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Defect-induced structural disorder in tetragonal $Cu(In_{1-x}Ga_x)_5Se_8$ thin films investigated by Raman spectroscopy: the effect of Ga addition

Chuan-Ming Xu[1,2,4]**, Wen-Hao Huang**[1]**, Jun Xu**[2]**, Xiao-Jie Yang**[2]**, Jian Zuo**[3]**, Xiao-Liang Xu**[2,3] **and Hong-Tu Liu**[2]

[1] Department of Precision Machinery and Precision Instrumentation, University of Science and Technology of China, Hefei 230027, People's Republic of China
[2] Department of Physics, University of Science and Technology of China, Hefei 230026, People's Republic of China
[3] Structure Research Laboratory, University of Science and Technology of China, Academia Sinica, Hefei 230026, People's Republic of China

E-mail: cmxu@ustc.edu

Abstract

The dependence of the phonon frequencies of the quaternary $Cu(In_{1-x}Ga_x)_5Se_8$ films with tetragonal structure on the Ga content have been systematically investigated by means of Raman scattering. The dominant A_1 mode shifts from 151 cm^{-1} for $CuIn_5Se_8$ to 160 cm^{-1} for $CuGa_5Se_8$ in an approximately polynomial but not linear curve, because different types of local tetrahedral cationic clusters around Se distribute in the defect crystal structures. The vibrational modes in the low-frequency region below 125 cm^{-1} clearly show one-mode behaviour, whereas significant changes in the frequency range from 160 to 235 cm^{-1} indicate defect-induced structural disorder and show two-mode behaviour due to Ga addition. Additionally, the quenching of the Raman band at 174 cm^{-1} for the Ga-rich films reveals that this mode should most probably originate from other similar localized structure phases in chalcopyrite-related $CuIn_5Se_8$ but not $CuGa_5Se_8$, due to the Ga inhibition effect. Such results should be ascribed to asymmetric distribution of Ga and In on a microscopic scale, resulting in the different properties of bonds between local clusters.

1. Introduction

Some ordered defect compounds (ODCs), such as $Cu(In, Ga)_5Se_8$ [1–3], $Cu(In, Ga)_3Se_5$ [4], have recently generated intense interest not only because of their potential applications in

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[4] Author to whom any correspondence should be addressed.

high-efficiency photovoltaic devices, but also as regards the understanding of structural properties of CuInSe$_2$ and its alloys. Due to the stable formation of the charge-neutral defect pair ($2V_{Cu^-} + In_{Cu^{2+}}/Ga_{Cu^{2+}}$) [5], ODCs are remarkably distinct from CuInSe$_2$ and CuGaSe$_2$ in structural and electrical properties [3, 6]. Raman spectroscopy has been used as a promising tool for both detecting traces of different structural phases and characterizing CuIn$_3$Se$_5$ [7, 8] and CuGa$_3$Se$_5$ [9, 10] compounds with the aid of a shift of phonon frequencies. However, there are still many unclear phenomena in Raman spectra of ODCs, such as the effect of defects on vibrational properties. These structural defects, i.e., cation vacancies, interstitials and antisites, can produce well-known local modes, and also reflect additional phonon energy associated with Urbach tails as an indicator of structural disorder in CuIn$_3$Se$_5$ and other Cu ternaries [11, 12]. We do not know to what extent the defect-induced structural disorders in ODCs should be correlated with the deviation from ideal stoichiometry (ideal cation to anion ratio) and molecularity (ideal cation to other cation ratio) [12], resulting in the different local environments in defect crystal structures. Zhang *et al* [5] suggested that any ODCs in chalcopyrite-related (CH) structure should have a weighted distribution of three types of local tetrahedral cationic clusters around Se. Thus, in such materials, the interaction between local clusters gives rise to the different bond properties in the lattice, and such an effect will be reflected in Raman spectra of ODCs. In our preliminary study, we found that the mode at around 174 cm^{-1} in CH–CuIn$_5$Se$_8$ is very sensitive to the chemical composition and local structure. No data on lattice vibration properties of Cu(In$_{1-x}$Ga$_x$)$_5$Se$_8$ compounds have been reported yet.

