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# Effects of partial anion substitution on the thermoelectric properties of silver(I) chalcogenide halides in the system $Ag_5Q_2X$ with $Q$=Te, Se and S and $X$=Br and Cl

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ABSTRACT

A selection of mixed conducting silver chalcogenide halides of the general formula $Ag_5Q_2X$ with $Q$=sulfur, selenium and tellurium and $X$=chlorine and bromine has been investigated due to their thermoelectric properties. Recently, the ternary counterpart $Ag_5Te_2Cl$ showed a defined $d^{10}$–$d^{10}$ interaction in the disordered cation substructure at elevated temperatures where $Ag_5Te_2Cl$ is present in its high temperature $\alpha$-phase. A significant drop of the thermal diffusivity has been observed during the $\beta-\alpha$ phase transition reducing the values from 0.12 close to 0.08 $mm^2\,s^{-1}$. At the same transition the thermopower reacts on the increasing silver mobility and jumps towards less negative values.

Thermal conductivities, thermopower and thermal diffusivity of selected compounds with various grades of anion substitution in $Ag_5Q_2X$ were determined around the silver-order/disorder $\beta-\alpha$ phase transition. A formation of attractive interactions could be observed for selenium substituted phases while no effect was detected for bromide and sulfide samples. Depending on the grade and type of substitution the thermopower changes significantly at and after the $\beta-\alpha$ phase transition. Thermal conductivities are low reaching values around 0.2–0.3 $W\,m^{-1}\,K^{-1}$ at 299 K. Partial anion exchange can substantially tune the thermoelectric properties in $Ag_5Q_2X$ phases.



## 1. Introduction

Energy conversion and storage is one of the most popular and also a continuously growing field in chemistry and physics at the moment [1,2]. This diverse field is divided into many different subtopics, where thermoelectrics and its development and optimization are the one only one small facet [3]. In thermoelectrics, the demand for new materials and the development of new concepts are challenges to be addressed and tackled in the future [4–7]. The optimization of physical properties and structural features in terms of thermoelectric performance like the architecture of building blocks [8], spinodal decomposition [9] the reduction of thermal conductivity [10,11], the diminishment of thermal diffusivity in combination with a drop of the thermopower is a field of scientific research aiming to obtain effective and energy-efficient thermoelectric materials [12]. Recently a new conceptual approach emerged, which leads to an improvement of the thermoelectric properties of compounds by the generation or use of low-dimensional attractive interactions in solids and the resulting effective modulation of the electronic structure [13,14].

Recently we started a systematic exploration of the phase field silver–chalcogen–halogen to find new compounds and to examine the influence of mobile cations and heavy anions on the thermoelectric properties [15–22]. A new concept to improve and tune the thermoelectric performance was derived from these results [23]. Low dimensional attractive interactions can positively influence the thermopower in such a way that the thermoelectric figure of merit can be varied over several orders of magnitude in a narrow temperature window [24,14].

A detailed examination of the thermopower, the thermal diffusivity and the heat capacity of polymorphic mixed ion and electron conducting $Ag_5Te_2Cl$ [25–27] was performed to verify the thermoelectric properties [28]. Significant variations of the electric and thermoelectric properties have been observed and are originated by the huge silver mobility and the occurrence of attractive $d^{10}$–$d^{10}$ interaction in the silver ion disordered high temperature polymorph. The thermoelectric properties can be tuned by such oriented, low dimensional interactions around the silver order/disorder phase transition.

It has been shown recently that telluride ions can be partially substituted by selenide and sulfide ions in $Ag_5Te_2Cl$ [29,30] and chloride can be fully exchanged by bromide without a change in

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the realized structure type [31,32]. This feature promises a reasonable chance for property tuning of this class of compounds because of the fact that the thermopower can be varied over a wide range of temperature by this substitution. It is not the intention of this paper to invent thermoelectric materials challenging the state of the art ones but it should point out that the combination of high ion mobility and attractive interactions can be helpful to manipulate the thermopower and therefore the thermoelectric properties in a significant way.

## 2. Materials and methods

### 2.1. Synthesis

$Ag_5Te_2Cl_{1-x}Br_x$ ($x$=0.2, 0.4, 0.6), $Ag_5Te_{2-y}S_yCl$ ($y$=0.1, 0.3) and $Ag_5Te_{2-z}Se_zCl$ ($z$=0.2, 0.4, 0.6) were prepared from stoichiometric mixtures of Ag (Haereus, 99.99%), S (AlfaAesar, 99.999%), Se (Chempur, 99.999%), Te (Chempur, 99.9999%), AgCl (AlfaAesar, 99.9%) and AgBr (AlfaAesar, >99%). All starting materials were used without further purification. The mixture was sealed in evacuated silica ampoules, heated to 1173 K, held at this temperature for 3 h, and quenched in an ice bath. After homogenization by grinding an annealing procedure was applied to the samples at temperatures between 623 and 603 K. In order to achieve homogeneous samples the annealing process was repeated 2–6 times for each sample after homogenization. The total annealing time was between 14 and 45 days.

**Table 1**
EDX analyses of $Ag_5Te_2Cl_{1-x}Br_x$, $Ag_5Te_{2-y}S_yCl$ and $Ag_5Te_{2-z}Se_zCl$. The values (in atomic per cent) were averaged from five to eight individual measurements. Estimated standard deviations are indicated in parentheses.

