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## Highly dynamic chalcogen chains in silver(I) (poly)chalcogenide halides: A new concept for thermoelectrics?

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Coinage metal(I) polychalcogenide halides are representing a new class of materials featuring high ion dynamics of different substructures capable to an effective phonon scattering process in the solid state. The interplay of mobile coinage metal ions like  $\text{Ag}^+$  or  $\text{Cu}^+$  on the one hand and the temperature driven redox reaction of a linear partially covalent-bonded Te chain on the other hand is responsible for tremendous variations in the electronic structure of such materials. A huge drop in the Seebeck coefficient within a very small temperature range and a extremely low thermal conductivity are the key properties of this substance class. Two different compounds with the general formula  $(\text{CM})_{10}\text{Q}_4\text{X}_3$  and  $(\text{CM})_{23}\text{Q}_{12}\text{X}$  (CM = coinage metal Cu and Ag, Q = chalcogen, X = halogen) exist and recent experiments point towards the existence of former unknown copper(I) (poly)chalcogenide halides and two more silver(I) (poly)chalcogenide halides in this field. A linear Te chain of comparable fashion is present in a number of different compounds like some alkaline earth polychalcogenides  $\text{M}_5\text{Te}_3$ , the mineral stuetzite  $\text{Ag}_{4.5}\text{Te}_3$  or closely in the closely related compounds  $\text{Ag}_{11}\text{AsTe}_7$  or  $\text{Ag}_{12}\text{Te}_6\text{S}$ . In most of the cases the thermoelectric potential is not verified. A topologic approach for the description of the structural features has been developed to understand the electronic properties of these complex materials in more detail.

**Key words:** Redox switches, chalcogen chains, ion dynamics, polychalcogenide halides, structure topology, effective phonon scattering

## Introduction

1  
2 A process which is capable to generate an effective phonon scattering in solids is a suitable to  
3 improve materials for thermoelectric devices in energy conversion applications. Recently,  
4 *Sales*<sup>1</sup> wrote in a nice manuscript reviewing the progress in this field. He stated: ‘It will  
5 probably be necessary to reduce  $\kappa$  and to improve the power factor in a *bulk material* in  
6 order to achieve a material at a reasonable cost that is efficient enough for many commercial  
7 applications’ and he pointed out that new ideas and concepts need to be found and developed  
8 to reach this goal. Even more critical statements are discussed in the literature for the future of  
9 thermoelectrics in general,<sup>2</sup> e.g. that all efforts and materials featuring ZT values  $> 2$  like  
10 quantum dots<sup>3</sup> and superlattices<sup>4-6</sup> are miles away from a production on commercial scales. It  
11 is also highly questionable how sintering of nanostructures materials can be avoided at high  
12 temperature gradients or how production costs can be reduced to make large scaled and nano-  
13 structured materials suitable for large scale applications. Herein we report on the structural  
14 and thermoelectric features of a new class of highly effective phonon scattering materials  
15 which show a high dynamic of different building blocks in the solid state. A partially  
16 covalent-bonded polyanion substructure seems to play a major role in this scattering process.  
17 The important covalent **and** ionic character of this group is denoted by a parentheses in the  
18 phrase (poly)anion hereof. Probably, the introduction of highly dynamic and well defined  
19 (poly)chalcogenide chains in the case of the coinage metal (poly)chalcogenide halides is a  
20 promising feature to lower the heat transport, determined by the crystalline lattice vibrations,  
21 as close as possible to zero. All results reported here are based on non-optimized bulk  
22 material without nano-structuring which is probably a reasonable chance to keep thermo-  
23 electrics in business for efficient energy conversion processes and applications.  
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## Experimental

45 All coinage metal (poly)chalcogenide halides were prepared by common solid state high  
46 temperature synthesis of stoichiometric mixtures of the starting materials (CM)*X*, *Q* and CM.  
47 The starting materials were fired at temperatures between 650 and 750 K in evacuated silica  
48 ampoules, quenched by removing the ampoules from the oven on air or by adding in water  
49 and subsequent homogenization and annealing processes for several days at temperatures  
50 below the respective peritectic decomposition temperatures. The phase purity of the resulting  
51 compounds were checked by X-ray powder phase analysis and the homogenization and  
52 annealing process was repeated until a phase pure sample was achieved. More detailed  
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1 information concerning the preparation conditions can be found in the literature (see citations  
2 in the results and discussion section).

