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Study of the $A_{1-x}B_xC$ Mixed Crystals by Raman Scattering

Observations of Raman scattering associated with vibrational modes in $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ semiconducting mixed crystals are reported. Measurements were made at room temperature for $Zn_{1-x}Mg_xSe$ crystals with Mg content in the range $0 < x < 0.43$ and $Zn_{1-x}Be_xSe$ crystals with Be content in the range $0 < x < 0.41$. From the polarized Raman spectra the longitudinal optical (LO) and transverse optical (TO) modes which corresponding to ZnSe-, MgSe- and BeSe-like single crystals are distinguished. Theoretical calculations of the frequencies of the ZnSe- and BeSe-like modes were also performed using modified random element isodisplacement (MREI) model. The optical modes of $Zn_{1-x}Be_xSe$ are compared with those of $Zn_{1-x}Mg_xSe$.

Keywords: semiconductors, mixed crystals, Raman spectra.

1. Introduction

The physical properties of wide-gap II-VI ternary mixed crystals have recently been studied extensively. These compounds are especially interesting in the context of the possibility of an additional control of band gap energies, lattice constants as well as conduction and valence band offsets in heterostructures. The vibrational spectra of mixed crystals are also of special interest in view of the many fundamental aspects of lattice vibrations. In the case of tetrahedrally coordinated semiconductors where a fraction of cations is replaced by an element whose atomic mass is smaller than that of constituent atoms of a host lattice, the optical modes can be described by the two-mode model (PETERSON et al.). Two mode mixed crystals always exhibit local and gap modes when one component or the other is infinitely diluted in the mixed system. The lighter component exhibits a vibrational mode (local mode) with frequency greater than that of perfect crystals. Such a behaviour can be expected both for $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$.

In this paper the results of an experimental study of the compositional dependence of Raman scattering spectra of $Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ crystals are described and discussed. Some results dealing with photoluminescence, electrical properties and Raman investigations in $Zn_{1-x}Mg_xSe$ have recently been published (FIRSZT et al.). However, no experimental data for $Zn_{1-x}Be_xSe$ bulk crystal are available so far.

2. Experimental

$Zn_{1-x}Mg_xSe$ and $Zn_{1-x}Be_xSe$ crystals were grown by the modified Bridgman method described in details elsewhere (SZATKOWSKI et al.). The composition of Mg or Be was determined by electron probe microanalysis. The samples used in Raman scattering experiments were

ground and polished to optical quality. The Raman spectra were taken at room temperature. An Ar-ion laser operating at 488 nm was used to excite the Raman spectra. The scattered radiation was observed at right angle to the incident beam and analyzed with a double-grating monochromator. The light was detected by a cooled photomultiplier, followed by a photon counter system. The experimental setup permitted the band positions of Raman spectra to be estimated with an accuracy of $\pm 2 \text{ cm}^{-1}$. The measurement were performed for mixed crystals in the range of composition $0 < x < 0.41$.

3. Result and discussion

The vibrational Raman spectra of $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ were described in our previous work (KOZIELSKI et al.). The Raman spectra for $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ at $x = 0.09$ are presented in Fig. 1. The typical spectrum consists of ZnSe- and BeSe-like transverse (TO) and longitudinal (LO) phonon peaks.

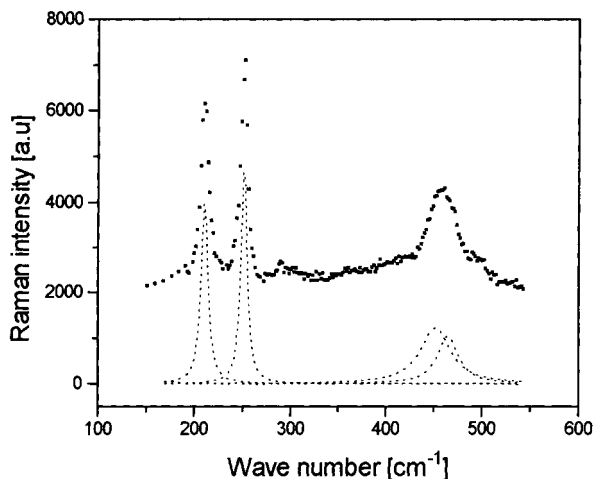


Fig. 1: Typical spectra of $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ mixed crystal (for $x = 0.09$). Dark points represented the experimental data and dashed lines the numerical fit.

Numerical fit of the experimental Raman bands shaped to Lorentzian functions is also presented in Fig. 1. The transverse and longitudinal modes in $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ mixed crystals as a function of mole concentration of Be is well described by the modified random element isodisplacement (MREI) model proposed for $\text{A}_{1-x}\text{B}_x\text{C}$ compounds (CHANG, MITRA). The $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ semiconductor shows a typical two-mode behaviour. The MREI model assumes that in a long-wavelength limit ($q \sim 0$) anion and cation of like species vibrate with the same phase and amplitude. 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 Be in ZnSe and gap mode for Zn in BeSe).

Figure 2 presents the position of ZnSe- and BeSe-like transverse (TO) and longitudinal (LO) modes as a function of beryllium content. The solid curves were determined from the MREI model using the literature data for ZnSe crystals. The data for BeSe crystal were obtained using the fitting procedure.

