Electrochemical Properties of $Ag_5Te_2Cl_{0.8}Br_{0.2}$, a Representative of the Solid Solutions $Ag_5Te_2Cl_{1-x}Br_x$

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Z. Naturforsch. **2008**, *63b,* 1083 – 1086; received May 27, 2008

Impedance spectroscopic investigations of $Ag_5Te_2Cl_{0.8}Br_{0.2}$, a selected representative of the solid solutions $Ag_5Te_2Cl_{1-x}Br_x$ with $x = 0-1$, proved the mixed-conducting property of this class of materials. Two polymorphs are realized in the temperature range of 309 to 410 K, the monoclinic β-phase (space group $P2_1/n$) and the tetragonal α-phase (space group $I4/mcm$) with an order-disorder phase transition temperature of 336 K (DSC). A sharp increase of the total and ionic conductivity can be observed at 337 K, in good accordance with the phase transition temperature. The electronic conductivity exceeds the ionic conductivity by approximately one order of magnitude over a wide range of temperature. Conductivities are $\sigma_{\text{ion}} = 6.9 \times 10^{-5}$ (309 K) and $\sigma_{\text{tot}} = 4.80 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$ (310 K) for β-$Ag_5Te_2Cl_{0.8}Br_{0.2}$ and $\sigma_{\text{ion}} = 1.6 \times 10^{-2}$ (395 K) and $\sigma_{\text{tot}} = 1.73 \times 10^{-1}\ \Omega^{-1}\ \text{cm}^{-1}$ (394 K) for α-$Ag_5Te_2Cl_{0.8}Br_{0.2}$.

Key words: Silver(I) Chalcogenide Halides, Impedance Spectroscopy, Mixed Conductors

Introduction

The exploration of the silver(I) chalcogenide halides with the composition Ag_5Q_2X (Q = chalcogenide and X = halide) started in the early 1980ies. Blachnik and co-workers reported on the discovery of α-Ag_5Te_2Cl [1] in the Ag-Te-Br section. Trimorphic Ag_5Te_2Cl was also investigated by Doert *et al.* who solved and described the low-temperature phase γ-Ag_5Te_2Cl [2]. Recently, we were able to address the structure of the intermediate β-Ag_5Te_2Cl phase at r. t. [3]. In the meantime we started a systematic investigation of the system coinage metal-chalcogen-halogen in order to find systems with large stability ranges of partially substituted compounds. Examples are Ag_3SX [4, 5], $Ag_{19}Q_6X_7$ [6, 7], $Ag_{10}Q_4X_3$ [8, 9] and $Ag_{23}Te_{12}X$ [10]. The Ag_5Q_2X system with Q = S, Se, Te and X = Cl, Br shows a great flexibility regarding partial substitution of the anions with retention of the structural features [11, 12]. This finding is in contrast to the $Ag_{19}Q_6X_7$ system where partial anion substitution leads to the formation of new structures. Physical properties like the stability ranges and the conductivity of the different phases can be varied and fine tuned by this process. Very recently, it was possible to prepare Ag_5Te_2Br, the second ternary representative of the class of Ag_5Q_2X compounds beside Ag_5Te_2Cl, by hydrothermal synthesis [13].

Beside the extensive structural characterization of the Ag_5Q_2X system, the electric properties have only barely been determined. Beeken [14] reported a study of the low-temperature (150 – 400 K) total conductivity of Ag_5Te_2Cl which was completed by a high-temperature study later on [3]. In addition, the total conductivities of selected substitution variants [11, 12] of the chloride were reported and were correlated with the structural properties of the different polymorphs. A detailed examination of the different contributions to the total conductivity and its separation into the electronic and ionic parts is still missing for all Ag_5Q_2X compounds.