3 The thermal diffusivity of  $\text{Ag}_{20}\text{Te}_{10}\text{BrI}$  was measured in the temperature range of 223 to 424  
4 K using a Netzsch Micro flash LFA 457. A pellet of 10 mm diameter and 1.32 mm thickness  
5 was examined under He gas flow of 100 mL/min. The pellet was prepared from a powdered  
6 sample of  $\text{Ag}_{20}\text{Te}_{10}\text{BrI}$  by cold pressing (pressure  $\sim 6000 \text{ kg cm}^{-2}$ ) achieving 98 % of the X-  
7 ray density. Five independent measurements were performed and averaged at each  
8 temperature. A MCT detector (HgCdTe) was used for detection purpose and the software  
9 packet Proteus (Netzsch, Germany) was applied to analyze the resulting raw data.  
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## 19 Results and discussion

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21 In order to understand the electronic properties of the coinage metal (poly)chalcogenide  
22 halides a deep and full understanding of the structural features is mandatory. Recently the  
23 exploration of new phases and members of coinage metal chalcogenide halides like  $\text{Ag}_5\text{Q}_2\text{X}^{7-}$   
24  $^{12}$ ,  $\text{Ag}_{19}\text{Q}_6\text{X}_7^{13,14}$  and the new class of coinage metal (poly)chalcogenide halides like  
25  $\text{Ag}_{10}\text{Q}_4\text{X}_3$  with  $\text{Q} = \text{S, Se or Te}$  and  $\text{X} = \text{Cl, Br or I}^{15-18}$  or  $\text{Ag}_{23}\text{Te}_{12}\text{X}$  with  $\text{X} = \text{Cl, Br}^{19}$   
26 demanded a new way of structure description due to its complexity and the high grade of  
27 dynamic disorder within the cation substructures. Defining and following a simple topologic  
28 principle the cation, anion and polyanion substructures of the coinage metal  
29 (poly)chalcogenide halides should be described separately. Isolated anions should be  
30 connected at distances around the sum of the van der Waals radii to form chains, honeycomb  
31  $6^3$  or Kagomé-like 3.6.3.6 nets, while the cations act as the coordinating species to separate  
32 the resulting units at usual bond lengths. The polyanion substructure can now be illustrated  
33 separately forming chains build up by isolated  $\text{Q}^{2-}$  ions and/or  $[\text{Q}_2]^{2-}$  dumbbells. Different  
34 linear units like isolated  $[\text{Q}_2]^{2-}$  dumbbell chains or slightly more complex  $-\text{Q}-[\text{Q}_2]-\text{Q}-$  strands  
35 result. Figure 1 illustrates the structural features of the (poly)anion substructures of  
36  $\text{Ag}_{10}\text{Te}_4\text{Br}_3^{16}$ ,  $\text{Ag}_{4.53}\text{Te}_3$  (stuetzite) $^{20}$  and  $\text{Ag}_{12}\text{Te}_6\text{S}^{21}$  applying this principle. The close  
37 structural relation according this topological approach becomes obvious and comparable  
38 building units can identified at once. In the present case, (poly)anionic  $\text{Q}$  chains, coordinated  
39 by the coinage metal in different fashions and its accommodation within the non-covalent  
40 bonded anion substructure, can be identified at once. The cations (not shown in Figure 1) are  
41 highly disordered and coordinate the different anion substructures in a comparable way in all  
42 cases. Such a topological approach is useful in three different ways:  
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1. ... as a useful tool for the structure solution of this compounds

Twinning caused by polymorphism, huge translation periods with several hundred atoms per unit cell, in combination with low scattering power at higher diffraction angles, are common features of these classes of compounds. These aspects neglect the use of direct, Patterson and charge flipping methods in some cases. If so, the electron density maps could not be interpreted properly after 'solving' the structures by the commonly used structure solution routines from single crystal data and even more problematic from powder data. Due to the reduced scattering power of silver atoms which are partially occupying the sites within the unit cell, a differentiation between silver and all sites covered by atoms having a lower scattering power than silver were not possible. Even the charge flipping approach<sup>22</sup> suitable to solve structures from powder<sup>23,24</sup> or single crystal data, implemented in modern computer programs like JANA 2006<sup>25</sup> (superflip), do not lead to an interpretable starting model.

