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INVESTIGATION OF THE ELECTRICAL PROPERTIES OF GLASSES OF Tm-As-S AND Tm-As-Se SYSTEMS

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Abstract. It was determined that electrical conductivity of the samples increases with the increase of concentration of thulium and its chalcogenides in the glasses based on As_2S_3 and As_2Se_3. According to our research of the $\sigma \sim f(10^3/T)$ dependence, for glasses containing As_2S_3 no impurity conductivity is observed, while for glasses containing thulium and its chalcogenides, in addition to a wide range of intrinsic conductivity, at relatively low temperatures, there is also an insignificant region of impurity conductivity, which slightly expands with increasing thulium content. The results of our research show that the most effective ohmic contact for the investigated alloys is aquadag. It has been determined that, in the wide range of values, current–voltage characteristic for all the studied systems, both in the dark and under illumination, is symmetric and linear, which indicates the ohmicity of the contacts.

Keywords: *Electrical conductivity, glass, width, band gap, properties, system dependence, photoconductivity.*

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1. Introduction

The interest in rare earth (REE) elements and their compounds is based on the possibility of their application in various fields of technology, including obtaining materials with a desired set of properties. Lanthanide compounds are used as catalysts, high-temperature superconducting (HTS) ceramics, additives to various alloys to improve mechanical strength and heat resistance.

Many research studies have been devoted to the system of the type As_2X_3-REE and REE chalcogenides (Barnier & Guittard, 1976; Ilyasly 1991; Xudieva *et al.*, 2017; Nasibova, 2015; Ilyasly *et al.*, 2016).

However, there are fragmentary data on the interaction of Tm and its chalcogenides with chalcogenides of the arsenic subgroup and intermediate phases formed as a result of this interaction (Ilyasly *et. al.*, 2018; Gahramanova *et. al.*, 2019; Ilyasly *et al.*, 2017).

Chalcogenide glassy semiconductors (CGS) based on arsenic chalcogenides exhibit significant photoinduced changes in optical, photoelectric, and electrical properties, which makes these compounds promising materials for creating a new type of photoresistors for the needs of microelectronics.

The investigation of electrical properties has long been one of the most important issues in the study of the glassy state. The most important difference between the crystalline and glassy states is that the electrical conductivity of glasses is less sensitive to the effects of impurities and their intrinsic conductivity region prevails at lower temperatures.

2. Experiments and results

2.1. Electrical properties of As_2Se_3 and AsSe based chalcogenide (selenide) glasses

To study these sections of Tm-AsS and As-TmS from the elements, TmS and AsS were synthesized using As arsenic of grade A-5 and Tm-A2, sulfur of high purity for synthesis. The synthesis mode was selected based on the physicochemical properties of the primary components and from the synthesis record.

The initial samples after evacuation of the ampule were placed in an oven and the oven was heated to 650-750 K for 8-10 hours, and then the temperatures were raised to 1200 K. At this temperature the ampules were kept for 5 hours and the ampule with the oven were slowly cooled to room temperature.

The alloys were homogenized by annealing for 650 hours depending on the concentration of the components in the alloys with TmS at a temperature of 750 K and with As and Tm at a temperature of 555 and 775 K.

Methods of differential thermal (DTA), X-ray phase (XRF) and micro-structural (MSA) analyzes, measurement of microhardness and electrophysical properties, studied the nature of the physicochemical interaction in the Tm-AsS and As-TmS. In the study of the high-temperature part, the installation VDTA 987 was used. DTA was performed using the PDS-021 installation (a two-coordinate self-feeding potentiometer, MIM microscope – 7 and PMT-3 microhardness tester) (3). After the separation of glassy alloys, the electrophysical properties were measured by the compensation method.

The measured temperature dependence of the electrical conductivity of the initial As_2S_3 and As_2Se_3, as well as glasses based on them and containing thulium and its chalcogenides, showed that they are high ohmic substances. To measure the physical properties of substances (alloys, glasses) alloys were synthesized according to the developed mode (Ilyasly *et. al.*, 2018; Gahramanova *et. al.*, 2019) cooling was carried out at a rate of $6 \cdot 10^3$ and 10 deg/min. The electrical conductivity of glassy substances was measured in the temperature range 300-450^{0}C.

According to our experimental data, the electrical conductivity of As_2S_3 and As_2Se_3 at 300K is $11,8 \cdot 10^{-11}$ и $6 \cdot 10^{-10}$ $ohm^{-1} \cdot cm^{-1}$, respectively.

