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OPTICAL AND STRUCTURAL PROPERTIES OF $Zn_{1-x}Be_xSe$ MIXED CRYSTALS

F. FIRSZT, S. ŁĘGOWSKI, H. MĘCZYŃSKA, J. SZATKOWSKI, J. ZAKRZEWSKI

Institute of Physics, N. Copernicus University
Grudziądzka 5/7, 87-100 Toruń, Poland

W. PASZKOWICZ, J. DOMAGAŁA

Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warsaw, Poland

AND M. MARCZAK

The State Mint, Pereca 21, 00-958 Warsaw, Poland

Optical and structural properties of $Zn_{1-x}Be_xSe$ bulk crystals in the range of composition $0 \leq x \leq 0.41$ have been studied. These crystals were grown by Bridgman method under an argon overpressure. Transmission, absorption, photoluminescence and photoacoustic spectra as a function of composition were investigated. It has been found that the crystal structure is of sphalerite type. The crystal quality increases when the crystallization process of the same boule is performed more than once. In the investigated composition range the lattice constant decreases and the energy gap increases with increasing beryllium content. From photoluminescence measurements the excitonic energy gap about 3.64 eV at 40 K was estimated for the highest obtained Be concentration ($x = 0.41$).

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Mixed crystals of wide gap II–VI compounds with Be chalcogenides are of particular interest because of their potential applications in constructing visible and UV lasers. The $Zn_{1-x}Be_xSe$ has a much higher degree of covalent bonding as compared to other (more ionic) wide gap II–VI compounds which modifies its mechanical properties [1]. This is expected to result in considerable lattice rigidity, a very important factor for reducing defects migration and multiplication. Until now, the published papers were concerned in thin films [2] but the fundamental properties of mixed $Zn_{1-x}Be_xSe$ bulk crystals remain unknown for the wide range of composition. Some preliminary results for $0 \leq x \leq 0.17$ have been recently published in Ref. [3].

$Zn_{1-x}Be_xSe$ crystals were grown by Bridgman method under an argon overpressure in the range of composition $0 \leq x \leq 0.41$ using a powder mixture of

ZnSe (6N), Be (2N) and Se (6N) as a starting material. Some crystals were grown from nonstoichiometric material, i.e., without Se. Typical dimensions of crystals obtained by this method were 10 mm in diameter and 40–50 mm in length. The crystals were cut into 1–1.5 mm thick plates and mechanically polished. The composition was determined with chemical analysis using an emission spectrometer with plasma excitation ICP2070. The phase analysis was performed with a standard X-ray Bragg–Brentano powder diffractometer and Ni-filtered Cu K_α radiation. Photoluminescence spectra were measured from 40 K up to room temperature (RT) in the energy range from 1.6 eV to 3.7 eV. The electron concentration, Hall mobility and conductivity were determined by the van der Pauw method in the temperature range from liquid nitrogen up to RT. For Hall measurements, indium contacts were alloyed in nitrogen atmosphere.

All investigated $Zn_{1-x}Be_xSe$ samples exhibit a sphalerite structure. The lattice constant decreases linearly with x [3]. The applied growth conditions and further annealing in zinc vapour are observed as having a strong influence on structural, mechanical and optical properties of the crystals. High-resolution diffraction indicates that repeating the crystallization process of the same boule more than once leads to a better homogeneity of the crystal as well as reduces or suppresses the presence of mosaic blocks.

As-grown $Zn_{1-x}Be_xSe$ samples exhibit a very high electrical resistivity. Annealing in zinc vapour at 1230 K improves their luminescence properties and for low beryllium content reduces the electric resistivity noticeably. For ZnSe crystals annealed in zinc vapour the resistivity is equal to about 0.1 Ω cm. With increasing Be content the resistivity increases very rapidly: $\rho = 1$ Ω cm for $x = 0.04$, $\rho = 30$ kΩ cm for $x = 0.09$ and ρ of the order MΩ cm for $x = 0.17$ in RT. This increase in resistivity with increasing Be content is much faster than in the case of $Zn_{1-x}Mg_xSe$ mixed crystals reported in Ref. [4].

The photoluminescence (PL) spectra of $Zn_{1-x}Be_xSe$ crystals for different compositions are presented in Fig. 1 ($x = 0.04$, $x = 0.17$ as-grown; $x = 0.26$, $x = 0.41$ annealed samples). PL spectra for as-grown crystals with a low Be concentration ($x < 0.17$) consist of near-band-edge (exciton), edge and deep-levels emission bands. The main features of PL spectra of $Zn_{1-x}Be_xSe$ samples are generally similar. Comparing the spectra of $Zn_{1-x}Be_xSe$ samples with different values of x with PL spectrum of pure ZnSe we conclude that the highest photon energy emission line observed in all investigated $Zn_{1-x}Be_xSe$ samples is associated with recombination of free excitons. With increasing Be content, the microscopic fluctuations of composition cause smearing of the band edges resulting in an observed broadening of exciton lines. This broadening, however, is lower than the analogous broadening of exciton luminescence lines in $Zn_{1-x}Mg_xSe$ solid solutions [5]. Annealing the as-grown samples with Be concentration $x < 0.3$ causes an increase in the intensity ratio of edge emission to deep levels one. It should be also noted that for samples with high beryllium content $x > 0.2$, the exciton line, not observed in as-grown samples, appears after annealing.

