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Original scientific paper

Fabrication possibilities and characterisation of chalcogenide glass-based sensors for bromide determination

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Abstract

The fabrication and characterisation of potentiometric chalcogenide glass (CG) electrodes with selectivity for bromide in aqueous media are reported. The focus is on the production of chalcogenide glasses of the material system AgBr Ag_2S As_2S_3 and their investigation by means of a series of physico-chemical methods, as well as on their fabrication with the aid of precision mechanical manufacturing and assembly techniques to form usable sensors and their testing. In addition to the production of conventional rod electrodes, it will be examined whether it is also possible to realize planar electrodes using thick-film technology.

Keywords
Potentiometric sensor; chalcogenide glasses; bromide selective rod-shaped electrode; ion selective solid-state electrode

Introduction

Potentiometry is often used as an analytical method for the quantitative determination of halide ions, which requires the availability of so-called ion-selective electrodes (ISE). These have been available for some time in the form of electrodes of the 2nd kind based on electrode membranes of homogeneous and heterogeneous compacts or single crystals of poorly soluble salts [1]. In the case of electrodes sensitive to bromide ions, the membrane usually consists of a moulded body formed by a mixture of Ag_2S and AgBr. The practically usable measuring range here is between 5 µmol/L and 0.1 mol/L Br^-.

In the literature [2], potentiometric electrodes based on glassy crystalline membranes of the composition AgBr Ag_2S As_2S_3 usable for Br^- determination are also described, which analytical properties are said to be superior in terms of Nernst response, as well as resistance to acids, strong oxidizing agents and corrosive media. To produce the chalcogenide glass electrodes, discs of up to 3 mm thickness were made from the reaction product obtained in evacuated quartz ampoules in a thermal manufacturing process, polished on one side and silver-plated on the other side by vacuum evaporation before the functional element was installed in a PVC pipe to produce the final sensor.

It is well known that due to the chemical composition required for functionality in chemosensors and the associated high brittleness, the processing of chalcogenide glasses (CGs) for electroanalytical purposes is not trivial in contrast to those glasses used for optical applications [3]. For example, the reaction products, which are in lumpy form after completion of the melting process, removal from the quartz ampoules and quenching in cold water, cannot usually be further processed into electrode membranes by sawing in larger quantities, as described in the above-mentioned publication. The pieces are available in different sizes and shapes and the application of mechanical processing methods very often leads to their pulverization. Therefore, the available pieces are often only coarsely crushed or used for further processing in their already existing form. This essentially involves making contact between the ion-selective chalcogenide glass and an electrical conductor by using electrically conductive adhesives, such as gold conductive lacquer [4], but also the use of conductive polymers [5]. Most of the sensors manufactured to date are used for the analysis of metallic cations [6]. Some of them are also commercially available [7].

In addition to improving analytical performance (lower detection limits, cross-sensitivities, ...), current research goals in the field addressed here primarily consist of optimizing sensor production. In this context, approaches to solutions are discussed in the scientific literature with regard to the use of pulsed laser deposition (PLD) [8] and thick-film technology [9,10], although none of the methods described has yet found broad acceptance due to numerous shortcomings. For example, there are sometimes problems with the formation of droplets inherent in the system when using PLD. Only thermally stable glass (paste) material that can be compacted during sintering while maintaining stoichiometry is suitable for the thick-film process. Thermal effects due to decomposition, crystallization and phase transformation of the chalcogenide glass may only occur above the sintering temperature, which does not apply, for example, to the production of thick-film electrodes selective for lead and iodide ions [11,12].

The present work focuses on finding an optimized chalcogenide glass composition for the production of electrodes selective for bromide ions and an optimized fabrication process for this. For the latter task, the focus will be on improving the classical precision manufacturing process and examining the possibility of using thick-film technology. The PLD method, on the other hand, is very cost-intensive, time-consuming and hardly suitable for mass production from the perspective. In addition to evaluating the various fabrication options, the manufactured sensors will be characterized chemically and analytically.

Experimental

Glassmaking

For the production of the CG, AgBr, Ag_2S and As_2S_3 powders were used, each with a purity of >99.99 wt.%, purchased from the companies Alfa Aesar GmbH Co KG and Sigma Aldrich Chemie GmbH. CG glass systems of different stoichiometries (Figure 1, Table 1) were melted in order to find the optimal glass composition for the production of bromide-sensitive sensors. From the literature [2,13] it was found that the bromide CG electrodes exhibit anion sensitivity when the composition is in a narrow concentration range of 55-65 mol % AgBr and when the Ag_2S to As_2S_3 ratio varies from 1:1 to 2:1.