2. ... as a formalism to understand some of the physical properties of this compounds

The different mobile coinage metals tend to be distributed in an anisotropic way in the coinage metal chalcogenides and (poly)chalcogenide halides under discussion. Using the afore mentioned formalism of a 'quasi-layered' arrangement of building blocks the anisotropy of the cations and the anisotropic ion mobility can be explained properly. In the case of  $\text{Ag}_5\text{Q}_2\text{X}$  and  $\text{Ag}_{23}\text{Q}_{12}\text{X}$  a non-corrugated or corrugated arrangement of interpenetrating honeycomb  $6^3\text{-Q}$  nets are interpenetrated by  $\text{X}$  chains. For  $\text{Ag}_5\text{Q}_2\text{X}$  a one-dimensional evolution of silver conductivity in direction of the halide chains was found.<sup>26,27</sup> The pronounced two dimensional mobility and transport of the coinage metals in the case of  $\text{Ag}_{10}\text{Q}_4\text{X}_3$  is now consistent with the layered arrangement of honeycomb  $\text{Q}$ - and Kagomé-like  $\text{X}$  nets (see Figure 1).

3. ... to identify and interpret the polyanionic part of anion substructures

Taking structure topologic aspects into account a simple Peierls-like arrangement of covalently bonded  $[\text{Q}_2]^{2-}$  and isolated  $\text{Q}^{2-}$  ions can be identified as the building block of the polyanion substructure in the coinage metal (poly)chalcogenide halides.<sup>16</sup> The mobility of the polyanionic chains causes a disorder in the structure which leads to closely neighbored and not fully occupied positions in the model derived from the averaging diffraction experiments. Diffuse scattering phenomena are common for such a behavior substantiating the accuracy of the averaged structure models. Applying a Peierls-model for the mobile  $\text{Q}$  chain with partially covalent interactions, like in the case of  $\text{Ag}_{10}\text{Te}_4\text{Br}_3$ , the band structure modulation could be predicted and substantiated in that case. Even more compounds like  $\text{Ag}_{4.53}\text{Te}_3$  (stuetzite)<sup>20</sup> and the closely related  $\text{Ag}_{11}\text{AsTe}_7$ <sup>28</sup> contain such a (poly)anion substructure which could not be

1 interpreted and identified properly before. For stuetzite no sharp order-disorder phase  
2 transition of silver ions can be observed but a structural transition was postulated by detailed  
3 electrochemical experiments at about 513 to 553 K.<sup>29</sup> The occurrence of a switching in the Te  
4 chains is at least a possible mechanism for this transition which can be derived from its  
5 comparable structural features. In the case of  $\text{Ag}_{12}\text{Te}_6\text{S}$  the disordered Te chain is substituted  
6 by a silver coordinated  $\text{S}^{2-}$  chain avoiding the structural disorder.<sup>21</sup>

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10 Some unusual structural properties and physical properties have been reported for  $M_5Q_3$   
11 compounds with  $M = \text{K}, \text{Cs}$  and  $Q = \text{Se}, \text{Te}$ .<sup>30-32</sup> A quite surprising and unbelievable structural  
12 feature of  $M_5Q_3$  compounds, the very short distance of some K sites  $d = 2.9\text{-}3.2 \text{ \AA}$  (30% less  
13 than in the element)<sup>32</sup> or Cs sites in the structure models (Figure 2) become understandable if  
14 the K sites (full occupancy in  $\text{K}_5\text{Te}_3$ ) or Cs sites (occupancy factor of 0.75 in  $\text{Cs}_5\text{Te}_3$ ) of  
15 interest are interpreted as linear polyanionic  $Q$  chains. Such an estimation would lead to a  
16 composition close to  $\text{KTe}$  or better  $\text{K}_2\text{Te}_2$  and would set some calculated properties<sup>32</sup> like the  
17 equilibrium volume per atom  $38.71 \text{ \AA}^3$  for ' $\text{K}_5\text{Te}_3$ ' in the right place between  $\alpha$ - or  $\beta$ - $\text{K}_2\text{Te}_2$ <sup>33</sup>  
18 (linear chains of  $\text{Te}^{2-}$  dumbbells; 43.66 and 42.70) and  $\text{K}_2\text{Te}_3$ <sup>34</sup> (chains of  $[\text{Te}_3]^{2-}$  units, 38.32  
19  $\text{ \AA}^3$ ).<sup>32</sup> Also some features in the partial DOS of the K3 site of ' $\text{K}_5\text{Te}_3$ ' a sharp and high peak  
20 right at the Fermi level<sup>32</sup> becomes understandable if partially covalent-bonded Te is present  
21 on this site instead of K. Such a replacement would result in minimal Te-Te distances not  
22 shorter than  $3.42 \text{ \AA}$  in  $\text{K}_5\text{Te}_3$  between the chains and neighbored Te positions. This  
23 assumption need to be verified and addressed by additional experiments which is not the  
24 scope of this work.

