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New membrane material for thallium (I)-selective sensors based on arsenic sulfide glasses

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ABSTRACT

New membrane materials were studied for thallium (I)-selective chemical sensors based on chalcogenide glasses in the TlI-Ag_2S-As_2S_3 system. Using these studies on the radioactive tracers diffusion (^{108m}Ag и ^{204}Tl) and electrical conductivity, an ionic conductivity of $\sigma_{ion} = 10^{-7}$ Ohm^{-1} cm^{-1} (20 °C) was found for the glass composition 27%TlI-20%Ag_2S-53%As_2S_3. This composition of chalcogenide glass was selected as a membrane material for the Tl-selective chemical sensor displaying a value of the electrode function of 57 mV/pTl and a detection limit of 3×10^{-6} mol l^{-1}.

1. Introduction

Sensors are the key components in the analysis, real-time and remote monitoring of trace metals in environmental science and technological process control. The most promising of these applications are potentiometric [1–6] and optical [7] sensors. Potentiometric sensors have the advantage of being small and portable devices, with low costs and low energy consumption compared to other analytical techniques [5,8].

Potentiometric sensors for heavy metal ions represent a wide class of sensors with sensitive membranes based on organic ion-exchangers and ionophores [9–11], chalcogenide glass and crystalline ionic conductors [12–14]. Chemical sensors were developed based on chalcogenide glass membrane materials for the selective determination of heavy metal ions (copper [15], lead [16–18], cadmium [19–21], mercury [22–25], and thallium [26–28]) in various liquid media. The advantages of chalcogenide glass membrane materials are: (1) continuously variable compositions offer a wide spectrum of material properties [29,30]; (2) glass materials provide the advantage of solid-state sensor devices, (3) high chemical stability of vitreous materials ensures an enhanced chemical durability of the chemical sensors based on chalcogenide glasses, and (4) possibility of fabricating thin films of chalcogenide glass materials for the miniaturization of sensors [31].

For the development of highly selective sensors with stable and reproducible electrode functions, the membrane materials should permit the ionic transport of a potential-determining ion or an ion related to a potential-determining ion by binding in a membrane matrix. Chalcogenide glasses of various compositions with an ionic conductivity value of 10^{-5}–10^{-3} Ohm^{-1} cm^{-1} are promising for the development of chemical sensor membranes. Studies on the structure and transport characteristics of new inorganic materials are very important for determining the possibility of using them in the development of new chemical sensors [32,33].

Results are reported here of the synthesis and complex studies of the transport characteristics of the chalcogenide glasses in the TlI-Ag_2S-As_2S_3 system. Along with the studies on the conductivity, the diffusion of the radioactive isotopes ^{108m}Ag and ^{204}Tl was investigated with the aim of identifying the ion transport characteristics and establishing the mechanism of ion transport. These data were used to select the optimal compositions of chalcogenide glass materials for preparing sensor membranes and studying the analytical characteristics of a new type of Tl-selective chemical sensors.

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2. Materials and methods

2.1. Glass preparation

Chalcogenide glasses in the TlI-Ag_2S-As_2S_3 system were synthesized using Ag_2S (99.9%, Aldrich) and TlI (99.999%, Aldrich) and synthesized As_2S_3 as starting materials.

The synthesis of As_2S_3 was carried out from the elements sulfur and antimony (puriss.p.a. Sigma–Aldrich, Fluka). The mixture of components (30 g) was sealed in evacuated quartz ampoules and the temperature was gradually raised to 350 °C within 3 h. The ampoules were further heated at this temperature for 1.5 h. After that the temperature was then gradually raised to 950 °C and hold at this temperature for 8–10 h, followed by air quenching.

Chalcogenide glasses in the TlI-Ag_2S-As_2S_3 system were synthesized using Ag_2S, TlI and As_2S_3 in quartz ampoules sealed under vacuum using 3 g of starting materials. The mixture of components was heated to a temperature of 350–400 °C, the ampoules were further heated at this temperature for 1–1.5 h. The temperature was then gradually raised to 750 °C for 4–5 h, followed by air quenching [34,35].

The glass phase and the homogeneity of the prepared alloys were verified by an X-ray phase analysis.

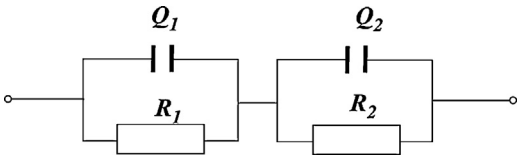
Thallium-containing chalcogenide glasses of four different compositions were obtained: 20 mol% TlI-40 mol% Ag_2S-40 mol% As_2S_3 (I), 23-30-47 (II), 27-20-53 (III), and 40-30-30 (IV) mol%, respectively, the sample (IV) with an As_2S_3 content of 30 mol% was glassy crystalline. These glass compositions with a variation of the content of Ag_2S of 20, 30, and 40 mol% are within the glass forming region of the TlI-Ag_2S-As_2S_3 system. Usually, the value of ionic conductivity in chalcogenide glasses of this system is determined by the concentration of Ag_2S [36,37]. The temperature dependence of the glass-transition temperature of the chalcogenide glasses, T_g, demonstrates that it is possible to study electrical conductivity and radioactive tracer diffusion up to 110 °C for the chalcogenide glass of 40 mol% TlI-30 mol% Ag_2S-30 mol% As_2S_3 composition, and up to ca. 130 °C for the chalcogenide glasses with 20, 23, 27 mol% TlI, compositions (I)–(III). Above this temperature the glasses soften.

