

## Chalcogenide Glass-based Chemosensors

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**Abstract** – A number of chalcogenide glasses for the fabrication of potentiometric electrodes selective for heavy metal ions were melted and characterized. The focus was directed on the detection of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions. In addition to the preparation of conventional rod electrodes, the purpose of the research was the realisation of corresponding planar electrodes in thick film technology. Until now, for measurements, only rod-electrodes were available. Miniaturized electrodes were achieved for the case of copper ion determination, whereupon several glass compositions were tested. The sintering behavior of the investigated lead ion selective glasses hitherto did not allow the fabrication by the thick film process. The requirement to add AgI to the initial mix is associated with light sensitivity of corresponding sensors.

**Keywords**–determination of heavy metals; potentiometric sensor; chalcogenide glasses; thick film technology; copper; lead.

### I. INTRODUCTION

Commonly used analytical procedures to detect heavy metals are Atom Absorption Spectroscopy (AAS), Optical Emission Spectrometry using Inductive Coupled Plasma (ICP-OES), Polarography and Ion Chromatography (IC) [1-4]. However, the devices needed are highly complex and require experienced operators. Measurements to be taken directly on-site are not possible by means of these methods. Other disadvantages are their high operational and equipment costs. A substantially more cost-effective alternative delivers the use of Ion Selective Electrodes (ISE) that allow continuous measurements in liquids [5]. Because of a simple experimental setup and a miniaturized sensor membrane, ion selective potentiometry is becoming increasingly important for the determination of ion activities and integrated sensor arrays [6]. For heavy metal ions, selective membranes chalcogenide glasses represent promising base materials. In the 1970s, Trachtenberg and Baker [7] introduced Ion-Selected Electrodes (ISEs) based on Chalcogenide Glasses (CG) to determine  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions.

At the end of the 1980s, Vlasov *et al.* [8]-[13] developed a systematic synthesis and carried out physical and electrochemical investigations at new CG-materials for the

detection of  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$  and  $\text{Sn}^{2+}$  ions in solutions. Further research results of CG for the analysis of liquids were presented by Vassiliev and Boycheva [14] in the year 2005. Conde Garrido investigated CG based on Ag-Ge-Se for the development of ISEs [15].

For the fabrication of such materials, in general, the required chemical compounds are heated in evacuated quartz ampoules and quenched, subsequently. In the process of making conventional potentiometric ISEs, the CG-bulk material is removed from the ampoules, cut into thin slices, mounted in a waterproof rod-shaped body and afterwards contacted. Pollrich [16] und Kloock [17] describe the fabrication of glasses. With regard to on-site analysis, currently, miniaturization of such as ISEs is at the core of research. During the on-site analysis, measurements can be carried out fast and easy at the sampling location with only reasonable effort and without equipped laboratory tests. Thus, quantitative and semi-quantitative statements about pollutant contents, e.g., in water, soil and solid waste, can be made. Therefore, especially small and robust sensors are required. For the miniaturization, several thin-film technologies are in use to deposit the CG-bulk material as thin membrane on, e.g., potentiometric or field effect based sensor structures. In the 1980s, Vlasov *et al.* [18] carried out first experiments to realize thin  $\text{Cu}^{2+}$ -ion sensitive CG-membranes by means of Radio Frequency (RF) Co-Sputtering on Ion Sensitive Field Effect Transistors (ISFETs). Further procedures to produce thin film sensors for heavy metal analysis in liquids are RF Magnetron Sputtering, Sputtering in combination with Ion Implementation, Evaporating, Flash Evaporating with Photo Doping as well as Electrochemical Deposition. All mentioned physical procedures have problems with respect to a stoichiometric deposition of thin CG-membranes based on multi-component mixtures. However, maintaining of the stoichiometry is of importance for the functionality of the CG-based ISEs. A method that realizes the stoichiometric deposition of glass membranes is Pulsed Laser Deposition (PLD). It was used by Schöning and Kloock [19]-[22]. In the PLD process, CG is rapidly removed from the bulk material and deposited on a transducer structure with remaining stoichiometry. Significant disadvantages of the procedure are high equipment

costs and enormous amount of time for the realization of the CG-thin film membrane.

The rest of the paper is structured as follows. In Section II, advantages of thick-film (TF)-technology as possible fabrication method of CG electrodes are highlighted. Section III contains the description of all experiments in connection with fabrication and characterization of the electrodes. In Section IV, the achieved results are presented and discussed. We conclude in Section V.

