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DTA STUDIES AND PHYSICAL PROPERTIES OF VITREOUS $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ ALLOYS

Viera Trnovcová, Claudia Ješková, Petr Řehůřek, Fyzikálny ústav
CEFV SAV, Bratislava, ČSSR
Walter Henrion, Zentralinstitut für Elektronenphysik AdW der DDR,
Berlin, DDR

ABSTRACT

DTA studies of vitreous $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ alloys, $0 \leq x \leq 35$, were performed and the concentration dependences of the temperatures of the glass transition, T_g, crystallization, T_{cr}, and melting T_m, have been determined. A special attention has been paid to the charge transport and dielectric response of the glasses.

INTRODUCTION

The electrical conductivities of vitreous semiconductors are much less sensitive to the presence of impurities than are those of crystalline semiconductors. The large conductivity changes caused by the additions of some heavy metals (U, Tl, Cu) in vitreous As_2Se_3 arise probably from the ionic nature of their incorporation [1]. In this paper, the nature of structural changes, the thermal stability, microhomogeneity and phase separation are examined in the glassy Cu-As-Se system and the influence of Cu on the electrical, dielectric and optical properties of vitreous As_2Se_3 is demonstrated. It is shown that the glassy system As_2Se_3:Cu represents a transition from a 3:2 coordinated short-range order to a tetrahedral one.

EXPERIMENTAL

The synthesis of glasses was carried out in evacuated, rocking, quartz ampoules using high-purity elements as starting materials. The glasses were melted at 700°C for 2h, at 900°C for 2h, quenched to 200°C and annealed for 1h. The homogeneity and amorphousness of samples were tested by the infrared and electron microscopy. DTA was performed in a flowing dry Ar at a rate of 10 K/min using DuPont Thermal Analyser 900. The electrical and dielectric measurements were made in vacuum and dry Ar, from LNT to 150°C, at both dc and ac (f=0.5-100 kHz). The optical band gap, E_o, was de-

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termined at the absorption coefficient α=100 cm^{-1}. The density was measured by a pycnometric method.

RESULTS AND DISCUSSION

The large influence of Cu doping on the electrical conductivity of glassy As_2Se_3 (Table 1) results from the way of incorporation of this additive and from its large glassforming region. The entropy of mixing favours a dissociation of neutral monovalent Cu atoms into 4-fold coordinated Cu^+ ions and charge compensating C_1^- defects, which is accompanied by a decrease of the concentration of C_3^+ defects [2]. At the same time,3-fold coordinated Se atoms are built-up, which use their "lone-pair" electrons to form coordination bonds with Cu^+. For non-zero width of the defect levels, this redistribution of the charged defects results in a continuous shift of the Fermi level [3] and a change of the electrical conductivity. A donor-like impurity, like Cu^+, reduces the conductivity of p-type glassy $AsSe_3$ until a minimum conductivity is reached (for Cu, at x=0.0021), then, the conductivity increases on further addition of impurity [4]. The absence of ESR signals over the whole concentration range confirms the ionic form of the Cu incorporation. For $x \gtrsim 0.02$, the increase of the electrical conductivity, $\sigma = \sigma_0 \exp(-E_\sigma/kT)$, with growing Cu contents is connected with a decrease of the optical band gap, E_0, due to structural changes in vitreous alloys. The activation energy, E_σ, also decreases and σ_0 is close to 10 Scm^{-1} indicating a conduction by a band-tail hopping. This conduction mechanism is confirmed by a temperature dependence of the ac component of the conductivity, $\sigma_\omega = A(T) f^{0.6 \pm 0.07}$ Above 8 at% Cu, both E_0 and E_σ decrease linearly with increasing Cu content and for x=0.3, both the E_0 and the oscillator strength (in the sigle-oscillator description of the permittivity) approach to the values which are characteristic for a tetrahedral coordination [5]. The average coordination number increases from 2.4 for x=0 to 3.83 for x=0.3 [6]. For $x \gtrsim 0.08$, the increase of the permittivity with increasing x saturates, reaching the value of $\varepsilon_s = 13.8 \pm 0.5$. For $x \gtrsim 0.1$, the diffraction patterns of partly devitrified glasses reveal structures close to sphalerite but they cannot resolve the similar structures of $CuAsSe_2$ and Cu_3AsSe_4 [6].

DTA studies are very useful for identification of the glassy and crystalline phases in As_2Se_3:Cu because the melting temperatu-

