INVESTIGATION OF TERNARY SEMICONDUCTING SYSTEM $(Al_xIn_{1-x})_2Se_3$

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Abstract: A series of samples in the system Al_2Se_3-In_2Se_3 have been synthesized and studied. The interval of the Al/In (molar) Ratio r from $r \gtrsim 0{,}02$ to $r \lesssim 0{,}05$ has been two phase region α and γ_1. For $r > 0{,}05$ ternary, γ_1 alloys $(Al_xIn_{1-x})_2Se_3$ have been present alone, and their unit cell parameters have decreased continuously as the Al content increased. The samples have also been studied by differential thermal analysis. Results of the optical and electrical conductivity measurements are presented.

A series of samples in the system Al_2Se_3-In_2Se_3 have been synthesized, firstly in the In-rich region, and then graduaLy increasing the Al content. All the crystals were prepared by the modified SSD (Synthesis, solute diffusion) method[1][2]. Selen, as the element with high vapour pressure was placed in the evacuated reaction vessel at 990 K, so that the resulting partial pressure was about $1{,}5 \cdot 10^5$ Pa. The mixture of Al and In (purity 6 N) in exact stoichiometric proportion for a given x, was in an alumina crucible in the upper part of a vessel, in a temperature gradient of aproximately 50 K cm^{-1}, around 1150 K. Se evaporated and diffused into the melted Al + In. As the temperature at the bottom of the crucible was chosen to be somewhat lower than the expected melting point of the finished ternary compound, the crystalization started there. The reaction was completed in 5-7 days.

The crystals obtained were mostly compact, polycrystalline ingots with colour changing, from black-greyish to dark-red, reddish, orange and yellow with the increase of the

Al content. The crystals with 60 % and 88 % of Al were not stable and in contact with air quickly decompose into the red powder.

The structural properties of the samples were studied by the X-ray diffraction analysis. The dependence of normalized unit cell parameters a_N and c_N on the concentration of Al, x, is shown on Fig. 1. For x=0, the black alloy obtained has been α, rhombohedral, In_2Se_3; the same phase was obtained by the usual direct synthesis of In and Se in exact stoichimetric amounts[3]. The addition of even very small amounts of Al (x = 0,02 and x = 0.04) produced the samples which were mixture of α and γ_1 phase. γ_1 phase is isostructural with the second high temperature modification, γ, of In_2Se_3. The unit cell parameters of α and γ_1 phases in this two-phase region, practicaly have not changed whith the Al content, the parameters of α being equal to the values for α In_2Se_3. The increase of the Al content results only in different fractions of α and γ_1 phases, namely, for x = 0.02 the fractions of α and γ_1 phases have been similar, but in the samples for x = 0.04, the γ_1 phase has been dominant with about 1 % α phase. For greater Al contents ($x \geq 0,14$) the samples have been homogeneous ternary alloys $(Al_xIn_{1-x})_2Se_3$ designated as γ_1. The unit cell parameters of this ternary alloys have decreased continuously as the concentration of Al increased.

Data for x = 0.6 and x = 0.88 have not been presented, as the instability of compounds caused great experimental errors.

Differential thermal analysis agrees with the X-ray diffraction data. The dependence of the melting point of the syntesized samples on the Al concentration x is shown on Fig. 2. For x=0, obtained signal at 1150 K represents the melting point of In_2Se_3. For x = 0.02, beside 1150 K signal, there is another signal at 1115 K which coresponds to the melting point of γ_1 phase. The same situation is for x = 0.04, but for the samples with higher contents of Al ($x \geq 0.14$) the system become mono--phase, the only value for melting point is 1115 K within the limits of experimental error.

