Structure Chemical Aspects of Silver(I) Chalcogenide Halides and Preparation of the $x = 1$ Member of the Solid Solution $Ag_5Te_2Cl_{1-x}Br_x$

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The maximum grade of substitution to be reached in solid solutions $Ag_5Te_2Cl_{1-x}Br_x$ by solid state melting reactions starting from the elements, is $x = 0.65$. Using solvothermal synthesis in aqueous ammonia solution, the area of stability can be extended to pure bromide ($x = 1$). X-Ray diffraction experiments have substantiated the isostructural features of Ag_5Te_2Br compared with the chlorine analog. At r. t. Ag_5Te_2Br crystallizes monoclinically, in the β-Ag_5Te_2Cl structure type, with lattice parameters of $a = 14.000(5)$, $b = 7.702(3)$, $c = 13.856(6)$ Å, $\beta = 90.61(4)°$, space group $P2_1/n$. A topological approach, first introduced for the characterization of complex structures of silver(I) (poly)chalcogenide halides, has been transferred to the Ag_5Q_2X system. Based on this formalism the anion substructures can be described by simple nets or strands created by the connection of positions at distances close to or even larger than the sum of the van der Waals radii. In case of the present system, only honeycomb-like telluride nets and halide strands are necessary to explain the complex anion substructure. A deeper understanding of the physical properties, like the anisotropic silver mobility, can be achieved by this topological approach which was not possible with other structure description models.

Key words: Silver(I) Chalcogenide Halides, Structure Topology, X-Ray Powder Diffraction, Solvothermal Synthesis

Introduction

Mixed silver conductors are of potential interest as new materials for electronic devices like non-volatile memories or sensors [1 – 4]. A wide range of physical properties like giant magneto resistance (GMR) [5 – 7], polymorphism [8 – 10] or the high silver mobility are key features of this class of compounds. The discovery of new materials is the essential first step for the improvement of the performance of devices for new applications. During the past two years we focussed our interest on the exploration of the ternary sections coinage metal-chalcogen-halogen.

Three different classes of compounds can be distinguished in the silver-tellurium-halogen section depending on the chemical bonding situation of the polyanion substructure. A purely covalent tellurium substructure is present in $AgITe_3$ [11, 12] or AgITe [13] characterized by tellurium rings and chains, respectively. Only partial covalent character is found for the recently discovered silver(I) (poly)chalcogenide halides with chain-like polyanionic substructures and isolated anions. Examples are $Ag_{10}Q_4X_3$ with Q = S to Te and X = Cl to I [14 – 17] or $Ag_{23}Te_{12}X$ with X = Cl, Br [18]. The most intensively investigated classes of compounds are the ones localized on the quasi-binary sections Ag_2Q – AgX with representatives like Ag_3SX [19 – 21] and $Ag_{19}Q_6X_7$ [22, 23].

In case of the Ag_5Q_2X system the exploration started in the early 1980ies with the examination of the Ag-Te-Br section by Blachnik and co-workers and the discovery and structure determination of α-Ag_5Te_2Cl [24]. The trimorphic Ag_5Te_2Cl was also investigated by Doert *et al.* who described the low-temperature phase γ-Ag_5Te_2Cl [25]. Later on, we were able to address the structure of the intermediate β-Ag_5Te_2Cl phase at r. t. [26] which marked the starting point for us to begin a systematic investigation of the stability ranges of partially substituted compounds. The Ag_5Q_2X system with Q = S, Se, Te and X = Cl, Br shows a great flexibility regarding substitution of the anions with retention of the structural features [27, 28].

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Physical properties like the thermal stability ranges of the different phases and the conductivities can be varied and fine-tuned by this process. Unfortunately, the chemical substitution within the anion substructures led only to a partial exchange of the telluride or chloride in Ag_5Te_2Cl. Ternary compounds like 'Ag_5Se_2Cl', 'Ag_5S_2Cl' or 'Ag_5Te_2I' are unknown. If classical solid state melting reactions are used, the maximum substitution degrees in $Ag_5Te_{2-x}Q'_xX_{1-y}X'_y$ are $x = 0.7$ for $Q' =$ Se [27] and $x = 0.3$ for $Q' =$ S [28]. Chloride can be substituted by $X =$ Br up to $y = 0.65$ [28]. Compounds with $X =$ F or I are unknown and can not be prepared by melting reactions.

