electrode was measured in a capacitive manner as a function of the photon energy of the probe beam by holding the grid fixed and chopping the probe beam at 200 Hz [14]. A 150 W xenon arc lamp filtered by a Photon Technology Inc. 0.25 m monochromator provided the monochromatic light. The incident light intensity was maintained at a constant level of $\sim 10^{-5}$ W/cm². A beam splitter was placed in the path of the incident light. The intensity of this radiation was monitored by a power meter and was kept constant by a stepping motor connected to a variable neutral-density filter placed in the path of the incident beam. The induced surface photovoltage on the metal grid was measured with a copper bottom as the ground electrode, using a buffer circuit and a lock-in amplifier.

3. Results and discussion

Figure 1 presents PL spectra measured at 10 K of three $\text{Zn}_{1-x-y}\text{Be}_x\text{Mg}_y\text{Se}$ mixed crystal samples with different Be/Mg content: sample A corresponds to content of 0.06/0.06 (Fig. 1(a)), sample B contains 0.14/0.06 (Fig. 1(b)) and sample C with 0.14/0.14 (Fig. 1(c)). Like other II-VI compounds [15–17], at low temperature, the PL spectra of $\text{Zn}_{1-x-y}\text{Be}_x\text{Mg}_y\text{Se}$ mixed crystals consist of a sharp peak followed by a broad edge-emission feature at the energy about 110 meV lower than the first peak and broad deep level (DL) bands. As shown in Fig. 1, the first peak denoted as exciton line X is located at 2.916 eV for sample A (Fig. 1(a)). This feature exhibits blue-shifted character with increasing of Be/Mg content and positioned at 3.086 eV for sample B (Fig. 1 (b)) and 3.185 eV for sample C (Fig. 1 (c)), respectively. Our results indicated a much faster rate of band gap increase of about 21 meV per mol % for Be in comparison to 11 meV per mol % for Mg. The line broadening for the samples with larger Mg/Zn or Be/Zn ratio can be attributed in part to the alloy scattering effects and also to the poorer crystalline quality of the samples with higher content of Mg or Be. The edge-emission band exhibits a shift towards higher energies with increasing of excitation intensity, so it is due to radiative recombination of shallow donor-acceptor pairs (DAP) [18].

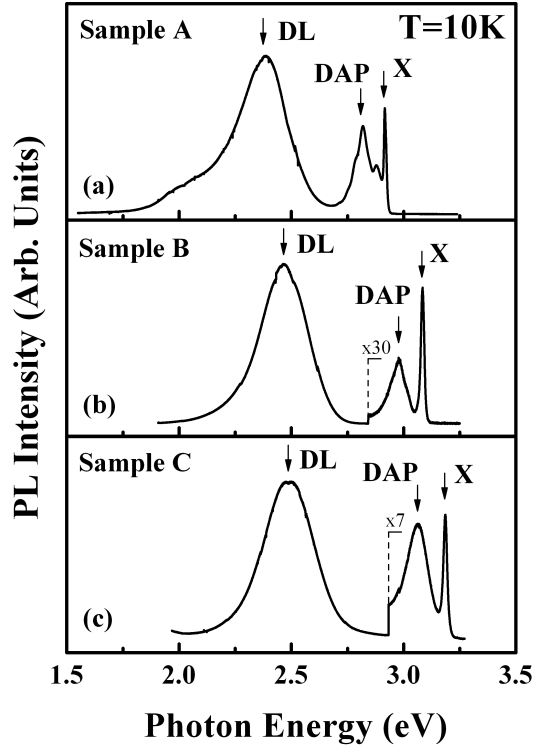
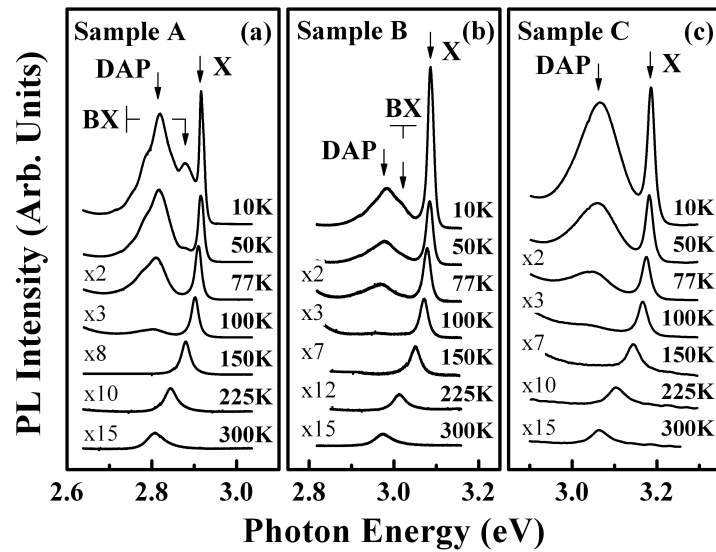