## II. OBJECTIVE

The goal of this work is the development of a cost-effective process for the manufacture of miniaturised CG-ISEs. This is given by thick-film (TF)-technology. Sensors for the determination of heavy metals fabricated by means of this technology would have the decisive advantage over those prepared with physical processes (like, e.g., PLD), namely, that they can be produced cost-effectively in small quantities.

The great potential that is offered by TF-technology, regarding market and technology, can be utilised for the development of electrochemical sensors. Advantages of a ceramic-TF based heavy metal sensor are its mechanical robustness, high chemical resistance and tightness, as well as the associated low susceptibility to cross influences. Thus, the aim is to create a TF-sensor for heavy metal ions, e.g., to be used in environmental analysis. In this paper,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions are the focus of interest. One challenge is the material and process development for the realisation of CG-membranes in TF-technology on ceramic substrates. From CG-bulk material, a submicron powder has to be produced for the realisation of a sinterable TF-paste. This requires fundamental tests of the sintering behaviour of chalcogenide glasses under inert conditions.

## III. EXPERIMENTS

Ag, Pb, Cu, As, S,  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{S}_5$ ,  $\text{As}_2\text{Se}_3$  and AgI, as well as PbS powders have been used for the fabrication of the glasses and Cu, Pb, K, Ca and Na nitrates for the preparation of the calibration solutions, in each case in a purity >99.99 wt.-% obtained from Alfa Aesar GmbH Co. KG and Sigma-Aldrich Chemie GmbH. For melting the CG, the individual glass components were inserted in a cylindrical quartz ampoule. This was filled with nitrogen in a reaction chamber, evacuated ( $<10^{-3}$  mbar) and hermetically sealed. The powder containing body was transferred in a quartz glass reactor, which then was placed in a tube furnace (B180, max. temperature:  $1300^\circ\text{C}$ , see Figure 1).

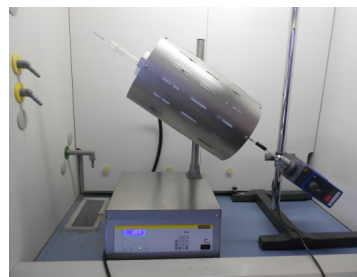


Figure 1. Tube furnace with laboratory stirrer

For the slow movement of the ampoule during the heat-up phase with 100-110 K/h until temperatures of  $1000\text{--}1100^\circ\text{C}$  and a melting process duration of 8-9h, a stirrer was used. Immediately after the melting process, the ampoule was quenched in cold water and destroyed for the collection of the glass. In particular, following heavy metal ion selective CG-glass systems of different stoichiometry were melted:  $\text{CuAsS}$ ,  $\text{CuAsSe}$ ,  $\text{CuAgAsSe}$  ( $\text{Cu}^{2+}$  sensitive) and  $\text{PbAgIAS}$  ( $\text{Pb}^{2+}$  sensitive)

Surface, structure, qualitative and quantitative composition as well as thermal expansion coefficient of the glasses and pastes that were later prepared for the screen printing process were characterised by means of following methods: Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectrometer (EDX), Microwave Digestion of the glasses with MARS 6 (CEM GmbH) and determination of the elements with Atom Absorption Spectrophotometer novAA400, X-ray Diffraction (XRD) by means of D8 advance from Bruker, Dilatometry and other thermoanalytic methods using several equipment from NETZSCH-Gerätebau GmbH.

As mentioned above, for the specific purpose of evaluation of TF-technology as manufacturing procedure for CG-glass electrodes, the determination of the sintering behaviour under inert conditions is important, for which several thermoanalytical investigations by means of Thermomechanical Analysis (TMA) were performed.

For orienting measurements of the electrochemical functionality of the glasses, initially the conventional electrode design, according to Figure 2a, was realised. Therefore, glass disks (thickness: 2mm) split by a diamond saw and embedded in epoxy resin were mounted in a liquid-tight polymer-pipe and encapsulated with epoxy resin. The electrical contact was realised by means of conductive silver lacquer via Ag or Cu wires. Later, impedance measurements were carried out to determine the internal electrode resistances using a GAMRY Electrochemical Measurement System. The determination of response times and slopes of the electrodes was performed in calibration solutions in the measuring range of  $10^{-2}$  M- $10^{-7}$  M  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  with a 0.1 M  $\text{KNO}_3$  amount to adjust the ionic strength. The cross-sensitivity of the glasses was determined in the calibration solutions specified above by adding of  $10^{-3}$  M interfering cation in each case. After having examined the electrode functions of the sensors, the CG that was found particularly