| $x$, $y$ or $z$ | Calculated compound | Measured compound |
|---|---|---|
| $Ag_5Te_2Cl_{1-x}Br_x$ | Ag:Te:Cl:Br | Ag:Te:Cl :Br |
| 0.2 | 62.5:25:10:2.5 | 61(2):26(2):11(2):2(2) |
| 0.4 | 62.5:25:7.5:5 | 60(2):26(2):8(2):6(2) |
| 0.6 | 62.5:25:5:7.5 | 61(2):25(2):6(2):8(2) |
| $Ag_5Te_{2-y}S_yCl$ | Ag:Te:S:Cl | Ag:Te:S:Cl |
| 0.1 | 62.5:23.75:1.25:12.5 | 61(2):25(2):1(2):13(2) |
| 0.3 | 62.5:21.25:3.75:12.5 | 62(2):23(2):2(2):13(2) |
| $Ag_5Te_{2-z}Se_zCl$ | Ag:Te:Se:Cl | Ag:Te:Se:Cl |
| 0.2 | 62.5:22.5:2.5:12.5 | 63(2):21(2):3(2):13(2) |
| 0.4 | 62.5:20:5:12.5 | 59(2):21(2):6(2):14(2) |
| 0.6 | 62.5:17.5:7.5:12.5 | 61(2):18(2):8(2):13(2) |

### 2.2. EDS analysis

Semi-quantitative analyses of the samples were performed using a Leica 420*i* scanning electron microscope (Zeiss) fitted with an electron dispersive detector unit (Oxford). Silver, selenium, HgTe (Te), KBr (Br), KCl (Cl) and $FeS_2$ (S) were used as standards for calibration. A voltage of 20 kV was applied to the samples. The postulated composition for each compound was substantiated within the standard deviations of the method. Details are summarized in Table 1.

### 2.3. X-ray powder diffraction

Phase analyses were performed by X-ray powder diffraction measurements. The samples $Ag_5Te_2Cl_{1-x}Br_x$ ($x$=0.2, 0.4, 0.6), $Ag_5Te_{2-y}S_yCl$ ($y$=0.1, 0.3) and $Ag_5Te_{2-z}Se_zCl$ ($z$=0.2, 0.4, 0.6) were characterized *via* Guinier powder patterns using Cu$K\alpha_1$ radiation and $\alpha$-quartz ($a$=4.913 and $c$=5.405 Å) as an internal standard at 298(2) 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 $\beta$-$Ag_5Te_2Cl$ structure type was observed for all $Ag_5Te_2Cl_{1-x}Br_x$ ($x$=0.2, 0.4, 0.6) materials, for $Ag_5Te_{1.9}S_{0.1}Cl$ and for $Ag_5Te_{1.8}Se_{0.2}Cl$ at room temperature. The lattice parameters are summarized in Table 2. Due to the variations in the measuring temperature during the phase analytical measurements and the dynamic silver distribution with temperature a slight deviation of lattice parameters has been observed.

### 2.4. Thermal diffusivity

Powdered samples were pressed at room temperature and 15 kN to pellets of 6 mm in diameter and 2 mm thickness reaching a value of >98% of the theoretical X-ray density. A sintering of the pellet was not performed prior to the measurements. Independent measurements were performed for each pellet covering the temperature range of 300–500 K. All data are summarized in Fig. 3. The thermal diffusivity was measured by a commercial Netzsch Laser Microflash apparatus in a SiC sample holder under Ar-atmosphere. The average values of five independent shots were calculated for each data point in the temperature range of 300–500 K. The thermal diffusivity was derived from the raw data using the Proteus software package.

### 2.5. Thermopower

The pellets from the measurement of Thermal Diffusivity (6 mm diameter and 18 mm thickness) were transferred to a

**Table 2**
Lattice parameters of the solid solutions $Ag_5Te_2Cl_{1-x}Br_x$ ($x$=0.2, 0.4, 0.6), $Ag_5Te_{2-y}S_yCl$ ($y$=0.1, 0.3) and $Ag_5Te_{2-z}Se_zCl$ ($z$=0.2, 0.4, 0.6) at 298 K. $V_{red}$ represents the volume per formula unit defined as $V_{red}=V/Z$. In case of the $\beta$-$Ag_5Te_2Cl$ structure type (space group $P2_1/n$) the number of formula units is $Z$=8 compared with $Z$=4 for the $\alpha$-$Ag_5Te_2Cl$ structure type (space group $I4/mcm$).

| $x$, $y$ or $z$ | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\beta$ (deg.) | $V_{red}$/Å$^3$ | structure type |
|---|---|---|---|---|---|---|
| $Ag_5Te_2Cl_{1-x}Br_x$ | | | | | | |
| 0.2 | 13.870(2) | 7.6785(6) | 13.692(2) | 90.127(12) | 182.3(1) | $\beta$-$Ag_5Te_2Cl$ |
| 0.4 | 13.903(3) | 7.694(2) | 13.763(3) | 90.090(15) | 184.1(1) | $\beta$-$Ag_5Te_2Cl$ |
| 0.6 | 13.934(4) | 7.702(3) | 13.788(4) | 90.10(4) | 185.0(1) | $\beta$-$Ag_5Te_2Cl$ |
| $Ag_5Te_{2-y}S_yCl$ | | | | | | |
| 0.1 | 13.748(9) | 7.594(4) | 13.570(8) | 91.14(3) | 177.1(3) | $\beta$-$Ag_5Te_2Cl$ |
| 0.3 | 9.6693(22) | | 7.7383(25) | | 180.9(1) | $\alpha$-$Ag_5Te_2Cl$ |
| $Ag_5Te_{2-z}Se_zCl$ | | | | | | |
| 0.2 | 13.809(5) | 7.629(4) | 13.588(6) | 90.893(24) | 182.3(1) | $\beta$-$Ag_5Te_2Cl$ |
| 0.4 | 9.703(3) | | 7.760(3) | | 182.7(2) | $\alpha$-$Ag_5Te_2Cl$ |
| 0.6 | 9.671(3) | | 7.715(3) | | 180.4.(2) | $\alpha$-$Ag_5Te_2Cl$ |

homemade thermopower machine and data were determined in the temperature range of 300–500 K. The thermopower measurements were carried out using a dynamic method (constant heating during the measurement, detection of the cell voltage versus time; accuracy of the thermopower within $\pm 1\%$), suitable for high-resistivity samples as well as metals featuring a thermopower lower than 10 $\mu V\,K^{-1}$. Details of the cell and measurement methods are described elsewhere [33].

