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Infrared reflectance and transmission spectra of semiconducting non-stoichiometric $CdGe_xAs_2$

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The infrared reflectance and transmission spectra of amorphous $CdGe_xAs_2$ were investigated to study the amorphous structure with varying Ge content. The mid-infrared optical absorption edges of amorphous $CdGe_xAs_2$ with $0 < x < 1.2$, were observed in the range 1.6–1.7 μm, indicating a structural similarity in short-range order throughout. Comparing the reflectance and transmission spectra of amorphous and devitrified crystalline phases established that the structures of amorphous $CdGe_xAs_2$ transformed from the $CdAs_2$ basic structure to the chalcopyrite ($CdGeAs_2$) structure, as one progressed from $x = 0$ to $x = 1.2$. The infrared spectra were interpreted interactively with radial distribution function, magnetic susceptibility, density measurements, and crystallization studies. The crystallization behaviour of amorphous $CdGe_xAs_2$ that was heat treated at different temperatures was investigated using far-infrared transmission spectra.

1. Introduction

$A^{II}B^{IV}C^{V}$ semiconducting compounds (chalcopyrite structure) are chemically and structurally close analogues of the $A^{III}B^{V}$ compounds [1–3]. Because of the difference between the A–C and B–C interatomic distances, the tetrahedra are slightly distorted [4]. When the A and B atoms form ordered sublattices, the crystals are tetragonal (chalcopyrite) rather than cubic (sphalerite structure). $CdGeAs_2$ is one of the ternary semiconducting compounds which can be prepared in either the crystalline or amorphous states [5, 6].

Knowledge of short-range atomic arrangement [7] in amorphous semiconducting $CdGeAs_2$ is necessary for understanding the electronic characteristics observed from electrical and optical property measurements. Proposals for structural models of amorphous $CdGeAs_2$ have been made from radial distribution function (RDF) [8], magnetic susceptibility [9], crystallization [10], and macroscopic density measurements [11]. From RDF analysis of amorphous $CdGeAs_2$, the coordination number of cations (Cd and Ge) was found to be close to four, indicating that the basic units in the amorphous structure are $CdAs_4$ and $GeAs_4$ tetrahedra. From magnetic susceptibility measurements as a function of temperature, it was proposed that the basic unit of amorphous non-stoichiometric $CdGe_xAs_2$ is the $CdAs_4$ tetrahedron [9]. By crystallization studies and macroscopic density measurements, a model of the transformation from the crystalline $CdAs_2$ structure to the chalcopyrite ($CdGeAs_2$) structure, was adopted from an abrupt change observed in behaviour at $x = 0.6$ [10, 11]. Amorphous structures of $CdGe_xAs_2$ were classified into two groups, depending on composition (Ge content): "$CdAs_2$ group" with $x \leq 0.6$ and "$CdGeAs_2$ group" with $x > 0.6$.

Crystalline $CdAs_2$ with tetrahedral coordination has the same electronic configuration as the $CdGeAs_2$ crystal. By the transfer of two electrons, one from every As atom, Cd changes its electronic configuration from $4d^{10}5s^2$ into $4d^{10}5s^25p^2$, while As changes from $3d^{10}4s^24p^3$ into $3d^{10}4s^24p^2$ (i.e. the configuration of group IV atoms). The crystalline form of $CdGeAs_2$ is related to the crystalline form of $CdAs_2$: with the addition of Ge atoms to $CdAs_2$ to form $CdGeAs_2$. The truly tetravalent Ge atoms lie at the centre of nearly undistorted tetrahedra, while the distortion around the Cd and As atoms is much higher, thus revealing the imperfect sp^3 character of their bonds. An alternative bond between two group IV atoms is the double bond which might be expressed in two different ways: either bent bonding or δ- and π-type orbital bonding [12].

Analysis of vibrational spectra provides a powerful tool for obtaining structural information concerning amorphous materials. Mid-infrared transmission spectra were measured to determine the transmission ranges of amorphous $CdGe_xAs_2$ along with studying structural units (short-range order) via optical band gaps. The effect of germanium content on the amorphous structures of $CdGe_xAs_2$ was investigated using far-infrared reflectance and transmission spectra because the structural units in the amorphous phase display characteristic absorption bands in this range. These spectra for amorphous $CdGe_xAs_2$ were interpreted on the basis of the corresponding crystalline

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spectra. The crystallization behaviour of amorphous $CdGe_xAs_2$ was also studied using the far-infrared transmission spectra and then interactively interpreting them along with XRD and DSC analysis.

