Conference paper

OPTO-ELECTRONICS REVIEW 7(2), 87–92 (1999)

# Photoluminescence and structural properties of selected wide-gap II–VI solid solutions*

F. FIRSZT[1], S. ŁĘGOWSKI[1], H. MĘCZYŃSKA[1], B. SEKULSKA[1], J. SZATKOWSKI[1*], W. PASZKOWICZ[2], and M. MARCZAK[3]

[1]Institute of Physics, N. Copernicus University, 5/7 Grudziądzka Str., 87-100 Toruń, Poland
[2]Institute of Physics, Academy of Sciences, 32/46 Al. Lotników, 02-668 Warsaw, Poland
[3]The State Mint, 21 Pereca Str., 00-958 Warsaw, Poland

*This work presents results of investigations of photoluminescence and structural properties of ternary $Zn_{1-x}Be_xSe$, $Cd_{1-x}Mg_xSe$, $Zn_{1-x}Mg_xSe$ and quaternary $Cd_{1-x-y}Mg_xZn_ySe$, $Zn_{1-x-y}Be_xMg_ySe$, $Zn_{1-x}Mg_xSe_{1-y}S_y$ mixed crystals. These crystals were grown from the melt by the high-pressure Bridgman method. $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Sr_xSe$ were also obtained by annealing of ZnSe crystals in evacuated quartz ampoules containing Mg or Sr metal. It has been found that admixing of Mg into ZnSe favours the formation of wurtzite $Zn_{1-x}Mg_xSe$ while Be – sphalerite $Zn_{1-x}Be_xSe$ structures. Low temperature (40 K) photoluminescence spectra consist of exciton, edge and deep levels emission bands. For most of investigated crystals the emission corresponding to the highest photon energy line in luminescence spectrum is observed up to room temperature.*

**Keywords:** II–VI mixed crystals, photoluminescence, chalcogenides, semiconductors, crystal structure, X-ray diffraction, crystal growth

## 1. Introduction

In the last few years there is an increasing interest in wide gap ternary and quaternary II–VI semiconductor solid solutions for their applications in optoelectronics, such as short wavelength light emitters and photodetectors [1,2]. Up to date, the blue-green II–VI laser structures based on ZnSe and ZnCdSe are grown mainly on GaAs.

Lack of high quality ZnSe bulk materials has prevented realising the superiority of ZnSe substrates over GaAs. New materials like $Zn_{1-x}Mg_xSe_{1-y}S_y$ and $Zn_{1-x-y}Mg_xBe_ySe$ can be used as alternative substrates due to their lattice matching to ZnSe. It is possible to change electronic properties, lattice parameters and band gap energies by adjusting the composition of mixed crystals. The change of band gap energy gives the desired optical properties and the lattice constant – the possibility of lattice matching to different compounds. Ternary $Zn_{1-x}Mg_xSe$ and quaternary $Zn_{1-x}Mg_xSe_{1-y}S_y$ compounds have been al-

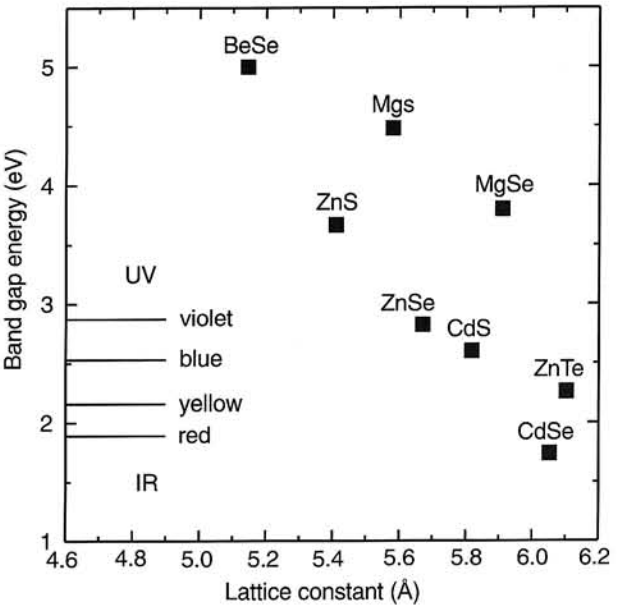


Fig. 1. Band gap energies plotted versus lattice constant for selected II–VI compounds.

