LONG WAVELENGTH OPTICAL LATTICE VIBRATIONS AND STRUCTURAL PHASE TRANSITION IN MIXED a-In$_2$S$_{3-x}$Se$_x$ CRYSTALS

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The subject of this work is to present a set of spectroscopy data of In-S-Se alloys together with the FIR spectra of the end members In$_2$S$_3$ and In$_2$Se$_3$. The fact that the end members crystalize in different structuresimplies a structural phase transition as a function of the concentration which is veryfied by the analysis of our results. We have studied the normal mode behavior for all concentrations and compared the spectra obtained for crystals after a long annealing and also for quenched samples. The structures of these compounds are defective that means that a great number of cation sites are vacant sites randomly distributed. This work is also an attempt to examine the influence of annealing process on the IR spectra.

In$_2$S$_3$ exists in three crystallographic modifications. The room temperature phase β-In$_2$S$_3$ has a defect spinel tetragonal superstructure with a high degree of ordering of octahedral and tetrahedral vacancies. Above 420°C a disordering of the tetrahedral vacancies takes place and a new modification a-In$_2$S$_3$ appears. Under certain conditions of preparation it is possible this phase to be stabilized into room temperature and this allows us to study this compound in comparison with the alloys, which after a slight amount of Se concentration have of about the same structure as the a-In$_2$S$_3$.

In$_2$S$_3$ in its a-phase has a defect spinel cubic structure and we have observed a large number of normal modes by IR reflectivity. When Se is introduced into In$_2$S$_3$ crystals we observe only two restrahlen bands whose frequencies shift monotonically with the concentration and evidences a one mode behavior. The bands in Raman spectra show also the continous shift with concentration. When we reach to a concentratiou x = 2.5 we observe a drastic change in the spectra.

134

The analysis of IR spectra show now three sets of normal modes which exhibit one mode behavior and in addition to this we observe also three other sets of vibrational modes which show a two mode behavior. The final frequencies for them for In_2Se_3 with a small concentration of S, correspond to the frequencies of the three localized modes belonging to each one of the three sets of normal modes of In_2Se_3.

An interesting characteristic feature concerning a-In_2Se_3 aud its alloys is the difference between the reflection spectra of quenced and annealed samples. Fig. 1 compares the spectra of the same sample taken by quenching (a), and after two months (b) annealing. We observe that all bands were modified after annealing but they remained in the same position with regard to the frequency and new bands did not appear. We also observe a very high reflectivity at low frequencies for the quenced phase.

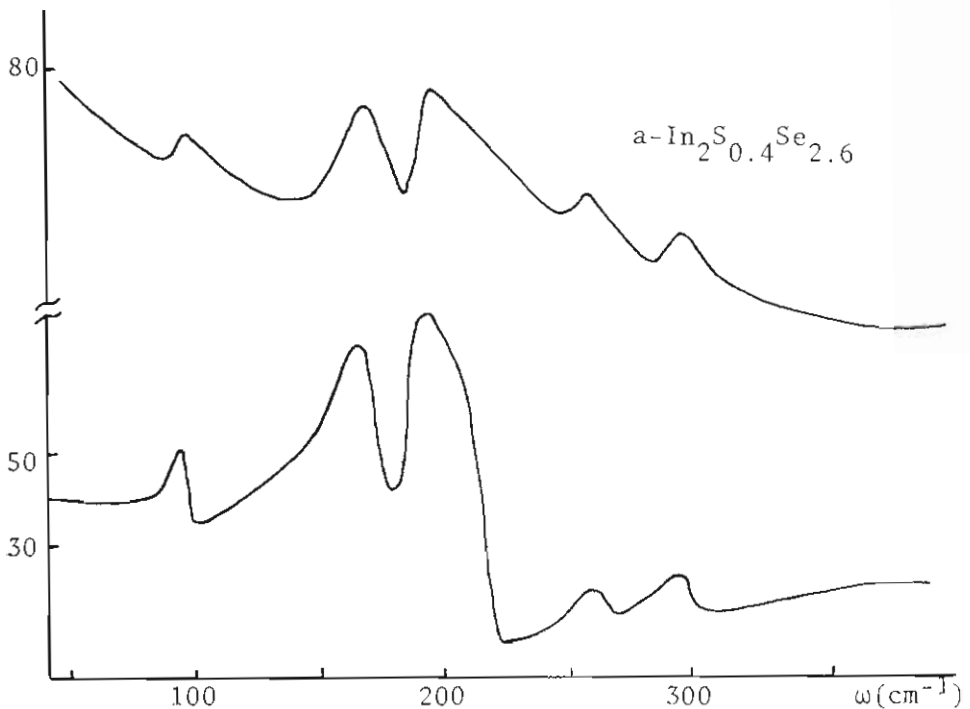Finally Fig. 2 shows the frequency distribution for the whole