Experimental Section

Preparation

Ag_5Te_2Br was prepared from a 4 : 2 : 1 molar mixture of Ag (Chempur, 99.9 %), Te (Chempur, 99.999 %), and AgBr (Chempur, $>$ 99 %). All starting materials were used without further purification. The mixture was sealed in evacuated silica ampoules, heated to 1200 K, held at this temperature for 1 day, and quenched in an ice bath. No formation of Ag_5Te_2Br was detected by X-ray powder phase analyses after this process, and Ag_2Te and AgBr were identified as binary reaction products instead. After homogenization by grinding, 400 mg of the mixture and an aqueous 12.5 % ammonia solution were sealed in an evacuated silica tube. The silica ampoule was filled with the ammonia solution to 40 – 50 % of its capacity. The silica tube was placed into a Teflon-lined, stainless steel autoclave which was filled with distilled water to 50 % of its volume. The autoclave was maintained at 453 K for 14 days and cooled down slowly to r. t. A silver-colored precipitate was filtered and washed several times with absolute ethanol to remove residual ammonia solution completely. Up to 5 – 10 mole-% of the starting materials Ag_2Te and AgBr were found in the phase analyses.

X-Ray powder diffraction

Phase analyses were performed by X-ray powder diffraction measurements. Ag_5Te_2Br was characterized *via* Guinier powder patterns using Cu$K\alpha_1$ radiation and α-quartz (a = 4.913 and c = 5.405 Å) as an internal standard at 298 K. The Guinier camera was operated with image plate technology, and read-out was achieved with a Fuji-film / BAS-1800 image plate system. The lattice parameters were refined from the powder data for Ag_5Te_2Br to a = 14.000(5), b = 7.702(3), c = 13.856(6) Å, β = 90.61(4)°, fitting the metric of the β-Ag_5Te_2Cl structure type.

X-Ray single crystal diffraction

Crystals were isolated from the solvothermal reaction batch to perform a single crystal structure determination. Intensity data of several crystals were collected on a IPDS II diffractometer operating with MoK_α radiation at r. t. All data sets were corrected for Lorentz, polarization, and absorption effects. The programs X-RED and X-SHAPE [29] were used to optimize the crystal shape from symmetry-equivalent reflections in order to perform a numerical absorption correction. Despite of all efforts to optimize the synthesis parameters it was not possible to obtain good quality crystals for single crystal structure determinations. The crystals of Ag_5Te_2Br are characterized by a strong anisotropic morphology (see inset of Fig. 3). Very thin plates with one pronounced growing direction could be obtained after solvothermal synthesis which are sensitive to touching. Most of the crystals showed a foil-like character preventing the isolation of high-quality crystals for a structure determination. Internal R values of several crystals were in the region of 0.40 – 0.50. The low crystal quality can have several reasons, starting with the extreme anisotropic morphology, the high grade of disorder in the system, massive stacking faults, and the somewhat unusual synthesis conditions in aqueous ammonia solution as a reaction medium at low temperatures. Nevertheless, the structure could be refined [30] based on a β-Ag_5Te_2Cl structure type model taken from $Ag_5Te_2Cl_{0.5}Br_{0.5}$, as reported in ref. [28]. Due to the low data quality, we do not go into great detail concerning the crystallographic data and atomic positions. Only a theoretical powder pattern was calculated from the resulting structure model to substantiate the isotypy of Ag_5Te_2Br with the chlorine analog.

EDX analyses

A semiquantitative analysis of Ag_5Te_2Br was performed using a Leica 420i scanning electron microscope (Zeiss) fitted with an energy 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. In both cases the postulated composition was confirmed within the standard deviation of the method. Results (in atom-%) averaged from selected crystals are Ag : Te : Br = 62(2) : 27(2) : 11(2), in good accordance with the theoretical value of Ag : Te : Br = 62.5 : 25 : 12.5.