### 2.6. Heat capacity

Finally ground samples were pressed at room temperature to a pellet (approx. 100 mg) and glued to the platform of a recalibrated heat capacity puck of a Quantum design physical property measurement system (PPMS). A density of 96% of the theoretical density was achieved for this pellet. $C_p$ measurements have been performed using the $C_p$ option of the PPMS in the temperature range from 150 to 390 K.

### 2.7. Differential scanning caloriometry (DSC)

DSC measurements were performed with a Netzsch differential scanning calorimeter DSC 204 at heating and cooling rates of 10 K $min^{-1}$ in the temperature range between 150 and 625 K. Mercury, indium, tin, bismuth, zinc and cesium chloride were used for temperature calibration. All samples were measured under a constant nitrogen flow of 50 ml $min^{-1}$ in sealed aluminum crucibles.

## 3. Results and discussion

$Ag_5Te_2Cl$, the ternary representative of the silver(I) chalcogenide halide series is a mixed conducting trimorphic system with one silver order/disorder phase transition ($\beta-\alpha$) at elevated temperature. A second transition occurs at lower temperatures, where the symmetry of the structure is further reduced but no substantial additional changes in the ion dynamics can be observed. The two reversible phase transitions have been observed at 240.9(2) and 334.2(5) K [27]. In Fig. 1a representative structure projection is given for each polymorph.

A recent study on the thermoelectric properties of $Ag_5Te_2Cl$ [28] proved the existence of attractive interactions in the cation substructure after the $\beta-\alpha$ phase transition in the high temperature α-phase which resulted in a pronounced modulation of the thermopower, thermal diffusivity and the thermoelectric figure of merit. Around the $\beta$-$\alpha$ order/disorder phase transition, the compound shows a significant drop of the thermopower from 397 $\mu VK^{-1}$ at 316 K to 105 $\mu VK^{-1}$ at 333.9 K. After a plateau regime with almost constant thermopower values the Seebeck coefficient starts rising again to a maximal value of 573 $\mu VK^{-1}$ at 441 K [28]. The absolute thermopower of $Ag_5Te_2Cl$ stays positive over the whole temperature range under investigation indicating a *p*-type (hole) conduction. The compound is characterized by low values of the thermal diffusivity in the order of 0.12 $mm^2\,s^{-1}$ for the different polymorphic forms comparable for instance with room temperature values of isolators [35,36]. At the $\beta$–$\alpha$ phase transition an additional and significant reduction of the thermal diffusivity to a very low value of 0.05 $mm^2\,s^{-1}$ has been observed which is equilibrating right after the transition to the values observed before. An attractive interaction of silver ions occurs at elevated temperatures in the highly silver-disordered α-phase which has been indicated and analyzed by single crystal X-ray structure determinations and $C_p$ measurements [28]. Our intention in this paper is to examine thermoelectric properties of the quaternary phases in order to identify additional compounds,

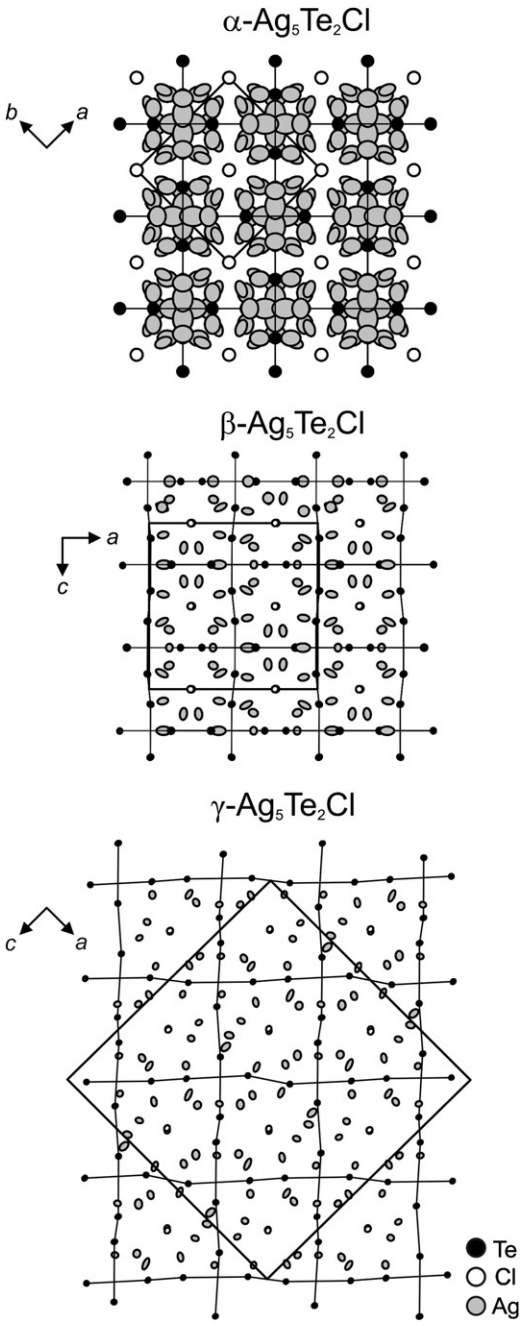


**Fig. 1.** Structure sections of α-, $\beta$- and $\gamma$-$Ag_5Te_2Cl$ (structure data are taken from [27]). Silver is quasi-molten in the high temperature α-phase. Displacement parameters are shown at 90% level.

where modulation of the thermopower and thermal diffusivity takes place. We would like to verify if a simple measurement of those values is sufficient to identify such phases, avoiding time consuming temperature dependent single crystal structure determinations followed by joint probability density function (jpdf) analysis of the silver distribution.