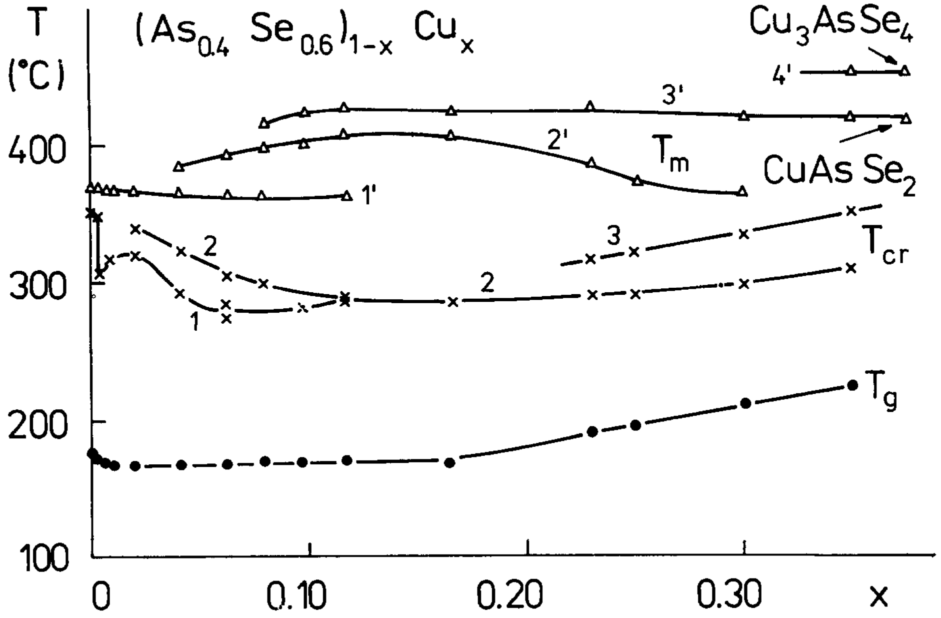

Fig. 1. The concentration dependences of the temperatures of glass transition, T_g, crystallization, T_{cr}, and melting, T_m, for various phases in glassy $(As_{0.4}Se_{0.6})_{1-x}Cu_x$

res of As_2Se_3 (372°C), $CuAsSe_2$ (415°C) and Cu_3AsSe_4 (450°C) differ appreciably. The "pure" As_2Se_3 changes continuously from the glassy state into the liquid one but already very small amounts of Cu cause a devitrification prior to melting, as is indicated by the exothermal crystallization peak and endothermal melting peak on the thermogram. Low concentrations of Cu decrease slightly the glass transition temperature, T_g, probably due to the incorporation of Cu^+ between "puckered", 3:2 coordinated As_2Se_3 layers. For $x \leqslant 0.08$, the main glassy phase is As_2Se_3 (curves 1,1′ in Fig. 1) and T_g is almost constant. For high concentrations of Cu, $x > 0.2$, the DTA diagrams show crystallization and melting of the tetrahedrally coordinated glassy $CuAsSe_2$ (curves 3,3′ in Fig. 1). For $x = 0.35$, the melting of both $CuAsSe_2$ and Cu_3AsSe_4 compounds is evident (curves 3′, 4′ in Fig. 1). The appearance of the glassy $CuAsSe_2$ brings about an increase of both the density (the density of $CuAsSe_2$, $d=5.28$ g/cm^3 [6], is higher than that of As_2Se_3)(Table 1) and T_g (due to the development of a 3-D tetrahedral network) of

Table 1
The optical band gaps, E_0, the activation energies, E_σ, and preexponential factors, σ_0, of the electrical conductivity, the dc conductivity σ_{300}, and static relative permittivity, ε_s, at 300 K and the density, d, for the concentrations, c, of Cu in glassy As_2Se_3

c (at %)	E_0 (eV)	E_σ (eV)	σ_0 (Scm^{-1})	σ_{300} (Scm^{-1})	ε_s	d (g/cm^3)
0.00	1.76	0.94	5200	$3\cdot10^{-12}$	10.5	4.620
0.21	1.63	0.95	19000	$7\cdot10^{-13}$	10.5	4.635
0.61	--	0.94	5200	$2\cdot10^{-12}$	11.0	4.646
1.04	1.50	0.80	120	$4\cdot10^{-12}$	11.6	4.662
1.19	--	0.77	330	$2\cdot10^{-11}$	11.8	--
2.17	1.42	0.67	12	$1\cdot10^{-10}$	12.7	4.708
3.14	1.37	--	--	--	--	4.738
4.16	1.33	0.56	11	$3\cdot10^{-9}$	12.8	4.776
6.27	1.30	0.52	7	$1\cdot10^{-8}$	13.1	4.821
7.89	1.27	0.49	8	$5\cdot10^{-8}$	13.8	4.865
9.72	--	0.48	9	$7\cdot10^{-8}$	12.8	4.924
11.76	1.20	0.44	15	$5\cdot10^{-7}$	13.9	4.982
16.67	1.13	0.39	14	$4\cdot10^{-6}$	14.1	5.224
23.08	1.03	0.33	18	$5\cdot10^{-5}$	--	5.34
25.00	--	0.19	0.02	$1\cdot10^{-5}$	--	--
30.00	--	0.16	0.04	$7\cdot10^{-5}$	--	--
35.00	--	0.13	0.05	$3\cdot10^{-4}$	--	--

glasses. At intermediate Cu concentrations, $0.04 < x < 0.3$, an unidentified As_2Se_3-like phase was observed (curves 2,2′ in Fig. 1) with the crystallization and melting temperatures lying between those of glassy As_2Se_3 and $CuAsSe_2$. Remelting of samples inside the DTA cell, followed by a free cooling, showed that this glassy phase needs higher quenching rates than glassy As_2Se_3. In the whole concentration range of Cu only one T_g was observed.

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