FIZIKA VOLUME 10 SUPPLEMENT 2, 1978
Proceedings of the VI Yugoslav Symposium of the Physics
of Condensed Matter, Kruševac, September, 18-22, 1978

ANALYSIS OF IONIC BONDS IN SEMICONDUCTING $A^{I}B^{III}C_2^{VI}$ COMPOUNDS

P.M.Nikolić, S.M.Stojilković+, Z.Petrović, P.Dimitrijević*

Institute of Physics, Electrotechnical Faculty,Belgrade University, +Electronic Faculty and *Philosophy Faculty, Niš Univesity, 11000 Belgrade, P.O.Box 57, Yugoslavia.

ABSTRACT

Semiconducting $A^{I}B^{III}C_2^{VI}$ compounds were obtained using the Bridgeman procedure. Far infrared reflectivity was measured in the range between 40 and 400 cm^{-1}. The experimental data were numericaly analysed and ionic bonds in: $AgInSe_2$, $CuInSe_2$, $AgInTe_2$ and $CuInTe_2$ were discussed.

1. INTRODUCTION

Many papers about $A^{I}B^{III}C_2^{VI}$ compounds have recently been published[1]. The main reson for this is the possible use their specific semiconducting properties have for producing light emitting diodes (LED), solar cells, lasers and nonlinear optical elements[2]. These compounds have a rather wide range of values for energy gaps so that there is a great possibility of choosing a suitable material for making devices. A good deal of work has been published on $CuInSe_2$ and $CuInS_2$. Both these compaunds have direct allowed energy gaps[3]. $CuInS_2$, $CuGaS_2$, $AgGaSe_2$ and $AgGaS_2$ are suitable for making lasers. Succesful p-n junctions have also been made from $CuInSe_2$ and $CuInS_2$.[4,5] Lattice reflectivity spectra of $CuGaS_2$, $AgGaS_2$[6,7], $AgInTe_2$[8], $AgInSe_2$[9] and even solid solutions of $CuGaS_2$-$CuGaSe_2$ have also been studied [10]

In this work we have investigated the lattice vibrations of $AgInTe_2$,$AgInSe_2$,$CuInTe_2$ and $CuInSe_2$. Also we discuss the consequencies of replacing Ag with Cu atoms and Se with Te atoms in the studied compounds.

2. EXPERIMENTAL

Single crystal samples of $AgInSe_2$ were made using the Bridgeman procedure. Using the same method only crystalline samples were produced of $AgInTe_2$, $CuInTe_2$ and $CuInSe_2$ compounds. The specimens for optical measurements were cut from ingots. Slices were between 0.5 and 2 mm thick. The samples were then polished on one side using a conventional polishing technique.

The far infrared reflectivity measurements were performed using a Beckman FS 720 Fourier spectrometer. The variation of near normal incidence reflectivity of $CuInSe_2$ is given in Figure 1.

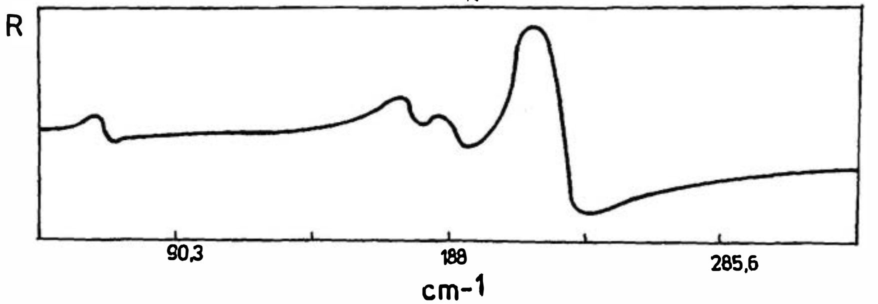

Fig.1. Nonpolarised far infrared reflectivity of $CuInSe_2$

Four reststrahlen bands occur in the range between 50 and 250 cm^{-1}. The variation of room temperature reflectivity of $AgInSe_2$ with wavenumber is given in figure 2. The light was polarised in the $\vec{E}\perp\vec{c}$ direction.

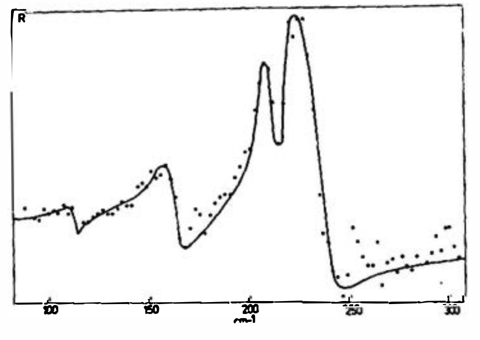

Fig.2. Polarised far infrared reflectivity of $AgInSe_2$ for $\vec{E}\perp\vec{c}$.