On Fig. 3. the results of optical measurements on the samples x = 0.04, x = 0.14, x = 0.33 and x = 0.45 are shown. The abrupt change in the absorption coefficient α represents the effect of direct electronic

transitions from the valence band to the conduction band. As the samples have been polycrystalline, the absorption at the grain boundaries is very strong so that the absorption coeficiente is too high even in the region of transparency and it cannot be said anything positive about indirect transitions. From the $(\alpha h\nu)^{2/3}$ vs, $h\nu$ representation, the width of the forbidden energy gap has been estimated:

$x = 0.04$ $E_g = 1.8$ eV , $x = 0.14$ $E_g = 2.0$ eV,
$x = 0,33$ $E_g = 2.2$ eV , $x = 0.45$ $E_g = 2.3$ eV .

Electrical conductivity measurements have also shown prevailed dependence on the Al content. The samples with small percentage of Al ($x=0$, $x = 0.02$, $x = 0.04$) had relatively low resistance at room temperature, order of magnitude 10^6 Ω cm, while for the samples $x \geq 0.14$ the resistance has been about 10^{12} Ω cm.

For thermal stability investigation and controlable structural defects introduction for identification and investigation, the crystals have been anealed several times at 250°C, 350°C, 450°C, 525°C and 650°C, for 30 min. The samples with higher Al contents have shown greater thermal stability and the significante increase in conductivity does not appear until anealing at 525°C.

Using thermoelectric probe it has been noticed that all the annealed compounds, with sufficiently lowered electrical resistivity, are n-type.

Fig. 4. represents temperature dependence of the conductivity after anealing at 650°C. All the defects for which the energy levels can be determinated or anticipated from the slope of $\log\sigma$ vs. $1/T$ courves are thermaly generated defects induced while the samples were anealed at high temperatures. As the high temperature anealing is acompained with strong Se evaporation, and colour change of crystalls from transparent red to a opaque black, it is reasonable to expect that the thermicaly induced defects corespond to singly or multiply ionized Se vacancies.

References:

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(2) D. Desnica, U. Desnica & B. Etlinger, Fizika 10 (1978) (Suppl. 2) pp 29-33
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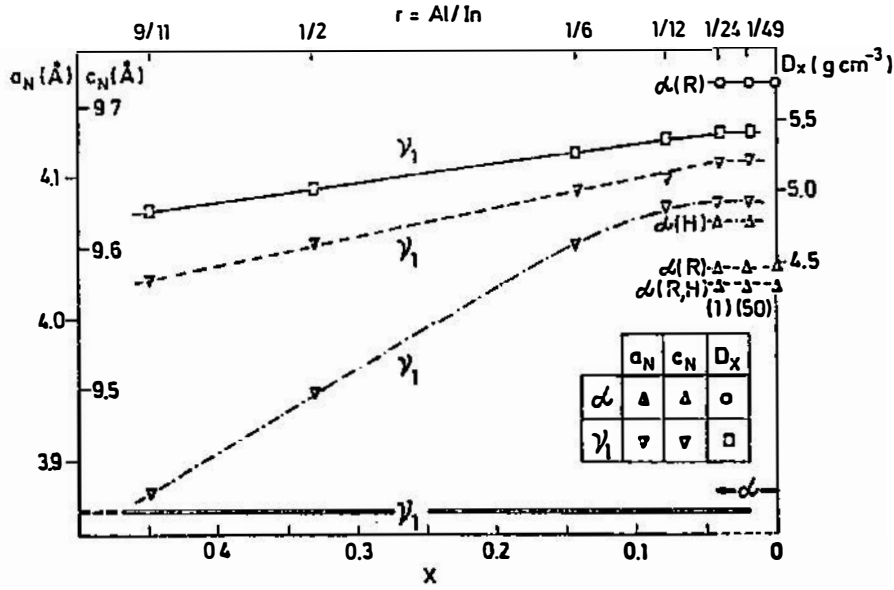