Based on the promising and surprising results of $Ag_5Te_2Cl$ the question arose how substitution in the anion substructure, representing the non-involved substructure according the interactions, can affect the physical properties in this sense. Partial exchange of the anions in this compound is possible under retention of the general structural features [29,30]. Samples of $Ag_5Te_2Cl_{1-x}Br_x$ ($x$=0.2, 0.4, 0.6), $Ag_5Te_{2-y}S_yCl$ ($y$=0.1, 0.3) and $Ag_5Te_{2-z}Se_zCl$ ($z$=0.2, 0.4, 0.6) were prepared by the literature

**Table 3**
Onset values of the DSC effects of $Ag_5Te_2Cl_{1-x}Br_x$ ($x$=0.2, 0.4, 0.6), $Ag_5Te_{2-y}S_yCl$ ($y$=0.1, 0.3) and $Ag_5Te_{2-z}Se_zCl$ ($z$=0.2, 0.4, 0.6). Each effect represents the order/disorder phase transition from the $\beta$- to the high temperature $\alpha$-phase in each sample.

| $x$ | Onset temperature (K) | Effect | Literature data |
|---|---|---|---|
| $Ag_5Te_2Cl_{1-x}Br_x$ | | | |
| 0.2 | 334(1) | Endothermic | 336.2(2) [30] |
| 0.4 | 337(1) | Endothermic | 340.2(2) [30] |
| 0.6 | 342(1) | Endothermic | 343.8(2) [30] |
| $Ag_5Te_{2-y}S_yCl$ | | | |
| 0.1 | 269(1) | Endothermic | 306.9(2) [30] |
| 0.3 | – | No effect | –[30] |
| $Ag_5Te_{2-z}Se_zCl$ | | | |
| 0.2 | 303(1) | Endothermic | 306.8(2) [29] |
| 0.4 | 273(1) | Endothermic | 277.1(2) [29] |
| 0.6 | 235(1) | Endothermic | 253.5(2) [29] |

procedures [29,30]. The characterization of the products was checked by X-ray powder phase analysis, EDX-measurements and differential scanning calorimetry-measurements. All samples were phase-pure according to the errors of the applied methods. Details of the X-ray phase analyses are given in Table 2 and thermoanalytical results in Table 3.

The degree of substitution in the $Ag_5Q_2X$ phases affects the temperature of the phase transitions, where the trend of the temperature shifts is consistent with previous studies in this class of materials [29–33]. In the case of the bromide substituted phases the literature data fit match quite well to the measured ones while a slightly larger deviation can be observed for the chalcogenide substituted phases. Such a variability or undercooling can occur in the case of fast ion conducting compounds because the transition is closely related to the crystallinity, the history (preparation, treatment and annealing) and the exact composition of the respective samples. In Fig. 2 the DSC curves of each sample under discussion is shown covering the temperature range of 230–370 K.

Each endothermic peak in each section represents the $\beta-\alpha$ phase transition. In the case of $Ag_5Te_{1.7}S_{0.3}Cl$ the transition is suppressed completely in the applied temperature range and no thermal peak has been observed. In addition we have checked this behavior by temperature dependent X-ray powder diffraction at various temperatures and could not find any hint for an ordering of silver. $Ag_5Te_{1.7}S_{0.3}Cl$ is present in its $\alpha$-phase during all experiments and applied temperature ranges. We have marked the onset temperature of the $\beta-\alpha$ phase transition for each compound of the different solid solutions in Figs. 3 (thermal diffusivity) and 4 (thermopower) in order to substantiate the relation between the structural transition and the respective peak present each case.

The evolution of thermopower for the $Ag_5Q_2X$ phases is dependent on the type and grade of substitution and n-type conduction has been identified for all quaternary compounds. This finding is in contrast to the ternary counterpart where p-type conduction is realized. The type of conduction is closely related to the exact silver content of the compounds and a very small excess or deficit (in the order of $10^{-6}$ in the stoichiometry coefficients) of silver can change the mechanism from p- to n-type conduction.

Three types of curves must be differentiated according the variations of the thermopower with temperature.

*Type* 1: A linear increase of the thermopower can be found for $Ag_5Te_{1.7}S_{0.3}Cl$ and $Ag_5Te_{1.4}Se_{0.6}Cl$. In these cases the $\beta-\alpha$ phase transition is completely suppressed or lies out of the applied temperature range. These compounds represent the chalcogenide phases with high grades of substitution.

*Type* 2: All bromide containing samples are characterized by a pronounced increase at the $\beta-\alpha$ phase transition. The thermopower is reduced from values larger than $-1000\ \mu V\ K^{-1}$ before to approx. $-750\ \mu V\ K^{-1}$ directly after the transition.

*Type* 3: In the case of the selenium containing phases with a small and a moderate grade of substitution ($Ag_5Te_{1.8}Se_{0.2}Cl$ and $Ag_5Te_{1.6}Se_{0.4}Cl$) a small bump is present at the low end of the applied temperature range around 300 K, where the thermopower shows a slight deviation from linearity. Whether $Ag_5Te_{1.7}S_{0.3}Cl$ is also a representative of this group cannot be decided due to the fact that the order/disorder phase transition at 269 K lies slightly below the lower end of the temperature range addressed by the thermopower measurements.

Recently, we have shown for $Ag_{10}Te_4Br_3$ [14] and $Ag_5Te_2Cl$ [28] that the formation of attractive interaction has a significant influence on the electronic structure and the density of states close to the Fermi level. Similar features have been identified in the tellurium substructure of $\{[Ga(en)_3]_2(Ge_2Te_{15})\}_n$ [34] as well as the in substructure of $In_4Se_{3-\delta}$ [13]. Obviously, the strong modulation of the electronic structure, while undergoing the order/disorder transition, has a definite influence on the absolute value of the Seebeck coefficient. It is worth to mention that the value of thermopower of all the different members (i.e. all compounds in their high temperature $\alpha$-phase) of the solid solutions lie in the same range at about $-750\ \mu V\ K^{-1}$ right after the transition and raises linearly in most of the cases (except the *Type* 3 members). It seems to be independent of the nature of substitution. The slightly higher thermopower of $Ag_5Te_{1.4}Se_{0.6}Cl$ compared to the other phases is due to the fact that the distance (in terms of temperature) to the phase transition is larger for this sample than for all the others. A completely different situation is present for $Ag_5Te_{1.7}S_{0.3}Cl$, where the $\beta-\alpha$ phase transition is suppressed. The thermopower of this compound is rather comparable to the majority of phases. More details can be found later on during the discussion of the $C_p$ measurements.

