Raman scattering in CuInS$_{2x}$Se$_{2(1-x)}$ mixed crystals

LETTER TO THE EDITOR

Raman scattering in $CuInS_{2x}Se_{2(1-x)}$ mixed crystals

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Abstract. Raman spectra of $CuInS_{2x}Se_{(1-x)}$ mixed crystals are reported. The dependence of the mode frequencies on the composition is studied. Two-mode behaviour is observed for the higher-frequency phonons. One-mode behaviour is found for the low-frequency modes corresponding to the zone-edge acoustic phonons of zincblende.

Solid solutions of $CuInS_{2x}Se_{2(1-x)}$ type are considered as an alternative for $CuInSe_2$ as an absorber in thin-film solar cells [1]. They crystallize in the chalcopyrite structure over the whole composition range. The band gap varies from 1.04 eV for $CuInSe_2$ to 1.53 eV for $CuInS_2$. To our knowledge no data on the lattice dynamics of this system have been published yet. The phonon spectra of the end members of the series are relatively well knowl from both infrared studies and Raman scattering ($CuInSe_2$ [2–4] and $CuInS_2$ [5–7]) though there are still some discrepancies concerning the mode assignment. In this letter we investigate the Raman spectra of $CuInS_{2x}Se_{2(1-x)}$ mixed crystals.

Raman-active modes in the centre of the Brillouin zone for chalcopyrite structure comprise the following symmetries: A_1, $3B_1$, $3B_2$ and $6E$ (B_2 and E modes are also infrared active). Because the chalcopyrite structure is directly related to the zincblende structure it is possible to find a correspondence of their zone-centre phonons in chalcopyrite to vibrations in different points of the zincblende Brillouin zone. Usually the highest-frequency nearly degenerate $E+B_2$ modes in chalcopyrite correspond to the zone-centre vibration of an analogue zincblende compound. The rest of the modes can be ascribed by the folding-down procedure to the phonons at the X and W points of the zincblende Brillouin zone [8].

$CuInSe_2$ crystals were grown by the gradient-freezing method and samples were prepared by cleaving. For all the other compositions the crystals were grown by the chemical vapour transport (CVT) method with iodine as a transport agent. The natural (112) crystal faces were used in the measurements. Raman spectra were taken on a triple XY-800 DILOR spectrometer with multichannel detection (CCD camera). Measurements were carried out in backscattering geometry at room temperatuure. The argon laser power (514.5 nm line) was kept below 40 mW to prevent sample damage. Samples were mounted in vacuum to avoid the Raman scattering from air.

The assignment of the modes observed in the Raman spectra was made on the basis of the known spectra of the end members and was in keeping with our measurements made in polarized light on the (112) faces. Though such a face geometry does not provide clear-cut discrimination between modes of different symmetry, it is basically possible to identify most of them [9]. Yet, not all allowed modes can be observed in that geometry. Besides this,
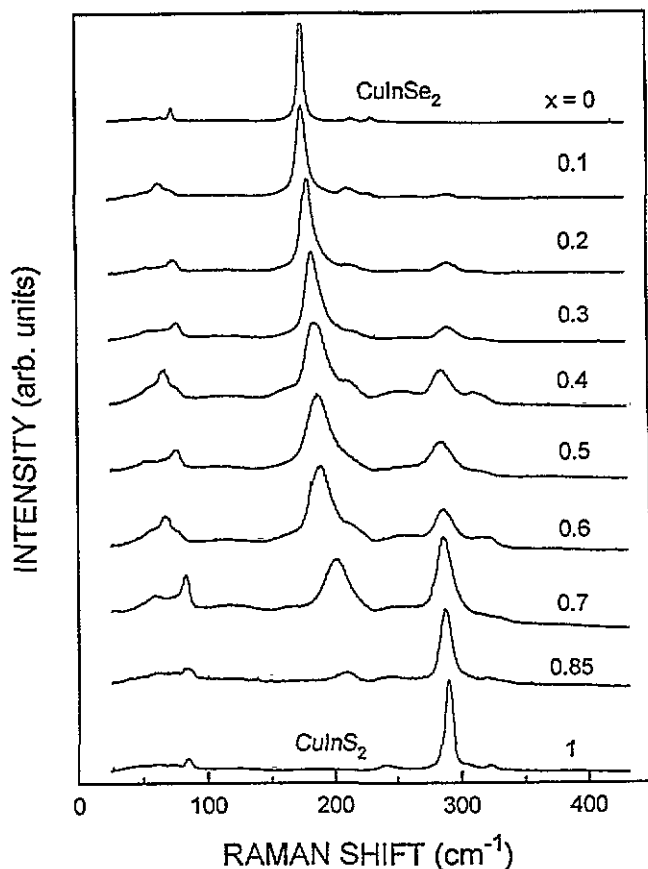
Figure 1. Unpolarized Raman spectra of the $CuInS_{2x}Se_{2(1-x)}$ mixed crystals.

the alloy broadening made it difficult to resolve closely spaced peaks in the Raman spectra of mixed crystals.

Raman spectra of $CuInS_{2x}Se_{2(1-x)}$ for different compositions are shown in figure 1. The strongest peaks for the end compositions (176 cm^{-1} in $CuInSe_2$ and 290 cm^{-1} in $CuInS_2$) are due to the A_1 symmetry mode of vibration. This corresponds to anion movement with cations at rest. According to the bond-stretching force constant model of Neumann [10], the squared frequency of the A_1 mode is give by $2(\alpha_A + \alpha_B)m_C$, where α_A and α_B are the force constants, and m_C is an anion mass. Using the values of α_A and α_B given in [10] one obtains the frequency ratio between the selenide and the sulphide 0.593 which is close to the experimental value 0.607.