Photoacoustic spectra of the as-grown and annealed samples were measured using an open cell with continuous wave excitation and piezoelectric transducer. The observed photoacoustic (PA) curves for the as-grown samples exhibit

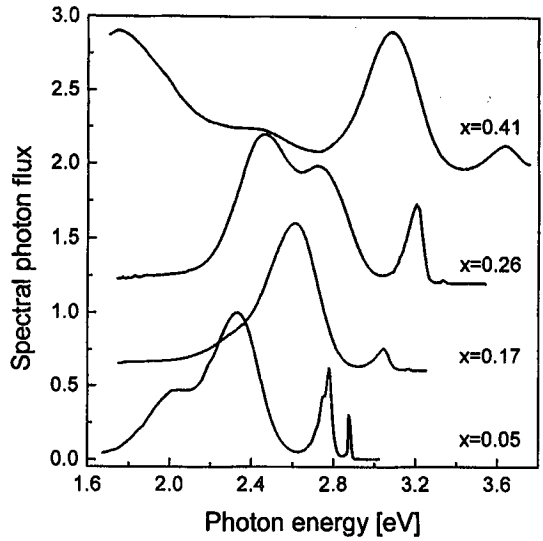

Fig. 1. Photoluminescence spectra (intensities in arbitrary units) measured at $T = 40$ K of $Zn_{1-x}Be_xSe$ for different compositions ($x = 0.04$, $x = 0.17$ as-grown; $x = 0.26$, $x = 0.41$ annealed samples).

well-expressed changes of the slope at points from which the energy gap could be determined. It was observed that the position of these points is frequency dependent. For frequencies less than 100 Hz the sub-band structure is observed which disappears when the frequency increases. For the annealed samples a noticeable decrease in low frequencies photoacoustic signal was observed at photon energies below the band gap. These results correlate with photoluminescence spectra indicating that the annealing of $Zn_{1-x}Be_xSe$ in zinc vapour causes a decrease in the concentration of defect centre and thus an increase in the crystal quality.

The Jackson–Amer model of the piezoelectrically detected photoacoustic effect was applied to analyse the obtained spectra. In order to determine the optical band gap energy the dependence of absorption coefficient on energy above the fundamental absorption edge has to be considered. The absorption coefficient does not depend on PA signal in the simple way. The appropriate formula was derived from the theory assuming a thermally thin and optically thick sample.

The dependence of exciton transition energy at $T = 40$ K determined from PL spectra and energy gap derived from photoacoustic spectra at RT on beryllium content are presented in Fig. 2. In the investigated composition range the energy gap increases almost linearly with increasing beryllium content. The experimental data give a variation of 20 meV per percent of Be content. From photoluminescence measurements the energy gap about 3.64 eV was estimated for the highest obtained Be concentration ($x = 0.41$).

Quite recently, the quaternary $Zn_{1-x-y}Be_xMg_ySe$ crystal of the sphalerite structure with the lattice constant ($a = 5.667$ Å) being nearly equal to that of ZnSe and energy gap 2.97 eV was also grown. Assuming the linear dependence

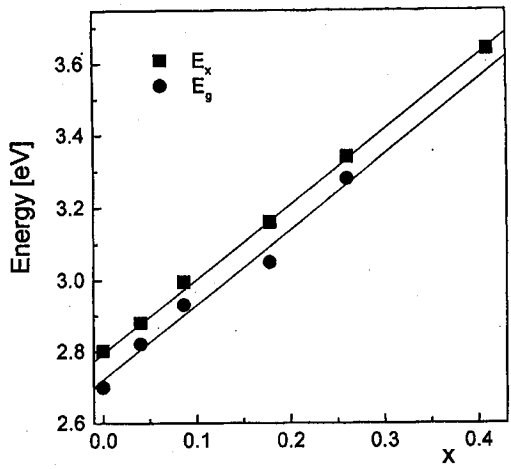

Fig. 2. The dependence of exciton transition energy (E_x) obtained from PL spectra at $T = 40$ K and energy gap (E_g) derived from photoacoustic spectra at RT in $Zn_{1-x}Be_xSe$ on composition.

of lattice constant and band gap energy on composition in ternary $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ compounds, the calculated concentrations of Be and Mg are: $x = 0.024$ and $y = 0.08$. These values are almost equal to the real values: $x = 0.03$ and $y = 0.10$ obtained from the chemical analysis.

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