Fig. 1. Infrared reflectivity spectra for different degree of annealing in a-$In_0S_{0.4}Se_{2.6}$.

concentration range $0 < x < 3$ in which one can see the discontinuity at $x \simeq 2.5$ which is due to a structural phase transition.
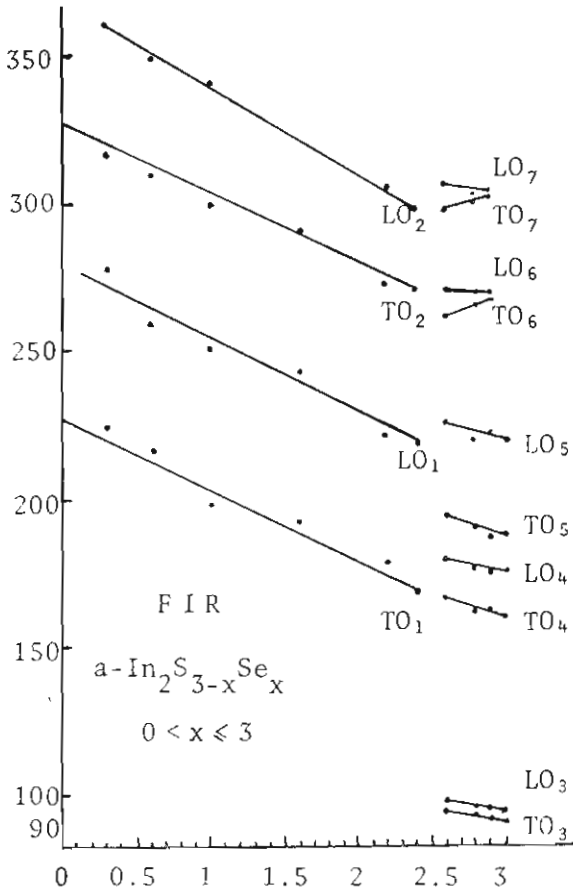

Fig. 2. Frequency dependence of $In_2S_{3-x}Se_x$ for the whole concentration range $0<x<3$.

ΠΕΡΙΛΗΨΗ

ΟΠΤΙΚΕΣ ΔΟΝΗΣΕΙΣ ΜΕΓΑΛΟΥ ΜΗΚΟΥΣ ΚΥΜΑΤΟΣ ΚΑΙ ΔΟΜΙΚΗ ΜΕΤΑΒΟΛΗ ΦΑΣΕΩΣ ΣΤΟΥΣ ΜΙΚΤΟΥΣ a-$In_2S_{3-x}Se_x$ ΚΡΥΣΤΑΛΛΟΥΣ

Ὑπὸ

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Φάσματα ἀνακλαστικότητας στὸ μακρὸ ὑπέρυθρο μελετῶνται συγκριτικὰ γιὰ μιὰ σειρὰ δειγμάτων ποὺ καλύπτει ὅλη τὴν περιοχὴ a-In_2S_3 - a-In_2-$S_{3-x}Se_x$ - a-In_2Se_3. Δείχνεται ἡ ἐπίδραση τῆς θερμικῆς ἀνόπτησης καθὼς καὶ ἡ δομικὴ μεταβολὴ φάσεως γιὰ x = 0.25 στοὺς μικτοὺς κρυστάλλους.