$CuInS_2$-like and $CuInS_2$-like A_1 peaks with different intensities are present in the Raman spectra of mixed crystals exhibiting the two-mode behaviour. Similar behaviour is noted also for the highest-frequency $E+B_2$ mode whose transverse components were observed for most compositions as searate $CuInSe_2$-like and $CuInS_2$-like peaks. The longitudinal counterpart of this mode has been detected only for the end members.

The two-mode evolution of the spectra has been found in a number of isocationic solid solutions where selenium was substituted by sulphur: $CuGaSe_2$–$GuGaS_2$ [11, 12], $AgGaSe_2$–$AgGaS_2$ [12, 13] as well as in $A^{II}B^{VI}$ mixed crystals [14, 15]. It can be explained in terms of the large mass difference between the two types of anion and the resulting
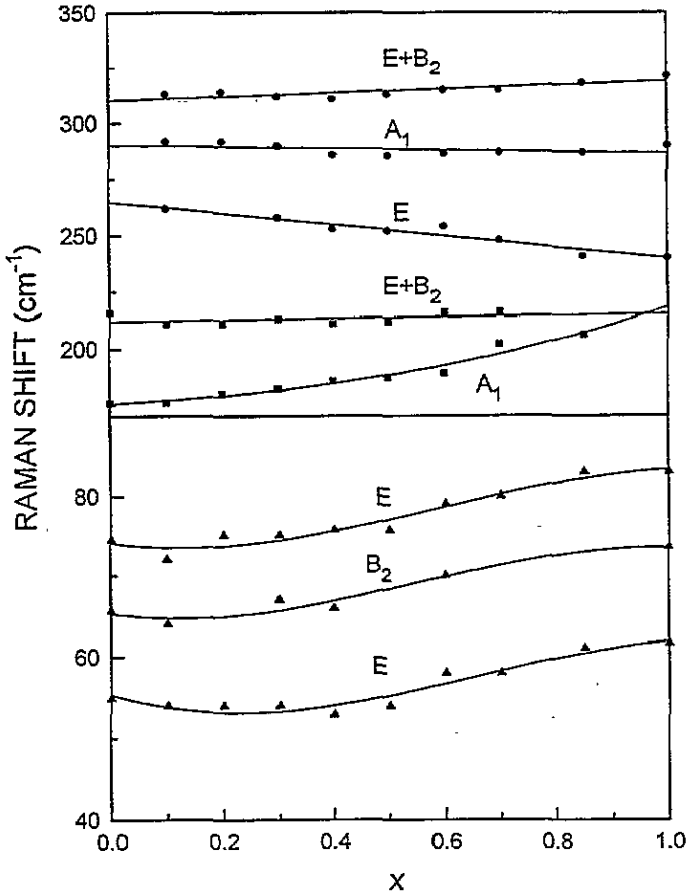
Figure 2. Composition dependence of the frequencies of different vibration modes in $CuInS_{2x}Se_{2(1-x)}$. Circles correspond to the $CuInS_2$-like modes, squres to $CuInSe_2$-like modes. Lines are guides for the eye only.

substantial difference between the frequencies of the respective phonons. In mixed crystals of binary compounds the characteristic feature of the two-mode behaviour is the existence (though not in all cases [16]) of localized and gap modes of substituting atoms in the dilute limit of their concentration.

The position of the $CuInS_2$-like A_1 mode is practically independent of the composition apart from a weak 'softening' for intermediate x-values (by ~ 2 cm^{-1}). The frequency of the $CuInSe_2$-like A_1 mode changes from 176 cm^{-1} for $x = 0$ to 206 cm^{-1} for $x = 0.85$ and converges with the practically constant 216 cm^{-1} mode, which is the transverse counterpart of the nearly degenerate zincblende-like $E+B_2$ mode in $CuInSe_2$. Apparently, the latter value yields an approximate frequency of the gap mode of selenium in $CuInS_2$. We have not observed analogous convergence for the $CuInS_2$-like modes so we could not identify a localized mode of vibration of sulphur in $CuInSe_2$.

In the low-frequency range 50–85 cm^{-1} we observe three closely spaced peaks, which are assigned to the E–B_2–E sequence in $CuInSe_2$ [3, 4] and in $CuInS_2$ [5]. They show continuous variation of the frequencies with the crystal composition therefore exhibiting the one-mode behaviour. The modes are the folded-down acoustic modes from the W and X

points of the Brillouin zone of the corresponding zincblende binary analogues [3]. Their frequencies are determined mainly by bond-bending force constants [10] and they depend weakly on anion mass.

Composition dependence of zone-centre phonons is usually treated in the random-element isodisplacement model [15, 16]. This was successfully applied to solid solutions of binary compounds where a number of criteria have been formulated to determine one-mode versus two-mode behaviour [16]. They are based mostly on evaluation of a mass ratio of constitutent atoms. In the $CuInS_{2x}Se_{2(1-x)}$ system, the higher-energy modes show two-mode behaviour in keeping with the large mass difference of sulphur and selenium, whereas the low-frequency acoustic-like modes exhibit one-mode evolution. The problem of the local and gap modes in this system awaits further study.

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