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Raman scattering in novel $(CuAlSe_2)_x(2ZnSe)_{1-x}$ and $(CuGaSe_2)_x(2ZnSe)_{1-x}$ mixed crystals

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Abstract. The new semiconductor materials $(CuAlSe_2)_x(2ZnSe)_{1-x}$ and $(CuGaSe_2)_x$ $(2ZnSe)_{1-x}$ are grown by the chemical transport method over all the compositional range. Raman spectra of the mixed crystals are measured at room temperature. Order–disorder phase transitions from chalcopyrite to disordered zincblende structure are observed in both materials. Phonon modes are identified on the basis of the phonon assignments of the end components. Some new bands assigned as vibrational modes of the CuSe and AlSe complexes in ZnSe are found.

1. Introduction

$(CuAlSe_2)_x(2ZnSe)_{1-x}$ and $(CuGaSe_2)_x(2ZnSe)_{1-x}$ mixed crystals belong to a large family of little-known $(A^IB^{III}C_2^{VI})_x(D^{II}C^{VI})_{1-x}$ semiconductors. It has been shown that many of them exhibit a strong energy gap dependence on the mixed crystal composition [1], a property important for energy band engineering. In addition, many of the compounds are stable in a wide compositional range [2, 3], which makes them interesting candidates for applications. Because crystal structures of the end components of the materials are different (chalcopyrite $A^IB^{III}C_2^{VI}$ compounds and zincblende or wurtzite $D^{II}C^{VI}$ materials), the mixed crystals examined are suitable candidates for studying the order–disorder phase transition.

In a few alloy systems the phase diagram has been measured and some information concerning the phase transition from chalcopyrite to a disordered zincblende structure is available in the literature [3]. It was reported recently that the phase transition from chalcopyrite to disordered zincblende structure in $(CuInS_2)_x(2ZnS)_{1-x}$ is sharp and well defined [4].

The end components of the alloys examined here, i.e. ZnSe, CuAlSe$_2$ and CuGaSe$_2$, are important semiconducting materials with prospective applications in photovoltaics and blue-light devices. Much effort has been made to study their physical properties and to find materials suitable for modern device technology. Special interest is devoted to mixed crystals with ZnSe and CuGaSe$_2$ as the end components and to semiconductor structures based on the compounds. CuAlSe$_2$ is less known, but the interest is growing.

Little is known of the lattice dynamics of the materials. Phonon dispersion curves were studied by the neutron diffraction method only for ZnSe [5]. Zone centre optical phonons of ZnSe, CuGaSe$_2$ and CuAlSe$_2$ were studied by Raman and infrared spectroscopy [6–12].

$(A^IB^{III}C_2^{VI})_x(D^{II}C^{VI})_{1-x}$ alloys are in general semiconducting materials about which little is known. Raman spectra of similar phase transitions were studied in some simpler

structures such as $Ge_{2x}(GaSb)_{1-x}$ and an order–disorder phase transition from one crystal structure to the other was evaluated experimentally and modelled numerically [13, 14]. Only a few papers have been published on the lattice dynamics of $(ABC_2)_x(DC)_{1-x}$ mixed crystals [15], and no information concerning the lattice dynamics of $(CuAlSe_2)_x(2ZnSe)_{1-x}$ and $(CuGaSe_2)_x(2ZnSe)_{1-x}$ mixed crystals is available.

In this study we report the growth and Raman scattering measurements of mixed crystals of both alloy types in the whole compositional range. The article is organized as follows: Firstly, by a short summary of lattice dynamics and Raman scattering in $(ABC_2)_x(DC)_{1-x}$ mixed crystals is presented, secondly the growth method and parameters are described and the experimental conditions of the Raman measurements are reported and then the experimental results are presented and discussed.