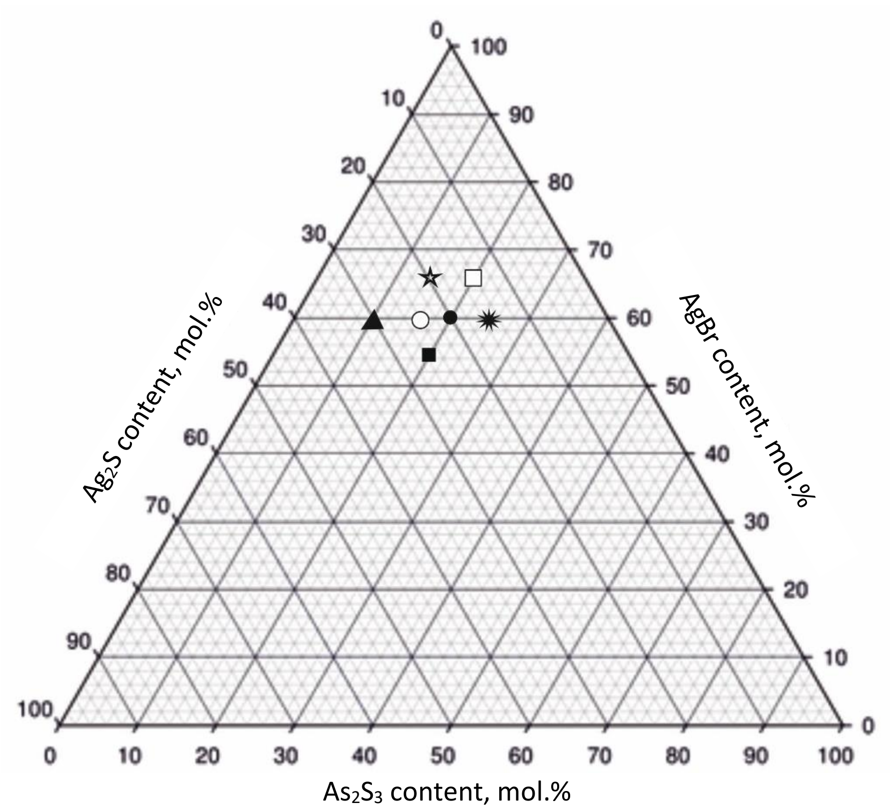

Figure 1. *Phase diagram AgBr - Ag$_2$S - As$_2$S$_3$*

Table 1. *Glass composition in mol %*

Signature	Content, mol %		
	AgBr	Ag$_2$S	As$_2$S$_3$
●	60	20	20
○	**60**	**24**	**16**
□	65	15	20
n	55	25	20
«	65	20	15
®	60	15	25
p	60	30	10

The melting of the sensor material of the compositions, according to Table 1 was carried out in a cylindrical quartz ampoule. This was evacuated (<10 µbar) and hermetically sealed in a reaction chamber filled with nitrogen. The powder-containing body was transferred to a quartz glass reactor, which was then placed in a Nabertherm tube furnace (B180, maximum temperature: 1300 °C). A stirrer was used for the slow movement of the ampoule during the heating phase with 100 to 110 °C/h up to a temperature of 980 °C and a melting process duration of 20 h. The stirrer was used for the heating of the ampoule. Immediately after the melting process, the ampoule was quenched in cold water and destroyed to collect the glass.

The smaller pieces were used for orientational examination by the following methods: Scanning electron microscopy (SEM) with energy dispersive X-ray spectrometer (EDX) using the QUANTA 200 measuring system (FEI company, NL) coupled with an energy dispersive X-ray spectrometer QantTAX QX2 (Röntec company), X-ray diffraction (XRD), using the D8 advance instrument from Bruker, and differential thermal analysis (DTA) and thermogravimetry (TG) with the STA 449 C instrument from NETZSCH-Gerätebau GmbH. The sintering behaviour of the CG powder was investigated with the thermomechanical analyzer TMA 402 F1 Hyperion, also from NETZSCH-Gerätebau GmbH, in order to determine whether the CG is suitable in perspective for the realization of CG ISEs with the aid of thick-film (TF) technology. For this purpose, cylindrical powder compacts were produced and measured by means of uniaxial pressing.