Fig. 1. The PL spectra of $\text{Zn}_{1-x-y}\text{Be}_x\text{Mg}_y\text{Se}$ with different Be and Mg content: (a) $\text{Zn}_{0.88}\text{Be}_{0.06}\text{Mg}_{0.06}\text{Se}$ (sample A), (b) $\text{Zn}_{0.80}\text{Be}_{0.14}\text{Mg}_{0.06}\text{Se}$ (sample B), and (c) $\text{Zn}_{0.72}\text{Be}_{0.14}\text{Mg}_{0.14}\text{Se}$ (sample C), measured at 10 K. The band edge excitonic line, donor-acceptor pair emission and deep levels emission bands are indicated by the arrows.

The DAP feature in PL spectra shows a blue-shift with increase of Mg and Be content and the intensity of this band diminishes rapidly for higher content of Mg (Fig. 1). The physical mechanism of radiative recombination responsible for the green broad band is not known; however, taking into account the positron annihilation experiment and luminescence data for $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ and $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ [19, 20], one can conclude that this broad band can be attributed to cation vacancy or some kind of defect containing a cation vacancy. The relative intensity of this band decreases with increasing Mg or Be content and noticeably decreases after annealing in zinc vapor at a temperature of 1230 K for two days [19, 20].

Figures 2 (a), 2 (b), and 2 (c) show the temperature evolution of the near-band-edge PL spectra for sample A, sample B, and sample C, respectively. The low temperature spectrum of sample A (Fig. 2 (a)) consists of a free exciton line, as was confirmed by measurements of electromodulation reflectance spectra, and the so called edge emission at 2.82 eV with clearly observed LO-phonon replicas ($\hbar\omega_{LO} = 33$ meV). The rather weak but well resolved peak at 2.88 eV is thermally quenched at temperatures higher than about 60 K. This feature labeled as BX is assigned to the radiative recombination of exciton bound to some defect-related center. With increasing Be or Mg content (Figs. 2 (b) and 2 (c)) at low temperature, the intensity of the edge emission lines positioned at 2.98 eV and 3.06 eV, respectively, become smaller in comparison with that in sample A. The BX feature diminishes with increasing of Be and Mg content.



As shown in Fig. 2, the excitonic peak shifts monotonically towards lower energy and broadens with increasing temperature in the range from 15 to 300 K. The shallow DAP feature is completely thermally quenched at temperatures higher than 120 K.

Fig. 2. The PL spectra of $\text{Zn}_{1-x-y}\text{Be}_x\text{Mg}_y\text{Se}$ mixed crystals at several temperatures between 10 and 300 K. The band edge excitonic line, free to band radiative recombination and donor-acceptor pair emission are indicated by the arrows.

Figures 3 (a), 3 (b), and 3 (c) present the temperature evolution of the near-band-edge CER/PR spectra for $\text{Zn}_{1-x-y}\text{Be}_x\text{Mg}_y\text{Se}$ mixed crystal samples A, B, and C, respectively, at 15, 77, 150, 300, and 400 K. As shown in Fig. 3, like for most semiconductors, when the temperature increases, the E_0 transition in CER/PR spectra exhibits a red-shift and lineshape broadening characteristics. The lineshape broadenings of the features are mainly due to the increase of electron (exciton)–phonon interaction effects. The solid curves are least-squares fits to the first derivative Lorentzian lineshape function of the form [21]