* e-mail: szatek@phys.uni.torun.pl

* The paper presented there appears in SPIE Proceedings Vol. 3724, pp. 234–238.

ready used in construction of some optoelectronic devices such as lasers and electroluminescent diodes.

For II–VI compounds one can obtain crystals with emission in entire visible and UV range of the spectrum (Fig. 1). There is a lot of work on thin films of wide gap II–VI compounds used for construction of optoelectronic devices, but the basic properties of bulk II–VI mixed crystals (e.g., structure, thermal properties, mechanical properties) remain unknown.

II–VI solid solutions crystallise in two basic structures, sphalerite and wurtzite. Because of the binary end compounds possess different structures: ZnSe, BeSe – zinc blende (ZB), CdSe, ZnS – wurtzite (W), MgSe, CaSe, SrSe – rock salt (NaCl), phase transitions, phase separations and crystal defects can occur in mixed crystals. Systematic investigations of the influence of growth conditions and further thermal treatment on crystal structure and defects are very important and necessary [3–6,11–13].

This paper deals with experimental study of structural and luminescent properties of various II–VI mixed crystals grown from the melt and layers obtained by thermal treatment of ZnSe crystals in Mg or Sr vapours.

## 2. Sample preparation and experimental procedure

The bulk crystals were grown from the melt by the high-pressure Bridgman method under argon overpressure [6]. The growth conditions and starting materials are listed in Table 1.

The obtained crystals of diameter (d) 8–10 mm and length (l) 40–50 mm were cut into about 1 mm thick plates, mechanically polished and chemically etched. The crystals with Mg concentration larger than about 50% are unstable in the air due to high hygroscopicity of MgSe.

Mixed crystals $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Sr_xSe$ were also obtained by thermal treatment of ZnSe plates (1 mm thick) in evacuated quartz ampoules containing Mg or Sr metal. The annealing process was carried out for 24–48 h in the temperature range from 1050 to 1200 K, followed by rapid quenching in water.

Phase analysis was performed in a step scanning mode with the standard X-ray Bragg-Brentano diffractometer and Ni-filtered Cu Kα radiation. The composition of samples was determined by electron microprobe and ICP chemical analysis. Photoluminescence (PL) spectra were measured in the temperature range from 40 K up to room temperature using a Zeiss monochromator followed by photomultiplier with S-20 photocathode spectral response and He-Cd laser (325 nm) as the excitation source.

## 3. Results and discussion

Measurements of luminescence spectra at different temperatures combined with X-ray measurements and analysis of composition enabled us to determine the dependence of lattice constants and energy gaps on composition for $Zn_{1-x}Be_xSe$ ($0 \le x \le 0.41$), $Cd_{1-x}Mg_xSe$ ($0 \le x \le 0.55$) and $Zn_{1-x}Mg_xSe$ ($0 \le x \le 0.61$). The excitonic energy gap was determined from the position of the free exciton emission line.

The structure of material is correlated to the ionicity of chemical bonds. The Phillips ionicity parameter for MgSe is $f_i = 0.790$ which is very close to the critical value $f_i = 0.786$ for transition between four-fold and six-fold coordinated crystal structures. MgSe can exist in wurtzite and rock salt structures [7]. $Zn_{1-x}Mg_xSe$ solid solution crystallises in sphalerite structure for x lower than about 0.18 and in wurtzite for higher magnesium concentrations. Polytypism is observed mainly for unannealed samples at the phase transition region. Results of investi-

Table 1. The growth conditions and starting mixtures for selected II–VI solid solutions. The last column presents the maximum value of x obtained for our particular crystals.