2. Systematics of the compounds

The chalcopyrite unit cell (D_{2d}^{12} ($I\bar{4}2d$) space group) may be roughly treated as a doubled zincblende cubic unit cell (T_d^2 ($F\bar{4}3m$) space group) with long dimension c equal to two cubic lengths and with eight instead of two atoms in the cubic elementary cell. The chalcopyrite unit cell may be formed by replacing two identical cationic species of zincblende by two different but well defined cations. When one or two of the cations are substituted by a third different cation, the chalcopyrite elementary cell is destroyed and two zincblende unit cells are created. In consequence, for some x, the $(ABC_2)_x(DC)_{1-x}$ mixed crystal may no longer be treated as a chalcopyrite compound but as a disordered zincblende crystal, and an order–disorder phase transition from chalcopyrite to a disordered zincblende structure is observed. This transition from one structure to the other causes a considerable change in the crystal lattice dynamics. The volume of the zincblende Brillouin zone (BZ) is four times that of the unrelaxed chalcopyrite BZ. In consequence the high-symmetry points of the zincblende BZ, i.e. $X(0, 0, 2\pi/a)$, $W(2\pi/a, 0, \pi/a)$ and $W(0, 2\pi/a, \pi/a)$, are folded to the Γ point of the unrelaxed chalcopyrite BZ. The two Raman-active BZ centre optical phonons of zincblende crystals are replaced by the vibrational modes of the D_{2d} chalcopyrite point group which are classified according to irreducible representations as follows:

$$A_1 + 2A_2 + 3B_1 + 3B_2 + 6E$$

where 13 vibrations $A_1 + 3B_1 + 3B_2 + 6E$ are Raman active.

In consequence, one can expect that the phase transition from one structure to the other will be strongly reflected in the Raman spectra. The compositional range of the coexistence of the two structures in the mixed crystal is not known. Recently Bente *et al* [16] examined a quite similar $ZnS–CuInS_2$ system by the x-ray diffraction method and showed that the range is relativity narrow. No x-ray results concerning the systems examined here are available in the literature. Our Raman results, which are quite contradictory to [16], will be discussed later.

Optical phonons of zincblende and chalcopyrite mixed crystals were intensively studied and the BZ centre phonon mode spectra were classified. In general, two major types of BZ centre optical phonon behaviour may be observed in mixed crystals, i.e. one-mode behaviour for which zone centre phonon frequencies vary continuously with the mixed crystal composition and two-mode behaviour for which two oscillators corresponding to the two constituents exist for all concentrations. In the framework of that classification the mode behaviours for both the zincblende and the chalcopyrite structures of $(CuAlSe_2)_x(2ZnSe)_{1-x}$ and $(CuGaSe_2)_x(2ZnSe)_{1-x}$ are discussed here.

3. Experiment

The mixed crystals examined were grown by the chemical transport method with iodine as the transport agent. Pure elements (99.9999% and 99.999%) were used in the technological process. The mixed crystal compositions were determined from the proportion of elements used in the technological processes and controlled with an electron microprobe. The microprobe analysis showed that the samples grown were quite homogeneous and deviations from the intended compositions of only a few per cent were observed. The materials obtained were mainly polycrystalline, and mixed crystals with compositions close to the end components were larger and of better quality and were also more homogeneous. We estimate that the accuracy of the composition is about 5% of the given value. No x-ray analysis was done.

Raman spectra were taken at room temperature with a Dilor XY-800 spectrometer equipped with a CCD multichannel detector. The 514.5 or 488 nm argon laser lines were used, depending on the mixed crystal compositions. Because of the quality of the material, the polarization dependence of the spectra was weak for majority of the crystals and is not considered here. Some of the crystals grown were too small for conventional Raman experiments and we used Raman microspectrometry when necessary. The majority of the samples here were large enough for conventional macroscopic Raman scattering.

4. Results and discussion

4.1. $(CuAlSe_2)_x (2ZnSe)_{1-x}$

Eight compositions of $(CuAlSe_2)_x(2ZnSe)_{1-x}$ mixed crystals with $x = 0.0$, 0.1, 0.2, 0.3, 0.5, 0.7, 0.85 and 1.0 were measured. The Raman spectra obtained are presented in figure 1. Because of weak inconsistent polarization dependence of the Raman spectra, the symmetry assignment is based mainly on the assignment of the respective modes of ZnSe ($x = 0$) [5–7] and CuAlSe$_2$ ($x = 1$) crystals [8, 9].