2. Experimental procedure

Six different compositions represented by the formula $CdGe_xAs_2$, where x-values were 0, 0.3, 0.6, 0.8, 1.0, and 1.2, were prepared with Cd and Ge of 99.999% purity and As of 99.99% purity. Amorphous $CdGe_xAs_2$ compounds were prepared by water-quenching of melts vacuum-sealed ($< 10^{-5}$ torr; $\sim 1.333 \times 10^3$ Pa) in carbon-coated (via pyrolysis) fused silica tubes (8 mm diameter, 1 mm thick). A motorized mixing furnace was used for enhancing homogenization, in which the melts were held for 24 h at a temperature 200 °C above the melting point.

Crystallization behaviour was investigated using DSC with 40–70 mesh amorphous powders hermetically sealed in aluminium pans, with a constant heating rate of 0.5 °C min^{-1}. Based on DSC crystallization traces, each sample was precisely heat-treated and quenched (~ 500 °C min^{-1}) using the DSC. Quenched powdered samples were used for XRD and spectroscopy analysis. Bulk pieces of amorphous samples were ground to ~ 110 µm thickness in the shapes of plane-parallel plates and polished to 0.05 µm for mid-infrared transmission spectral measurements.

A Nicolet 60SX Fourier transform infrared (FTIR) spectrometer was used to measure the transmission spectra in the region 400–6000 cm^{-1}. The accuracy of the spectrometer is 0.01 cm^{-1}. Each spectrum was scanned 32 times with a resolution of 4 cm^{-1}. A Nicolet 20F Far FTIR spectrometer was used to measure the reflectance spectra and transmission spectra in the region 50–500 cm^{-1}. The accuracy of the spectrometer is 0.01 cm^{-1}. Each spectrum was scanned 300 times with a resolution of 4.0 cm^{-1}. For far-infrared transmission spectra measurements, powdered samples were mixed with polyethylene powder. Film samples were formed from the mixture by first placing the sealed dies containing them into boiling water, and cooling the dies with the material in air. Far-infrared reflectance spectra were measured directly from the polished samples using a diffuse reflectance accessory.

3. Results and discussion

The compositions of six samples G0, G0.3, G0.6, G0.8, G1.0, and G1.2 represent x-values of 0, 0.3, 0.6, 0.8, 1.0, and 1.2 in $CdGe_xAs_2$, respectively. The mid-infrared transmission spectra of amorphous $CdGe_xAs_2$ are illustrated in Fig. 1. The optical absorption edges of amorphous $CdGe_xAs_2$ are determined as 0.73–0.77 eV ($\sim$ 1.6–1.7 µm), which contrasts with the broad differences in absorption edges between crystalline $CdGeAs_2$ ($\sim$ 0.53 eV) and $CdAs_2$ ($\sim$ 1.0 eV) [9, 13]. This relation indicates that there exists a structural similarity in the short-range order in the family of amorphous $CdGe_xAs_2$, implying the structural basic units throughout remain $CdAs_4$ tetrahedra. Using the multiple scattering formalism, Klima *et al.* [7] suggested that the existence of an optical energy gap in the spectrum of amorphous covalent semiconductors is a result of short-range order. The strong lattice absorption bands at 15 µm in Fig. 1 are ascribed to a band structure change (near the boundary of the Brillioúin zone) of the amorphous $CdGe_xAs_2$, which was discussed in detail in [14].

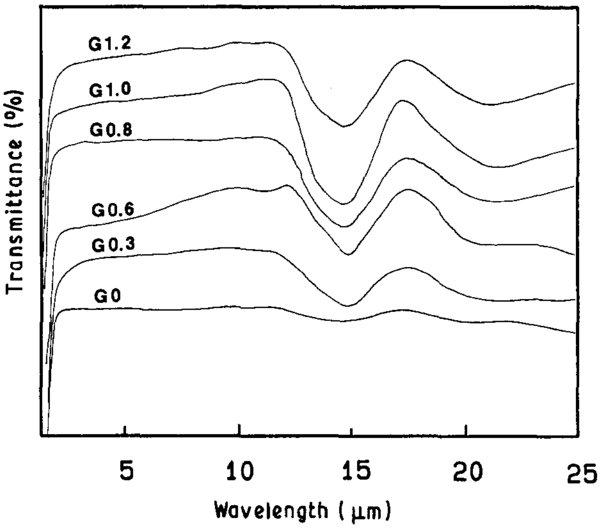

Figure 1 Infrared spectra of amorphous $CdGe_xAs_2$.