| Material | Temperature (K) | Starting mixture | Maximum x value |
|---|---|---|---|
| $Cd_{1-x}Mg_xSe$ | 1600–1650 | CdSe+Mg | 0.55 |
| $Zn_{1-x}Mg_xSe$ | 1840–1860 | ZnSe+Mg, ZnSe+Mg+Se | 0.61 |
| $Zn_{1-x}Be_xSe$ | 1820–1850 | ZnSe+Be, ZnSe+Be+Se | 0.41 |
| $Cd_{1-x-y}Mg_xZn_ySe$ | 1820 | CdSe+ZnSe+Mg+Se | ? |
| $Zn_{1-x-y}Be_xMg_ySe$ | 1850 | ZnSe+Mg+Be+Se | ? |
| $Zn_{1-x}Mg_xSe_{1-y}S_y$ | 1970 | ZnSe+ZnS+Mg | ? |

 

gations of high-resolution X-ray diffraction and cathodoluminescence were already published and details of polytypes occurrence near the phase transition were discussed [6,8]. In sphalerite structure a large density of {111} twins was observed. Their origin (in analogy to "pure" ZnSe) may be closely correlated with the solid-solid phase transition taking place below the melting point. The crystals with $x > 0.25$ are of single wurtzite 2H type. Noticeable increase of Mg concentration along the growth direction was observed. The Mg content is always lower at the tip and higher at the end of the crystal boule.

The colour of the obtained $Zn_{1-x}Mg_xSe$ crystals changes from yellow through yellow-green towards almost colourless with increasing x value. The photoluminescence spectra of $Zn_{1-x}Mg_xSe$ crystals, measured at 40 K, consist of near-band-edge (exciton), edge and deep levels emission bands. In the region of sphalerite-wurtzite phase transition the broadening of photoluminescence bands due to compositional and structural disorder is observed. The details of temperature evolution and dependence of photoluminescence spectra on composition were already published [6]. For $Zn_{1-x}Mg_xSe$ the dependence of excitonic energy gap on composition (Fig. 2a) is almost linear for both structures. At $x \approx 0.18$ there is a discontinuity connected with the phase transition.

$Zn_{1-x}Mg_xSe$ layers obtained by thermal diffusion of Mg metal into ZnSe crystals are of good quality. This is demonstrated by the presence of blue-violet emission at room temperature. Photoluminescence spectra at low temperatures are dominated by narrow blue and UV emission bands originated form radiative recombination of excitons and shallow donor--acceptor pairs. The efficiency of radiative recombination has been found to be higher than the efficiency of blue PL in ZnSe reference samples [9].

BeSe has a higher degree of covalent bonding ($f_i$ = 0.261) as compared to other wide gap II–VI compounds. For this reason $Zn_{1-x}Be_xSe$ is expected to have larger lattice rigidity than ZnSe. This is very important for reducing the defect migration and multiplication in laser structures [10]. A noticeable increase in microhardness with increasing Be content in $Zn_{1-x}Be_xSe$ mixed crystals was already reported [11,12]. The lattice hardening is found to depend strongly on growth conditions. The improvement in crystallographic structure by repeating the crystallisation process more than once, results in slight decrease in microhardness (e.g., from 2.37 GPa to 1.54 GPa for $Zn_{0.83}Be_{0.17}Se$ crystal for which the crystallisation process was performed once and four times, respectively).

The beryllium concentration decreases along the growth direction of the crystal. For crystals with low Be content the gradient of berylium concentration is very small, but is noticeable for crystal with $x \approx 0.4$ ($\Delta x/\Delta l = -0.02$ cm$^{-1}$). The $Zn_{1-x}Be_xSe$ solid solutions form sphalerite structure with lattice constant decreasing with increasing x value, according to the formula: $a(x) = 5.67 - 0.52x$ in Å. The crystals quality can be improved when the crystallisation process is per-