The *Type* 3 compounds are showing a modulation of the thermopower right after the structural phase transition pointing towards an occurrence of attractive interactions in these cases. We have performed a detailed temperature dependent structure analysis for $Ag_5Te_{1.8}Se_{0.2}Cl$ and we detected attractive $d^{10}$–$d^{10}$ interactions in the same temperature range. Details of these investigations will be presented elsewhere.

Obviously, a small modification of the anion substructure by substitution of small portions of tellurium by selenium does not affect the formation of Ag–Ag bonds in the disordered phase while a higher grade of substitution results in the opposite. The silver mobility increases significantly at higher grades of substitution which can directly be related to the shift of the order/disorder ($\beta-\alpha$) phase transition towards lower temperatures. In the case of $Ag_5Te_{1.7}S_{0.3}Cl$ the shift of the DSC peak ($\beta-\alpha$ phase transition) is reduced to 269 K. Whether this reduction is sufficient to suppress the $d^{10}$–$d^{10}$ interaction cannot be judged properly. A slight anomaly or upwards trend of the thermopower close to 300 K cannot be more than a first and weak hint for such a process.

The $\beta-\alpha$ phase transition has also a significant influence on the thermal diffusivity of the $Ag_5Q_2X$ phases. In the case of $Ag_5Te_2Cl$ thermal diffusivities of 0.11–0.12 $mm^2\ s^{-1}$, where observed over a temperature range of 298–473 K [28] which are comparable with room temperature values of isolators [35,36]. At the $\beta$–$\alpha$ phase transition a significant reduction of the thermal diffusivity occurred dropping down to a very low value of 0.05 $mm^2\ s^{-1}$ at 329 K. This finding substantiated the effective phonon scattering due to the huge mobility of the silver cations [37] and the rearrangement of the anions during the transition.

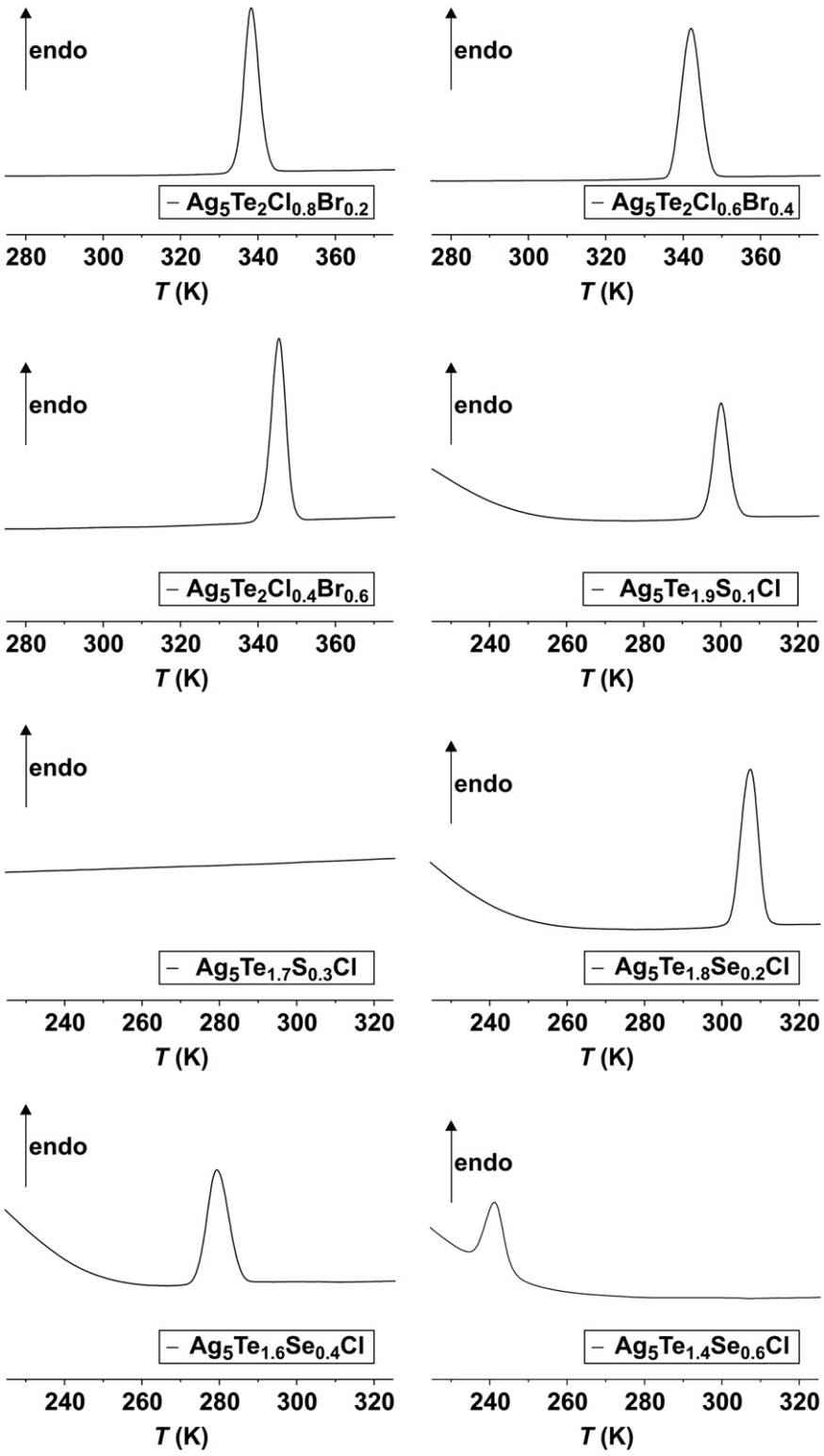


**Fig. 2.** DSC curves of selected $Ag_5Q_2X$ phases representing the $\beta-\alpha$ phase transitions. The exact compositions are given in the respective figure sections. Data are measured in the temperature range of 225–375 K and only sections with thermal effects are shown for each sample. The $\beta-\alpha$ phase transition of $Ag_5Te_2Cl$ (not shown) is located at 334 K [27]. Thermal effects are separating the $\beta$-and $\alpha$-phase in all cases.

