Anomalous composition and temperature dependence of the energy gap of $AgGa_{1-x}In_xSe_2$ mixed crystals

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Lattice constants a and c were measured in the mixed crystals $AgGa_{1-x}In_xSe_2$ for $0 \leq x \leq 1$. They showed a miscibility region from $x=0.0$ to $x=0.4$ and from $x=0.8$ to 1.0, and then immiscibility near $x=0.6$ in the composition dependence of the lattice constants a and c. Also, the photoconductivity peak energy and the energy gap measured in the composition range from $x=0.0$ to 1.0 showed a discontinuity near $x=0.6$. The temperature coefficient of the photoconductivity peak energy is $(1.4-2.8)\times10^{-4}$ eV/K and that of the energy gap $(2.3-3.8)\times10^{-4}$ eV/K in the temperature range 25–75 K. The sign of the temperature coefficient reverses and the values are $-(2.4-4.1)\times10^{-4}$ and $-(2.4-5.1)\times10^{-4}$ eV/K, respectively, in the temperature range 100–300 K.

In recent years, the physical properties of I-III-VI_2-type compounds with the chalcopyrite structure[1–8] have attracted considerable interest because the specific energy band and crystal structure of these materials make them promising objects in solid-state physics and semiconductor electronics. In the present paper, we report some measurements of the composition dependence of the lattice constants a and c, the composition and the temperature dependence of the photoconductivity peak energy, and the energy gap from optical absorption in the mixed crystals $AgGa_{1-x}In_xSe_2$ for $0 \leq x \leq 1$.

The ingots of $AgGa_{1-x}In_xSe_2$ used in this experiment were prepared for high-purity (99.999%) elements in powder form. The elements were mixed and sealed in evacuated quartz tubes at 2×10^{-6} Torr. The tubes were heated at a rate of 40 °C per h, up to 890 °C, held for 40 h and cooled to room temperature over 48 h. The crystal structure obtained from the powder x-ray diffraction was chalcopyrite. The composition dependence of the lattice constants a and c measured in $AgGa_{1-x}In_xSe_2$ crystals is presented in Fig. 1. The lattice constants a and c for $x=0$ ($AgGaSe_2$) are $a=5.9930$ Å, $c=10.8474$ Å and for $x=1.0$ ($AgInSe_2$), $a=6.1027$ Å, $c=11.7122$ Å. The lattice constants of mixed crystals $AgGa_{1-x}In_xSe_2$ are found to be in good agreement with Shaukat and Singh's[9] experimental data; $a=5.9920$ Å, $c=10.8863$ Å for $AgGaSe_2$ and 6.0913 Å, $c=11.7122$ Å for $AgInSe_2$. Figure 1 shows the miscibility regions for $x=0.0-0.4$ and $x=0.8-1.0$ and the immiscibility near $x=0.6$ which has an undefined other phase that is probably a different kind of chalcopyrite.

The photoconductivity peak energy and the energy gap from optical absorption were measured in the mixed crystals $AgGa_{1-x}In_xSe_2$ for $0 \leq x \leq 1$. The composition dependence of both the photoconductivity peak energy and the energy gap is presented in Fig. 2. The energy gap of $AgGa_{1-x}In_xSe_2$ increases from 1.24 to 1.78 eV with decreasing x. The energy gap in the regions $x=0.0-0.4$ and $x=0.8-1.0$ varies linearly with x. The discontinuity near $x=0.6$ is ascribed to another chalcopyrite phase as in the case of the lattice constant behavior, Fig. 1.

The temperature dependence of the photoconductivity peak energy is presented in Fig. 3. The energy of the photoconductivity peak increases with increasing temperature and the temperature coefficient is $(1.4-2.8)\times10^{-4}$ eV/K in the temperature range 25–75 K. The energy of the photoconductivity peak decreases with increasing temperature and the temperature coefficient is $-(2.4-4.1)\times10^{-4}$ eV/K at 100–300 K.

The temperature dependence of the energy gap of

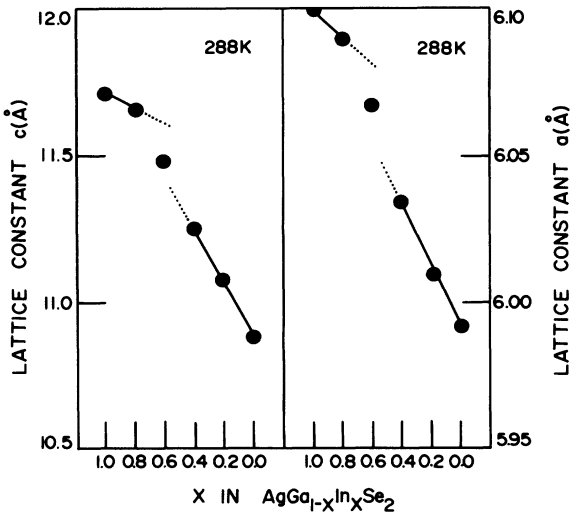

FIG. 1. Composition dependence of the lattice constants a and c.