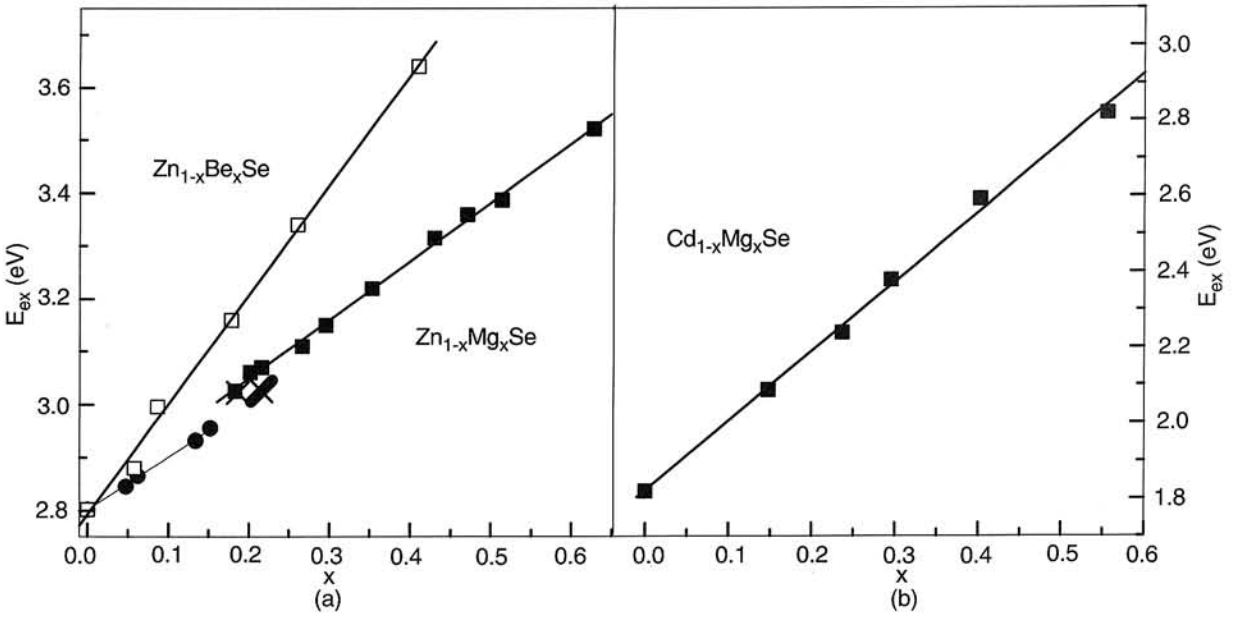


Fig. 2. The dependence of excitonic energy gap on composition determined from PL spectra at T = 40 K in: (a) – $Zn_{1-x}Mg_xSe$ (solid circles – sphalerite structure, solid squares – wurtzite structure, crosses – 4H polytype), $Zn_{1-x}Be_xSe$ – open squares and (b) – $Zn_{1-x}Mg_xSe$.

formed more than once. In such a case the sizes of grains increase from sub-millimetre scale up to millimetre one. The crystals are transparent with colour changing from yellow for x = 0 to colourless for x = 0.41. The photoluminescence spectra depend on growth conditions and post-growth thermal treatment. Annealing in liquid zinc causes an increase in the intensity ratio of near band edge emission to deep levels emission bands. For crystals with high Be content, the exciton emission line, not observed in as-grown samples, appears after annealing in zinc vapour. The broadening of photoluminescence bands due to statistical fluctuation of composition was also observed in these crystals [12], however, the broadening of exciton emission lines is smaller than that in $Zn_{1-x}Mg_xSe$. The dependence of the excitonic energy gap on composition is presented in Fig. 2(a).

$Cd_{1-x}Mg_xSe$ solid solution forms hexagonal structure in the investigated range of composition ($0 \le x \le 0.55$) with the lattice constant decreasing with increasing x value. The gradient of magnesium concentration $\Delta x/\Delta l$ for $Cd_{0.7}Mg_{0.3}Se$ crystal is about 0.01 $cm^{-1}$. The samples with Mg concentration x larger than about 0.5 are unstable in moist air. Their colour changes from black (x = 0) through purple to yellow (x = 0.55). The photoluminescence spectra at 40 K consist of exciton line, edge emission and deep levels bands. The edge emission was not observed for samples with x > 0.3. The position of the highest photon energy line at T = 40 K varies from 1.82 eV for CdSe up to 2.82 eV for $Cd_{0.45}Mg_{0.55}Se$ [Fig. 2(b)]. This line is observed up to room temperature. Some details concerning electrical and optical parameters of these crystals have been already published [13].