Results and Discussion

Structure chemical considerations using a topological approach

Compounds with a high grade of disorder and mobile ions are often polymorphic systems with huge unit cells and complex structures. In addition, the temperature-dependent mobility of the ions often results in order-disorder phenomena and twinning prob-

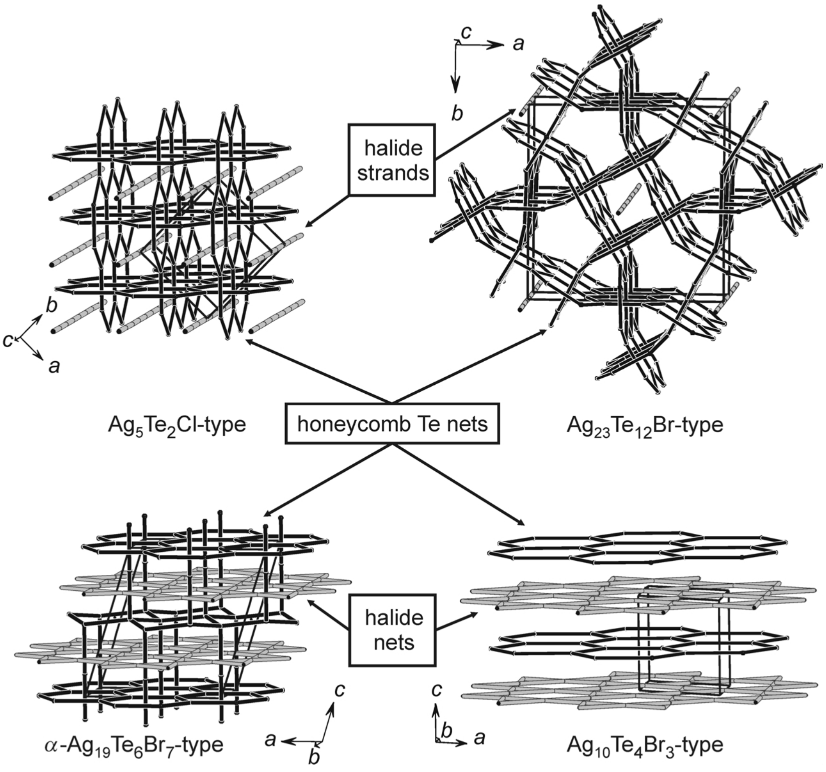


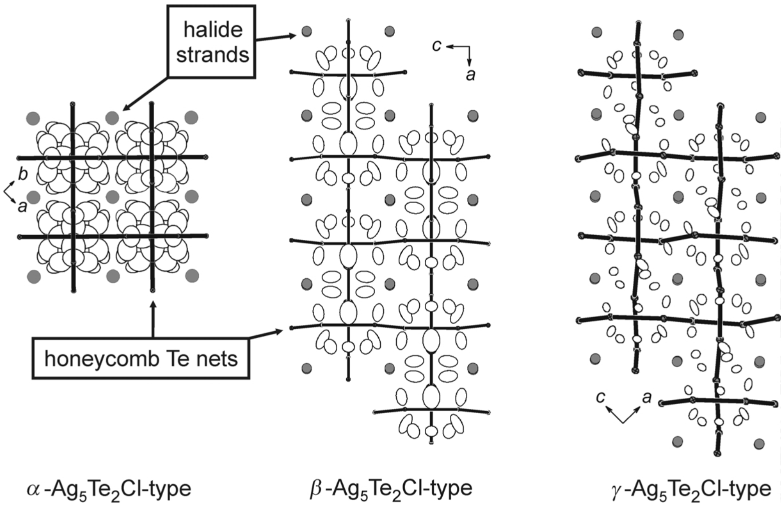
Fig. 1. Topology of the anion substructures of the silver(I) chalcogenide halide structure types Ag_5Te_2Cl [24], $Ag_{23}Te_{12}Br$ [18], $Ag_{19}Te_6Br_7$ [22] and $Ag_{10}Te_4Br_3$ [14]. The polyanion substructures of the $Ag_{23}Te_{12}Br$ and $Ag_{10}Te_4Br_3$ types are omitted. The lines of the nets and strands represent the sum of the van der Waals radii of the respective atoms. No bonding interaction is present between the different positions.