The thermal bandgap calculated from the slope of the conductivity curves is for As_2S_3 $\Delta E = 2.1$ eV and for As_2Se_3 $\Delta E = 1.96$ eV. Figure 1. shows the curves dependences $\sigma \sim f(10^3/T)$ for the initial As_2S_3 and glasses of the As_2S_3-Tm, Tm_2S_3 and TmS systems (Ilyasly *et al.*, 2018).

As shown in the Fig. 1, with the increase of thulium and its chalcogenides content in the As_2S_3 composition, the specific electrical conductivity of the samples also increases. In the entire investigated temperature range, a semiconductor behavior of the conductivity is observed. According to our research of the $\sigma \sim f(10^3/T)$ dependence, for glasses containing As_2S_3 no impurity conductivity is observed, while for glasses containing thulium and its chalcogenides, in addition to a wide range of intrinsic conductivity, at relatively low temperatures, there is also an insignificant region of impurity conductivity, which slightly expands with increasing thulium content.

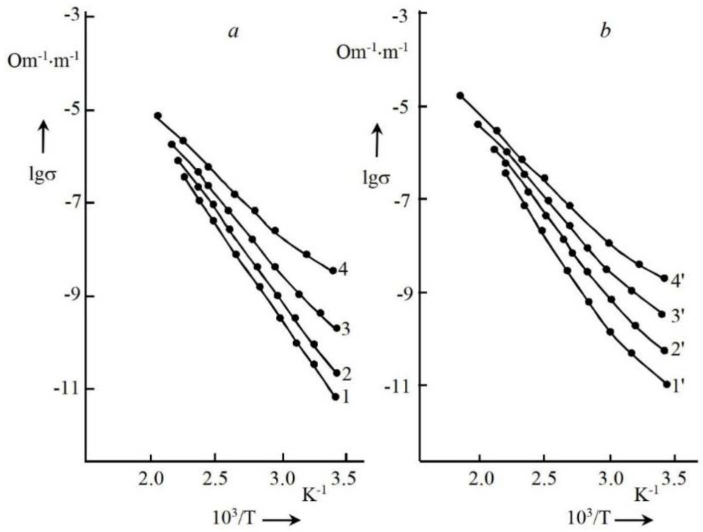

Fig. 1 (a, b). Temperature dependence of the electrical conductivity of glasses based on As_2S_3

1 – As_2S_3 ;
2 – 99,5 As_2S_3 + 0,5 at.% Tm ;
3 – 99,0 mol. % As_2S_3 + 1 at.% Tm;
4 – 98 mol. % As_2S_3 + 2 at.% Tm;

1′ – 99,5 mol. % As_2S_3 + 0,5 м mol. % Tm_2S_3;
2′ – 99,0 mol. % As_2S_3 + 1 моль % Tm_2S_3;
3′ – 99,5 mol. % As_2S_3 + 1,5 mol. % Tm_2S_3;
4′ – 99,5 mol. % As_2S_3 + 1,5 mol. % TmS;

Consequently, the higher the concentration of thulium and its chalcogenides in the glass composition, the more impurity zones there are.

A similar picture is observed with the addition of mono and sesquisulfides to As_2S_3 (Fig. 1 a,b). These samples are also characterized by a narrow region of impurity conductivity. It was found that impurities introduced into the chalcogenide glass matrix in the amount of up to 10-11% have almost no effect on the value of electrical conductivity. As shown in Fig. 1 (a), As_2S_3 has no «impurity» slopes. This can be explained by the presence in As_2S_3 of a large number of local centers caused by the loss of long-range order and having a quasi-continuous energy distribution. These local centers provide «recharge» of the impurity centers, which makes the impurities electrically inactive.

Thus, if we generalize the results of studies, it can be noted that the electrical conductivity of glasses obeys the law $\sigma = V_0 \exp\left(-\frac{\Delta E}{kT}\right)$ and increases with an increase in the concentration of Tm, TmS, Tm_2S_3 in them. The regular change in the electrophysical parameters of the studied samples suggests that these samples do not contain any microinclusions that interact with the main matrix of the chalcogenide glass.

Based on the results of the studies, it was established that the specific electrical conductivity of glassy As_2Se_3 is 10^{10} $Ohm \cdot m^{-1}$ at 300 K and the temperature dependence of the electrical conductivity of alloys of the As_2Se_3-TmSe; As_2Se_3-Tm_2Se_3 и AsSe-TmSe systems decreases with the addition of thulium chalcogenides (Fig. 2).