These reflectance and transmission spectra of polycrystalline $CdGe_xAs_2$ after full crystallization (at 500 °C) are illustrated in Fig. 2. The spectra of devitrified polycrystalline $CdGe_xAs_2$ appeared as two distinct groups, depending on composition (Ge content): the first group being $x = 0.8, 1.0, 1.2$, with their spectra similar to that of stoichiometric $CdGeAs_2$ ("$CdGeAs_2$ group"); the other group is $x = 0, 0.3, 0.6$, with their spectra similar to that of stoichiometric $CdAs_2$ ("$CdAs_2$ group"). In the case of the $CdGeAs_2$ group, a small amount of second phases of Ge in G1.2, and $CdAs_2$ in G0.8, were observed in X-ray diffraction patterns [10], as expected from the deviation from stoichiometry. These second phases were not observed in Fig. 2. In the case of the $CdAs_2$ group, Ge-doped $CdAs_2$ and Cd_3As_2 phases were observed in the X-ray diffraction patterns [10]. On the basis of comparisons with the spectra of $CdSiAs_2$, $CdAs_2$, and GaAs [14], the three main bands of crystalline $CdGeAs_2$ (G1.0) at wave numbers of 274, 199, and 155 cm^{-1} were assigned. The bands at 274 cm^{-1} are due to vibrational modes involving Ge and As, while the bands at 199 cm^{-1} are due to modes involving Cd and As. The bands at 155 cm^{-1} are due to the vibrational modes involving the cations alone (principally Ge because of the reduced contribution of the heavier cation (Cd)). In the $CdAs_2$ group these (155 cm^{-1}) vibrational modes are observed at lower wave numbers because of the change in basic structure (137 cm^{-1} for G0.3 and G0.6) and the unmasking of the Cd vibration (120 cm^{-1} for G0). The microstructures of as-quenched G0.3 and G0.6 glasses showed that Ge content in excess of $x \simeq 0.2$ was rejected from the $CdAs_2$ matrix in the melt and formed spherical Ge-rich segregates [10]. The weak intensity of the bands (vibrational

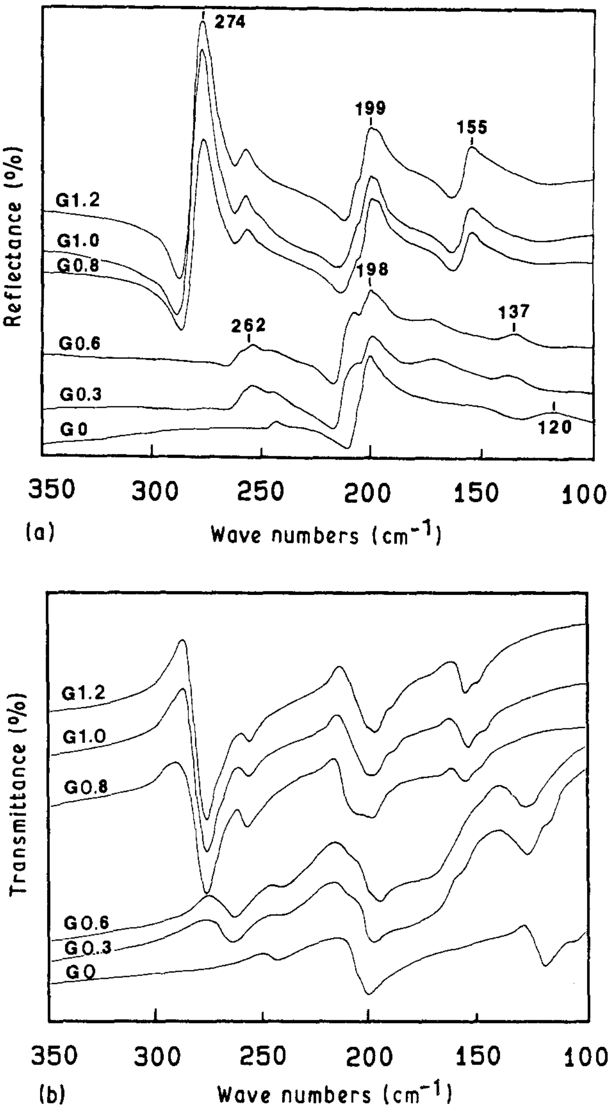

Figure 2 Far infrared spectra of devitrified polycrystalline $CdGe_xAs_2$: (a) reflection and (b) transmission.