The same behavior is present in the solid solutions. In each case, where the $\beta-\alpha$ phase transition lies in the range of the thermal diffusion experiment a significant drop of the diffusivity was observed.

The heat capacity of the compounds $Ag_5Te_2Cl_{1.4}Br_{0.6}$, $Ag_5Te_{1.7}S_{0.3}Cl$ and $Ag_5Te_{1.4}Se_{0.6}Cl$ was measured (Fig. 5). In the heat capacity measurement of $Ag_5Te_2Cl_{0.4}Br_{0.6}$ three effects were observed: one huge effect at 340 K, is followed by two small effects at 362.3 and 366.5 K. The huge λ-shaped effect in the $C_p$ curve comes along with the second phase transition at 341.6 K featuring a heat capacity maximum of 299.3 J $kg^{-1}$ $K^{-1}$. The small effects at 362.3 K and at 366.5 K with $C_p$ maxima of 192.4 and 190.4 J $kg^{-1}$ $K^{-1}$ cannot be assigned to a structural phase transitions known so far.

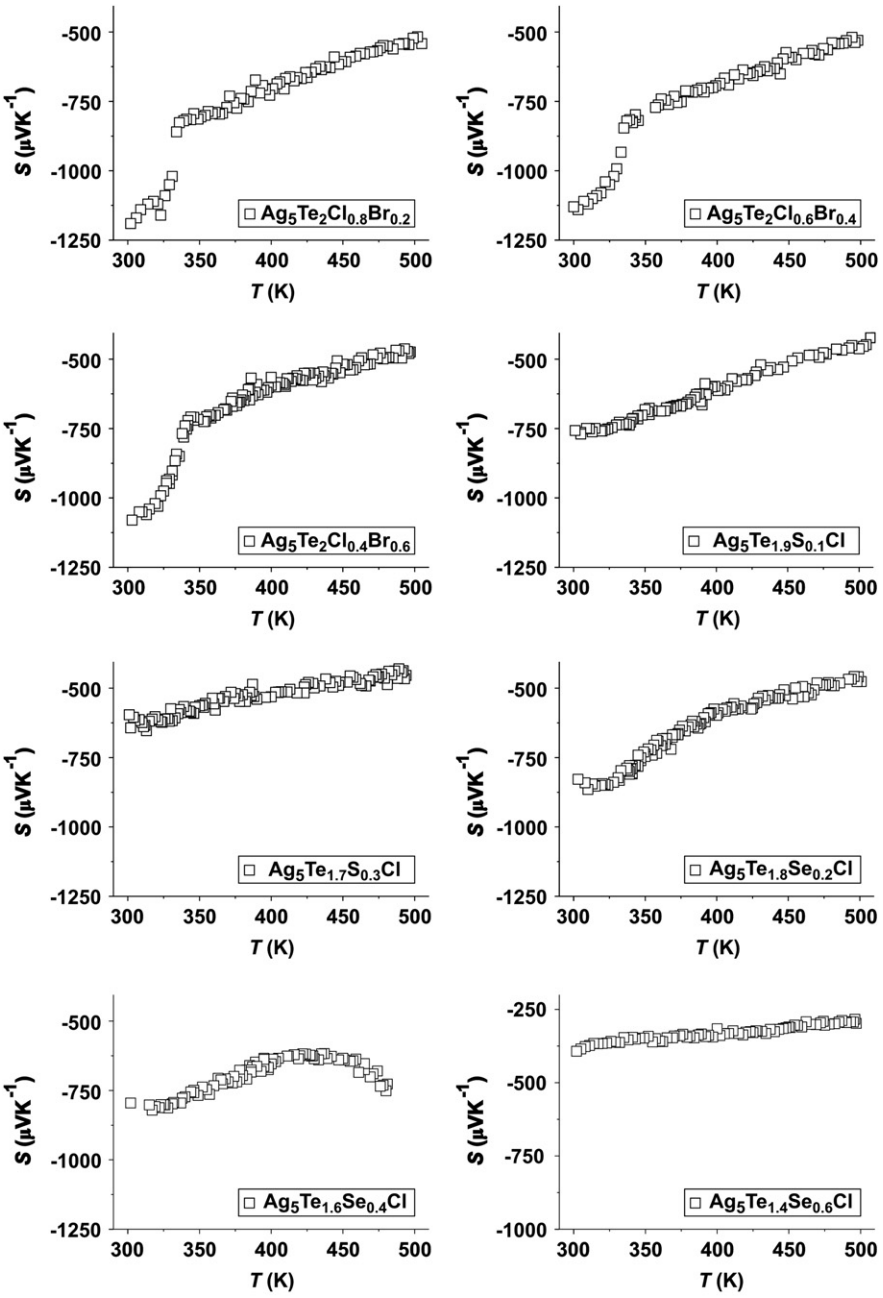


**Fig. 3.** Thermopower $S$ ($\mu$V K$^{-1}$) of selected $Ag_5Q_2X$ phases. The exact compositions are given in the respective figure sections.

The same general features are present in the $C_p$ measurement of $Ag_5Te_{1.4}Se_{0.6}Cl$. Around the $\beta$–$\alpha$-phase transition the heat capacity measurement of $Ag_5Te_{1.4}Se_{0.6}Cl$ shows a maximum at 238.0 K ($C_p$=354.6 J kg$^{-1}$ K$^{-1}$) in good accordance to the respective DSC peak at 235(1) K. Additionally, an effect at 381.6 K with $C_p$ of 197.6 J kg$^{-1}$ K$^{-1}$ is present, which cannot be explained by any known phase transition. It seems to be highly probable that those effects are first indicators of an emerging attractive interaction somewhere in the sample as already proved for $d^{10}$–$d^{10}$ interactions in the ternary counterpart. A detailed examination of the structural features and especially the behavior within the silver substructure is currently underway. Since this point is not totally clarified by an examination of the silver distribution or by the use of more local probes like solid state NMR spectroscopy this aspect remains speculative.