Experimental Section

Synthesis

$Ag_5Te_2Cl_{0.8}Br_{0.2}$ was prepared by classical solid state flux synthesis mixing Ag (Chempur, 99.9 %), Te (AlfaAesar, 99.9999 %), AgCl (Merck, > 99.3 %) and AgBr (Chempur, 99.9 %) in an ideal molar ratio in evacuated silica ampoules [12]. After a heating stage to 753 K, the mixture was quenched in an ice bath, homogenized, and resealed in an ampoule to add an annealing period at 713 K lasting several

0932–0776 / 08 / 0900–1083 $ 06.00 © 2008 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

days. The homogenization and annealing processes were repeated twice to achieve phase purity of the sample. Dark grey to black $Ag_5Te_2Cl_{0.8}Br_{0.2}$ is not light sensitive and stable on air over months.

X-Ray powder diffraction

X-Ray powder diffraction experiments for $Ag_5Te_2Cl_{0.8}$-$Br_{0.2}$ were performed using a Stoe StadiP diffractometer, equipped with a linear 5° position-sensitive detector (PSD, Braun). A finely ground sample was examined in transmission geometry applying $CuK_{\alpha 1}$ radiation (λ = 1.54051 Å, germanium monochromator). Lattice parameters at 298 K of the present sample were identical within two times the standard deviation to the values of a = 13.879(3), b = 7.678(2), c = 13.704(2) Å, β = 90.10° for the β-Ag_5Te_2Cl structure type as reported in [12]. The sample was phase-pure and suitable for the impedance spectroscopic investigations.

Impedance spectroscopy

A symmetric cell with two electron-blocking but silver ion-conducting electrodes was used to measure the partial silver ionic conductivity of $Ag_5Te_2Cl_{0.8}Br_{0.2}$, according to the well-known electrochemical concepts introduced by Wagner [15]. These concepts have since been applied frequently by many others [16 – 18]. Electron-blocking electrodes were prepared by cold pressing of 6 mm pellets of a mixture of $RbAg_4I_5$, $RbAg_4I_5$/Ag (1 : 1), and Ag powder in a volume ratio of 6 : 1 : 1 at 15 kN. $RbAg_4I_5$ was synthesized by mixing AgI (Sigma-Aldrich, 99 %) and RbI (Alfa Aesar, 99.8 %) in a 4 : 1 molar ratio in evacuated silica ampoules, followed by heating to 970 K and quenching in an ice bath. $RbAg_4I_5$ was stored at 323 K prior to use, and each electrode was prepared directly before the measurements after an X-ray powder phase analysis. The silver ion-conducting electrodes were contacted on both sides of a cold-pressed $Ag_5Te_2Cl_{0.8}Br_{0.2}$ pellet achieving the phase sequence Ag/$RbAg_4I_5$/$Ag_5Te_2Cl_{0.8}Br_{0.2}$ /$RbAg_4I_5$/Ag. This setup was mounted between Pt electrodes and connected to a Solartron 1287 potentiostat which was controlled by a Solartron 1260 frequency response analyzer. All measurements were performed under an N_2 atmosphere. Impedance spectra were recorded within a frequency range of 1 MHz to 0.1 Hz applying a temperature range of 309 – 395 K. 1 h of equilibration time was granted prior to each impedance measurement after reaching a new temperature. After each impedance measurement, a dc measurement was carried out by applying a dc potential difference in the cell and taking the steady-state ionic current after 400 s. The impedance data and resulting dc resistance was used to calculate the ionic conductivity. Conductivity values as evaluated from the low-frequency part of the impedance spectra and from the steady-state dc currents agreed well within the experimental errors.

Data of the total conductivity of $Ag_5Te_2Cl_{0.8}Br_{0.2}$ were taken from the literature [12]. The total conductivity was measured with a Zahner IM6 impedance analyzer in the frequency range of 4 MHz to 100 mHz and within a temperature range of 306 – 414 K. Ion-blocking gold electrodes were contacted to cold-pressed pellets, and impedance spectra were recorded under an oxygen- and moisture-free nitrogen atmosphere.

EDX analyses

Semi-quantitative analysis of $Ag_5Te_2Cl_{0.8}Br_{0.2}$ was performed using a Leica 420i scanning electron microscope (Zeiss) fitted with an electron dispersive detector unit (Oxford). Silver, HgTe (Te), and KBr (Br) were used as standards for calibration. A voltage of 20 kV was applied to the samples. The postulated composition was substantiated within the standard deviations of the method.