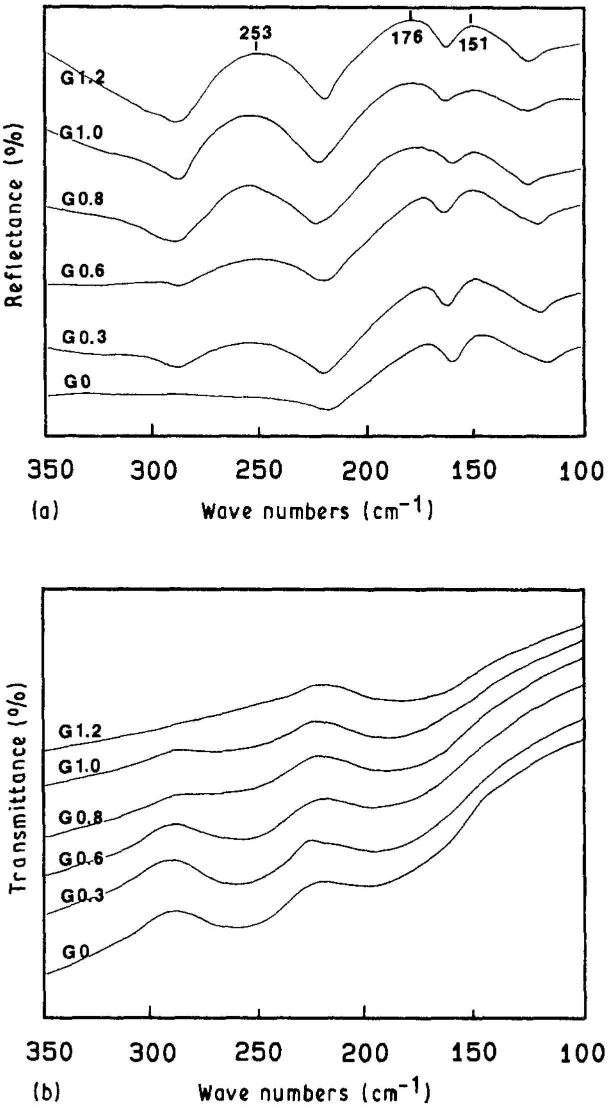

Figure 3 Far-infrared spectra of amorphous $CdGe_xAs_2$: (a) reflection and (b) transmission.

modes involving Ge and As) at ~ 262 cm^{-1} in both G0.3 and G0.6 that are shown in Fig. 2a, are ascribed to the doped Ge in the $CdAs_2$ structure to the limit of $x \simeq 0.2$. One may note that the intensity of the bands at ~ 262 cm^{-1} is almost the same for both G0.3 and G0.6 (see Figs 2 and 3), confirming the limited solubility of Ge in the $CdAs_2$ structure ($x \simeq 0.2$), regardless of the extent of doping (up to $x \simeq 0.6$). The infrared reflectance and transmission spectra of amorphous $CdGe_xAs_2$ are illustrated in Fig. 3. From the assignment of vibrational bands made for crystalline $CdGe_xAs_2$, the bands observed at ~ 253, 176, and 151 cm^{-1} in Fig. 3a, were assigned to vibrational modes involving mainly Ge–As bonds, Cd–As bonds, and cations (Cd and Ge), respectively.

The maxima of the broad vibrational bands observed in amorphous $CdGe_xAs_2$ show a shift to lower wave numbers compared with those of the corresponding crystalline phases. The origin of this shift will be discussed subsequently in the spectroscopic study of crystallization behaviour.