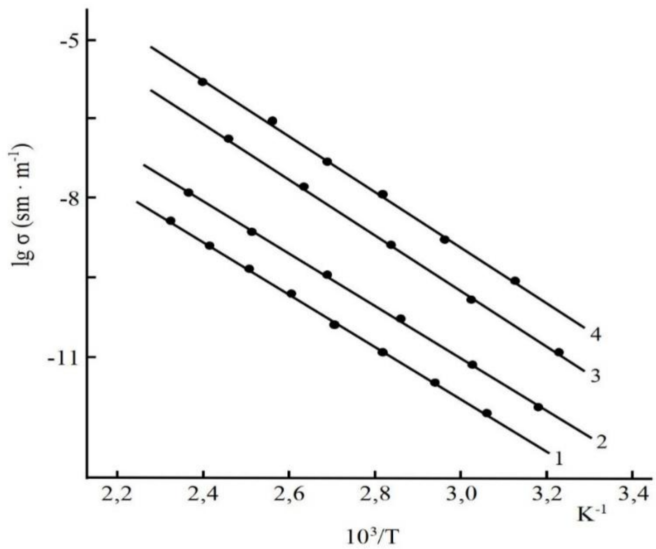

Fig. 2. Temperature dependence of the electrical conductivity of the glasses of the As_2Se_3-TmSe system

1 – As_2Se_3; 2 – 1 mol. % TmSe; 3 – 3 mol.% TmSe; 4 – 5 mol. % TmSe.

As seen in figures, the temperature dependences of the electrical conductivity of the studied samples are well described by the relation

$$\sigma = c\exp\left(-\frac{\Delta E}{kT}\right).$$

ΔE for pure As_2Se_3 and AsSe is 0.92 and 0.96, respectively, and decreases with the addition of the second component.

To analyze the measurement results, we used the energy model of a glassy semiconductor proposed by Mott and Davis (2012). According to the model, in the conduction band and in the valence band of a glassy semiconductor, localized states appear due to the absence of long-range order, and there are boundary energies E_C and E_V, which separate the localized states from the non-localized ones.

When the energy of the charge carrier passes through the boundary values, the mobility changes by about a thousand times. In this case, the energy difference E_C-E_V is called the mobility gap. The energy dependence of the density of states is shown in Fig. 3.

If we take into account that the materials studied by us have the «p» -type of conductivity and the current is mainly carried by holes, then:

$$\sigma = c\exp\left(-\frac{E-E_0}{kT}\right) = c\exp\left(-\frac{\Delta E}{kT}\right),$$

where ΔE is approximately equal to half the band gap (Fig. 3).

In this case, if the value of ΔE in the temperature range in which the measurement is made can be interpolated by a linear dependence, then the graph of the function log σ from $10^3/T$ should be a straight line, $\Delta E = \Delta E_{(0)} - \gamma^T$, where $\Delta E_{(0)}$ – Is the activation energy at zero temperature.

With the addition of the second component, ΔE decreases; thus, it can be concluded that the addition of the second component leads to a decrease in the mobility gap, i.e. the difference E_C - E_V. Activation energy ΔE decreases with the increase in the concentration of the second component.

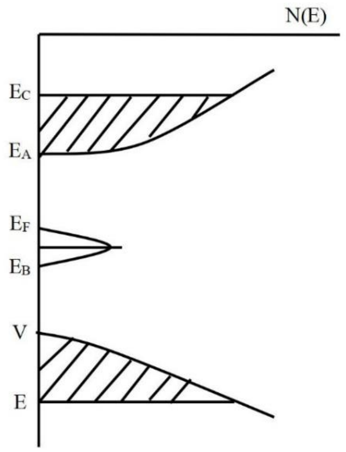

Fig. 3. Dependence of the state's density on energy

2.2. Photoconductivity of As_2Se_3 and AsSe based chalcogenide (selenide) glasses

To select contacts, we checked their differences by measuring the current-voltage characteristic (CVC) of samples with symmetrical contacts. As our research has shown, the most effective ohmic contact for the investigated alloys is aquadag.