2.2. Conductivity and tracer diffusion measurements

The temperature dependence of the total electrical conductivity of the samples was studied by impedance spectroscopy ("Novocontrol Concept 40") in a frequency range of 20 MHz–10 Hz and a temperature range of 0–120 °C. Silver contact paste ("Degussa") was deposited on the parallel sample sides polished to form contact electrodes. The resistivity of the samples was found using equivalent circuit software [38].

Radioactive tracers ^{204}Tl ($T_{1/2}$ = 3.78 y.) and ^{108m}Ag ($T_{1/2}$ = 418 y.) were used to study ionic diffusion in the chalcogenide glass samples. Radioactive tracers were deposited on one of the flat polished surfaces of the chalcogenide glass samples as a drop of Tl^*NO_3 or Ag^*NO_3 solution, which remained on the surface for 20–80 min. Subsequently, the solutions were washed off with distilled water and ethanol and then dried. The radioactivity of the specimen was measured using gamma spectroscopy with a semiconductor(Ge)-based detector (GX1018, Canberra Ind.). The activity measured on the surface of the samples after radioactive tracer deposition was: (3-6) × 10^5 impulses/100 s for the chalcogenide glasses in which the diffusion of ^{204}Tl was studied and (3-8) × 10^4 impulses/1000 s for the glasses in which the diffusion of ^{108m}Ag was studied.

To find the diffusion coefficients of ^{204}Tl and ^{108m}Ag radioactive tracers, further experiments were performed by the method of diffusion from an "infinitely" thin layer with subsequent sectioning of the samples and measurements of the radioactivity of the ground-off layers. For this, the samples were subjected to annealing in the temperature range of 20–120 °C for 10–30 days. After diffusion annealing, thin layers of 5–100 μm were ground off from the ≪radioactive≫ surface. The dependence of the activity on the distance from the surface was studied for various temperatures and diffusion times [39].



Scheme 1. The equivalent circuit for the analysis of the impedance spectra, where R_1 is the bulk resistance of the sample, R_2 is the charge transfer resistance, Q_1 and Q_2 are constant phase elements (CPE).

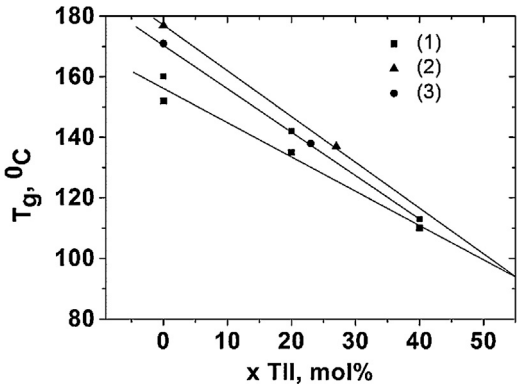


Fig. 1. Dependence of the glass-transition temperature, T_g, on the composition of chalcogenide glasses in the system TlI-Ag_2S-As_2S_3: (1) – xTlI-(50-x/2)Ag_2S-(50-x/2)As_2S_3, (2) – xTlI-20Ag_2S-(80-x)As_2S_3 and (3) – xTlI-30Ag_2S-(70-x)As_2S_3.

2.3. Potentiometric measurements

The four compositions of the chalcogenide glasses (I)–(IV) were studied as membrane materials for potentiometric chemical sensors. Membranes of chalcogenide glass materials were prepared with a diameter of 8 mm and a thickness of 2 mm. A solid-state silver contact was attached to the membranes and the membranes with a contact were glued with epoxy compound into PVC tubes. The potentiometric measurements were performed in the electrochemical cell:

Ag | AgCl | KCl 0.1 M ⋮ KNO_3 0.1 M ⋮ Analyzed Solution | Sensor Membrane | Ag.

The potentials of this cell were measured using a voltmeter/pH meter Mettler Toledo S40 SevenEasy with an input resistance of 10^{11} Ohm. The sensors were connected to a potentiometer through a commutator to measure the emf of twelve sensors. The sensor response was investigated in a concentration range of 10^{-1}–10^{-6} mol l^{-1} $TlNO_3$. A constant background electrolyte solution (0.1 M KNO_3) was used in a concentration range of 10^{-2}–10^{-6} mol l^{-1} $TlNO_3$ to ensure practically a constant ionic strength.

3. Results and discussion

The total electrical conductivity of the synthesized membrane materials of compositions (I)–(IV) was studied by the method of impedance spectroscopy in a temperature range of 0–120 °C. The impedance spectra were analyzed using a Boukamp equivalent circuit program. The equivalent circuit used for fitting procedure is shown in Scheme 1 (Fig. 1).