In Fig. 3a and b, the broad bands assigned to vibrational modes involving Ge–As bonds are observed at almost the same location for all glasses. However, the intensity of those bands observed in the spectra of G0.3 and G0.6 samples is weak, and those bands logically do not exist in the spectra of the G0 sample. The broad bands at 151 cm^{-1} (cation alone) of amorphous $CdGe_xAs_2$ are shown in the reflectance spectra in Fig. 3a, but were not observed in the transmission spectra in Fig. 3b. From Figs 2 and 3, the structure of amorphous $CdGe_xAs_2$ is interpreted to transfer from the $CdAs_2$ basic structure to the $CdGeAs_2$ structure with increasing Ge content, which is in good agreement with crystallization studies [10] and macroscopic density measurements [11].

Crystallization behaviour of amorphous $CdGe_xAs_2$ was investigated using far-infrared transmission spectra after heat treatment at various temperatures using DSC. The transmission spectra for crystallization behaviour were interpreted with DSC traces and XRD analysis reported in [10]. In the $CdGeAs_2$ group, the transmission spectra of G1.2 and G0.8 for crystallization are similar to that of stoichiometric $CdGeAs_2$ (G1.0) (the latter shown in Fig. 4). The maxima of broad bands near 272 and 198 cm^{-1} in as-quenched glasses that were heat-treated at 405 °C, and at 412 °C shifted to higher wave numbers and approached the

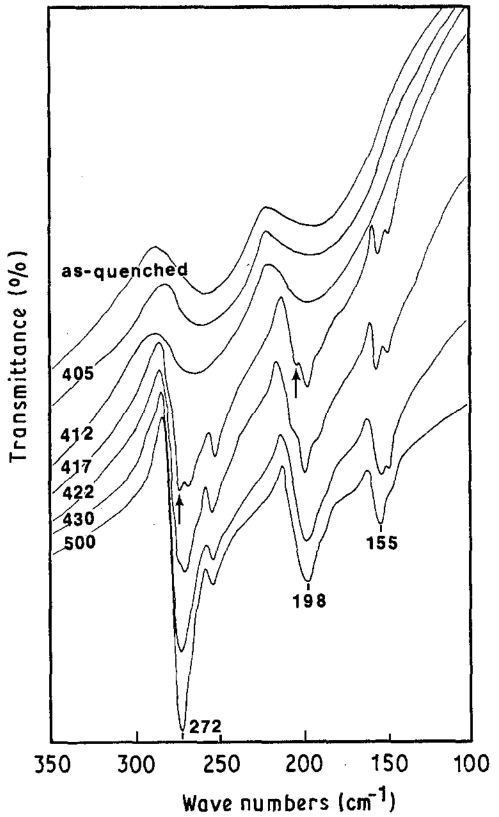

Figure 4 Far-infrared transmission spectra of amorphous $CdGeAs_2$ (G1.0) heat treated at various temperatures.

positions of the corresponding crystalline bands with increasing temperature. This can be explained by the higher coordination for cations or bent bonds in as-quenched glass. From RDF analysis [8], it was proposed that a strong disturbance of the amorphous lattice enhances the probability of some development of higher coordination for cations ($CdAs_6$ or $GeAs_6$) and hence weaker individual Cd–As and Ge–As bonds. From macroscopic density measurements, the density of amorphous $CdGeAs_2$ was ~ 2% higher than that of the crystalline compound [11], implying closer interatomic distances which can be interpreted to cause increasing bond strength (increasing wave number) in the amorphous state. However, the shift to lower wave numbers in Fig. 4 implies weaker bonding, thus the double bond of sp^3 may be a bent bond [12]. Below the crystallization temperature (417 °C in Fig. 4), the spectral changes in as-quenched glasses that were heat treated at 405 °C, and 412 °C indicate that a change in local atomic order in the amorphous phase begins to occur with a gradual increase in temperature.

The bands marked with an arrow in Fig. 4 near 272 and 198 cm^{-1} were observed from glass heat treated at 417 °C. At 417 °C, it was found from XRD and microstructure [10] that the Ge-rich precursor phase ($Cd_{0.24}Ge_{0.28}As_{0.48}$) with a pseudo-cubic structure coexists with the chalcopyrite phase grown spherulitically from the precursors. The bands marked as an arrow near 272 and 198 cm^{-1} are believed to be due to the precursor phase. The intensity of these bands become comparatively weaker than that of the major chalcopyrite $CdGeAs_2$ phase at 422 °C as this latter phase grows. After full crystallization to 500 °C, these bands disappear due to the recrystallization of the precursor phase to a stable phase (chalcopyrite).