For the determination of resistivity, large chalcogenide glass pieces (Ø = 8 mm, length = 2 cm) were cast with two-component adhesive Epoxy 4439 (KAGER GmbH) and cut into approximately 1 to 2 mm thick slices using an Accutom 50 diamond saw from Struers. For impedance measurements (Gamry Electrochemical Measurement System of the company Gamry Instruments, Inc., USA), leakage leads consisting of silver wire (ϕ = 0.3 mm) were attached with the aid of silver adhesive to both sides of the surfaces of the cut pieces that were fully contacted with silver conductive lacquer. A resistivity of 1.1 to 1.35 MΩ was determined from recorded ground diagrams in the frequency range from 10 mHz to 100 kHz, the thickness and area of the fused bodies.

Electrode fabrication

From a series of CG melts for the detection of bromide ions, sample structures, so-called rod electrodes, were prepared for initial evaluations of the electrochemical properties. For this purpose, glass fragments were electrically contacted, metallographically prepared and converted into a measurable structure. The starting point for the production of the rod electrodes are CG fragments of various sizes and shapes (Figure 2).

Figure 2. *Chalcogenide glass fragments*

The greatest difficulty in using the CG fragments arose from their extremely inhomogeneous shape and extreme brittleness. Fragments had to be selected that could be sufficiently contacted electrically and had a shape that was largely suitable for subsequent metallographic preparation.

The electrically conductive polymer-based adhesives known from microelectronic packaging were not suitable for this due to their chemical and physical properties. Instead, adhesives with strong bonding properties and favorable curing characteristics were used. The 2-component adhesive CW 2400 from Chemtronics proved itself. Contrary to the usual assembly methods/bonding technologies, this was only done manually, without dispensing technologies and special annealing conditions. The use of a soldering lug as an aid for contacting the CG fragments has proven itself.

The contacted glass fragments with the copper or silver (Ø = 0.35 mm) electrical connecting wire were then inserted and embedded in a suitable glass tube to be transformed into the shape and homogeneity required for the subsequent measurements by means of metallographic preparation (embedding, grinding and polishing of the CG surface). EpoFix from the company Struers proved to be a suitable embedding medium. The aim was to achieve the largest possible and most homogeneous glass ground surface without cracks and inhomogeneities (Figure 3).

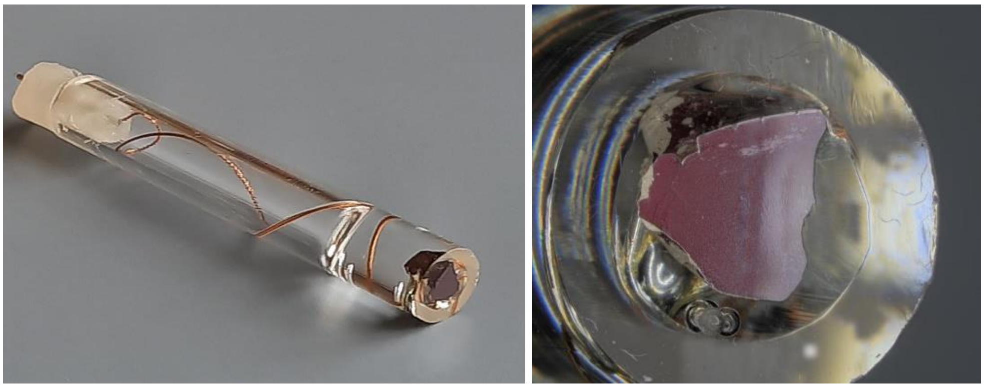

Figure 3. *Overall structure of a CG electrode, diameter 12 mm, length 9 cm (left), glass surface (right)*

Potentiometric measurements

The determination of the response times and slopes of the electrodes was carried out in calibration solutions in the measuring range from 10 to 10^{-3} mM Br^- with 0.1 M KNO_3 in each case to adjust the ionic strength. The solutions were prepared from a 0.1 M KBr stock solution according to the dilution method. The potassium bromide standard in purity of >99.99 wt. % was purchased from Sigma Aldrich Chemie GmbH. An Ag/AgCl, sat. KCl reference electrode (RE) was used as a reference electrode. Stirring the measuring solution led to higher sensitivities, as this avoided saturation and enrichment effects on the surface of the electrode. A salt bridge filled with 0.1 M KNO_3 was used to separate the reference electrode from the measuring solution and to prevent precipitation, *e.g.,* of silver chloride. The LM 3000 measuring system from Sensortechnik Meinsberg GmbH (Xylem Analytics Germany Sales GmbH & Co. KG) served as the measuring device for electrode potential measurement and data recording. Conditioning of the CG electrodes was performed in 10 or 1 mM potassium bromide calibration solutions over a period of 30 min.