In this figure the experimental values are given with points. The solid line was calculated using the oscillator parameters obtained by numerical analysis, which was carried out with the aid of a fitting procedure according to Gervai's four parameter model[11].

The values of transversal (ω_{TO}) and longitudinal (ω_{LO}) optical modes are given in table 1, together with their damping factors (γ_{TO}) and γ_{LO}, respectively) for all four compounds studied.

In figure 3 are given experimental values of the reflectivity versus wavenumber for $CuInSe_2$ while the broken line represents the theoretical curve which best fits the values of the parameters given in table 1.

The real [Re(EPS)(—)] and imaginary [Im(EPS)(--)] parts of the complex dielectric function for $CuInSe_2$ are given i figure 4.

TABLE 1. Optical parameters used to fit far infrared reflectivity spectra. Frequencies and damping factors are expressed in units of cm^{-1}.

	$AgInSe_2$				$AgInTe_2$	$CuInSe_2$				$CuInTe_2$
	I	II	III	IV		I	II	III	IV	
ε_{TO}	113	158	200	219	168	67	175	190	212	145
ε_{LO}	114	166	214	239	184	70	183	197	236	179
γ_{TO}	5	10	2.3	2.3	4.13	10	12	10	0.7	21.5
γ_{LO}	4	9	9	9	4.13	15	14	15	13	32.8
ε_{∞}		12			9.84		16			14.8

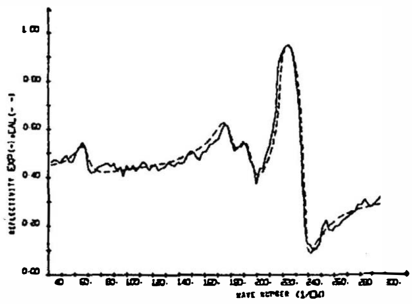

Fig.3. Experimental far infrared reflectivity (solid line) of $CuInSe_2$. Broken line represents theoretical curve.

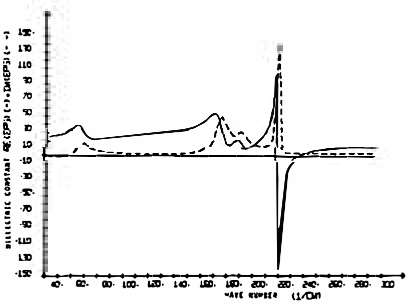

Fig.4. The real and imaginary parts of the complex dielectric function.

4. ANALYSIS AND DISCUSSION OF RESULTS

As far as we know, our experimental and numerical data could be compared with the only literature data published for $CuInSe_2$[7]. We have also observed four infrared active modes, but there are differencies in the position of transverse and longitudinal optical frequencies for first, second and fourth oscillators. Gan et al[7] did not determine the values of damping factors so that we cannot compare our values with any literature data. It is interesting to emphasise that Gan et al[7] could not distingnish longitudinal from transverse optical modes for the first two oscillators. In our case we obtained the values 67 and 70 for the first and 175 and 183 for the second oscillator and that is what one would expect.

We have also checked the composition of our $CuInSe_2$ samples using X-ray analysis, and the obtained values for the lattice parameters were in good agreement with the literature values.

As far as we know there are no previous studies of lattice vibrations in $AgInSe_2$. Our experimental data where we have observed four active infrared modes for $\vec{E}\perp\vec{c}$, are in good agrement with the group theory prediction[7].

Knowing that the atomic weights of Cu and Ag are rather big, one would expect that the oscillator frequencies are much lower for $AgInSe_2$ samples compared with $CuInSe_2$. In practice this is not the case and even more some $AgInSe_2$ modes are moved towards higher frequencies. These results are in agreement with the literature data obtained by Koschel et al[6] for $CuGaS_2$ and $AgGaS_2$. This means that the role of either Ag or Cu atoms in forming ionic bonds is relatively small. If, on the contrary, we compare the positions of the optical modes for $CuInS_2$ and $CuGaS_2$ it is obvious that the changes in position of their optical modes is in agreement with the differences in the atomic weights of indium and galium.

REFERENCES

1. Journal De Physique, V.36,Coloque C-3 suppl.,No9,1-191,1975.
2. Cardona M., Jerphagnon J., J. De Physique, C3,189,1975
3. Smith R.C, J. De Physique C3, 89,1975.
4. Parkers et al.,J.Cryst.Growth,20,315,1973.
5. Shay J.L., et al.,Appl.Phys.Lett.,19,366,1971
6. Koschel et al. Journal De Physique, C3,177,1975.
7. Gan J.N.,et al. Phys.Rev.,B13,3610,1976.
8. Nikolić P.M., et al.J.Engineer.Phys.13,45,1975.
9. Petrović Z.. Nikolić P.M.,J.Engineer.Phys.17,1978(to be published)
10. Bodnar I.V.,Karoza A.G.,Smirnova G.F.,Phys.Stat.Sol(b)84,K65,q977.
11. Gervais F. et al.J.Phys.C.,2374,1974.