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Study of $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ semiconducting crystals by Raman scattering*

M. SZYBOWICZ[1], M. KOZIELSKI[1*], F. FIRSZT[2], S. ŁĘGOWSKI[2], H. MĘCZYŃSKA[2], J. SZATKOWSKI[2], W. PASZKOWICZ[3]

[1]Institute of Physics, Poznań University of Technology, 3 Piotrowo Str., 60-965 Poznań, Poland
[2]Institute of Physics, N. Copernicus University, 5/7 Grudziądzka Str., 87-100 Toruń, Poland
[3]Institute of Physics, Polish Academy of Science, 32/46 Al. Lotników, 02-668 Warszawa, Poland

Wide gap II–VI mixed crystals containing Mg and Be are recently studied extensively for their application in constructing blue-green laser diodes. This work deals with experimental study of optical modes in $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ semiconductors using Raman scattering method.

Measurements have been performed at room and liquid nitrogen temperatures for $Zn_{1-x}Mg_xSe$ crystals with Mg content in the range $0 < x < 0.34$ and for $Zn_{1-x}Be_xSe$ with Be content in the range $0 < x < 0.26$. From polarised Raman spectra the longitudinal (LO) and the transverse (TO) optical mode, corresponding to ZnSe- and MgSe-like modes in $Zn_{1-x}Mg_xSe$ and to ZnSe- and BeSe-like modes in $Zn_{1-x}Be_xSe$, were determined. These lattice vibrations can be described by the modified random element isodisplacement (MREI) model.

Keywords: II–VI semiconductors, mixed crystals, Raman spectra

1. Introduction

Recently, physical properties of wide-gap II–VI mixed crystals have been studied extensively. These compounds are interesting in the context of the control of band gap energies, lattice constants as well as conduction and valence band offsets in heterostructures. In $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ crystals the optical modes can be described by the two-mode model [1]. This feature is demonstrated in mixed crystals by the presence of the local and gap modes when one component is infinitely diluted in the mixed system. The lighter component exhibits a vibrational mode (local mode) with frequency greater than that of perfect crystals.

In this paper the study of Raman scattering spectra at room and liquid nitrogen temperature for $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ crystals are presented. Some results concerning Raman investigations performed at room temperature for $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ have recently been published [2–5].

2. Experimental

The $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ crystals were grown by the modified Bridgman method described in details elsewhere [6]. The crystal composition was determined by electron microprobe ($Zn_{1-x}Mg_xSe$) and chemical wet ($Zn_{1-x}Be_xSe$) analysis. The samples used in Raman scattering experiment were ground and polished to optical quality. The Raman spectra were measured at room temperature (RT) and liquid nitrogen temperature (LNT). The measurements at LNT were performed with the use of the helium cryostat (Optistat^{CF} static continuos flow cryostat). An Ar-ion laser, operating at 477 nm and 488 nm, was used to excite the Raman spectra. Due to relatively large absorption coefficient of

* e-mail: markoz@phys.put.poznan.pl
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$Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ crystal at LNT the output power was kept below 150 mW. The scattered radiation was analysed with a double-grating monochromator and was detected by a cooled EMI photomultiplier, followed by a photon counting system. The experimental setup permitted the band positions of Raman spectra to be estimated with an accuracy of ± 2 cm^{-1}. The measurements were performed for mixed crystals in the range of composition $0 < x < 0.34$ for $Zn_{1-x}Mg_xSe$ and $0 < x < 0.26$ for $Zn_{1-x}Be_xSe$.

3. Results and discussion

The vibrational Raman spectra of $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ mixed crystals for selected Mg ($x = 0.065$) and Be ($x = 0.09$) contents, obtained at RT and LNT are presented in Fig. 1. The typical spectra at room and liquid nitrogen temperature consists of ZnSe-like, MgSe-like and BeSe-like transverse (TO) and longitudinal (LO) phonon peaks. The $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ mixed crystals show a typical two-mode behaviour described by the modified random element isodisplacement model (MREI) [7].

This model assumes that in a long-wavelength limit ($q \approx 0$) anion and cation of like species vibrate with the same phase and amplitude [7]. Such assumptions are connected with a local and a gap mode in the limit of small concentrations of the light and heavy constituents, where each TO-LO mode pair for the binary compounds degenerates to an impurity mode (local mode for Mg and Be in ZnSe and gap mode for Zn in MgSe and BeSe).