In the case of the $CdAs_2$ group (G0, G0.3, G0.6), the crystallization behaviour had the common feature of a large low-temperature DSC exotherm between the glass transition and crystallization exotherm [10]. This exotherm was proposed to correspond to a glass to glass transformation for a chemical ordering process by the reaction: $Cd_3As_2 + 4\ As \rightarrow CdAs_2$. The broad amorphous humps in the X-ray diffraction patterns were found to become sharper after this exotherm. The far-infrared transmission spectra of amorphous $CdAs_2$ (G0) that was heat treated at different temperatures are shown in Fig. 5. The broad bands (~ 201 cm^{-1}) of Cd–As bonds in the glass that was heat treated at 325 °C after the glass to glass exotherm became sharper than that of the as-quenched glass. Also, the maxima of broad bands of Cd–As bonds shifted to that of the corresponding crystalline bands. At 344 °C, the shoulder (marked with an arrow in Fig. 5) of the bands at 201 cm^{-1} are believed to be the initial crystalline phase of $CdAs_2$ adopting a structure slightly different from the stable $CdAs_2$ crystalline phase. The glass structure was preserved initially in this initial crystalline phase resulting after the crystallization of the glass and then the crystalline phase relaxed into the normal strucure [8].

The far-infrared transmission spectra of G0.6 for crystallization are similar to those of G0.3, the latter of which is shown in Fig. 6. The intensity and the position of bands at 198 and 241 cm^{-1} in G0.3 change similarly with those of G0 in Fig. 5 with heat treat-

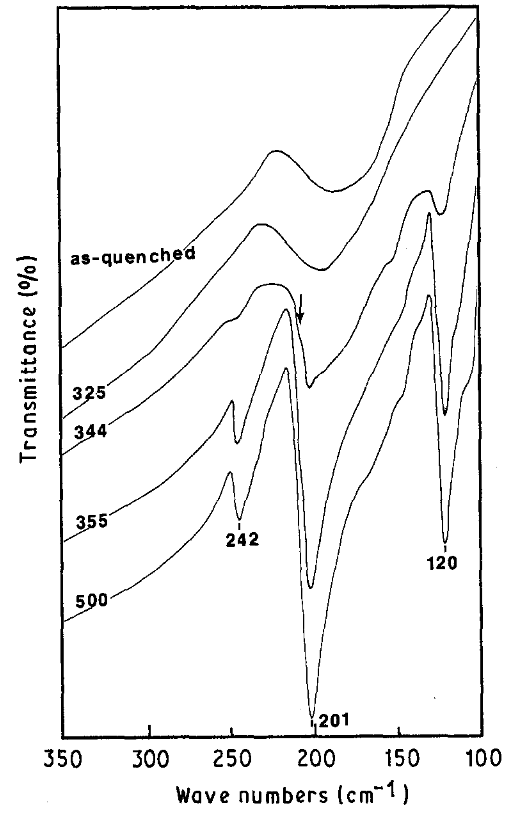

Figure 5 Far-infrared transmission spectra of amorphous $CdAs_2$ (G0) heat treated at various temperatures.

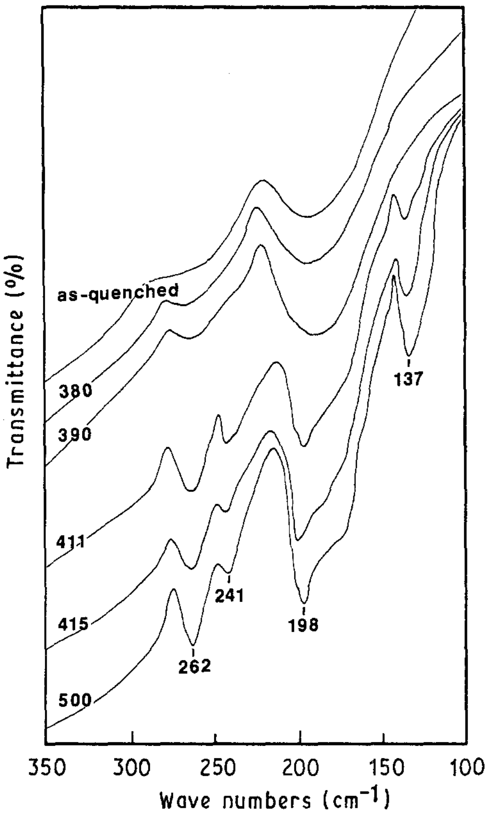

Figure 6 Far-infrared transmission spectra of amorphous $CdGe_{0.3}As_2$ (G0.3) heat treated at various temperatures.