Calcium and strontium selenides exhibit very high ionicity of chemical bonds; $f_i$(CaSe) = 0.90 and $f_i$(SrSe) = 0.92. An attempt to obtain homogeneous solid solutions of $Zn_{1-x}Ca_xSe$ (from ZnSe + Ca or ZnSe + CaSe), $Zn_{1-x}Sr_xSe$ (from ZnSe + Sr) and $Cd_{1-x}Be_xSe$ (from CdSe + Be) by the described Bridgman method has failed. The thermal treatment of ZnSe crystals in Ca + Za vapour was also unsuccessful.

In the case of $Zn_{1-x}Ca_xSe$, $Zn_{1-x}Sr_xSe$, $Cd_{1-x}Be_xSe$ it has been observed that the applied growth method prefers creation of binary compounds rather than uniform ternary alloys. After annealing of $Zn_{1-x}Ca_xSe$ (prepared by the used Bridgman method) in vacuum at the temperature about 2000 K, almost perfect "pure" CaSe was obtained as thin needles in the tungsten crucible.

Thin layers prepared by thermal annealing of ZnSe plates in Sr vapour have shown a shift of all

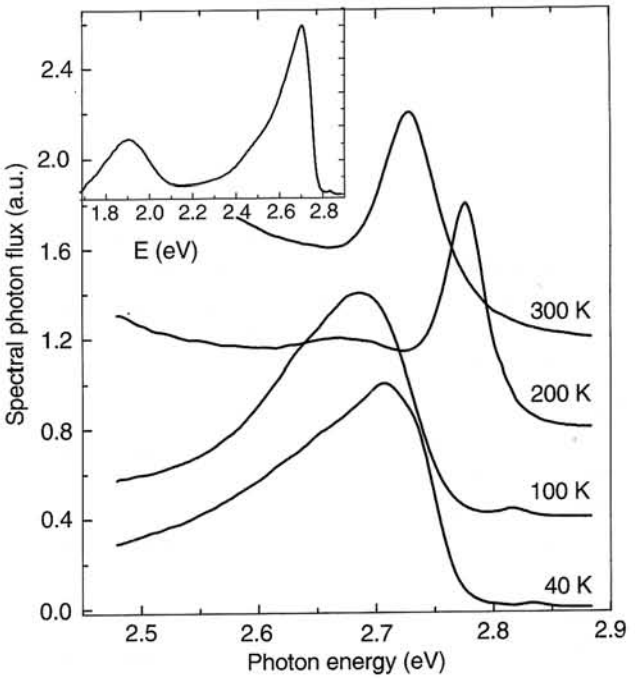


Fig. 3. The temperature evolution of the high energy part of $Zn_{1-x}Sr_xSe$ photoluminescence spectrum. The inset shows the whole emmission spectrum at T = 40 K.

photoluminescence bands towards higher photon energies in comparison with PL of "pure" ZnSe indicating that $Zn_{1-x}Sr_xSe$ mixed crystal surface layer was obtained. Figure 3 presents the temperature evolution of the high-energy part of the photoluminescence spectrum of $Zn_{1-x}Sr_xSe$ layer. The edge emission is completely thermally quenched at temperatures higher than about 200 K but the highest photon energy line is observed up to room temperature.

For $Zn_{1-x}Mg_xSe_{1-y}S_y$ solid solution the excitonic energy gap 3.15 eV at 40 K has been estimated from photoluminescence measurements. The X-ray diffraction showed the wurtzite structure (a = 3.993 Å, c = 6.537 Å) and high crystallographic quality of the grown material. The calculated hypothetical cubic lattice constant is equal to 5.652 Å that is very close to that of GaAs (5.654 Å). Assuming the linear dependence of lattice constants and band gap energies on composition for ternary $Zn_{1-x}Mg_xSe$ and $ZnSe_{1-x}S_x$ alloys the calculated concentration of Mg and S are x = 0.15 and y = 0.19.