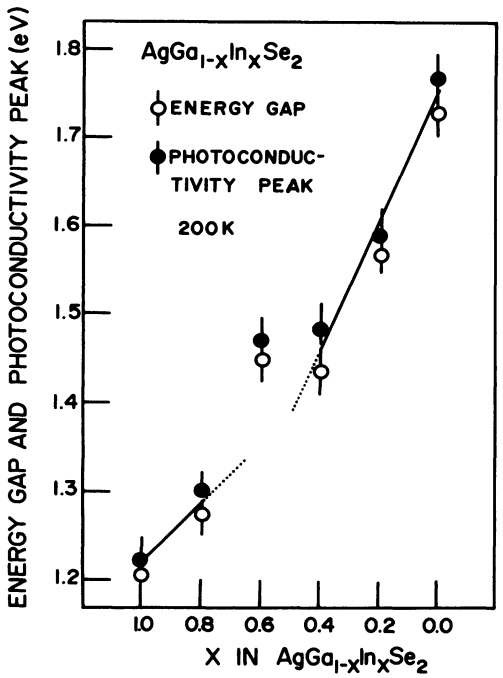

FIG. 2. Composition dependence of photoconductivity peak energy and energy gap.

$AgGa_{1-x}In_xSe_2$ is shown in Fig. 4. The energy gap increases with increasing temperature and the temperature coefficient is $(2.3-3.6)\times10^{-4}$ eV/K for the temperatures 25–75 K. The energy gap decreases with increasing temperature and the temperature coefficient is $-(2.4-5.1)\times10^{-4}$ eV/K over the temperatures 100–300 K. Hörig *et al.*[2] reported that in the temperature range 22–296 K the temperature coefficient of $CuGa_{0.52}In_{0.48}Se_2$ mixed crystals was -1×10^{-5} eV/K. Yu *et al.*[10] reported that the temperature coefficient for $AgGaS_2$ is 6×10^{-5} eV/K over the temperatures 4.2–80 K and -1.8×10^{-4} eV/K in the temperature range 80–300 K. From a comparison of our data with the above two and other reports[11,12] it would seem that a small value of the temperature coefficient is a property of both I-III-VI_2 Ag and Cu chalcopyrite compounds and the change of temperature coefficient sign near 75–100 K is a property of I-III-VI_2 Ag chalcopyrite compounds.

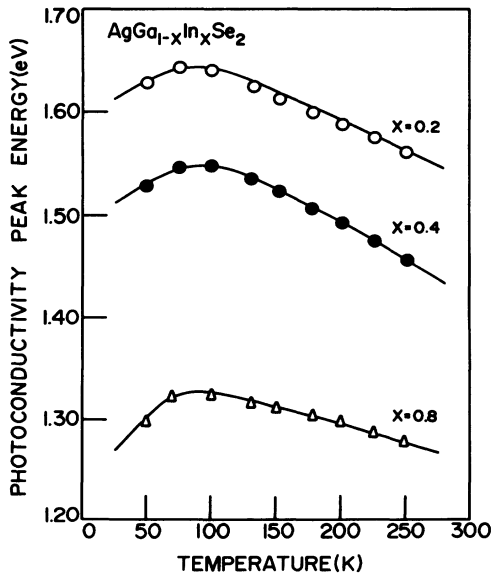

FIG. 3. Temperature dependence of photoconductivity peak energy for $x=0.2$, 0.4, and 0.8.

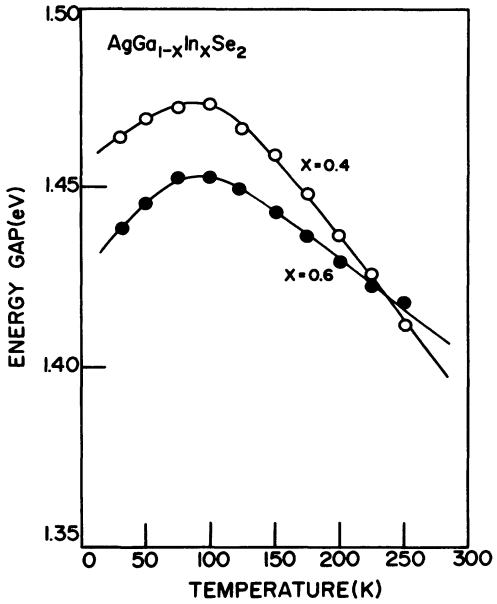

FIG. 4. Temperature dependence of energy gap for $x=0.4$ and 0.6.

The temperature dependence of the energy gap in semiconductors is caused by the thermal expansion of the lattice and the electron-phonon interaction. The thermal expansion represents the positive temperature coefficient[13] and the electron-phonon interaction has the negative sign.[14] Therefore it is considered that in $AgGa_{1-x}In_xSe_2$ the thermal expansion is dominant below ~75 K and the electron-phonon interaction above ~100 K. However, we cannot determine the absolute magnitude of each of these effects, since there are no band-structure calculations and the temperature dependence of $AgGa_{1-x}In_xSe_2$ lattice constants is not known. We are planning to remedy the latter situation by carrying out lattice constant measurements at other temperatures.

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