The cross-sensitivity of the glasses was determined in the calibration solutions by adding 1 mM interfering anions (Cl^-, SO_4^{2-}, SCN^-, and I^-) according to the mixed solution method recommended by IUPAC (International Union of Pure and Applied Chemistry). The determination of the selectivity coefficients of a Br^- sensitive electrode based on the material system 60AgBr $24Ag_2S$ $16As_2S_3$ was carried out in a measurement range 10 to 10^{-4} mM KBr, 0.1 M KNO_3 with the addition of interfering ions in a constant concentration of 1 mM in each case. We added KCl, KI, KSCN and K_2SO_4. For the calculations, concentrations instead of activities were considered because we adjusted the ionic strength of the solutions with 0.1 M KNO_3.

Results and discussion

Scanning electron micrographs at 20000× magnification of the CG of composition 60AgBr $24Ag_2S$ $16As_2S_3$ (mol %) in Figure 4, reveal the formation of butterfly-shaped crystalline formations on the surface of the selective powder material. The CG shows a tendency to recrystallize due to the grinding of the bulk material in the vibrating disc mill and planetary ball mill.

Figure 5 shows X-ray diffraction patterns of powder samples of a CG of the above composition. The reflection line shows visible peaks of the compounds AgBr. This clearly shows the glassy-crystalline character of the material. This state seems to cause Br^- sensitivity and thus usability as a functional element as an anion-sensitive material. In work on the sensitivity of chalcogenide glassy-crystalline materials based on silver bromide, it has been reported that the ISEs have far better analytical properties in terms of the measured electrode potentials and the resulting Nernst slope than those sensors based on conventional fully crystalline AgBr Ag_2S or AgBr membranes [2,12].

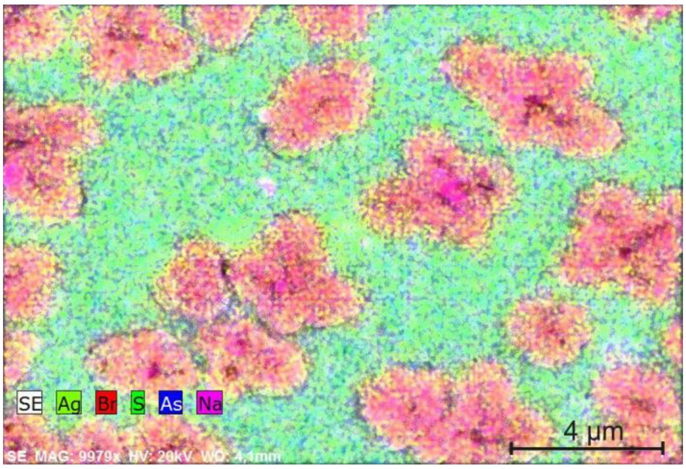

Figure 4. *Scanning electron micrographs of AgBr Ag_2S As_2S_3 CG (SE-secondary electron detector)*

However, in the pulverization of CG necessary for the preparation of TF pastes, the occurrence of undesirable partial recrystallization is not conducive. However, the solidified CGs show high chemical stability in aqueous solutions, comparable to completely amorphous glasses.

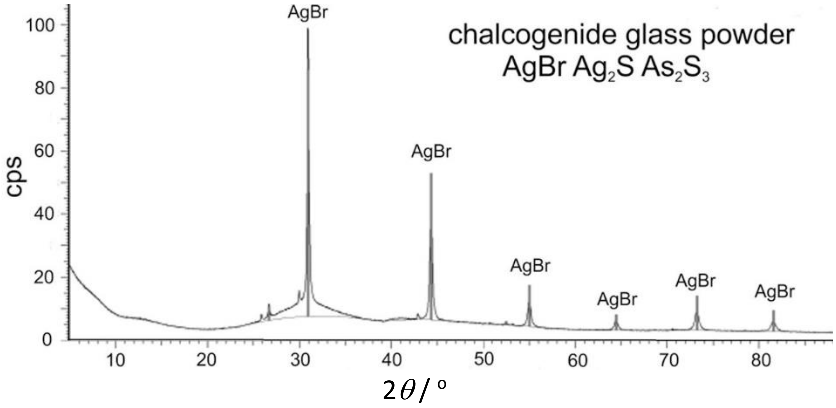

Figure 5. *X-ray diffraction diagram of Br^- sensitive CG powder with AgBr peaks*