Strong Raman modes at 251 and 204 cm^{-1} observed in polycrystalline ZnSe ($x = 0$) are attributed to LO(Γ) and TO(Γ) phonons. The other bands are due to 2LO at 495 cm^{-1} and 2TA(X) at 139 cm^{-1} and were also observed by Henion *et al* and Irwin and LaCombe [6, 7].

12 Raman modes are found for CuAlSe$_2$. The frequencies and proposed symmetry identifications of Raman modes for ZnSe and CuAlSe$_2$ are presented in table 1.

In general the spectra of the end components are in good agreement with those in the literature [10, 12]. Only small differences between the experimental mode frequencies and the published data are found. One weak mode not reported in literature is found at about 43 cm^{-1} in the chalcopyrite range of the mixed crystal composition. Two quite strong bands at about 245 and 260 cm^{-1} in CuAlSe$_2$ were only observed by Chichibu and Kamata [12] and were not interpreted. The compositional dependence of the phonon modes is illustrated graphically in figure 2.

The strong band easily seen in all the crystals with $x \leqslant 0.7$ at about 239 cm^{-1} is interpreted as the ZnSe-like LO(Γ) phonon mode. The pronounced mode at about 182 cm^{-1} with A$_1$ symmetry is characteristic of the chalcopyrite crystal structure and may be treated as its indicator. This mode is present for the $x = 1.0$ and $x = 0.85$ mixed crystals and was also found for the $x = 0.7$ mixed crystal. We conclude that the phase transition from chalcopyrite to disordered zincblende crystal takes place for $x = 0.7$. The ZnSe-like TO phonon mode is easily seen for ZnSe polycrystalline material (204 cm^{-1}) and is
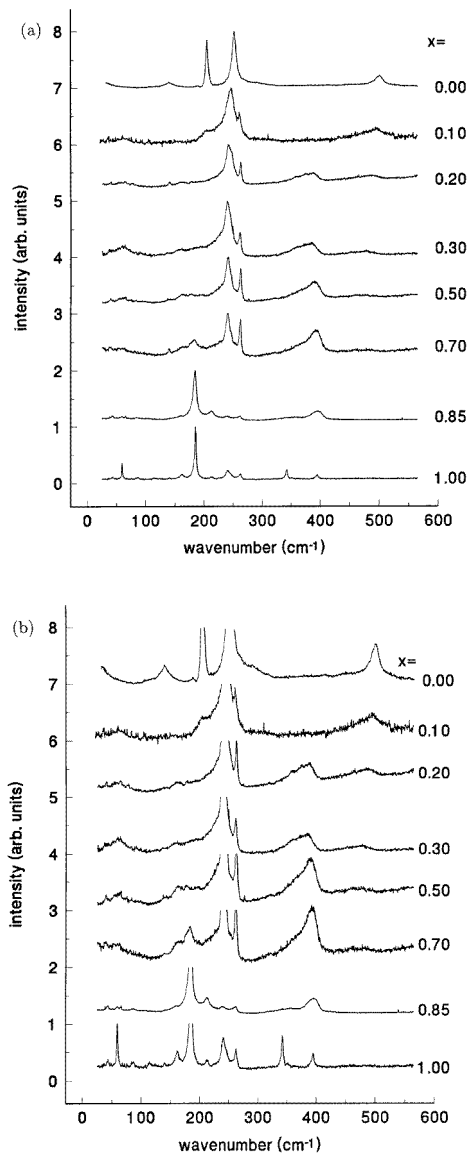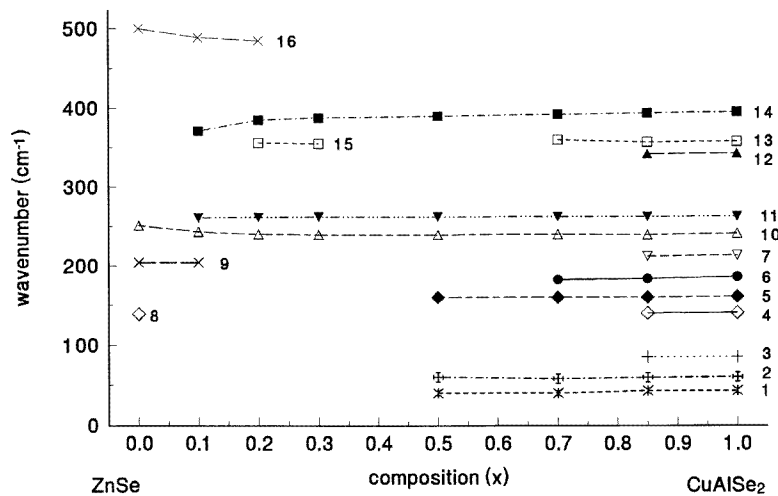
Figure 1. Raman scattering spectra of $(CuAlSe_2)_x(2ZnSe)_{1-x}$ mixed crystals. The values of the mixed crystal compositions x are indicated on the right-hand side of the figure. (*a*) The scattering intensities are normalized to unity. (*b*) The strongest modes are cut off to visualize the weaker modes.