In order to get a deeper understanding of both the origin of the additional mode at 174 cm^{-1} in CuIn$_5$Se$_8$ and the structural information on quaternary Cu(In$_{1-x}$Ga$_x$)$_5$Se$_8$ films from their lattice vibration behaviours, the effects of Ga addition to CuIn$_5$Se$_8$ on its vibrational properties are systematically investigated by Raman spectroscopy in this paper. Considering the effect of defect-induced structural disorder, the change of the Raman modes with Ga content x is qualitatively discussed on the basis of our experimental data.

2. Experimental results and discussion

The Cu(In$_{1-x}$Ga$_x$)$_5$Se$_8$ films with Ga content $x = 0, 0.3, 0.5, 0.7$ and 1.0 investigated were grown on Na-free glass substrates by the periodic sequential evaporation method (i.e., In/Ga/Cu/In... for $0 < x < 1$ and Ga/Cu/Ga... for the $x = 1$ stacking sequence) [13] and this was followed by a vacuum-selenized annealing (at an annealing temperature of 673 K and with the annealing time 3 h) process. The chemical composition of all the films with nominal 60 nm thickness obtained was confirmed by an XRF-1800 x-ray fluorescence spectrometer with a Rh anode. On the other hand, these films with tetragonal CH structure, characterized by x-ray diffraction spectra, grow mainly with (112) and (220)/(204) preferred orientations. For Cu(In$_{1-x}$Ga$_x$)$_5$Se$_8$ films, the unpolarized Raman spectra in the wavenumber region from 50 to 350 cm^{-1} were recorded with the spectral resolution of 1 cm^{-1} at room temperature, using a triple-monochromator spectrometer (LABRAM-HR) equipped with a multichannel detector in the backscattering configuration. A 514.53 nm Ar$^+$ laser, which has a penetration depth of more than 100 nm, was used as the excitation source.

Like the other chalcopyrite compounds CuInSe$_2$ and CuGaSe$_2$, the Cu(In$_{1-x}$Ga$_x$)$_5$Se$_8$ films in this work crystallize in the tetragonal CH structure analogously to CuIn$_3$Se$_5$ [7] and CuGa$_3$Se$_5$ [9]. The lattice vibrations of Cu(In$_{1-x}$Ga$_x$)$_5$Se$_8$ films should be similar to those of chalcopyrite compounds. Therefore, the irreducible representations for the zone-centre Raman active optical modes in these structures are expressed as [14]: $1A_1 + 3B_1 + 3B_2 + 6E$. The long-range electrostatic interaction causes the splitting of the longitudinal optical (LO) and transversal optical (TO) high-frequency B$_2$ and E modes.
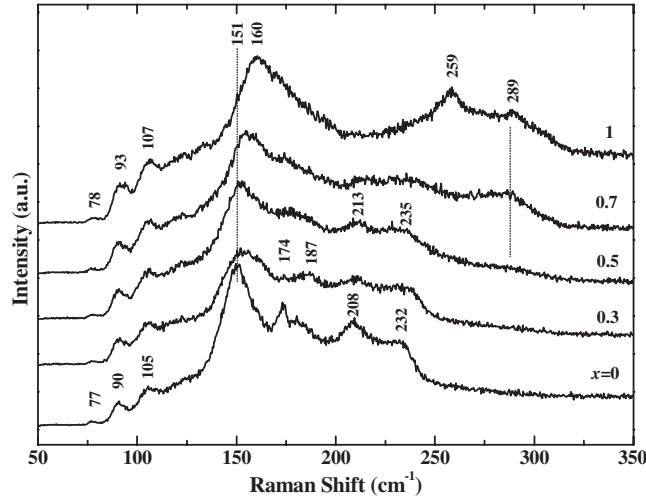
Figure 1. Unpolarized Raman spectra of $Cu(In_{1-x}Ga_x)_5Se_8$ films.