lems during the phase transitions. The structure solution and the description of the sometimes complex arrangement of ions in the mobile and rigid part of the structure can be a serious problem. Simple and well defined methods need to be developed as auxiliaries for the structure solution and refinement process. We have established such a method for coinage metal chalcogenides and polychalcogenide halides, based on a topological description of the anion substructures by simple nets and strands (examples are given in Fig. 1). The knowledge of such characteristic structure units helps to accelerate the structure solution process drastically.

It has to be stated at this point that no bonding interaction takes place between and within the strands or nets, and distances between the positions are equal to or slightly higher than the sum of the van der Waals radii of the respective atoms. The difficulty in a structure solution, especially in the case of strongly disordered systems, is the resulting low scattering power of partially occupied sites. In most of these cases the common structure solution routines can not handle such a problem properly which leads to a misinterpretation of the electron density map.

In addition to the positive effect for the structure solution process (detection or identification of well defined subunits in large unit cells), this way of structure description helps to understand the electrical properties of the coinage metal compounds in more detail. Silver tends to be delocalized parallel to the chalcogenide nets or at the intersection of the honeycomb nets which becomes clear after applying the present structure topology to the structure description. The halide substructure acts as a separator between the chalcogenide/silver units and has a certain structure-directing influence. In all of the cases included in Fig. 1, silver tends to avoid a close neighborhood to halides and shows a low tendency to interpenetrate the halide substructures.

In the literature, the anion substructure of Ag_5Q_2X compounds has been described as a 3-dimensional network of corner-shearing, strongly distorted octahedra, resembling the ReO_3 structure type [25]. After separation of the anion substructures of Ag_5Te_2Cl into the telluride- and chloride substructures, the arrangement of telluride ions was characterized as a 3^2434-net, known from the boron positions in Cr_5B_3 or the bismuth atoms in In_5Bi_3 [31]. Following this approach,



α-Ag_5Te_2Cl-type β-Ag_5Te_2Cl-type γ-Ag_5Te_2Cl-type

Fig. 2. Structure topology (structural data for the Ag_5Te_2Cl type taken from [26]) of the three existing polymorphs realized in the solid solution $Ag_5Te_2Cl_{1-x}Br_x$. It is based on the topological approach of interpenetrating honeycomb-like Te nets (black lines) and Cl strands (grey spheres). View parallel the Cl strands for each polymorph. Silver becomes disordered in the α-phase and tends to form 1-dimensional strands along the intersection of the interpenetrating Te nets.

the chloride ions form 4^4 nets. In the context of this description, the distribution of silver relative to the nets is randomly.

Based on the afore mentioned topology approach, only two different units, honeycomb nets of chalcogenide ions and strands of halides, are sufficient to describe the anion substructure of the Ag_5Q_2X compounds in the present case (see Fig. 1). Now, the distribution and silver mobility of the quasi-molten cation substructure in the high-temperature α-phase of the Ag_5Q_2X system can be understood. Silver is located at the intersections of the interpenetrating honeycomb chalcogenide nets forming areas of silver strands along one crystallographic axis (Fig. 2).

Upon reduction of the temperature, silver tends to localize at distinct positions. The well pronounced 1-dimensional silver distribution becomes more diffuse. Presently, there is a structure determination of a coinage metal (poly)chalcogenide halide in progress where lattice parameters exceeding the 50 Å regime are present.