The frequencies of the vibrational modes in $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ as a function of beryllium content were determined using macroscopic parameters listed in Table 1. To fit the computed values to experimental data in the MREI model we estimated all parameters of BeSe crystal. The

following linear dependence of cubic lattice constant on Be content x was used:

$$a(x) = 5.67 - 0.53 x \text{ \AA}. \quad (1)$$

As seen from Fig. 2, the curves obtained from the MREI model are in good agreement with the experimental results. For comparison, in Table 2 we list the parameters of the MREI model for $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$, which were published elsewhere (KOZIELSKI et al.).

An important difference between the two systems of $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ and $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ is value of the local mode (e.g. impurity modes Mg and Be in ZnSe). We calculated the local mode frequencies in $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ and $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ for comparison with the experimental data using the modified diatomic linear chain model (LUCOVSKY et al.).

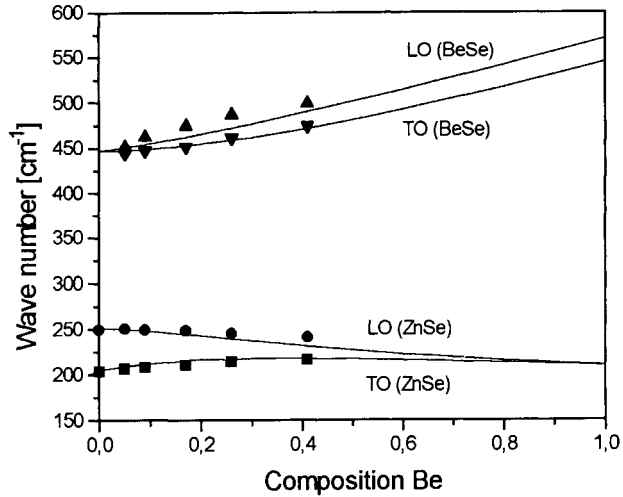


Fig.2: Dependences of ZnSe- and BeSe-like transverse (TO) and longitudinal (LO) modes as a function of Be content.

Experimental	Fitting parameters
$\omega_{\text{TO}}(\text{ZnSe}) = 205 \text{ cm}^{-1}$	$\omega_{\text{TO}}(\text{BeSe}) = 546 \text{ cm}^{-1}$
$\omega_{\text{LO}}(\text{ZnSe}) = 252 \text{ cm}^{-1}$	$\omega_{\text{LO}}(\text{BeSe}) = 578 \text{ cm}^{-1}$
$\omega_{\text{loc}}(\text{ZnSe:Be}) = 447 \text{ cm}^{-1}$	$\omega_{\text{gap}}(\text{BeSe:Zn}) = 210 \text{ cm}^{-1}$
$\epsilon_0(\text{ZnSe}) = 9.2$	

Table 1: Parameters in the MREI model for $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ mixed crystal

Experimental	Fitting parameters
$\omega_{\text{TO}}(\text{ZnSe}) = 205 \text{ cm}^{-1}$	$\omega_{\text{TO}}(\text{MgSe}) = 237 \text{ cm}^{-1}$
$\omega_{\text{LO}}(\text{ZnSe}) = 252 \text{ cm}^{-1}$	$\omega_{\text{LO}}(\text{MgSe}) = 340 \text{ cm}^{-1}$
$\omega_{\text{loc}}(\text{ZnSe:Mg}) = 300 \text{ cm}^{-1}$	$\omega_{\text{gap}}(\text{MgSe:Zn}) = 192 \text{ cm}^{-1}$
$\epsilon_n(\text{ZnSe}) = 9.2$	

Table 2: Parameters in the MREI model for $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ mixed crystal

The frequencies of the local modes were calculated as a function of the mass defect parameter $\epsilon_j = 1 - M/M_j$ where M is the mass of impurity atom and M_j is the mass of host-crystal atom. The results for $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ and $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ semiconducting crystals are: $\text{ZnSe:Mg} = 294 \text{ cm}^{-1}$ and $\text{ZnSe:Be} = 448 \text{ cm}^{-1}$. These values are in good agreement with the experimental data listed in Tables 1 and 2.

By comparing the fitted curves presented in Fig. 2 with the data listed in Tables 1 and 2 it may be concluded that for $Zn_{1-x}Mg_xSe$ the LO-TO modes splitting for MgSe is larger than for ZnSe. This is caused by a stronger ionic character of the chemical bonds in MgSe in comparison with ZnSe crystal. For the $Zn_{1-x}Be_xSe$ crystal we observe larger LO-TO modes splitting in ZnSe crystal in comparison with BeSe crystal. This phenomenon is caused by a stronger covalent character of the chemical bonds in BeSe.

Using the MREI model we also estimated for $Zn_{1-x}Be_xSe$ crystal the force constants F_{Zn-Se}^* , F_{Zn-Be}^* , F_{Be-Se}^* . The obtained values are as follows: $F_{Zn-Se} = 4.48$, $F_{Zn-Be} = 1.60$, $F_{Be-Se} = 5.50$ (in 10^6 amu/cm²). These values are similar to the analogous parameter obtained earlier for $Zn_{1-x}Mg_xSe$ crystal: $F_{Zn-Se} = 1.82$, $F_{Zn-Mg} = 0.30$, $F_{Mg-Se} = 1.57$ (in 10^6 amu/cm²) (KOZIELSKI et al.).

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