The result of the heat capacity measurement of $Ag_5Te_{1.7}S_{0.3}Cl$ exhibits only a broad effect at 229.5 K with a $C_p$ maximum of 292.0 J kg$^{-1}$ K$^{-1}$. Neither any observable feature in the respective DSC experiment (see Fig. 2, third row on the left) which could be assigned to a structural transition nor any crystallographic hints were found for the existence of a $\beta$-$\alpha$-phase transition so far. In the case of the sulfur substitution the anion substructure is disturbed drastically and the obviously present large difference in the size and the chemical properties of sulfur and tellurium seems to substantially change silver dynamics in the present case. The shape of the effect and the lack of any DSC peaks points towards a different dynamic response of silver in the sulfur containing samples. A smaller grade of chalcogenide substitution has a much stronger influence on the silver ion properties resulting in an increased mobility (lower phase transition temperatures). We therefore interpret the broad $C_p$ effect as a change in the silver distribution and mobility from a dynamic to a static one without a detectable structural phase transition.

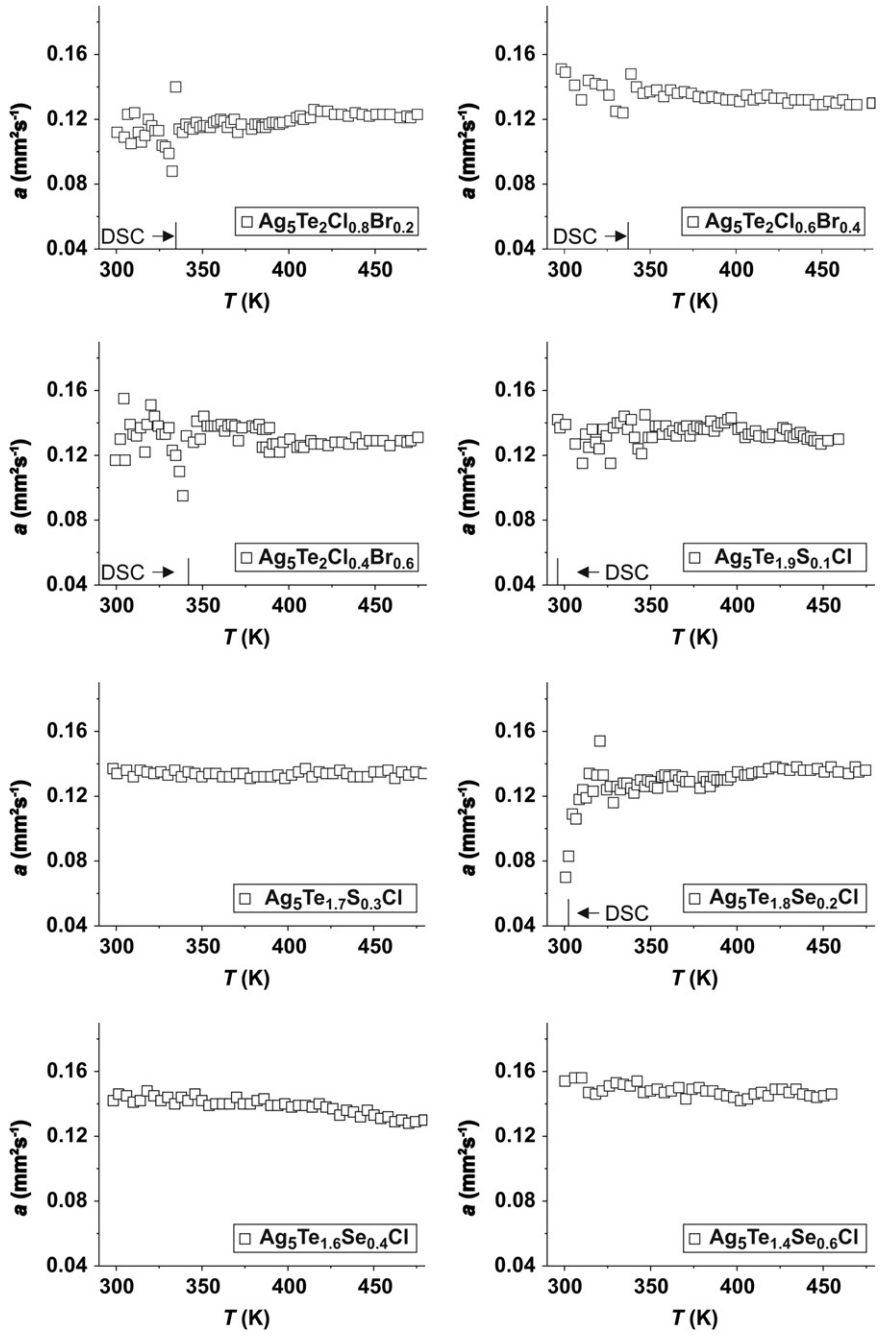


**Fig. 4.** Thermal diffusivity a ($mm^2\ s^{-1}$) of selected $Ag_5Q_2X$ phases. The exact compositions are given in the respective figure sections. Data are plotted in the range of 300–475 K. The temperature of the $\beta-\alpha$ phase transition of each representative, as shown in Fig. 2, is denoted by a vertical line.