In the following, the main features of our experimental data for $Cu(In_{1-x}Ga_x)_5Se_8$ will be presented and briefly analysed.

2.1. The Raman shift of the A_1 band

Raman spectra of $Cu(In_{1-x}Ga_x)_5Se_8$ films with varying x are depicted in figure 1. It is clearly observed that the most intense Raman band for $CuIn_5Se_8$ and $CuGa_5Se_8$ in figure 1 is the A_1 one, at around 151 and 160 cm^{-1}, respectively. This mode corresponds to Se anion movement with cations at rest. According to the force model of Neumann [15], the frequency of the A_1 mode is given by $\nu \approx (k/M_{Se})^{1/2}$ [9], where M_{Se} is the Se mass and k is the cation–Se bond-stretching force describing the interaction between nearest neighbours. Since one vacancy V_{Cu} exists for each four Se atoms in the $CuIn_5Se_8$ and $CuGa_5Se_8$ [5], in analogy to the analysis of Raman studies on $CuIn_3Se_5$ and $CuGa_3Se_5$ [9, 10], it is justified to hypothesize that k for A_1 is reduced by 25% relative to its values in the normal chalcopyrites. In this case, it is expected that the A_1 frequency $\nu' \approx (0.75k/M_{Se})^{1/2} \approx 0.87\nu$, where ν is the A_1 frequency in the normal chalcopyrites. According to the A_1 band being at 174 cm^{-1} for $CuInSe_2$ and 184 cm^{-1} for $CuGaSe_2$ at room temperature [9, 16], the ν' for $CuIn_5Se_8$ and $CuGa_5Se_8$ is 151 and 160 cm^{-1}, respectively, in fairly good agreement with the observed bands in figure 1.

For $Cu(In_{1-x}Ga_x)_5Se_8$, the frequency of the A_1 mode with increasing x value is shown in figure 2. The frequency of the A_1 mode in the interval $0 < x < 0.5$ varies slightly with increasing x and significantly shifts toward higher wavenumbers with $x \geqslant 0.5$, as shown in figure 2. Over the whole x range, the shift of the A_1 band in $Cu(In_{1-x}Ga_x)_5Se_8$, unlike those of the lattice constants a and c [3], does not follow the linear Vegard law. The variation of the A_1 mode with x can be obtained by using a polynomial curve

$$A_1 \text{ Raman shift (cm}^{-1}) = 150.8 - 0.8x + 9.6x^2 \tag{1}$$

with a standard deviation of around 0.003 cm^{-1}. Similar behaviour has been observed in $CuIn_{1-x}Ga_xSe_2$ ($0 < x \leqslant 0.29$) [17], $Cu(In_{1-x}Ga_x)_3Se_5$ [18] films and $Ag_xCu_{1-x}GaS_2$ mixed crystals [19]. Some shoulder peaks at A_1 band are distinctly found due to Ga addition, resulting in the asymmetric broadening of the corresponding A_1 band relative to that of $CuIn_5Se_8$.
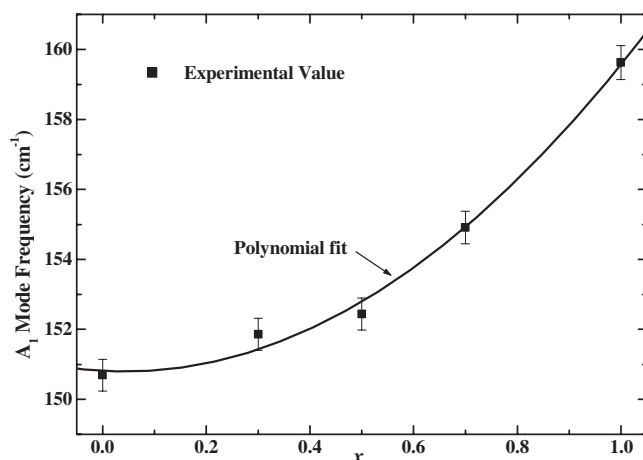
Figure 2. The composition dependence of the A_1 band frequency in $Cu(In_{1-x}Ga_x)_5Se_8$ films.

