

PRODUCTION CRYSTALLOGRAPHIC AND OPTICAL PROPERTIES OF
 $A^{II}B^{III}_2C^{VI}_4$ SEMICONDUCTING MATERIALS

P.M.Nikolić, S.M.Stojilković, P.Dimitrijević, S.S.Vujatović and
M.Rakić

Institute of Physics, Electrotechnical Faculty, Belgrade University,
Electronic Faculty and Philosophy Faculty Niš University.

ABSTRACT

Some $A^{II}B^{III}_2C^{VI}_4$ samples have been produced such as $CdGa_2Te_4$, $CdGa_2S_4$, $ZnIn_2S_4$ and $HgIn_2Se_4$ and their crystallographic and some optical properties have been studied. The optical properties were measured in the range of the absorption edge and also in the far infrared range where some ionic resonances were observed. The experimental results were numerically analysed and the value of some optical parameters calculated in the range of ionic resonances.

1. INTRODUCTION

A great deal of work about $A^{II}B^{III}_2C^{VI}_4$ compounds has been published mainly on $CdIn_2S_4$ and a cubic modification of $ZnIn_2S_4$. Both these semiconducting materials have the spinel structure with the space group O_h^7 and two molecules per Bravais cell. Practically all other semiconductors $A^{II}B^{III}_2C^{VI}_4$ have the S_4^2 space group and crystallise in a tetragonal lattice.

Ternary $A^{II}B^{III}_2C^{VI}_4$ compounds have well exposed photoelectric and luminescent properties¹⁾. In addition these semiconductors are interesting because they have some sort of defective diamond like structure and can be treated as materials which are intermediate between ordered crystals and disordered glassy semiconductors²⁾. They are sometimes called quasicrystalline materials³⁾. Some interesting reports have been published about $CdIn_2S_4$ including its photoconductivity properties in the visible range⁴⁾. For this material and also for $ZnIn_2S_4$ Raman and infrared spectra were reported⁵⁾. $CdGa_2Se_4$ and $CdGa_2S_4$ exhibit strong photosensitivity and luminescence effects which could be probably used in practice.

In this work some optical properties of several $A^{II}B^{III}_2C^{VI}_4$ compounds were investigated in the far infrared range.

2. EXPERIMENTAL

The samples of $CdGa_2S_4$, $CdGa_2Te_4$, $CdGa_2Se_4$, $ZnIn_2S_4$ and $HgIn_2Se_4$ were prepared using a standard Bridgeman method starting with spec-

troscopy pure elements. All the semiconductors made were polycrystalline except for HgIn_2Se_4 . The composition of the samples was checked by comparing the values of the calculated lattice parameters with the literature data. For CdGa_2S_4 which crystallise in a tetrahedral lattice the American ASTM standards were used, while for CdGa_2Se_4 and CdGa_2Te_4 the values of the parameters which were given by Hahn et al⁷⁾ were employed.

The reflectivity diagrams were obtained in both near and far infrared ranges using a Perkin Elmer 577 spectrophotometer and a Fourier spectrometer Beckman FS 702.

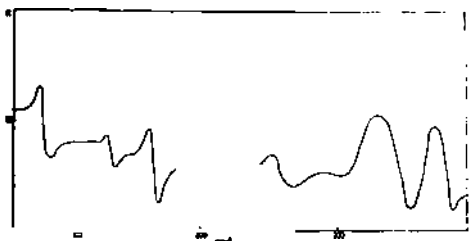


Figure 1. Far infrared reflectivity of CdGa_2S_4

In figure 1 the change of the far infrared reflectivity coefficient is given as a function of wavenumber for a polycrystalline sample CdGa_2S_4 . In this range there are six well exposed ionic resonances. It is obvious that one should know how these oscillators are directed in connection with the three existing crystallographic axes. For these measurements one needs sufficient large single crystal samples which we have not yet managed to obtain.

We also have made some far infrared transmission measurements on CdGa_2S_4 . These samples were made from a powder when it was mixed with powdered polyethylene. This mixture was then compressed at a pressure of 5t/cm^2 . The change of the transmission curve in the range between 40 and 250 cm^{-1} is given in figure 2

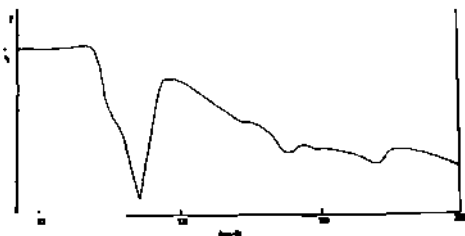


Figure 2. Far infrared transmission of CdGa_2S_4

where it is possible to see one very obvious absorption band at about 85cm^{-1} and also two less exposed absorption bands at about 136 and 170cm^{-1} . The reflectivity diagram versus wavenumber for CdGa_2Te_4 in the range between 40 and 400cm^{-1} is given in figure 3.

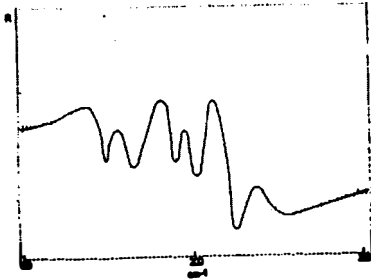


Figure 3. Far infrared reflectivity of CdGa_2Te_4 . Experimental points and curve obtained by a computer fitting procedure.