Figure 2 presents the dielectric constant as a functions of energy gap and reduced masses for BeSe, MgSe, ZnSe and CdSe compounds and ionic radii for Be, Mg, Zn, and Cd elements. Presented data have been obtained by different authors [8]. On the basis of the dependencies shown in Fig. 2, the value of dielectric constant $\varepsilon_0 = 7.65$ (for MgSe) and $\varepsilon_0 = 6.46$ (for BeSe) has been calculated and averaged.

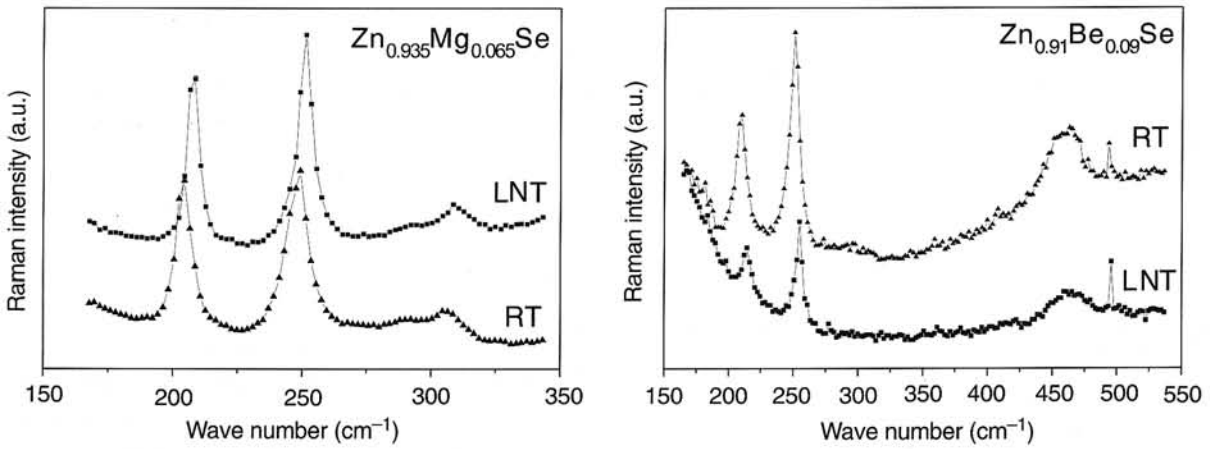

Fig. 1. Spectra of $Zn_{0.935}Mg_{0.065}Se$ and $Zn_{0.91}Be_{0.09}Se$ mixed crystals at room temperature (RT) and liquid nitrogen temperature (LNT).

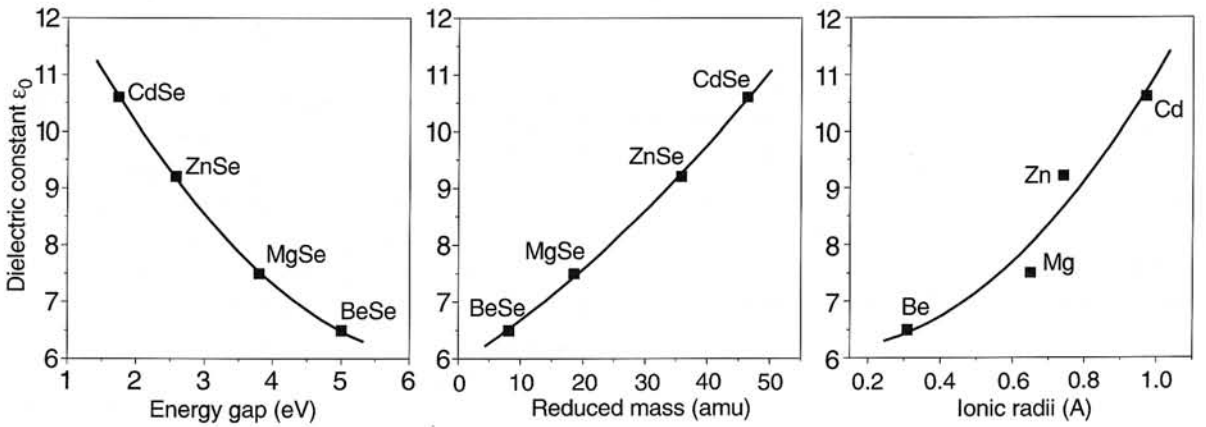

Fig. 2. The dielectric constant as a functions of the energy gap, reduced masses for BeSe, MgSe, ZnSe and CdSe, and ionic radii for Be, Mg, Zn and Cd (after Ref. 8).