The solid solutions $Ag_5Te_2Cl_{1-x}Br_x$ up to $x = 1$

Classical synthesis strategies like thermodynamically controlled melting reactions can be used to stabilize compounds with a substitution grade up to $x = 0.65$ in $Ag_5Te_2Cl_{1-x}Br_x$ [28]. Since we started our systematic investigations of the silver chalcogenide halide systems, we are looking for ways to prepare solid solutions to fine-tune electrical and structural properties. In most of our investigated cases (*e. g.* Ag_5Q_2X [27, 28], $Ag_{19}Q_6X_7$ [22, 23] or $Ag_{10}Q_4X_3$ [16, 17],) only one ternary phase exists, and anions can only be partially substituted. One example of a complete silver chalcogenide halide solid solution is Ag_3SX with X = Br, I [32]. In case of $Ag_{23}Te_{12}X$ with X = Cl, Br [18] the formation of a complete solid solution is probably due to the structure isotypy. Experiments to address this assumption are currently underway.

Due to the fact that thermodynamically controlled syntheses obviously did not lead to a successful preparation of a complete $Ag_5Te_2Cl_{1-x}Br_x$ solid solution, we tried to find more kinetically controlled ways to solve this problem. Schnieders and Böttcher [13] reported on the successful preparation of AgITe by a kinetically controlled solvothermal synthesis using concentrated aqueous HI. All efforts to transfer this synthetic concept, and to prepare Ag_5Te_2Br in an acidic solvent like aqueous HBr failed. Surprisingly, a solvothermal synthesis in a 12.5 % ammonia solution led to the formation of Ag_5Te_2Br, the first ternary end member of a solid solution in the Ag_5Q_2X system with Q = Te and $X \neq$ Cl. A solvothermal reaction at a neutral pH value in deionized water also resulted in the formation of Ag_5Te_2Br, but the yields were much lower than in case of higher pH values. Under the applied conditions using aqueous ammonia solution the formation of Ag_5Te_2Br took place but, in some cases, some rounded crystal edges pointed towards a certain solubility of Ag_5Te_2Br under the solvothermal conditions. Nevertheless, X-ray phase analysis proved the formation of Ag_5Te_2Br, and first single crystal structure determinations substantiate the β-Ag_5Te_2Cl structure type at r. t. (Fig. 3).

Table 1. Lattice parameters of the solid solution $Ag_5Te_2Cl_{1-x}Br_x$ with $x = 0-1$. $V_{red.}$ = volume per formula unit based on $Z = 8$.

x(Br)	a (Å)	b (Å)	c (Å)	β (deg)	$V_{red.}$ (Å^3)	Lit.
0	13.852(3)	7.663(2)	13.661(3)	90.09(1)	181.3	[28]
0.1	13.877(4)	7.671(2)	13.668(7)	90.07(3)	182.1	[28]
0.2	13.879(3)	7.678(2)	13.704(2)	90.10(1)	182.6	[28]
0.3	13.902(2)	7.686(2)	13.733(3)	90.09(2)	183.4	[28]
0.4	13.909(6)	7.687(3)	13.753(8)	90.09(5)	183.8	[28]
0.5	13.922(6)	7.691(6)	13.769(6)	90.08(6)	184.3	[28]
0.6	13.933(2)	7.704(1)	13.782(2)	90.07(2)	184.9	[28]
0.65	13.947(6)	7.709(5)	13.799(6)	90.11(3)	185.5	[28]
1.0	14.000(5)	7.702(3)	13.856(6)	90.61(4)	186.8	this work