In this case one can also distinguish six well determined oscillators. Finally in figure 4 is given the reflectivity diagram for ZnIn_2S_4 , where only three oscillators are obvious.

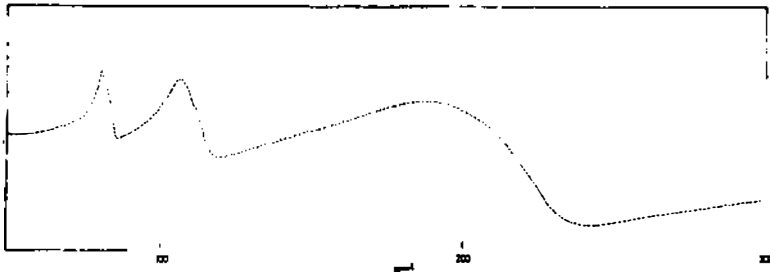


Figure 4. Far infrared reflectivity of ZnIn_2S_4 .

3. ANALYSIS AND DISCUSSION OF RESULTS

All experimentally obtained reflectivity diagrams were numerically analysed using a classical fitting procedure. In figure 3 a theoretical curve obtained with the best chosen values of the optical parameters is given together with experimental data represented by dots. There are obvious minor disagreements between these two sets of data, and that could be expected because in this case one should fit 25 parameters for the six oscillators.

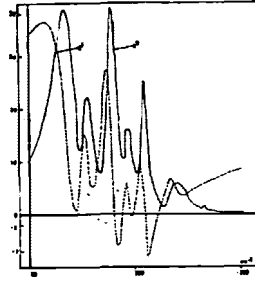


Figure 5. The real ϵ' and imaginary ϵ'' parts of the complex dielectric function for CdGa_2Te_4

The way of change of the real ϵ' and imaginary ϵ'' component of the dielectric constant is shown in figure 5. One can also see the effects of the well exposed six oscillators. The values of transversal and longitudinal optical modes together with their damping factors are given in Table 1

Table 1

cm^{-1}	CdGa_2Te_4	CdGa_2S_4	ZnIn_2S_4
ω_{T01}	141	84	80
ω_{L01}	148	86	83
γ_{T01}	30	0.8	1.95
γ_{L01}	6	6	5.55
ω_{T02}	153	134	104
ω_{L02}	164	136	113
γ_{T02}	12	6	6.15
γ_{L02}	10	4	12.45
ω_{T03}	178	163.5	175.5
ω_{L03}	190	168	230
γ_{T03}	11	8	42.5
γ_{L03}	5	3	26.5
ω_{T04}	193	258	
ω_{L04}	201.5	268	
γ_{T04}	6.1	43	
γ_{L04}	9	15	

Table 1 continued

cm^{-1}	CdGa_2Te_4	CdGa_2S_4	ZnIn_2S_4
ω_{T05}	209.5	322	
ω_{L05}	223.5	353	
γ_{T05}	6	28	
γ_{L05}	6	5.5	
ω_{T06}	236	368	
ω_{L06}	246	383	
γ_{T06}	15	4.8	
γ_{L06}	25	15	
ϵ_{∞}	14	12	11.45

It is well known that for ZnIn_2S_4 there are four infrared active modes according to the theory of groups, at the centre of the Brillouin zone⁵. We obviously did not succeed in observing the fourth oscillator for the spinel structure of ZnIn_2S_4 . The other $\text{A}_{\text{II}}^{\text{III}}\text{B}_{\text{III}}^{\text{II}}\text{C}_{\text{VI}}^{\text{IV}}$ compounds which have space group S_4^2 according Radatsan⁶ have got six infrared active modes and that is in good agreement with our experimental results.

If we compare the values of the optical parameters for CdGa_2Te_4 and CdGa_2S_4 it is obvious that when the "heavier" atoms of tellurium are replaced with the much "lighter" sulphur atoms the resonance frequencies are moved towards the higher energies. This is in good agreement with the well known behaviour of tin chalcogenide compounds and alloys^{8,9}.

In conclusion one can say that this is the first time that the lattice vibration of Cd,Zn,Ga chalcogenide alloys have been studied. They have interesting photoconductivity and luminescence properties, so that it is possible to expect further increased interest in these ternary compounds.

4. REFERENCES

1. Shionoya S., Tomoto Y., J. Phys. Soc. Japan, **19**, 1142, 1974
2. Fritzsche H., J. Non Cryst. Solids, **6**, 49, 1971
3. Bosacchi A., et al., Solid State Comm., **13**, 1805, 1973.
4. Nakanishi H., Endr S., Irei T., J. Physiq. C, Tome 36, 163, 1975
5. Unger W.K. et al. Solid St. Comm., **25**, 913, 1978.
6. Radatsan S.I., et al. Fiz. Tehn. Poluprov., **11**, 69, 1977.
7. Hahn H., et al., Zeit für Anorg. Chem. **5-6**, 241, 1955.
8. Chandrasekar H.R., Zwick U., Solid St. Comm., **18**, 1509, 1976.
9. Popović Z., Nikolić P.M., Chamberlain J.M., Physics Lett., **64A**, 123, 1977.