The thermoanalytical behaviour of AgBr Ag_2S As_2S_3 CG powder was studied under a nitrogen atmosphere using equipment from NETZSCH-Gerätebau GmbH. Figure 6 shows the measured curves of TG and DTA. According to the TG curve, the glass is thermally stable up to about 260 °C. At higher temperatures, there is a significant loss of mass caused by thermal decomposition. In the DTA curve, exothermic signals at 190 and 250 °C indicate phase formation.

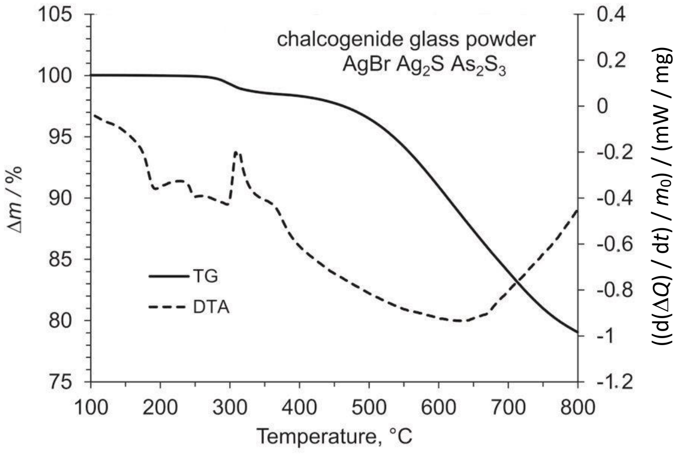

Figure 6. *Mass change (TG signal) and heat flow (DTA signal) of AgBr Ag_2S As_2S_3 CG*

Another endothermic signal at 310 °C indicates thermal decomposition or phase transformation. The results of the thermal analysis show that the glass is not thermally stable at temperatures above 260 °C due to thermal decomposition.

The sintering behaviour of AgBr Ag_2S As_2S_3 CG powder was also investigated (Figure 7). The sintering curve of a powder compact was measured with thermomechanical analysis TMA 402 F1 Hyperion from NETZSCH-Gerätebau GmbH. The glass begins to sinter homogeneously at 225 °C. After a shrinkage of 8 % at 305 °C, the thermal decomposition of the glass dominates. The decomposition causes the sintered body to bubble, which is indicated by the rise of the shrinkage curve. Above 330 °C, shrinkage increases again due to the evaporation of the decomposition products. Thus, the thermal decomposition of the bromide glass influences its sintering. The glass cannot be sufficiently compressed and is therefore unsuitable for the thick-film process.

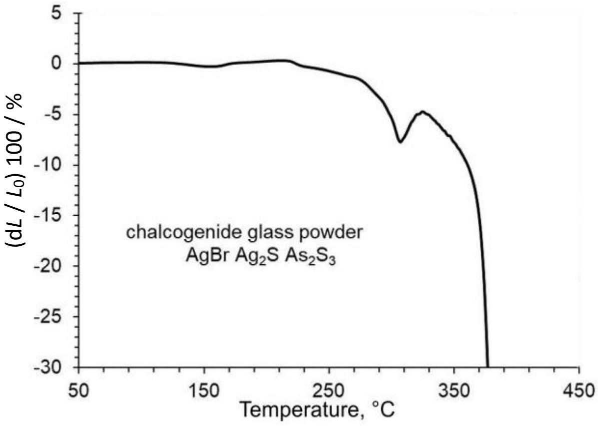

Figure 7. *Linear shrinkage vs. temperature of AgBr Ag_2S As_2S_3 CG (L = Length of the measurement sample, L_o = Length of the sample at the beginning of the measurement*

All configured ISEs, with chalcogenide glasses of the stoichiometric composition given in Table 1, were subjected to potentiometric measurement to determine the most optimal glass composition in terms of their electrode properties. Here, the CG sensors of the composition 60 AgBr 24 Ag_2S 16 As_2S_3 (mol %) showed the highest sensitivity to bromide ions (Figure 8). The response time t_{90} of the electrode was determined to be 0.5 to 1 min.