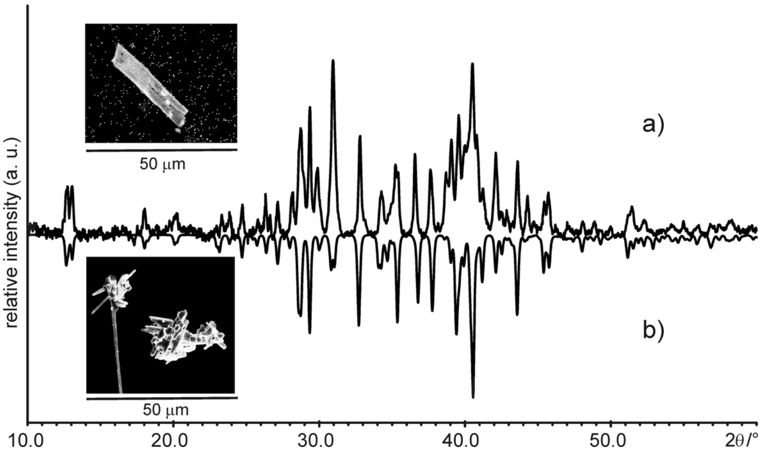


Fig. 3. a) X-Ray powder diffractogramm ($CuK\alpha_1$ radiation) of Ag_5Te_2Br at 298 K. Lattice parameters are a = 14.000(5), b = 7.702(3), c = 13.856(6) Å, β = 90.61(4)°, space group $P2_1/n$; b) calculated powder diffractogram based on single crystal data. Insets: Selected Ag_5Te_2Br crystals.

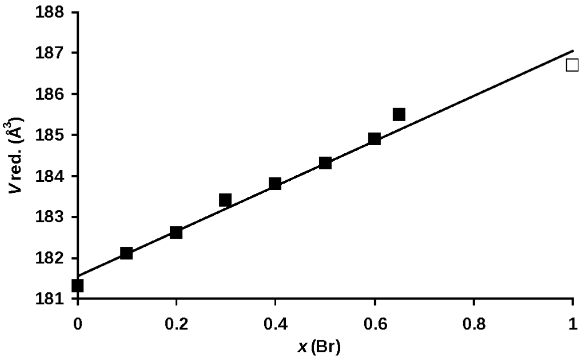


Fig. 4. Plot of V_{red}. (volume per formula unit) *vs*. x(Br) of the solid solution $Ag_5Te_2Cl_{1-x}Br_x$ substantiating the Vegard-like behavior. Data for $x = 0$ to 0.65 (black squares) are taken from the literature [28]. The open square represents the data point for Ag_5Te_2Br.

The purity of the product can be estimated to be around 90 – 95 %. Approximately 5 – 10 % of non-reacted starting material was separated from the product prior to the phase analysis. Unfortunately, the crystal quality we achieved after the solvothermal synthesis in ammonia solution is not sufficient to perform a proper structure determination at the present stage (details see Experimental Section). At the moment we are trying to optimize the synthesis conditions and the solvent to prepare better crystals for a high-quality structure determination. Nevertheless, the measured and calculated X-ray powder diffractogram, calculated from the crude structure model after a preliminary structure determination as given in Fig. 3, substantiates the β-Ag_5Te_2Cl structure type. Lattice parameters of a = 14.000(5), b = 7.702(3), c = 13.856(6) Å, β = 90.61(4)° and V = 1494.0(4) Å^3 were derived from the powder pattern. The parameters correspond well to the ones reported for other compounds of the solid solutions $Ag_5Te_2Cl_{1-x}Br_x$ (Fig. 4).

With Z = 8, according to the β-Ag_5Te_2Cl structure type (space group $P2_1/n$), a reduced volume of 186.8 Å^3 results. This volume fits to a Vegard-like behavior in the solid solution.

Conclusion

The topological description of the anion substructure using Te nets and Br strands in Ag_5Te_2Br is a useful tool to elucidate the structural pattern with a minimum of structure units. This concept was developed for (poly)chalcogenide halides and has now been applied to the present chalcogenide halide system. It has the perspective to be general and applicable to other systems with a high degree of disorder and major crystallographic problems. The structure solution can be simplified due to a fast recognition of defined structure units.

In case of the Ag_5Q_2X system, the distribution of silver within the structure can be described by a delocalization along the intersections of the honeycomb-like Te nets. Using this model, the topological approach can be used to discuss the structure-property relations in more detail.

A kinetically controlled solvothermal synthesis route using aqueous ammonia solution was successfully established to prepare Ag_5Te_2Br, the first representative of a silver(I) chalcogenide halide in the Ag_5Q_2X system with Q = Te and $X \neq$ Cl. X-Ray powder diffraction studies substantiated the Vegard-like behavior of the heavy-end member of the solid solution $Ag_5Te_2Cl_{1-x}Br_x$.

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