$$\frac{\Delta R}{R} = \text{Re} \sum_{j=1} A_j e^{i\Phi_j} (E - E_j + i\Gamma_j)^{-n}, \quad (1)$$

where A_j and Φ_j are the amplitude and phase of the lineshape, E_j and Γ_j are the energy and broadening parameter of the transitions, and the value of n depends on the origin of the transitions. For the first-derivative functional form, $n = 2$ is appropriate for excitonic transitions. The CER spectra at 15 K consist of two distinct features, denoted as $E_0^{n=1}$ and $E_0^{n=2}$, and indicated by vertical arrows, where $E_0^{n=1}$ and $E_0^{n=2}$ are the ground state and the first excited state of the band-edge excitonic transitions. These two excitonic features are not clearly resolved at temperatures higher than 150 K. The transition energies of $E_0^{n=1}$ and $E_0^{n=2}$ at 15 K are determined to be 2.925 ± 0.003 and 2.942 ± 0.005 eV, 3.096 ± 0.003 and 3.119 ± 0.005 eV, and 3.195 ± 0.003 and 3.220 ± 0.005 eV for samples A, B, and C, respectively. Using the hydrogenic model, the binding energy of the band edge exciton is determined to be 23 ± 8 meV, 31 ± 8 meV, and 33 ± 8 meV, respectively. These values are compatible with that obtained from the relation for exciton binding energy of $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ thin films [22]. At room temperature (RT), the values of excitonic transition energies of CER measurements are matched with the results determined from PR. The values of band-edge excitonic transitions at RT for samples A, B, and C correspond, respectively, to 2.816 ± 0.005 eV, 2.987 ± 0.005 eV, and 3.073 ± 0.005 eV.

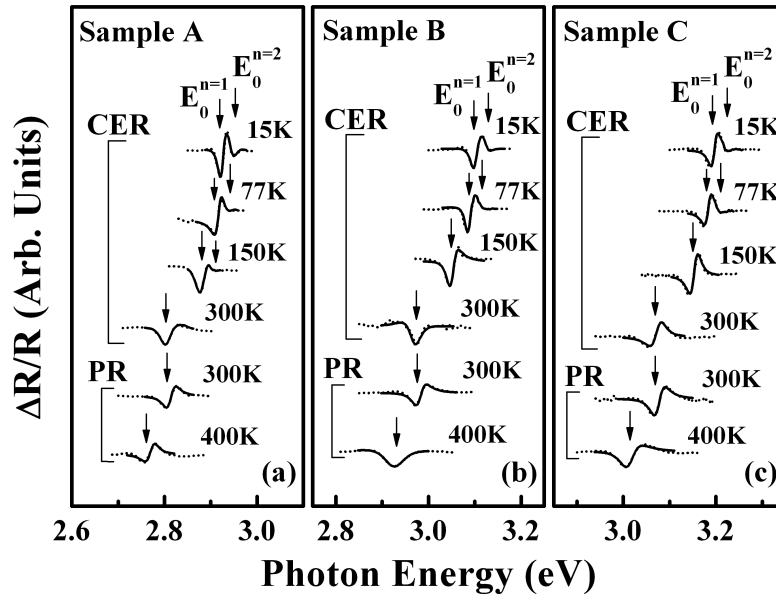


Fig. 3. Experimental CER/PR spectra (dot curves) near band-edge excitonic transitions of three mixed crystal samples: (a) $\text{Zn}_{0.88}\text{Be}_{0.06}\text{Mg}_{0.06}\text{Se}$ (sample A), (b) $\text{Zn}_{0.80}\text{Be}_{0.14}\text{Mg}_{0.06}\text{Se}$ (sample B), and (c) $\text{Zn}_{0.72}\text{Be}_{0.014}\text{Mg}_{0.14}\text{Se}$ (sample C) at 15, 77, 150, 300, and 400 K. The solid lines are least-squares fits to Eq (1). The obtained values of the transition energies are indicated by the arrows.