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To best of our knowledge, none of the afore mentioned compounds, except the evaluation of  
the thermomagnetic properties and the magnetic field dependence of the Seebeck coefficient  
of stuetzite<sup>35</sup>, were checked according their thermoelectric properties.

Based on this simple but fundamental structural approach an interpretation of the unexpected  
electronic and thermoelectric properties of the coinage metal (poly)chalcogenide halides can  
be achieved.

$\text{Ag}_{10}\text{Te}_4\text{Br}_3$ , the first discovered representative<sup>15</sup> of this class of materials is a tetramorphic  
system<sup>16</sup> with four polymorphs in the small temperature range of 290 to 390 K. Chains of Te-  
 $[\text{Te}_2]$ -Te units coordinated linearly by Ag are running perpendicular to alternating  $6^3$  Te and  
3.6.3.6 Br nets. The occurrence of a diffuse scattering phenomena for the two high  
temperature polymorphs is in good accordance to a model of an emerging Peierls-distortion of  
a linear  $[(-\text{Te}-[\text{Te}_2]-\text{Te}-\text{Ag})_n]$  chain (see Figure 1) after the temperature driven removal of the

1 silver ions. This feature causes a split arrangement of half occupied and closely neighbored Te  
2 positions in the structure model. A comparable diffuse scattering effect has been observed for  
3 compounds with the nominal composition  $\text{Ag}:\text{Te}:\text{X} = 20:10:2$  like  $\text{Ag}_{20}\text{Te}_{10}\text{BrI}$  and  
4  $\text{Ag}_{20}\text{Te}_{10}\text{I}_2$ .<sup>36</sup>

5 Quantum chemical calculations of the polyanionic Te chain and solid state  $^{125}\text{Te}$ -NMR  
6 spectroscopy of  $\text{Ag}_{10}\text{Te}_4\text{Br}_3$  substantiated the increasing mobility (forming and breaking of  
7 covalent Te-Te bonds along the chain) of the Te chain overtaking the NMR timescale at  
8 elevated temperatures.<sup>37</sup> A development of a Peierls distorted towards an equidistant chain  
9 results in a significant closing of the band gap which is a well known fact in the case of Sb- or  
10 Te chains.<sup>37,38</sup> Exactly, when the  $Q$  chain mobility becomes high and the band gap gets closed  
11 from 1.1 eV to approx. 0.7 eV, a huge and former unseen thermopower drop of about 1400  
12  $\mu\text{V}/\text{K}$  occurs. The band gap tuning results in a change of the semiconduction mechanism from  
13  $p$  to  $n$  and back to  $p$  conduction at the same time within a temperature region of 375 to 410  
14 K.<sup>37</sup> This process was substantiated by temperature dependent potentiometric measurements  
15 and Hebb-Wagner polarization experiments. Recent experiments point towards the same  
16 polarization behavior in the case of  $\text{Ag}_{23}\text{Te}_{12}\text{Br}$ .<sup>39</sup>

17 As an result of two mobile substructures (cations and polyanionic chalcogen part) the coinage  
18 metal (poly)chalcogenide halides are effective phonon scattering materials. For  $\text{Ag}_{10}\text{Te}_4\text{Br}_3$  a  
19 thermal conductivity of 0.27 to 0.43  $\text{W m}^{-1} \text{K}^{-1}$  was observed in the temperature range of 250  
20 to 350 K.<sup>37</sup> Compared with the room temperature thermal conductivity of  $\text{Ag}_2\text{Te}$ <sup>40</sup> of 0.93  $\text{W}$   
21  $\text{m}^{-1} \text{K}^{-1}$  the conductivity is reduced by a factor of  $\sim 3$  at this temperature. Figure 2 shows the  
22 results of thermal diffusivity measurements for  $\text{Ag}_{10}\text{Te}_4\text{Br}_3$  and  $\text{Ag}_{20}\text{Te}_{10}\text{BrI}$ . The low thermal  
23 diffusivity of  $\text{Ag}_{10}\text{Te}_4\text{Br}_3$  of about  $1.9 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$  is again lowered to  $1.1 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$  in the  
24 case of  $\text{Ag}_{20}\text{Te}_{10}\text{BrI}$  (Figure 3). Both thermal diffusivities are comparable to the values of  
25 classical isolators like polyethylene ( $2.2 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$ )<sup>41</sup> or polyvinylchloride ( $1 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$ )<sup>42</sup>. A brief summary of the thermal diffusivity data is given in Table I.