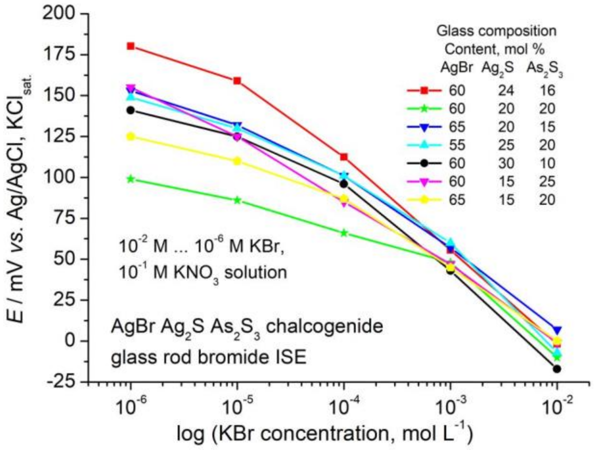

Figure 8. *Calibration curves of bromide electrodes of different compositions*

The response of a bromide ISE in a range of 10 to 10^{-3} mM KBr, 0.1 M KNO_3 measured on different days is shown in Figure 9.

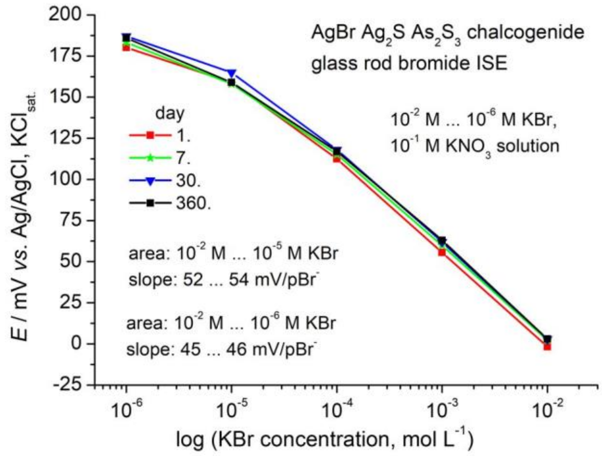

Figure 9. *Calibration curves of a bromide ion-sensitive electrode of the material system 60AgBr 24Ag$_2$S 16As$_2$S$_3$ (mol %)*

The linear measuring range of the electrode extends in a range from 10 M to 0.01 mM KBr, 0.1 M KNO$_3$. The slope of the measuring electrode in this range was 53 ± 5 mV/pBr$^-$. This value is slightly lower than the index of 59 mV/pBr$^-$ for monovalent ions given according to the Nernst equation. Even after one year, no decrease in the slope can be observed. The detection limit is about 0.1 μM KBr. At even lower concentrations, the electrode does not show any potential changes. A great advantage is the dry storage of the ISEs. However, it is necessary that the sensor is conditioned and calibrated before measurement.

The temperature dependence of the electrode voltage of a Br$^-$-sensitive ISE based on the material system 60AgBr 24Ag$_2$S 16As$_2$S$_3$ (mol %) *vs*. Ag/AgCl, sat. KCl reference electrode is shown in Figure 10. For a precise determination of the bromide concentration, temperature compensation is necessary since the electrode signal increases by approx. 1 to 2 mV at a temperature increase of 1 °C.

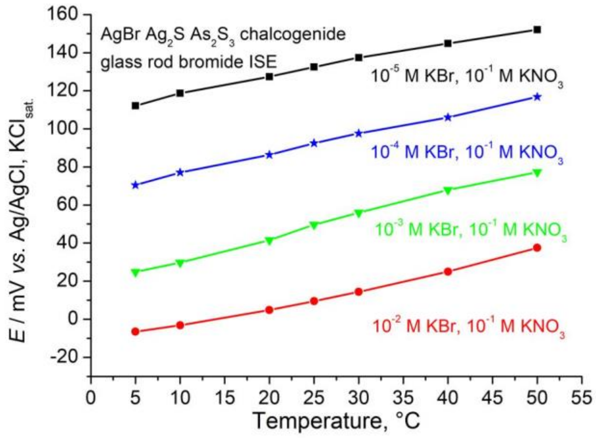

Figure 10. *Temperature dependence of the measurement signal of a CG bromide electrode*

