

PARALLEL OPTICAL PROPERTIES OF SINGLE CRYSTAL AND AMORPHOUS
 $\text{GeS}_{2-x}\text{Se}_x$ ALLOYS

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Abstract: Single crystals of $\text{GeS}_{2-x}\text{Se}_x$ were grown by the vertical Bridgman technique. It was shown that a complete range of solid solutions was formed and that lattice parameter "c" increased, beginning with GeS_2 , following Vegard's law. For both single crystal and amorphous sample, the optical properties were investigated in the range near to the absorption edge and the variation of the energy gap with composition was determined. Beginning with GeS_2 the energy gap decreased when the content of GeS_2 increased, for both single crystal and amorphous alloys. Infrared transmission spectra of the amorphous samples showed that the samples with more a 50 mol% GeS_2 were very transparent at the wavelength of 10.6 μm . This indicated that these amorphous alloys could be used for making optical fibers in communication systems where CO_2 lasers could be employed as light sources.

EXPERIMENTAL:

Crystallographic and optical properties of single crystals of GeS_2 and GeSe_2 have been investigated previously (1, 2, 3, 4). The optical properties of amorphous samples of both components have also been published recently (5, 6, 7). In particular GeSe_2 has become a very interesting material because it is useful as a resist in the lithography procedure for making submicron devices in integrated circuits (8). In this work we have investigated the optical properties of both amorphous and single crystal $\text{GeS}_{2-x}\text{Se}_x$ alloys. Special attention was paid to the amorphous alloys assuming that these materials might be suitable for making optical fiber in optical communications.

Single crystal $\text{GeS}_{2-x}\text{Se}_x$ samples were synthesized using the Bridgman technique. They could be easily cleaved on (001) plate. Using X-ray diffraction the change of their "c" lattice constant with composition was obtained and is given in figure 1. Beginning with GeS_2 it increased linearly to the value for GeSe_2 , following Vegard's law. The amorphous samples were

amorphous state were confirmed using microprobe analysis.

Transmission of monochromatic light in the range of the absorption edge was measured in all single crystal and amorphous samples using Perkin-Elmer UV spectrometer "Lambda 5". For single crystal samples of $\text{GeS}_{2-x}\text{Se}_x$ the change of direct energy gap was then calculated and its change with composition for E_g is given in figure 2. (broken line). The optical energy gap values for amorphous samples was obtained using an arbitrary method, where the linear part of $T = f(\lambda)$ was extended until it intersected the horizontal axes. The calculated change of the energy gap with composition for amorphous $\text{GeS}_{2-x}\text{Se}_x$ alloys is given in figure 2. (solid line).

The transmission spectra for the amorphous samples with various compositions were measured using a Perkin-Elmer 9830 spectrophotometer. These diagrams are given in figure 3. as a function of reciprocal wavelength. It is obvious that these amorphous alloys become transparent at larger wavelengths when the content of the Se is increased. First of all it may be noticed that these amorphous samples are very transparent in the range above 900 cm^{-1} , which means that these glassy materials could be used for making optical fibers in communications where CO_2 lasers are expected to be used as light sources.

DISCUSSIONS:

In this work it has been shown, for the first time, by X-ray analysis that complete solid solution existed throughout the whole composition range and that the variation of the lattice parameter "c" changed according to Vegard's law. This way of behavior is important confirmation that the quality and composition of the produced samples was as expected.

The change of the energy gap with composition, given in figure 2. for both single crystal and amorphous samples, is in agreement with earlier data for the starting compounds (3, 9, 10). While the energy gap changed almost linearly for the amorphous sample, the decrease was nonlinear for single crystal samples containing less than 25 mol% GeSe_2 . The energy gap values were found to be larger for single crystals than for amorphous samples of the same composition. That is in agreement with some recent data (11). This problem can be analysed by comparing the bond energy between various atoms. In table 1. are given the bond energies for various combinations of the

obtained when the melted sample, previously evacuated in quartz ampoules, were quenched in cold water. Their compositions in the

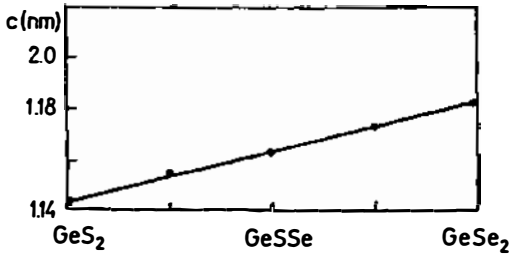


Fig. 1. The change of lattice constant "c" with composition for single crystal $\text{GeS}_{2-x}\text{Se}_x$ samples.

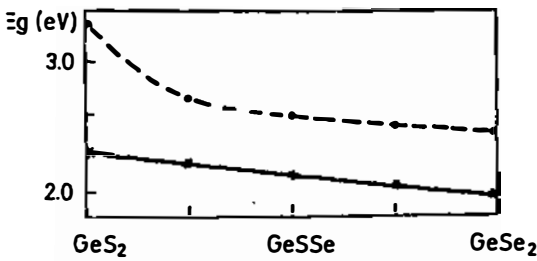


Fig. 2. The change of energy gap with composition for $(\text{GeS}_{2-x}\text{Se}_x)$. Solid line represents amorphous and broken line single crystal (E || b) samples.

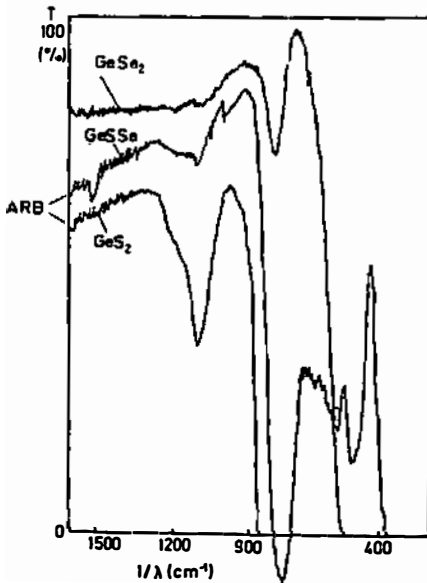


Fig. 3. The transmission spectra for some amorphous samples with compositions. Spectra for GeSSe and GeS_2 are given in arbitrary units.

elements: Ge, S and Se.

Table 1 - bond energy

bond	energy (Kcal/mol)	energy (eV)
Ge-Se	49	2.1
Ge-S	55.5	2.41
Se-Se	44	1.91
S-S	50.9	2.21
Se-S	49.7	2.16

These energies were calculated following Pauling (12). The larger concentration of S which combines preferentially with Ge, and Ge-S bond energies are larger than that of Ge-Se, S-S and S-Se, are followed by an decrease in the concentration of either S-S or S-Se bonds, which results in increase in the energy gap. The most important property of these amorphous alloys is that they are very transparent even at wavelengths above $11\mu\text{m}$ which means that these glassy materials could probably find an application in the construction of optical fibers in communication systems in which CO_2 lasers would be used as light sources.

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