rapidly identified in mixed crystals. A similar effect was observed in some II–VI mixed crystals and interpreted in terms of the anharmonic interaction of TO phonons with other vibrational modes [17], but still the nature of the effect is not clear. The vibrational mode at 139 cm^{-1} interpreted as the 2TA(X) mode in ZnSe is also easily distinguished in the mixed crystal. Special interest should be devoted to a narrow mode near 262 cm^{-1} seen in all the zincblende $(CuAlSe_2)_x(2ZnSe)_{1-x}$ crystals. The frequency of the mode is in good agreement with the Cu local mode frequency in ZnSe calculated in the simple mass defect

Table 1. Mode assignment of $(CuAlSe_2)_x(2ZnSe)_{1-x}$.

Mode number	Frequency (cm^{-1}) $x = 0$	$x = 1$	Mode symmetry	Mode assignment
1		43	Unknown	
2		60	B_2	
3		85	B_2	
4		139	?	
5		161	E	
6		186	A_1	
7		213	B_1	
8	139			2TA(X)
9	204		F_2 and E	TO(Γ)
10	251	245	F_2 and ?	LO(Γ)?
11		260	Unknown	LO(Γ)?
12		342	E	
13		358	$B_2 + E$	
14		395	E	
15				TO(Γ)?
16	500			2LO(Γ)

Figure 2. Composition dependence of the frequencies of different Raman modes in $(CuAlSe_2)_x(2ZnSe)_{1-x}$. The lines are guides for the eye only.

approximation [18] and the maximum of the mode intensity is observed at $x = 0.5$. We suggest that the mode is related to the independent vibration of CuSe units in the mixed crystals. The 260 cm^{-1} band intensity dependence on the mixed crystal composition was not systematic, so we are not able to distinguish between vibrations of CuSe clusters and CuSe-like vibrations of the two-mode mixed crystals. Further research is needed to clarify the problem.

The strong 342 and 395 cm^{-1} modes and a very weak 358 cm^{-1} mode in $CuAlSe_2$ ($x = 1.0$) are identified as vibrations of Al and Cu–Al pairs [8, 9]. With increasing ZnSe content the intensity of the modes increases and only one broad band may be found for

$x = 0.7$. In the zincblende compositional range, two broad bands at about 350 and 400 cm^{-1} are found. They seem to converge to one mode, the local vibration of Al in ZnSe for $x = 0$. Local vibrations of Al in the ZnSe matrix at 348 cm^{-1} has been reported in the literature [19]. The two modes may be interpreted as strongly damped AlSe-like TO and LO phonons. This mode behaviour is typical for two-mode mixed crystals, when the mode behaviour of the end component units is preserved.