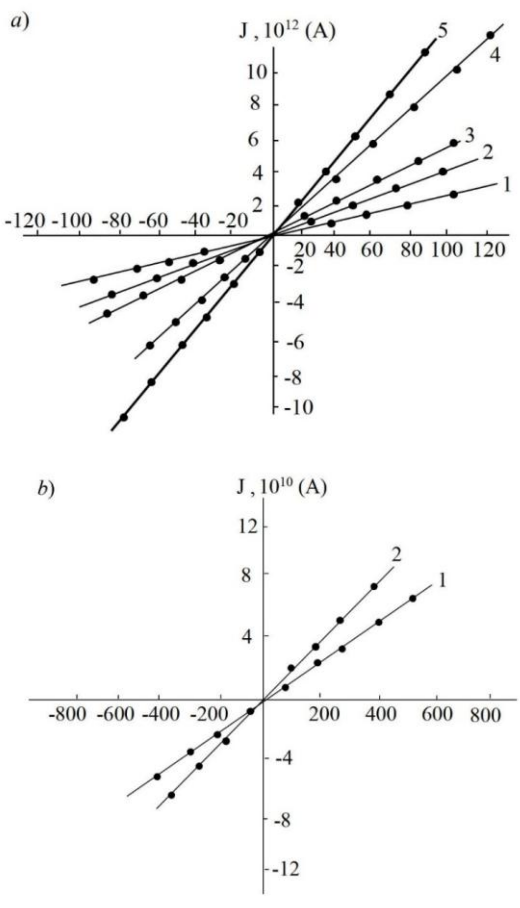

Figure 4. a) CVC of AsSe-Tm system at 800 K:
1 – 1 mol.% TmSe, 2 – 3 mol.% TmSe, 3 – 5 mol. % TmSe, 4 – 7 mol.% TmSe, 5 – 10 mol.% TmSe
b) CVC of AsSe-Tm system with aquadag contact in the dark (1) and under illumination (2)

As seen in the figures, in the wide range of values, current–voltage characteristic for all the studied systems, both in the dark and under illumination, is symmetric and linear, which indicates the ohmicity of the contacts.

After measuring the ohmicity of the contacts, we investigated the photoconductivity of AsSe and As_2Se_3 based alloys (glasses) (Figs. 5,6) containing 1 – 3 mol% TmSe, 2 – 10 mol% TmSe, 3 – 5 mol% TmSe, 4 – 7 mol% % TmSe.

As shown in Fig. 5 and Fig. 6, with introduction of Tm into the composition of AsSe and As_2Se_3, the spectral distribution curves of the samples are shifted towards the IR region. The maximum photoconductivity is observed in samples containing 7 mol% TmSe. The optical band gap is 1.49 and 1.63 eV, respectively, for samples based on As_2Se_3, and on AsSe, while maximum photosensitivity for alloys based on As_2Se_3 corresponds to λ = 985 nm, and for AsSe – to λ = 0.845 nm.

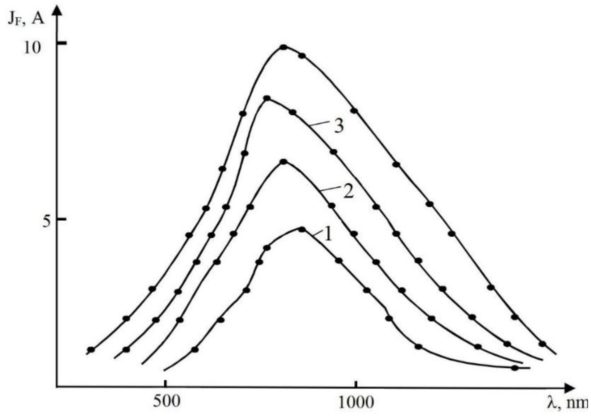

Figure 5. Curve of the spectral distribution of AsSe based glasses:
1 – 3 mol.% TmSe; 2 – 10 mol.% TmSe; 3 – 5 mol.% TmSe; 4 – 7 mol.% TmSe

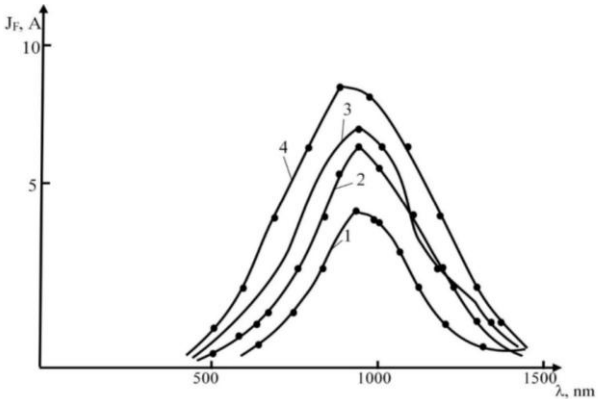

Figure 6. Curve of the spectral distribution of As_2Se_3 based glasses:
1 – 3 mol% TmSe; 2 – 10 mol.% TmSe; 3 – 5 mol.% TmSe; 4 – 7 mol.% TmSe

3. Conclusion

Glassy alloys have been synthesized and their electrical and photoconductivity in the temperature range 298-720^{0}C It was found that the studied glasses have "P" type conductivity. It was found that the introduction of thulium and its chalcogenides into As_2S_3.

The values of electrical conductivity increase, and the band gap decreases. In glasses based on arsenic selenides, the photoconductivity is shifted towards longer waves.

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