During phase formation, it is expected that different gradients in Cu, In or Ga concentrations will exist on a microscopic scale in films [20], thereby leading to different local environments in crystal structures. From this consideration, due to the difference in defect pair between $(2V_{Cu^-} + In_{Cu^{2+}})$ for $CuIn_5Se_8$ and $(2V_{Cu^-} + Ga_{Cu^{2+}})$ for $CuGa_5Se_8$, it is apparent that two crystal structures should have different local environments although the anion Se is the same. When In is partially replaced by Ga in $Cu(In_{1-x}Ga_x)_5Se_8$ with x varying, the cation sites in the lattice are shared by Cu, In, Ga and the vacancy V_{Cu} in varying degrees [21], resulting in asymmetric distribution of In and Ga cations in different local clusters and disorder in the cation sublattice. Such defect-induced disorder should be responsible for the nonlinear shift of the A_1 peak position with x and for the development of shoulder peaks at the A_1 band.

2.2. Evolutionary history of Raman bands between 160 and 289 cm^{-1}

It is obviously found that the positions and intensities of those peaks between 160 and 289 cm^{-1} are changed due to Ga addition, with x changing. For the film with $x = 0.3$, the intensity of the peak at 174 cm^{-1} is remarkably decreased and as a result this mode is barely discernible above the noise; on the other hand, the peaks related to In–Se vibration at 187 and 208 and 232 cm^{-1} are weakened, and this is accompanied by the presence of weaker features at 259 cm^{-1} for local Ga–Se vibration. For the films with $x > 0.3$, the peak at 187 cm^{-1} and the other two bands at 213 and 235 cm^{-1} are gradually widened, resulting in formation of the wide shoulder peak at A_1 band in the range from 160 to 199 cm^{-1} in $CuGa_5Se_8$, whereas the intensity of the two peaks at 259 and 289 cm^{-1} is gradually enhanced. These bands in the region between 160 and 289 cm^{-1} are identified with the end members and are exhibited in figure 3. Since discrepancies between the assignments of Raman modes are usually present for $CuInSe_2$ [22] and $CuGaSe_2$ [16] as well as $CuIn_3Se_5$ and $CuGa_3Se_5$ [9, 10], a possible assignment for $CuIn_5Se_8$ and $CuGa_5Se_8$ is proposed on the basis of references [22] and [10, 16], respectively. For $Cu(In_{1-x}Ga_x)_5Se_8$ films with $0 < x < 1$ in this work, the assignments are mainly based on both the mode assignment of the end members and the shift history of the corresponding phonon frequencies in films with x. Figure 3 shows a graphical comparison between all the observed curves in figure 1 and the reference data both for $CuInSe_2$ [14, 22] and $CuGaSe_2$ [16] and for $CuIn_3Se_5$ [9] and $CuGa_3Se_5$ [9, 10].
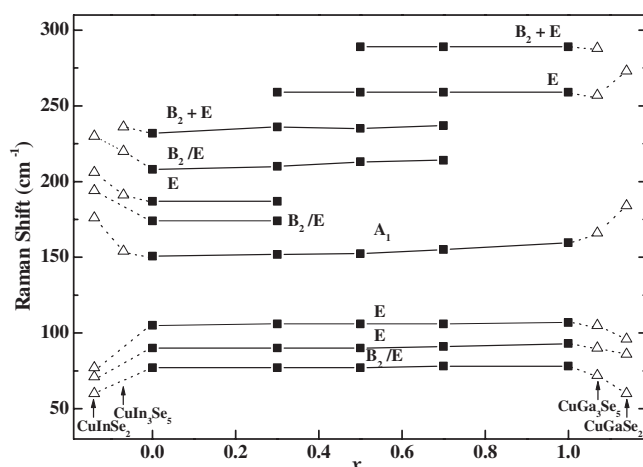
Figure 3. The composition dependence of the phonon frequencies of different vibration modes in $Cu(In_{1-x}Ga_x)_5Se_8$ films. The solid squares correspond to the $CuIn_5Se_8$-like and $CuGa_5Se_8$-like modes in this work; additionally, the triangles denote reference data (lines are guides for the eye only). These data follow the analysis of the spectra shown in figure 1.