appropriate (sensitivity:  $>25$  mV/pX,  $X = \text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ; measuring range:  $>10^{-5}$  M; lower detection limit:  $<10^{-5}$  M, pH-range: pH = 2- 7; response time:  $< 3$  min) was chosen for the later fabrication of the TF-electrodes (Figure 2b). Therefore, the CG-bulk materials are milled to glass powder and brought into an organic vehicle, which is added to achieve screen printability. Afterwards, the pastes were processed on a three roll mill to make sure the particles were finely-dispersed. The pastes have been screen printed on  $\text{Al}_2\text{O}_3$  substrates over a metallised layer (Au). The CG layers were fired according to the sintering temperature of the respective glass.

Potentiometric measurements with conventionally produced rod-shaped CG-electrodes, as well as with prepared TF-sensors were carried out by means of the multiple channel measuring instrument KM 3000 of Sensortechnik Meinsberg GmbH usually in connection with a saturated silver/ silver chloride reference electrode. On a specific occasion, the influence of light on the electrode potential of individual electrodes was determined, too.

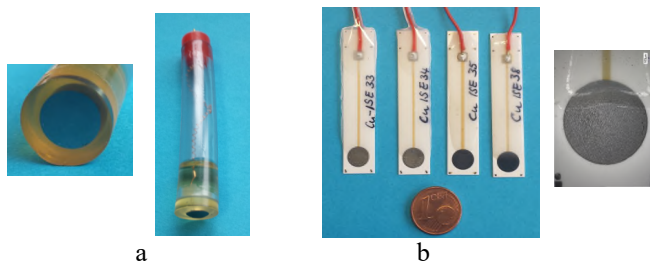


Figure 2. Heavy metal ion sensitive chalcogenide glass electrodes (a rod-shaped electrode, b thick film electrode)

#### IV. RESULTS AND DISCUSSION

The results presented below relate to the relevant material science tests and to the investigations in connection with the use of the electrodes.

In Figure 3, an EDX measurement of a  $\text{Cu}^{2+}$  ion selective glass suitable for the thick-film process is presented; it shows a uniform distribution of the elements within the selective material. However, from AAS analyses, it can be concluded that there is a slight stoichiometric difference between weighed crystalline starting mixture and glass.

In particular, pulverisation of bulk glasses necessary for the preparation of TF-pastes causes sometimes unwanted partial recrystallisation for materials without silver. This becomes clear in the XRD diagrams of the relevant copper and lead ion selective materials shown in Figure 4.

Knowledge of the sintering behaviour of the glass powder is of great importance for the realisation of glass-based TF-sensors. By means of TMA, the shrinkage was measured of glass powder compacts (of cylindrical shape). During sintering, the glass powder should compress without crystallisation.

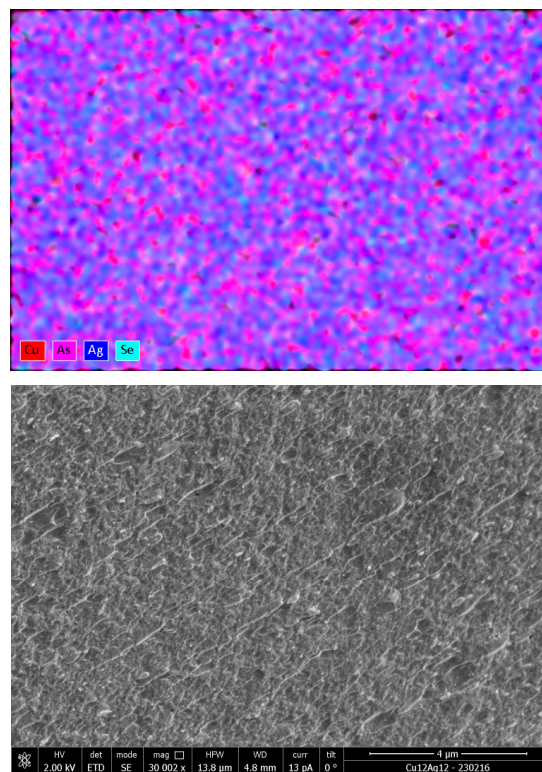


Figure 3. EDX-recordings of distribution of the elements copper, silver, arsenic, selenic in a chalcogenide glass with the composition:

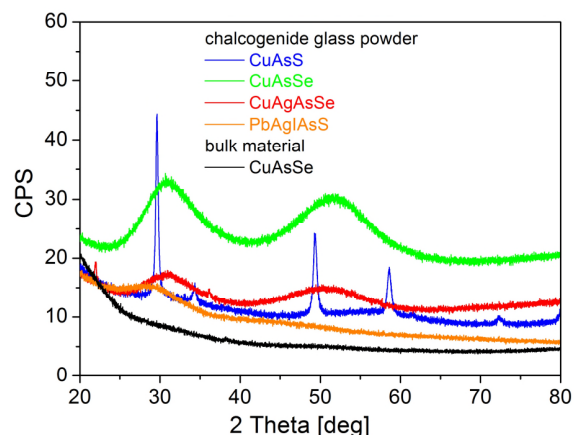
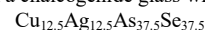


Figure 4. X-ray diffraction diagrams of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  sensitive chalcogenide glasses

As a result of all orienting investigations on CG-bulk material and on CG-powder including Differential Thermal Analysis (DTA), Thermogravimetry (TG) and sintering behaviour, it could be concluded that all proposed systems of copper ion selective CG with copper contents  $>10$  at.-% should be suitable for paste preparation. Due to phase formation/crystallisation of the investigated lead selective glass

(see Figure 5) at 190°C, it should be sintered at temperatures <190°C what is possible in air and nitrogen, in principle. Using a heating rate of 10 K/min, an end of the sintering would be expected at 355°C. This corresponds to sufficient material shrinkages of 17% (see Figure 6).

Assuming a sintering temperature of 180°C that is relevant in the present case to prevent crystallisation, it would lead to shrinkage of only 4%; then, the glass is not sufficiently compressed. The available lead ion selective CG is, therefore, unsuited for the TF-process.

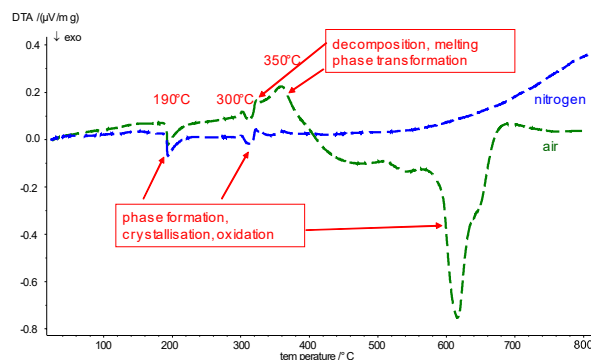


Figure 5. DTA investigations for a chalcogenide glass system PbAgIAsS

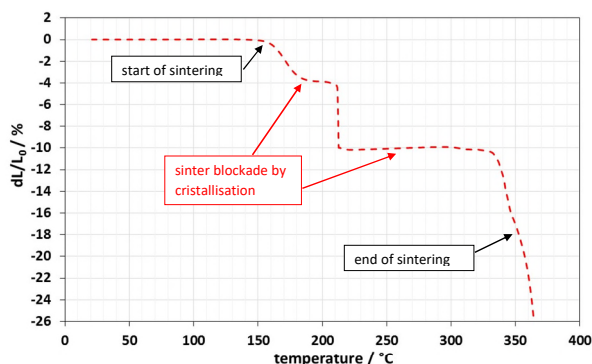


Figure 6: Linear shrinkage vs. temperature of PbAgIAsS-powder compact

For impedance measurements carried out with all rod-shaped and TF-electrodes, a 3-electrode arrangement was chosen, consisting of CG-working electrode, platinum-sheet counter electrode and saturated silver/ silver chloride reference electrode. The internal resistances are presented in Figure 7. Since conventional ion-meters have input resistances of about  $10^{13} \Omega$ , no measurement problems are expected.