26 All experiments performed in the present class of materials point towards the fact that the  
27 linear partially covalent-bonded  $Q$  chain, in addition to the high and effective coordination  
28 behavior of the coinage metal cations is an effective way to generate favorable electronic  
29 properties. The redox reaction itself has maybe a certain potential to be used as electro-  
30 chemical redox switch or as current driven resistance switch after material optimization and a  
31 successful thin-film preparation of the materials.<sup>40</sup> At least the evolution of the thermopower  
32 as well as the thermal diffusivity are promising features to check the opportunity of this

1 materials as potential thermoelectrics or sensors. Even a use of the drastic switching effect in  
2 data storage applications can be possible if a properly ordered and oriented thin-film  
3 preparation of the crystalline material can be achieved. Each chain shows a distance of  
4 approximately 0.75 nm to the next neighbor chain which reduces the density of switch-able  
5 substructures the to the sub-nanometer regime.  
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## 10 11 **Conclusions**

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14 An easy and straight forward principle of structure topology is the basis for a deep  
15 understanding of the electronic structure of a new class of highly dynamic coinage metal  
16 (poly)chalcogenide halides. A linear partially covalent-bonded and mobile chain of chalcogen  
17 has been identified as the origin of a temperature driven redox reaction in the solid state. In  
18 combination with the intrinsically mobile cation substructure of this mixed ion and electron  
19 conducting semiconductors, this class of materials is a rare example of a system combining  
20 two independent mobile substructures in the solid state. As a result, the thermal conductivity  
21 of such systems is drastically reduced to values comparable and even slightly lower than  
22 today's state of the art nano-structured thermoelectrics (like superlattices and quantum dots).  
23 This extremely low thermal conductivity is reached by bulk phase material without nano-  
24 structuring or material optimization. Such a redox-reaction causes a band gap tuning due to  
25 modification of the units (Q chains), having a major contribution to electronic states around  
26 the band gap. A *pn*p transition of the semiconduction mechanism was found for  $\text{Ag}_{10}\text{Te}_4\text{Br}_3$   
27 within a very small temperature range of approx 40 K at 390 K leading to a reversible drop of  
28 the Seebeck coefficient of about 1400 mV/K within this gradient.  
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48 motion in materials with disordered structures. We thank Netzsch, Germany for the  
49 measurement of the thermal diffusivity of  $\text{Ag}_{20}\text{Te}_{10}\text{BrI}$ .  
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## Figures

captions:

**Figure 1:** Structure relations and topology between  $\beta$ - $\text{Ag}_{10}\text{Te}_4\text{Br}_3$ <sup>16</sup>, stuetzite ( $\text{Ag}_{4.53}\text{Te}_3$ )<sup>20</sup> and  $\text{Ag}_{12}\text{Te}_6\text{S}$ .<sup>21</sup> *Polyanion substructure:* Predominantly covalent-bonded linear Te chains form  $\text{Te}_4$  units. These units are drawn as black (disordered), blue and red (ordered) spheres. A topological relation of  $[(\text{Te}_2)\text{Te}]_3$  units (triangularly connected  $\text{Te}_4$  units) in  $\text{Ag}_{4.53}\text{Te}_3$  and  $\text{Ag}_{12}\text{Te}_6\text{S}$ , compared with the Kagomé-type 3.6.3.6 bromide nets in  $\beta$ - $\text{Ag}_{10}\text{Te}_4\text{Br}_3$ , can be observed.  $[\text{Te}_2]^{2-}$  units are denoted as light blue dumbbells and  $[\text{S}_2]^{2-}$  units as yellow dumbbells are forming a linear  $Q_2$  chain which is sometimes coordinated by Ag. *Anion substructure:* Isolated  $\text{Te}^{2-}$  and  $\text{Br}^-$  ions are connected at distances around the sum of the van der Waals radii by solid dark grey or light grey lines to form  $6^3$  and 3.6.3.6 nets, respectively. Further atoms in the Figure: Silver (orange spheres) and sulphur (yellow spheres).