$Cd_{1-x-y}Zn_xMg_ySe$ mixed crystal of wurtzite structure were grown from CdSe (50%), ZnSe (20%) and Mg (30%) starting mixture. The real composition of the crystal was: x = 0.25 and y = 0.36 measured by chemical analysis. The photoluminescence spectrum of $Cd_{0.39}Zn_{0.25}Mg_{0.36}Se$ crystal is presented in Fig. 4.

 

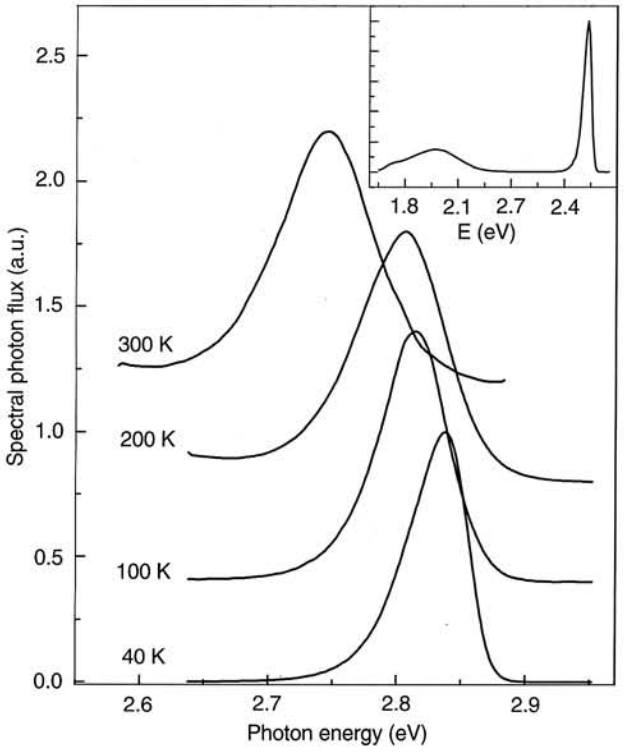


Fig. 4. The temperature evolution of the high energy part of $Cd_{0.39}Zn_{0.25}Mg_{0.36}Se$ photoluminescence spectrum. The inset shows the whole emission spectrum at T = 40 K.

The highest photon energy emission line is observed up to room temperature.

The $Zn_{0.87}Be_{0.03}Mg_{0.1}Se$ crystal of sphalerite structure and the lattice constant nearly equal to that of ZnSe with the energy gap of 2.97 eV, was also grown. The photoluminescence spectrum of this crystal is generally similar to that of $Zn_{1-x}Be_xSe$ and was presented in [12].

For quaternary compounds the structure and composition was measured only for some selected plates from the crystals and detailed systematic investigations are necessary.

## 4. Conclusions

Mixed crystals of wide gap II–VI binary compounds with Mg, Be and Sr chalcogenides have been obtained. These compounds are very interesting because of their potential applications in optoelectronic devices as well as because of their basic physical properties. Three of them ($Zn_{1-x}Be_xSe$, $Cd_{1-x}Mg_xSe$, $Zn_{1-x}Mg_xSe$) have been obtained in wide range of composition. It has been found that admixing of Mg into ZnSe favours the formation of wurtzite $Zn_{1-x}Mg_xSe$ while Be – sphalerite $Zn_{1-x}Be_xSe$ structures. The photoluminescence spectra of these crystals are generally similar and consist of exciton, edge, and deep levels emission bands. The broadening of photoluminescence bands due to compositional disorder and in the case of $Zn_{1-x}Mg_xSe$ also structural disorder is always observed.

Some quaternary crystals such as $Zn_{1-x-y}Mg_xBe_ySe$, $Cd_{1-x-y}Zn_xMg_ySe$ and $Zn_{1-x}Mg_xSe_{1-y}S_y$ were also grown but these materials need further systematic investigations.