For $Ag_5Te_2Cl_{0.4}Br_{0.6}$, $Ag_5Te_{1.7}S_{0.3}Cl$ and $Ag_5Te_{1.4}Se_{0.6}Cl$ the thermal conductivities $\kappa_{tot}$ at 299 K are calculated according to Eq. 1 (with $a$=thermal diffusivity, $C_p$=heat capacity and $\rho$=density).

$$\kappa_{tot} = aC_p\rho \quad (1)$$

The values are 0.18 $W\,m^{-1}\,K^{-1}$, 0.25 $W\,m^{-1}\,K^{-1}$, and 0.29 $W\,m^{-1}\,K^{-1}$, respectively. These low values are comparable to the ternary phase ($Ag_5Te_2Cl$ 0.19 at 329 K [28]. All quaternary phases overcome the thermal conductivities of isostructural $Tl_{10-x}La_xTe_6$ [38] or $Tl_9BiTe_6$ [39] featuring 0.5 $W\,m^{-1}\,K^{-1}$ or 0.4 $W\,m^{-1}\,K^{-1}$ at 300 K, respectively. The reduction is likely due to the contribution of the mobile silver ions to effective phonon scattering processes in the $Ag_5Q_2X$ phases compared to the immobile ions in the latter examples. Elements like phosphorus and sulfur are showing comparable thermal conductivities in this temperature region [40].

## 4. Conclusion

The substituted phases $Ag_5Te_2Cl_{1-x}Br_x$ ($x$=0.2, 0.4, 0.6), $Ag_5Te_{2-y}S_yCl$ ($y$=0.1, 0.3) and $Ag_5Te_{2-z}Se_zCl$ ($z$=0.2, 0.4, 0.6) exhibit similar thermoelectric characteristics, which were already found in the ternary connection. A jump of the Seebeck coefficient connected with the $\beta-\alpha$ phase transition was observed in the bromine-substituted phases. Two deviations from linearity in the thermopower of $Ag_5Te_{1.8}Se_{0.2}Cl$ and $Ag_5Te_{1.6}Se_{0.4}Cl$ point towards the occurrence of attractive interactions in the cation

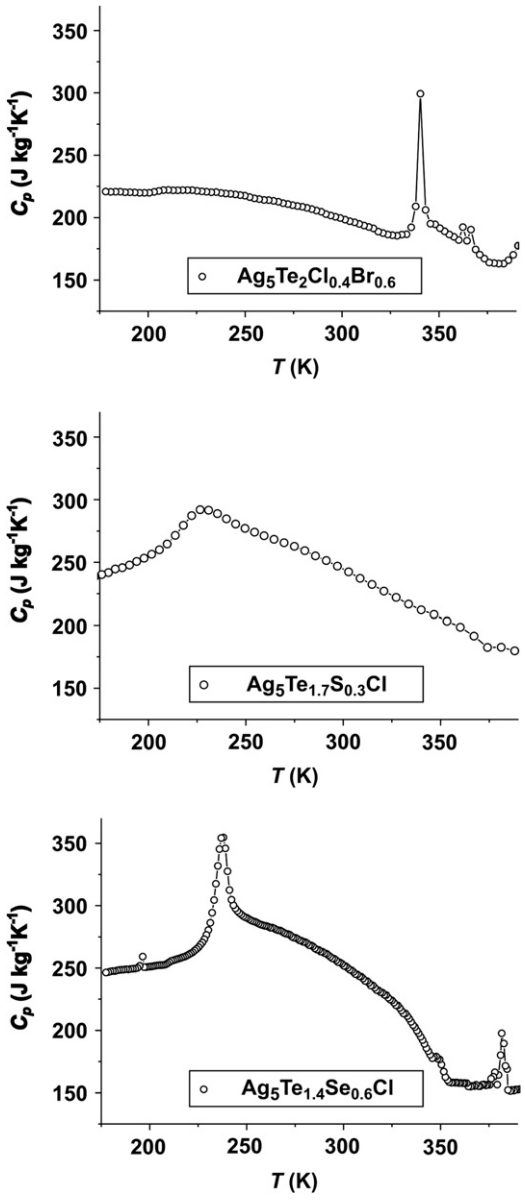


**Fig. 5.** Heat capacity $C_p$ (J kg$^{-1}$ K$^{-1}$) of selected $Ag_5Q_2X$ phases. The exact compositions are given in the respective figure sections. Strong effects are correlated with the $\beta-\alpha$ phase transitions of $Ag_5Te_2Cl_{0.4}Br_{0.6}$ and $Ag_5Te_{1.4}Se_{0.6}Cl$. Small effects are similar to the one in $Ag_5Te_2Cl$ where attractive $d^{10}$–$d^{10}$ interactions occurred.

substructure as already observed for the ternary counterpart $Ag_5Te_2Cl$. The Seebeck coefficients of $Ag_5Te_{1.7}S_{0.3}Cl$ and $Ag_5Te_{1.4}Se_{0.6}Cl$ show a linear rise with temperature between 300 and 500 K, which is consistent with the thermopower evolution in the ternary phase far away from the phase transition. The absolute thermopower stays negative over the whole temperature range of investigation indicating an n-type behavior.

The thermal diffusivity of the substituted phases of $Ag_5Te_2Cl$ lies, in analogy to the ternary compound, in the range of classical isolators at the low end of the thermal diffusivity range. A significant drop has been observed at the point of the $\beta-\alpha$ phase transition indicating the huge mobility of the whole structure at this point. In heat capacity measurements of $Ag_5Te_2Cl_{1.4}Br_{0.6}$, $Ag_5Te_{1.7}S_{0.3}Cl$ and $Ag_5Te_{1.4}Se_{0.6}Cl$ new effects have been identified which could not be assigned to structural phase transitions with defined thermal effects in thermal analyses or X-ray phase analyses. These new effects are probably first indicators of attractive interactions in these compounds. The thermoelectric properties of $Ag_5Q_2X$ phases can be tuned by partial anion substitution in a rather simple way. It has to be stated at this point that the overall resistivity of the title compounds is rather high limiting the potential use of this class of compounds as thermoelectric devices drastically. Nevertheless the general concept of property tuning by simple chemical modifications in combination with low dimensional interactions is attractive and should be considered for the improvement of other thermoelectric materials.

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