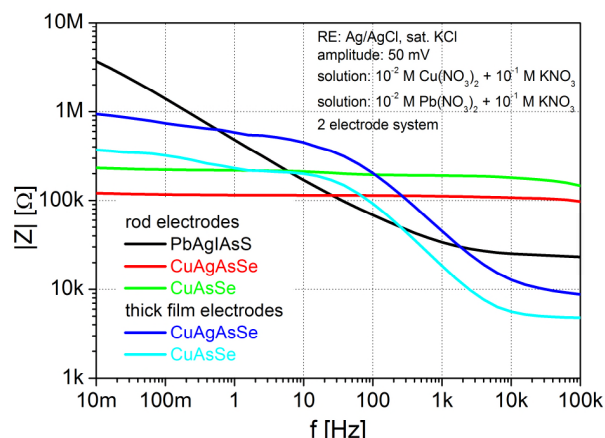


Figure 7. Impedance measurements with chalcogenide glass electrodes

Rod-shaped and TF-electrodes based on the glass systems CuAsS, CuAsSe and CuAgAsSe have been used for the potentiometric determination of  $\text{Cu}^{2+}$  ions. Lead analyses were performed only by means of rod-shaped sensors. It was ascertained that glass compositions with Ag content and the use of Se instead of S resulted in improved properties concerning the lower detection limit of the corresponding electrodes. The slopes of the measuring chains in the linear measurement range from  $10^{-2}$  M-  $10^{-8}$  M  $\text{Cu}(\text{NO}_3)_2$ , 0.1  $\text{KNO}_3$  with  $28.7 \pm 0.5$  mV/p $\text{Cu}^{2+}$  were in good agreement with the Nernst equation for bivalent ions. The calibration curve of a corresponding TF-electrode is shown in Figure 8. The electrode sensitivities of lead selective rod-shaped electrodes obtained in calibration solutions of  $10^{-2}$  M-  $10^{-8}$  M  $\text{Pb}(\text{NO}_3)_2$ , 0.1 M  $\text{KNO}_3$  had with  $28.6 \pm 0.5$  mV/p $\text{Pb}^{2+}$  similar values. Furthermore, an extreme influence of light on the electrode potential of these (silver iodide containing) electrodes (see Figure 9) was detected. Strong responses of the potential of a corresponding electrode located in a black box under the influence of light with varying intensity were observed. This circumstance should be considered for practical measurements.

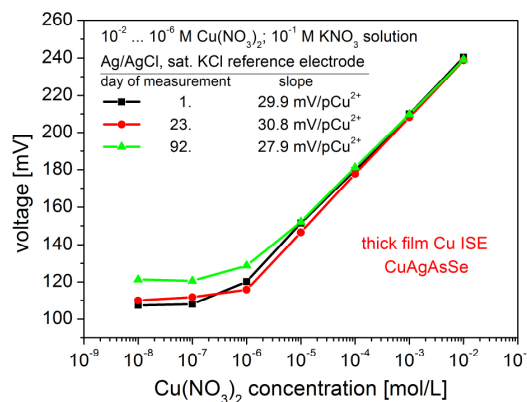


Figure 8. Calibration curve of a copper electrode in thick film technology



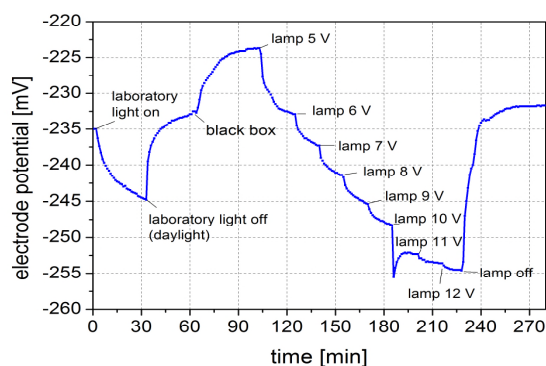


Figure 9. Light sensitivity of a lead ion selective chalcogenide glass electrode with AgI as component of the membrane

Finally, for the favoured copper ion selective TF-electrode the selectivity coefficients were determined according to the method of mixed solutions (see Table 1).

TABLE 1. SELECTIVITY COEFFICIENTS OF A  $\text{Cu}^{2+}$  CG-ISE

cation	$K_{A,B}^{\text{pot}}$
$\text{Cd}^{2+}$	$3.5 \cdot 10^{-4}$
$\text{Pb}^{2+}$	$5.0 \cdot 10^{-4}$
$\text{Na}^+$	$4.5 \cdot 10^{-1}$
$\text{Ca}^{2+}$	$3.0 \cdot 10^{-4}$

## V. CONCLUSION

CGs of different stoichiometric compositions were melted. They were characterised by a number of physico-chemical methods with the aim to fabricate copper and lead ISEs in TF-technology. The focus was on the material systems  $\text{CuAgS}$ ,  $\text{CuAsSe}$ ,  $\text{CuAgAsSe}$  and  $\text{PbAgIAsS}$ . In a first step, rod-shaped electrodes were fabricated in conventional manner from these glasses. While the material properties of the lead selective glasses did not allow a preparation of processable TF-pastes, corresponding screen printed copper selective electrodes could be realised. Their measuring performances were comparable with those known from rod-shaped electrodes. By an optimisation of the glass composition, the electrode properties were improved.

## ACKNOWLEDGEMENT

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