Results and Discussion

During the past few years the renaissance of mixed electron and ionic conducting silver chalcogenides and related compounds for data storage applications in the form of non-volatile memory devices is remarkable. Nanosized resistivity-switching memories based on silver chalcogenides [19] as well as phase-change materials based on GeSbTe alloys, doped with coinage metals for rewriteable data storage [20], are examples of this rapidly growing field of interest. Physical properties like semi-conduction and high ion mobility, leading to materials which can be switched with minimum power from one state to another, are of particular interest.

The substance class Ag_5Q_2X is characterized by a pronounced structure retention during the partial exchange of chalcogenide or halide ions [11, 12]. Most of the compounds are di- or trimorphic depending on the degree and type of substitution, and the transition temperatures can be varied in an interesting temperature window around r. t. The transition from the silver-ordered β-phase in Ag_5Te_2Cl to the disordered α-phase can be shifted from 334 to 336 K (DSC data). A high ion mobility could be estimated from the structural data, and all compounds are light- and moisture-stable over month. Details concerning the structural properties can be found in [12].

Impedance spectroscopic measurements of the total and partial ionic conductivity (Fig. 1, black squares) were now performed in a temperature range around the reported phase transition at 338 K from the or-

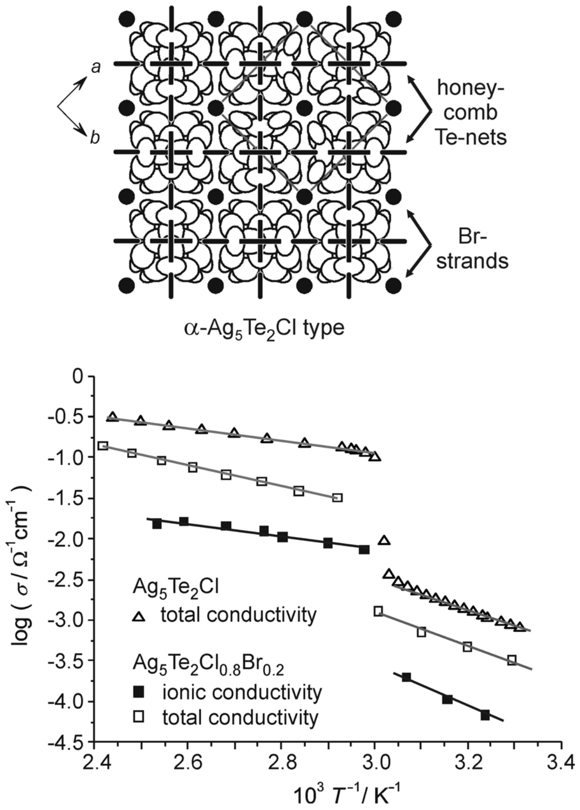

Fig. 1. Top: α-Ag_5Te_2Cl structure type; view parallel to the 6^3 Te nets (fragmented lines) and Br strands (black spheres). Bottom: Arrhenius representation of the specific ionic (black squares) and total conductivity (open spheres) of $Ag_5Te_2Cl_{0.8}Br_{0.2}$. The total conductivity exceeds the ionic conductivity by approximately one order of magnitude over the whole temperature range. A jump of two orders of magnitude is present at 338 K in good accordance with the order-disorder phase transition at 335 K observed by DSC measurements. Data of the total conductivities and of DSC experiments with $Ag_5Te_2Cl_{0.8}Br_{0.2}$ [12] and Ag_5Te_2Cl [3] were taken from the literature.

dered β-phase to the disordered α-phase. In the high-temperature α-phase the silver substructure is quasi-molten, and ion mobility takes place anisotropically along the crystallographic *c* axis in a 1-dimensional fashion. A conductivity jump of two orders of magnitude can be observed in the impedance measurements at 337 K while passing the phase transition. Details concerning the conductivity values are summarized in Table 1.