2.3. The origin of the Raman mode at 174 cm^{-1}

For the band at 174 cm^{-1}, in contrast to other bands (i.e., those at 232, 208 and 187 cm^{-1}) for $CuIn_5Se_8$, the intensity is significantly decreased with increasing x while the frequency is unchanged. Since this band becomes barely discernible above the noise with $x > 0$, it is expected that Ga addition could inhibit formation of the phase related to such modes but not modify its structure. Furthermore, the fraction of such phase domains in CH–$CuIn_5Se_8$ should be relatively small. Recently, Chang *et al* [21] analysed several possible crystal structures for $CuIn_5Se_8$ by means of first-principles calculations, and found that the total energy of the CuAu-related $CuIn_5Se_8$ structure derived from $CuAu$–$CuInSe_2(100)$ is only 1 meV/atom higher than that of CH–$CuIn_5Se_8$ with the lowest energy, since the two structures have the same types of local clusters. On the other hand, the transmission electron measurements on $CuGaSe_2$ films [23] have confirmed the theoretical prediction [24] that the CuAu-like phase is less likely in $CuGaSe_2$ than in $CuInSe_2$. Therefore, due to the large formation energy of the Ga_{Cu} in $CuGa_5Se_8$ relative to In_{Cu} in $CuIn_5Se_8$ [25], in analogy to the above results, the coexistence of CuAu-like and CH phases is less likely in $CuGa_5Se_8$. Considering the sensitivity of Raman spectra to x, together with the Ga inhibition effect in this work, it seems justified to suppose that the band at 174 cm^{-1} is derived from metastable CuAu-related $CuIn_5Se_8$ in CH–$CuIn_5Se_8$ and not CH–$CuGa_5Se_8$. This band may shift from the 194 cm^{-1} modes of $CuInSe_2$. To a great extent, the presence of such CuAu-related $CuIn_5Se_8$ should be correlated with spontaneous migration and a defect (i.e., V_{Cu} and In_{Cu}) formation mechanism controlled by bulk thermodynamics, and hence deserves further investigation.

2.4. Assignment of the highest-frequency mode

For the peak at 232 cm^{-1} in $CuIn_5Se_8$, the intensity is gradually decreased with increasing x and it disappears in $CuGa_5Se_8$, whereas the peak at 289 cm^{-1} can be clearly observed in films with $x \geqslant 0.5$. The two bands show distinct two-mode behaviour. Although the origins of the two bands are not still clear, it is found that they basically exist in Raman spectra of ODCs

and hence must be associated with the vacancies and antisites in the defect crystal structure. Thus, they should share a common origin. According to assignment of the Raman mode at 286 cm^{-1} in CuGa$_3$Se$_5$ single crystals proposed by Rincón *et al* [9, 10], the band at 289 cm^{-1} for CuGa$_5$Se$_8$ and 232 cm^{-1} in CuIn$_5$Se$_8$ is most probably corresponding to the combination of the B$_2$ and E modes. Usually the highest-frequency two-phonon combination modes related to B$_2$ + E are also observed in CuInS$_{2x}$Se$_{2(1-x)}$ [26] as well as in analogue chalcopyrite-related compounds [18].