All the phonon modes of CuAlSe$_2$ gradually broaden with increasing ZnSe content in the mixed crystal in general for the Raman spectra of the chalcopyrite mixed crystals. One low-frequency broad band is identified over all the mixed crystal composition. We ascribe this band disorder to activated BZ boundary acoustic phonons. This band may be observed owing to relaxation of Raman scattering selection rules and amorphization of the sample.

Table 2. Mode assignment of $(CuGaSe_2)_x(2ZnSe)_{1-x}$.

Mode number	Frequency (cm^{-1})		Mode symmetry	Mode assignment
	$x = 0$	$x = 1$		
1		57	B$_2$	
2		93	B$_1$	
3		182	A$_1$	
4		204	E	
5	251	242	F$_2$ and E	LO(Γ)
6		267	E	
7		269	E	
8	139			2TA(L)
9	187			2TA(X)
10	202		F$_2$	TO(Γ)
11	213			
12	289			
13	502			2LO(Γ)

4.2. $(CuGaSe_2)_x(2ZnSe)_{1-x}$

The Raman spectra of $(CuGaSe_2)_x(2ZuSe)_{1-x}$ are presented at figure 3. The frequency dependence of the Raman modes on the mixed crystal composition is presented in figure 4. The proposed assignment of the phonon modes is presented in table 2. The presented spectra are in many aspects similar to those of $(CuAlSe_2)_x(2ZnSe)_{1-x}$ mixed crystals. The end-component phonon modes are in good agreement with those in the literature [6–9]. Broadening and merging of the low-frequency chalcopyrite phonon modes are observed for x close to 0.5. This behaviour is typical of low quality, fairly amorphous samples where selection rules are violated and Raman spectra are proportional to the phonon density of states. The A$_1$ symmetric chalcopyrite mode at 185 cm^{-1} may be observed in the compositional region from $x = 1$ to $x = 0.5$. The ZnSe-like LO mode at 251 cm^{-1} is seen from $x = 0$ to $x = 0.7$ but is well defined only in the range from $x = 0$ to $x = 0.5$. We conclude that the phase transition from the chalcopyrite to the disordered zicblende structure takes place for $x \simeq 0.6$. It seems also that the compositional range of coexistence of the two phases is larger than in the case of $(CuAlSe_2)_x(2ZnSe)_{1-x}$. As in the previous case, we observe strong discrimination of the ZnSe-like TO(Γ) mode in $(CuGaSe_2)_x(2ZnSe)_{1-x}$ mixed crystals. The 262 cm^{-1} mode is observed in zincblende compositional range of the
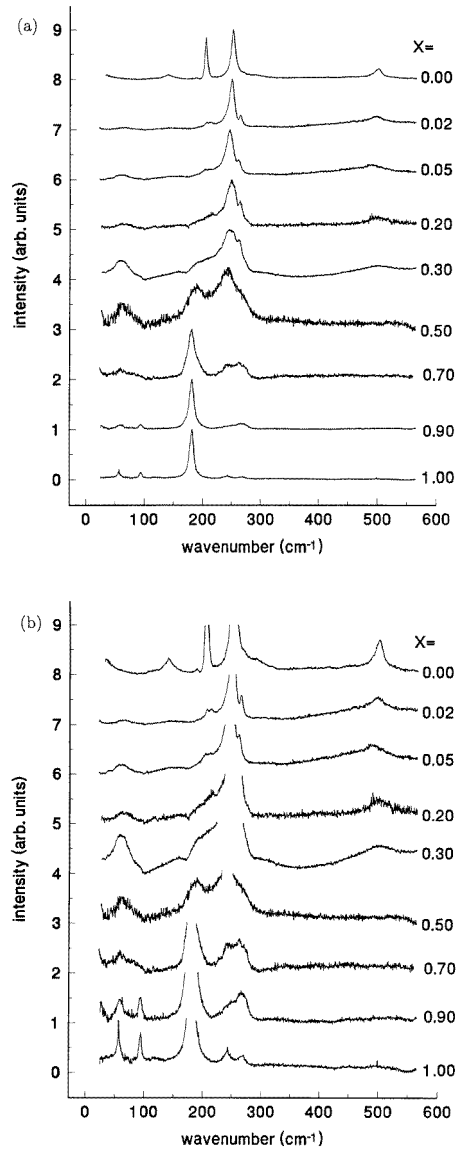
Figure 3. Raman scattering spectra of $(CuGaSe_2)_x(2ZnSe)_{1-x}$ mixed crystals. The values of the mixed crystal compositions x are indicated on the right-hand side of the figure. (*a*) The scattering intensities are normalized to unity. (*b*) The strongest modes are cut off to visualize the weaker modes.