Table 1. Impedance spectroscopic data of $Ag_5Te_2Cl_{0.8}Br_{0.2}$; σ_{ion} = specific ionic conductivity (this work), σ_{tot} = specific total conductivity (data taken from ref. [12]).

$Ag_5Te_2Cl_{0.8}Br_{0.2}$	Partial ionic conductivity		Total conductivity
T (K)	σ_{ion} (Ω^{-1} cm^{-1})	T (K)	σ_{tot} (Ω^{-1} cm^{-1})
		306	$3.80 \cdot 10^{-4}$
309	$6.9 \cdot 10^{-5}$	310	$4.80 \cdot 10^{-4}$
317	$1.1 \cdot 10^{-4}$	314	$6.16 \cdot 10^{-4}$
		319	$8.00 \cdot 10^{-4}$
326	$2.0 \cdot 10^{-4}$	323	$1.08 \cdot 10^{-3}$
		328	$1.59 \cdot 10^{-3}$
336	$7.5 \cdot 10^{-3}$	334	$5.67 \cdot 10^{-3}$
		338	$6.65 \cdot 10^{-2}$
345	$9.0 \cdot 10^{-3}$	343	$7.54 \cdot 10^{-2}$
		348	$8.17 \cdot 10^{-2}$
357	$1.1 \cdot 10^{-2}$	354	$9.07 \cdot 10^{-2}$
362	$1.3 \cdot 10^{-2}$	364	$1.08 \cdot 10^{-1}$
373	$1.5 \cdot 10^{-2}$	374	$1.28 \cdot 10^{-1}$
386	$1.7 \cdot 10^{-2}$	384	$1.49 \cdot 10^{-1}$
395	$1.6 \cdot 10^{-2}$	394	$1.73 \cdot 10^{-1}$
		404	$1.95 \cdot 10^{-1}$
		414	$2.83 \cdot 10^{-1}$

The pronounced silver mobility leads to an enhanced ionic conductivity which is only one order of magnitude lower than the electric conductivity. Activation energies for the ionic conductivity of the two polymorphs were derived from the Arrhenius-type representation. β-$Ag_5Te_2Cl_{0.8}Br_{0.2}$ shows an activation energy of approximately 0.55 eV which is reduced to 0.16 eV in the α-phase. It has to be stated that the 0.55 eV value is based on a small number of datapoints, and interpretations must be made carefully. Activation energies derived from the total conductivity of the non-substituted Ag_5Te_2Cl are 0.44 eV (β-phase) and 0.14 eV (α-phase), respectively [3] (see Fig. 1, open triangles and squares). In the disordered modification the activation energies are equal within the error of the experiment. The partial substitution of Cl by Br reduces the total conductivity not significantly. A reduction of approximately half an order of magnitude can be observed in the case of $Ag_5Te_2Cl_{0.8}Br_{0.2}$ compared with Ag_5Te_2Cl. The reduction correlates with the increase in the phase transition-temperature, pointing towards a slightly reduced silver mobility for the title compound.

Conclusion

An electrochemical investigation of $Ag_5Te_2Cl_{0.8}Br_{0.2}$ was performed in the temperature range of 306 to 395 K, covering the area of an order-disorder phase transition of the silver substructure. $Ag_5Te_2Cl_{0.8}Br_{0.2}$, a selected sample of the solid solution $Ag_5Te_2Cl_{1-x}Br_x$ with x = 0 to 1, is a mixed conductor with a reasonably high partial ionic conductivity. The electronic conductivity is increasing the ionic conductivity by approximately one order of magnitude over the whole temperature range. This behavior fits the general trend of electrical properties on the quasi-binary section AgX-Ag_2Q, heading from the insulating halides to the semi-conducting chalcogenides with predominantly electronic conductivity.

Acknowledgements

The authors thank the Deutsche Forschungsgemeinschaft DFG (SFB 458, Project A5) for the kind support of this project and Prof. Dr. H.-D. Wiemhöfer, University Münster, for the possibility to use his impedance spectroscopy equipment.

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