2.5. One-mode behaviour in the low-frequency region below 125 cm^{-1}

For low-frequency bands at 77, 90 and 105 cm^{-1} in CuIn$_5$Se$_8$, the intensities are unchanged with increasing x and their frequencies slightly shift toward high wavenumbers within 3 cm^{-1}. Such continuous shifting exhibits typical one-mode behaviour. Similar behaviour has been observed in CuIn$_{1-x}$Ga$_x$Se$_2$ solid solutions [27]. These low-frequency peaks for CuGa$_5$Se$_8$ are similar to those for CuGa$_3$Se$_5$ [10]. However, the discrepancies related to low-frequency Raman modes, such as in the assignment and the peak position, are present in both theoretical studies and experimental data on CuInSe$_2$ and CuGaSe$_2$ [16, 22]. Wei *et al* [25] suggested that the change of the lattice mismatch between CuIn$_{1-x}$Ga$_x$Se$_2$ and Cu(In$_{1-x}$Ga$_x$)$_3$Se$_5$ due to Ga addition is small. Considering the similar lattice constants of Cu(In$_{1-x}$Ga$_x$)$_3$Se$_5$ [18] and Cu(In$_{1-x}$Ga$_x$)$_5$Se$_8$ [3], it is expected that the variation of the lattice mismatch with x is also small in Cu(In$_{1-x}$Ga$_x$)$_5$Se$_8$. Considering the previous studies on CuIn$_{1-x}$Ga$_x$Se$_2$ [27] and CuGa$_3$Se$_5$ [10], together with our present study, the shift trend of low-frequency bands in this work is unlike that of high-frequency bands mainly affected by In(Ga)–Se bonds. The 77 (B$_2$/E), 90 (E) and 105 cm^{-1} (E) bands are mainly determined by the bond-bending forces which preserve the tetragonal structure and they depend weakly on the anion mass [26].

According to the ODC model proposed by Zhang *et al* [5], CH–CuIn$_5$Se$_8$ has 50% each of two types of local tetrahedral cationic clusters around Se: 2In + Cu + V$_{Cu}$ (denoted as $N = 7$) and 3In + V$_{Cu}$ (denoted as $N = 9$). Here N denotes the sum of valence electrons of Se-centred nearest neighbour cations. For the In–Se bond length, the distance in $N = 9$ clusters is slightly larger than that in $N = 7$ clusters [21], resulting in a displacement of the Se atom between the different N and the same N clusters according to its local environment. Thus, there are different bond properties of local clusters: namely, the Cu–Se, In–Se and Ga–Se bond forces vary with the different local clusters.

Due to the introduction of Ga, the defects and defect pairs distributed in local clusters should be extended to any spatial scale and hence lead to the formation of concentration fluctuations in varying degrees in Cu(In$_{1-x}$Ga$_x$)$_5$Se$_8$ films with $0 < x < 1$. Such spatially extended effects caused by mixed defects and clusters can decrease the phonon lifetimes, which may be responsible for the increase in the asymmetric broadening of Raman bands around A$_1$. The increase in asymmetric broadening of Raman bands around A$_1$ in Cu(In$_{1-x}$Ga$_x$)$_5$Se$_8$ with increasing x should be indicative of the presence of a large density of defects and hence lead to a reduction in crystalline quality.

On the other hand, the local and gap modes in intergranular regions can be produced in polycrystalline films due to the formation of a large number of mixed defects and clusters. Thus, these local modes can also contribute to the observed broadening and overlapping of Raman bands.

3. Conclusions

From the systematic analysis of Raman spectra in Cu(In$_{1-x}$Ga$_x$)$_5$Se$_8$ with varying x, it is found for the first time that with increasing Ga content, the A$_1$ frequency shifts from 151 to 160 cm^{-1}

in an approximately polynomial curve, and the low frequencies below 125 cm^{-1} clearly show one-mode behaviour, whereas the high frequencies in the region between 160 and 289 cm^{-1} exhibit two-mode behaviour. Additionally, the quenching of the Raman band at 174 cm^{-1} for the Ga-rich films gives a hint of the presence of other similar localized structure phases in chalcopyrite-related CuIn$_5$Se$_8$, but not CuGa$_5$Se$_8$, due to the Ga inhibition effect. The changes in Raman modes have been qualitatively discussed in terms of the effect of local clusters in defect chalcopyrite structure. Due to Ga addition, mixed defects associated with concentration fluctuations on a microscopic scale increase the disorder in the cation sublattice and structure, resulting in the broadening and overlapping of Raman bands. The interaction between local clusters should change the bond properties in the lattice and needs further investigation.

Acknowledgments

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