material and, as previously, we attribute it to the vibration of CuSe complexes. We do not observe a pronounced band at about 350 cm^{-1}, which was easily seen in the previous case. Because of the small mass difference between Ga and Cu these bands may be degenerate and difficult to observe separately. Only small bands observed in zincblende crystals at 213 and 220 cm^{-1} may be attributed to local vibrations of Ga and GaSe complexes [20] in the ZnSe matrix.
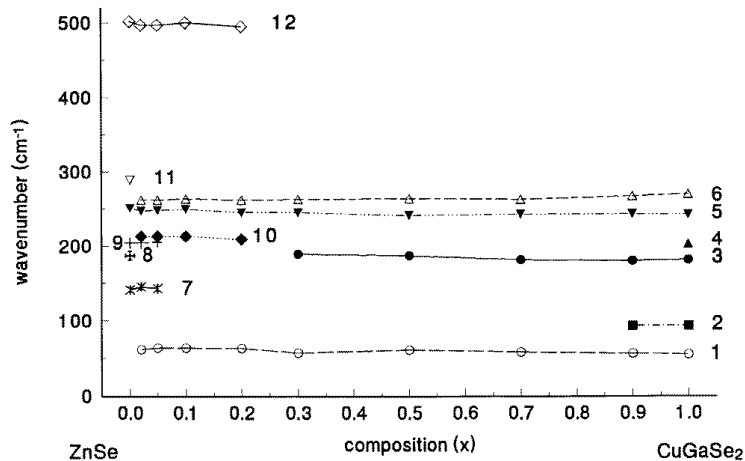
Figure 4. Composition dependence of the frequencies of different Raman modes in $(CuGaSe_2)_x(2ZnSe)_{1-x}$. The lines are guides for the eye only.

5. Conclusions

The little-known semiconductor mixed crystals $(CuAlSe_2)_x(2ZnSe)_{1-x}$ and $(CuGaSe_2)_x$ $(2ZnSe)_{1-x}$ are grown for the first time and examined using Raman spectroscopy. It is shown that the phase transition from the chalcopyrite to the disordered zincblende structure is not sharp and a compositional range of zincblende and chalcopyrite structure coexistence may be found. This conclusion is different from the results [16] obtained for $(CuInS_2)_x(2ZnS)_{1-x}$ but the sensitivity of Raman spectroscopy may be different from the results of x-ray diffraction spectroscopy [15]. One of the reasons for this may be connected with disorder-activated phonon modes from the BZ boundaries, which may also be observed in first-order Raman scattering and may be difficult to distinguish from symmetry folded modes. This effect may broaden the observed compositional range of the coexistence of the two phases. The x-values of the phase transition are determined as 0.7 and 0.6 for $(CuAlSe_2)_x(2ZnSe)_{1-x}$ and $(CuGaSe_2)_x(2ZnSe)_{1-x}$, respectively. In both materials, in the zincblende range of the mixed crystal composition, we observe ZnSe-like first-order LO and TO vibrational modes. The intensities of the TO modes are strongly dependent on the mixed crystal compositions and disappear quickly in the mixed crystals. A new band at about 260 cm^{-1} is observed in both mixed crystals. The band is attributed to vibrations of CuSe complexes in the mixed crystal matrix. Two vibrational modes near 350 cm^{-1} are observed for $(CuAlSe_2)_x(2ZnSe)_{1-x}$. The modes are attributed to AlSe-like vibrations. A possible convergence of the mode frequencies to the Al local frequency is reported, which suggests a behaviour typical for two-mode zincblende mixed crystals.

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