ment. Also, the changes of intensity and position of bands at 262 cm^{-1} which can be assigned to the vibrational mode involving Ge and As, follow similar trends. However, the maxima of broad bands of as-quenched glass corresponding to the crystalline 262 cm^{-1} band (Ge–As bonds) appear at a much lower wave number compared with the band maximum of the glass heat treated at 380 °C. With initial Ge additions to $CdAs_2$, forming a glass with $x \lesssim 0.2$, Ge atoms predominantly occupied the larger vacancy sites (A-sites) formed in channels shaped spirally with As atoms [11]. The doped Ge atoms in the $CdAs_2$ structure are believed to bind weakly with As atoms in the as-quenched state. After thermal processing to 380 °C, Ge bonding adjustment results in a comparatively large shift toward lower wave numbers.

The intensity of the bands at 198 cm^{-1} in Fig. 6 increased markedly with temperature. As with the discussion for G0 samples, this increase of intensity indicates that the number of Cd–As bonds were increased by a glass to glass reaction: $Cd_3As_2 + 4\,As \rightarrow CdAs_2$. Below the crystallization temperature (here at 411 °C), a change in local atomic order in the amorphous phase begins to occur with a gradual increase in temperature.

4. Conclusions

The optical absorption edges of amorphous $CdGe_xAs_2$ were observed at ~ 1.6–1.7 µm, indicating a structural similarity in the short-range order of amorphous $CdGe_xAs_2$ for $0 < x < 1.2$. This implies that the structural basic units are $CdAs_4$ tetrahedra. From the far-infrared reflectance and transmission spectra of $CdGe_xAs_2$ in the amorphous and devitrified crystalline states, the amorphous structure was found to transfer from the $CdAs_2$ basic structure to the chalcopyrite structure ($CdGeAs_2$) with Ge content more than $x = 0.6$. The intensity of broad bands at 274 cm^{-1} in amorphous $CdGe_xAs_2$ increased with Ge content but the intensity of the Cd–As bond at 199 cm^{-1} did not change. The infrared reflectance and transmission spectra of amorphous $CdGe_xAs_2$ were interpreted on the basis of spectra of devitrified crystalline phases. In the amorphous $CdAs_2$ group (G0, G0.3, G0.6), the intensity of the bands of Cd–As at 201 cm^{-1} did not show any change. The bands at 262 cm^{-1} due to vibrational modes involving the Ge–As bonds showed almost the same intensity for G0.3 and G0.6 but, of course, did not exist in G0, implying Ge atoms in excess of $x \simeq 0.2$ were rejected from the $CdAs_2$ matrix in the melt.

The crystallization behaviour of amorphous $CdGe_xAs_2$ was investigated using far-infrared transmission spectra. In the $CdGeAs_2$ group, the spectra of G0.8 and G1.2 were similar to that of stoichiometric $CdGeAs_2$ (G1.0). The Ge-rich precursor phase was observed to coexist with the $CdGeAs_2$ phase grown heterogeneously from this precursor. The precursor bands were found to disappear after full crystallization due to recrystallization to a stable phase. In the $CdAs_2$ group (G0, G0.3, G0.6), the bands of Cd–As in G0.3 and G0.6 were found to change in a similar manner to those in G0 during crystallization. The intensity of Ge–As bands in G0.3 and G0.6 increased after a glass to glass exotherm but was almost constant thereafter below the crystallization temperature. However, the intensity of Cd–As bands increased with temperature prior to crystallization.

The maxima of broad bands in as-quenched $CdGe_xAs_2$ glasses were observed at lower wave numbers compared to the corresponding crystalline bands. This may be explained by the higher coordination for cations and bent bonds in as-quenched glasses. The higher coordinations were due to a strong disturbance of the amorphous lattice and the bent bonds were postulated to explain the higher density of the amorphous phase than crystalline phase contrasting against a shift to lower wave numbers for amorphous samples. The shifting and sharpening of broad bands of amorphous $CdGe_xAs_2$ with increasing temperature indicates that a change in local atomic order in the amorphous phase begins to occur with a gradual increase in temperature below the crystallization temperature.

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