The following data were taken for MREI model calculations
at room temperature:
experimental data: $\omega_{TO}(ZnSe) = 205\ cm^{-1}$, $\omega_{LO}(ZnSe) = 251\ cm^{-1}$, $\omega_{loc}(ZnSe:Mg) = 300\ cm^{-1}$, $\omega_{loc}(ZnSe:Be) = 448\ cm^{-1}$,
and theoretical data: $\varepsilon_\infty = 5.8$, $\varepsilon_0 = 9.2$
at liquid nitrogen temperature [9,10]:
experimental data: $\omega_{TO}(ZnSe) = 207\ cm^{-1}$, $\omega_{LO}(ZnSe) = 257\ cm^{-1}$, $\omega_{loc}(ZnSe:Mg) = 303\ cm^{-1}$, $\omega_{loc}(ZnSe:Be) = 450\ cm^{-1}$, and
theoretical data: $\varepsilon_\infty = 5.95$, $\varepsilon_0 = 9.2$.

Estimated parameters from fitting of experimental data at RT and LNT to the MREI model are listed in Table 1.

Table 1. Parameters estimated from fitting of experimental data to the MREI model for $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ mixed crystals.

Fitting parameters (RT)	Fitting parameters (LNT)
ω_{TO} (MgSe) = 237 cm^{-1}	ω_{TO} (MgSe) = 239 cm^{-1}
ω_{LO} (MgSe) = 340 cm^{-1}	ω_{LO} (MgSe) = 342 cm^{-1}
ω_{gap} (MgSe:Zn) = 192 cm^{-1}	ω_{gap} (MgSe:Zn) = 198 cm^{-1}
$\varepsilon_0 = 7.65$	$\varepsilon_0 = 7.65$
$\varepsilon_\infty = 3.8$	$\varepsilon_\infty = 3.74$
ω_{TO} (BeSe) = 501 cm^{-1}	ω_{TO} (BeSe) = 504 cm^{-1}
ω_{LO} (BeSe) = 578 cm^{-1}	ω_{LO} (BeSe) = 580 cm^{-1}
ω_{gap} (BeSe:Zn) = 220 cm^{-1}	ω_{gap} (BeSe:Zn) = 222 cm^{-1}
$\varepsilon_0 = 7.9$ (exp. – $\varepsilon_0 = 6.46$)	$\varepsilon_0 = 7.7$ (exp. – $\varepsilon_0 = 6.46$)
$\varepsilon_\infty = 6.0$	$\varepsilon_\infty = 6.0$

As it can be seen from Table 1, the fitting for BeSe-like compound has been obtained for the theoretical value $\varepsilon_0 = 7.9$ at RT and $\varepsilon_0 = 7.7$ at LNT, instead of $\varepsilon_0 = 6.46$ determined from Fig. 2. In the case of MgSe-like modes, the both values are the same. As it can be also seen from Table 1, phonon energies of the TO and LO modes increase with temperature decreasing. As an example, the energy of LO (MgSe) phonon increases from 41.7 meV at RT to 42.4 meV at LNT for $Zn_{1-x}Mg_xSe$ mixed crystal with x = 0.065 Mg content.

4. Conclusions

Using the theoretical MREI model we have estimated the force constants between different atoms for $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ mixed crystals. The obtained values are presented in Table 2.

Table 2. The values of the force constants for $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ mixed crystals.

Mixed crystal	Force constant	Value (10^6 amu/cm^2) (RT)	Value (10^6 amu/cm^2) (LNT)
	F_{Zn-Se}	2.05	2.12
$Zn_{1-x}Mg_xSe$	F_{Mg-Se}	1.71	1.76
	F_{Zn-Mg}	0.36	0.44
	F_{Zn-Se}	3.09	3.13
$Zn_{1-x}Be_xSe$	F_{Be-Se}	2.52	2.55
	F_{Zn-Be}	0.07	0.09

These values of force constants obtained at room temperature are similar to the analogous values obtained for other wide-gap II–VI mixed compounds [1,11]. As it can be seen from Table 2, all values of force constants for liquid nitrogen temperature are larger then those for room temperature.

A mixed crystal model has been presented which is completely defined by macroscopic parameter of the pure end members at room and liquid nitrogen temperature. The upward shift of the Raman modes with decreasing temperatures is the manifestation of anharmonicity. We suggest that experimental evidence already exists which supports this classification scheme.

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