The calibration curves without interfering ions addition and each with a constant interfering ions concentration of a bromide-CG-ISE of the composition 60AgBr 24Ag$_2$S 16As$_2$S$_3$ (mol %) are shown in Figure 11. The determination of the selectivity coefficients (Table 2) was carried out in the measuring range from 10 to 10^{-5} mM KBr, 0.1 M KNO$_3$ of the measuring ion. Iodide ions interfere with the measurements or have a strong influence on the electrode potential and were therefore not included in the determination of the selectivity coefficient. Thus, extreme errors or inaccuracies can occur in the presence of I$^-$ ions in the measuring solution. This circumstance should be taken into account for practical measurements. Furthermore, all chalcogenide glasses of the AgBr Ag_2S As_2S_3 system show a high sensitivity to silver ions.

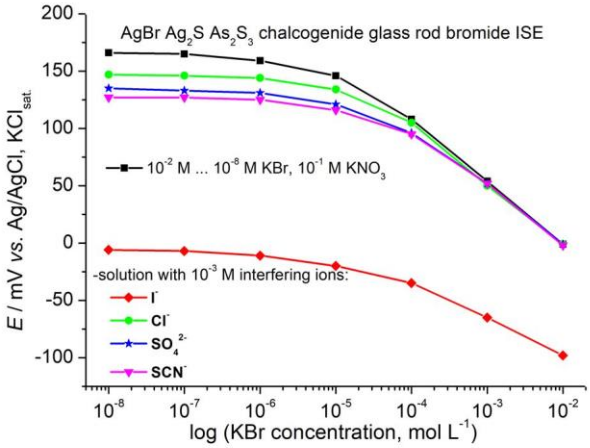

Figure 11. *Determination of the selectivity coefficient of the AgBr Ag_2S As_2S_3 CG electrode*

Table 2*. Selectivity coefficients of a Br^- CG with the mixed solution method*
(primary ion Br^- against the interfering ion)

Interfering ion (1 mM)	Selectivity coefficient
SO_4^{2-}	7.9×10^{-4}
Cl^-	1.1×10^{-2}
SCN^-	3.9×10^{-2}
I^-	-

For practically-relevant applications of the sensors, the applicable pH range is another important parameter. Figure 12 shows that the measurement signals of a Br^-sensitive rod electrode remain stable in the pH range from pH 2 to 12, independent of pH changes in the test solution. Measurements were made in 10 and 0.1 mM concentrations of bromide, with the ionic strength being constant at 0.1 M KNO_3. The respective pH value of the test solution was adjusted using potassium hydroxide solution or nitric acid.

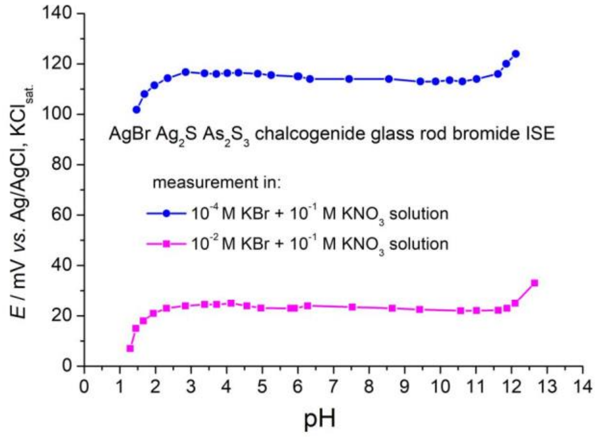

Figure 12. *pH dependency of the measuring signal*

Conclusions

A series of chalcogenide glasses for the determination of bromide in aqueous solutions of different stoichiometric compositions were melted and characterized using various physico-chemical methods. The focus was on the material system AgBr Ag_2S As_2S_3, whereby the CG glass of the composition 60AgBr $24Ag_2S$ $16As_2S_3$ (mol %) showed the most optimal results in terms of Nernst behaviour, signal stability and reproducibility of sensitivities. By improving the classical precision manufacturing process, it was possible to configure measurable ISEs in rod form by means of an optimal metallographic preparation and the use of new processing materials. It was found that due to its thermal decomposition behaviour in the sintered region of the glass, the AgBr Ag_2S As_2S_3 CG material is not suitable for processing into a glass paste and screen printing and firing it onto a ceramic substrate to produce a dense glass membrane using the thick film method. However, it is the crystalline-glassy character that seems to be responsible for the ionic sensitivity of the CG.

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