Fig.1

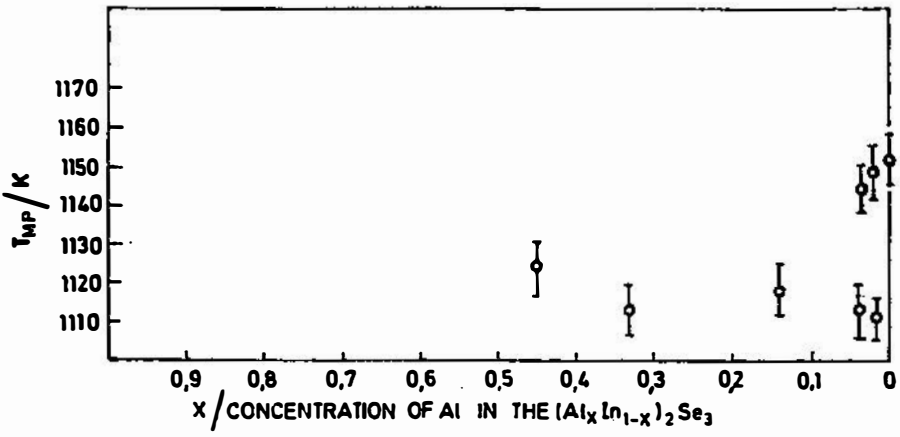

Fig. 2

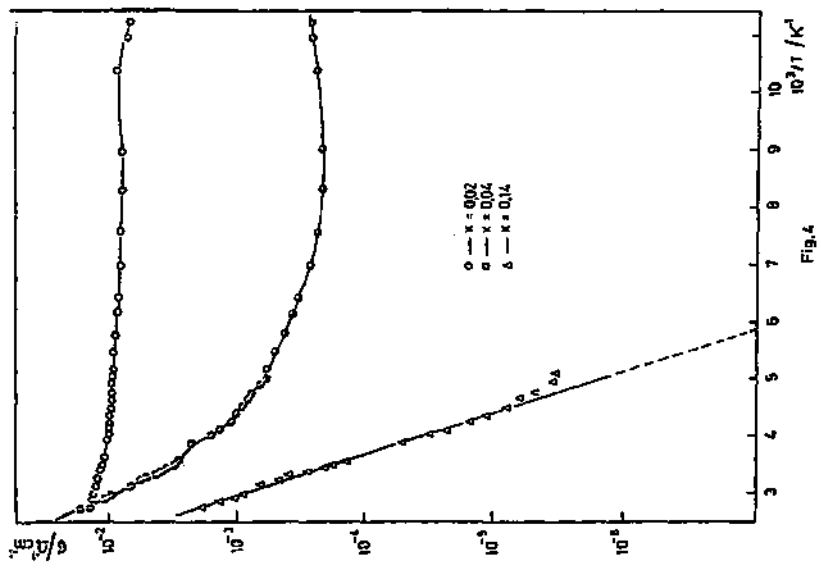

Fig.4

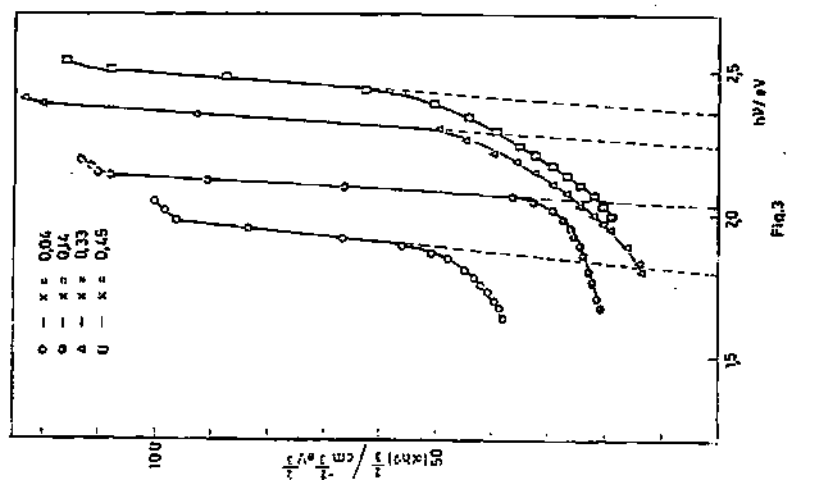

Fig.3