## Acknowledgements

This work was partly supported by the State Council of Science through the grant No 2 PO3B 127 14.

## References

1. A. Nurmikko and R. Gunshor, "Blue and green semiconductors lasers: a status report," *Semicond. Sci. Technol.* **12**, 1337–1347 (1997).
2. A. Waag, Th. Litz, F. Fisher, H.J. Lugauer, T. Baron, K. Schüll, U. Zehnder, T. Gerchard, U. Lunz, M. Keim, G. Reuscher, and G. Landwehr, "Novell beryllium containing II–VI compounds: basic properties and potential applications," *J. Cryst. Growth* **184/185**, 1–10 (1998).
3. D. Shin, C. Kim, H. Jang, S. Choe, D. Kim, C. Yoon, and W. Kim, "Growth and characterisation of $Mg_xCd_{1-x}Se$ mixed crystals," *J. Cryst. Growth* **177**, 167–170 (1997).
4. S. Park, H. Song, W. Kim, H. Kim, M. Jin, C. Kim, and C. Yoon, "Photoluminescence properties of $Mg_xZn_{1-x}Se$ single crystals," *J. Appl. Phys.* **83**, 3429–3431 (1998).
5. S. Park, H. Song, D. Kim, H. Kim, M. Jim, C Kim, C. Yoon, and W. Kim, "Structural and optical properties of $Mg_xZn_{1-x}Se$ and $Mg_xZn_{1-x}Se$: $Co^{2+}$ single crystals", *Semicond. Sci. Technol.* **13**, 1011–1015 (1998).
6. F. Firszt, H. Męczyńska, S. Łęgowski, J. Szatkowski, U. Falke, M. Hietschold, W. Paszkowicz, and P. Dłużewski, "Growth and characterisation of $Zn_{1-x}Mg_xSe$ mixed crystals," *Proc. SPIE* **3178**, 205–212 (1997).
7. J. A. Van Vechten, "Quantum dielectric theory of electronegativity in covalent systems," *Phys. Rev.* **187**, 1007–1020, (1969).
8. U. Falke, A. Cichoś, F. Firszt, H. Męczyńska, P. Dłużewski, W. Paszkowicz, J. Lenzner, and M. Hietschold, "Structural investigations of polytypes in $Zn_{1-x}Mg_xSe$ by transmission electron

microscopy and cathodoluminescence," *J. Cryst. Growth* **184/185**, 1015–1020 (1998).

9. F. Firszt, "Radiative recombination processes in $Zn_{1-x}Mg_xSe$ layers," *Semicond. Sci. Technol.* **12**, 272–279 (1997).
10. Ch. Vèrié, "Beryllium substitution-mediated covalency engineering of II–VI alloys for lattice elastic rigidity reinforcement," *J. Cryst. Growth* **184/185**, 1061–1066 (1998).
11. W. Paszkowicz, K. Godwod, J. Domagała, F. Firszt, J. Szatkowski, H. Męczyńska, and S. Łęgowski, "Lattice parameter, microhardness and energy gap of bulk $Zn_{1-x}Be_xSe$ alloys," *Solid State Commun.* **107**, 735–740 (1998).
12. F. Firszt, H. Męczyńska, S. Łęgowski, J. Szatkowski, W. Paszkowicz, J. Domagała, M. Kozielski, M. Szybowicz, and M. Marczak, "Structure, luminescence and lattice hardening of Be-rich $Zn_{1-x}Be_xSe$ bulk crystals," *Proc. 2nd International Symposium on Blue Lasers and Light Emitting Diodes,* Chiba, Japan, 335–338 (1998).
13. F. Firszt, S. Łęgowski, H. Męczyńska, J. Szatkowski, W. Paszkowicz, and M. Marczak, "Growth and characterisation of $Cd_{1-x}Mg_xSe$ mixed crystals," *J. Cryst. Growth* **184/185**, 1053–1056 (1998).

 