**Figure 2:** Structure topological aspects of potassium (poly)tellurides.  $\text{Te}_4$  units or K coordinated  $[\text{Te}_2]^{2-}$  dumbbells are present in  $\alpha$ - $\text{K}_2\text{Te}_2$  and  $\beta$ - $\text{K}_2\text{Te}_2$ .<sup>33</sup>  $\text{Te}_4$  units can also be found in  $\text{K}_5Q_3$  with  $Q = \text{Se}, \text{Te}$ .<sup>30, 31</sup> Very short K distances and high displacements are unusual findings in these structure models which can be easily avoided by a replacement of K by Te. The respective smeared out electron density should then be interpreted as polyanionic disordered Te strands like in the case of the coinage metal (poly)telluride halides.

**Figure 3:** Thermal diffusivity data of  $\text{Ag}_{10}\text{Te}_4\text{Br}_3$  and  $\text{Ag}_{20}\text{Te}_{10}\text{BrI}$ .

Figure 1

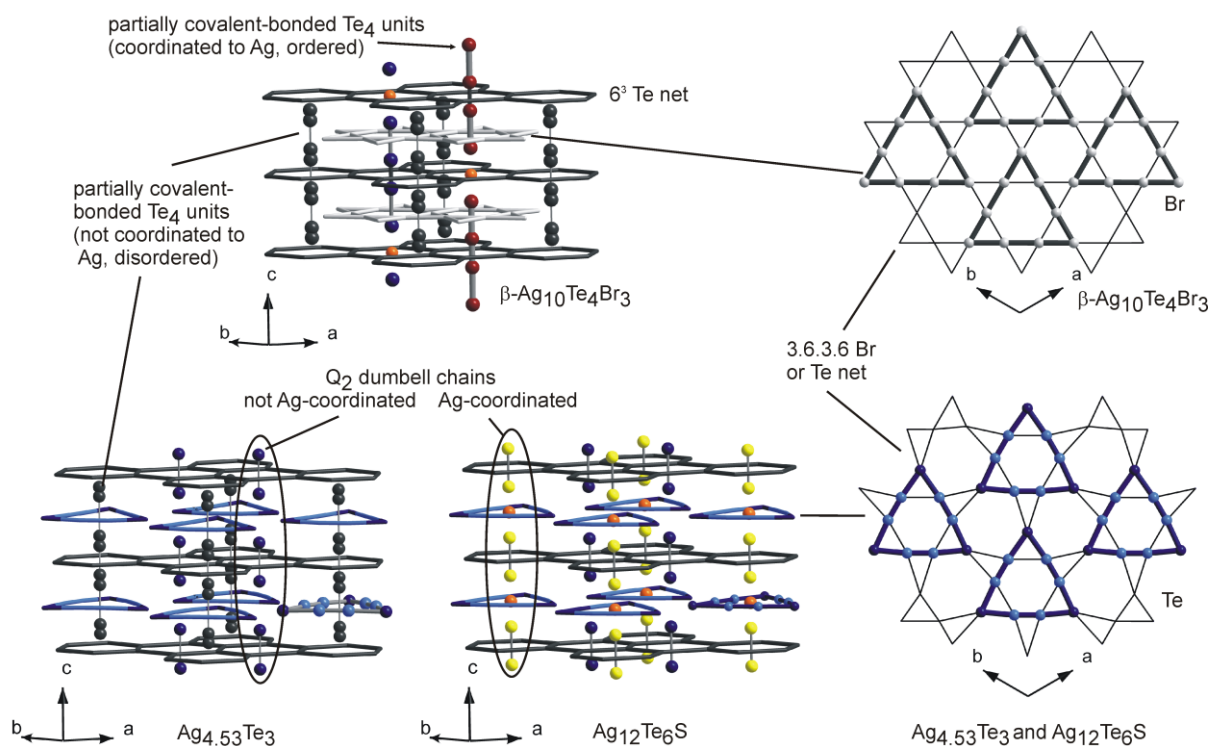


Figure 2

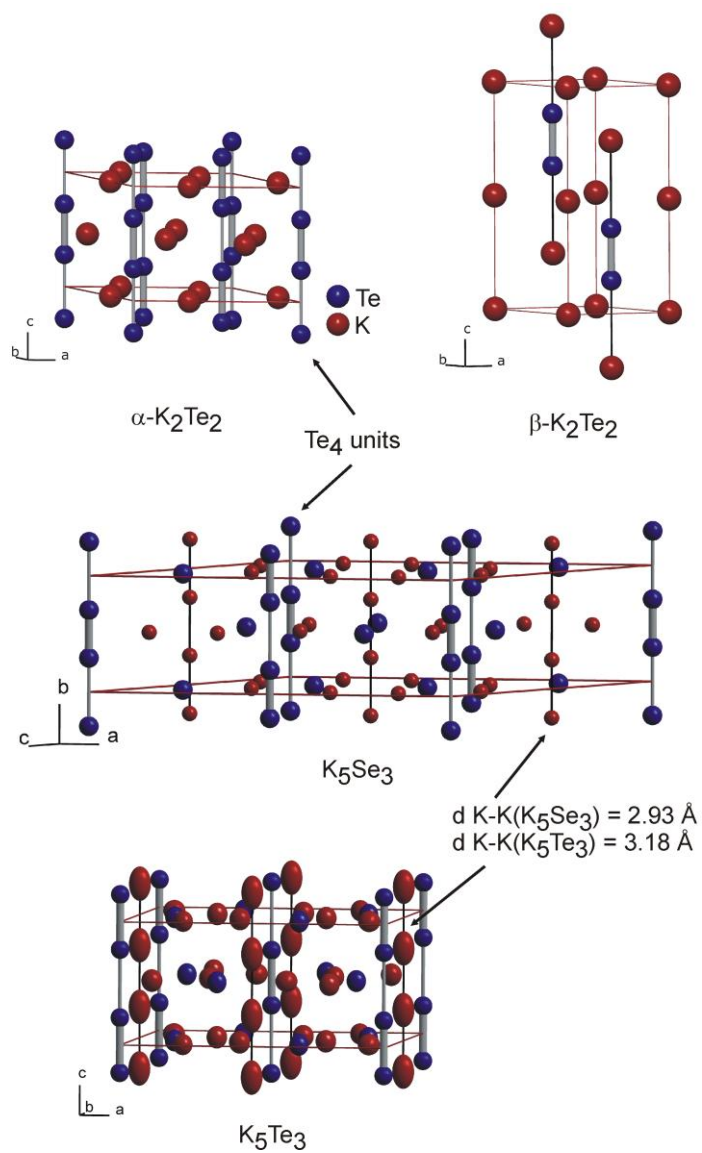
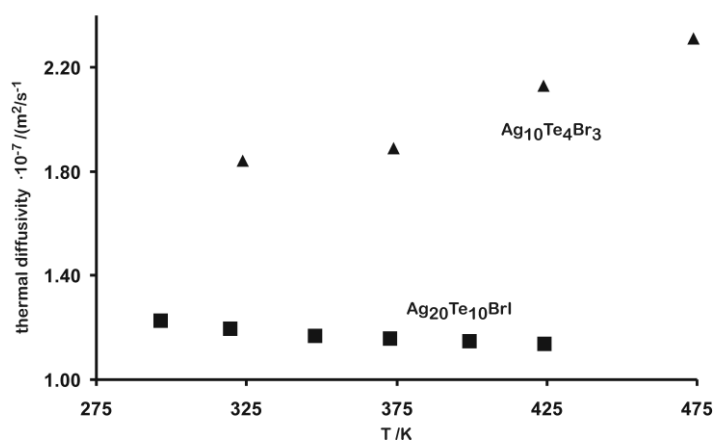


Figure 3



## Tables

Table I. Thermal diffusivity data of  $\text{Ag}_{10}\text{Te}_4\text{Br}_3$  and  $\text{Ag}_{20}\text{Te}_{10}\text{BrI}$ .

$\text{Ag}_{10}\text{Te}_4\text{Br}_3$	Temperature $T$ /K	Thermal diffusivity $a \cdot 10^{-7} /(\text{m}^2 \text{s}^{-1})$	Lit.
	324(1)	1.84	37
	374 (1)	1.89	
	424 (1)	2.13	
	474 (1)	2.31	
$\text{Ag}_{20}\text{Te}_{10}\text{BrI}$	223(1)	1.44(7)	this work
	248(1)	1.33(5)	
	273(1)	1.28(7)	
	296(1)	1.23(6)	
	319(1)	1.20(6)	
	348(1)	1.17(4)	
	372(1)	1.16(3)	
	399(1)	1.15(3)	
	424(1)	1.144(8)	