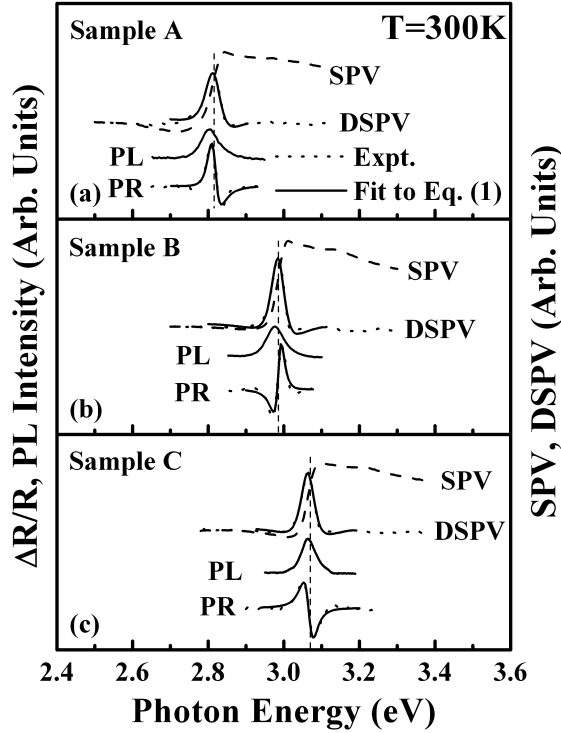


Fig. 4. Room temperature experimental SPS, PL, and PR spectra as well as calculated $(\Delta V_{SPS}/\Delta E)/V_{SPS}$ for $Zn_{1-x-y}Be_xMg_ySe$ with different x and y content: (a) $x=0.06$ and $y=0.06$, (b) $x=0.14$ and $y=0.06$, and (c) $x=0.06$ and $y=0.26$, respectively. The full curves in PR and DSPV spectra are least-squares fits to Eq. (1).

A proper surface treatment of the sample must be performed to eliminate the damaged layer formed on the surface caused by mechanical polishing. The surface photovoltage spectroscopy (SPS) technique can be utilized to check the condition of the surface layer. The detailed procedure of SPS has been described in [23]. Figure 4 shows the surface photovoltage (SPV), and the first derivative of the SPV (DSPV) and PR spectra near the band edge at 300 K for three $Zn_{1-x-y}Be_xMg_ySe$ mixed crystal samples with different containing of Be and Mg.

As shown in Fig. 3, the typical SPS spectra (dashed curves) have a step-like shape characteristic of excitonic transitions, in the spectral range around the fundamental transition. In order to determine the values of the transition energies, we have numerically calculated the DSPV signal with respect to photon energy $(\Delta V_{SPS}/\Delta E)$ and then divided this quantity by the value of the photovoltage itself V_{SPS} . The ratio $(\Delta V_{SPS}/\Delta E)/V_{SPS}$ is proportional to $(\Delta\alpha/\Delta E)/\alpha$ [24], where α is the absorption coefficient. The obtained curves are displayed by the dotted lines in Fig. 4. The DSPV data were fitted to Eq. (1), which is appropriate for excitonic transitions. The band-edge excitonic transition energies determined from SPS measurements corresponds quite well to that obtained from CER/PR and slightly higher in contrast to the position of PL excitonic features that is in accordance with the Stokes shift partly attributed to a relaxation of the carriers into defect or surface states.

4. Summary

In summary, the investigations of the near band-edge transitions of high-pressure Bridgman-grown $Zn_{1-x-y}Be_xMg_ySe$ mixed crystal samples have been carried out by temperature-dependent PL, CER/PR, and SPS. PL spectra at low temperatures consist of an exciton line, a broader emission band due to recombination of shallow donor-acceptor pairs, and a broad band related to recombination through deep level defects. Interband transitions determined from CER/PR have been observed in the SPV spectra. The peak positions of the excitonic emission lines in PL spectra correspond quite well to the energies of the fundamental transitions determined from CER, PR, and SPV. The band edge excitonic transition features show a blue-shift in the transition energy and a broadened linewidth with the increase of Be/Mg contents. Our results indicated a much faster rate of band gap increase of about 21 meV per mol % for Be in comparison to 11 meV per mol % for Mg.

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