Crystal structure of $\sim R\mathrm{Cu_3S_3}$ and $\sim R\mathrm{CuTe_2}$ (R=Gd–Lu) compounds

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ABSTRACT

The crystal structures of ternary compounds $\mathrm{TbCu_3S_3}$, $\mathrm{Dy_{1.06}Cu_{2.84}S_3}$ (space group $R\bar{3}$), $\mathrm{Ho_{0.67}Cu_2S_2}$ (space group $P\bar{3}m1$), $\mathrm{ErCu_3S_3}$ (space group $P\bar{3}1c$), $\mathrm{Yb_{0.80}Cu_{1.60}S_2}$, $\mathrm{Lu_{0.67}Cu_2S_2}$, $\mathrm{TbCuTe_2}$, $\mathrm{DyCuTe_2}$, $\mathrm{Tm_{1.07}Cu_{0.78}Te_2}$, $\mathrm{LuCuTe_2}$ (space group $P\bar{3}m1$), $\mathrm{Gd_{0.75}Cu_{1.74}Te_2}$ (space group $P\bar{3}1m$) were determined by means of X-ray single crystal diffraction. The S(Te) atoms are stacked in a close packed arrangement with the layers in the sequence AB. The R atoms are distributed over octahedral interstices whereas Cu atoms are located in tetrahedral interstices. Disorder of R and Cu atoms in studied chalcogenides is found. Crystal structure comparison showed that $\mathrm{TbCuTe_2}$ and $\mathrm{DyCuTe_2}$ crystallize as superstructure $2a \times 2a \times {_2}c$ to $\mathrm{CaAl_2Si_2}$ structure type, whereas $\mathrm{Gd_{0.75}Cu_{1.74}Te_2}$, $\mathrm{ErCu_3S_3}$ and $\mathrm{TbCu_3S_3}$ ($\mathrm{Dy_{1.06}Cu_{2.84}S_3}$) have superstructure $\sqrt{3}a \times \sqrt{3}a \times nc$ with n=1, 2, 3.

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1. Introduction

Designing of new functional materials with increasingly complex compositions has become a primary direction in modern science and technology. Complex rare-earth-based chalcogenides are interesting due to their specific thermal, electrical, magnetic and optical properties [1,2]. Various chalcogenide materials have application in the field of infrared and nonlinear optics. Systematic investigation of complex chalcogenide systems is important way for searching of new materials with interesting properties [3].

The formation of the compounds $R\mathrm{Cu_3S_3}$, $R\mathrm{CuSe_2}$ and $R\mathrm{CuTe_2}$ (R—Y, Gd–Lu) with $\mathrm{Er_{2/3}Cu_2S_2}$ structure type (space group $P\bar{3}$) has been originally reported in Refs. [4–7]. The crystal structure of $\mathrm{Er_{2/3}Cu_2S_2}$ has been determined using X-ray single crystal data. Aforementioned compounds have been investigated using X-ray powder diffraction and lattice parameters have been determined. The crystal structure of $\mathrm{Er_{0.85}Cu_{1.45}S_2}$ has been investigated using X-ray single crystal data ($\mathrm{CaAl_2Si_2}$ structure type, space group $P\bar{3}m1$) [8]. The crystal structure of $R\mathrm{CuSe_2}$ (R—Gd–Lu) has been reinvestigated using X-ray single crystal data ($\mathrm{CaAl_2Si_2}$ structure type, space group $P\bar{3}m1$) [9].

In this paper we present results of the single crystal structure reinvestigation of the $\sim R\mathrm{Cu_3S_3}$ and $\sim R\mathrm{CuTe_2}$ (R=Gd–Lu) compounds.

2. Experimental details

The samples of the compositions $R\mathrm{Cu_3S_3}$ and $R\mathrm{CuTe_2}$ (R=Gd–Lu) were prepared by sintering the elemental constituents of the purity better than 99.9 wt% in evacuated quartz tubes. The syntheses were carried out in a tube resistance furnace. The ampoules were first heated with a rate of $30\,\mathrm{K\,h^{-1}}$ up to 1420 K and then kept at this temperature for 3 h. Afterwards, the samples were cooled slowly ($10\,\mathrm{K\,h^{-1}}$) down to 870 K, and annealed at this temperature for 720 h. Subsequently, the furnace was turn off and ampoules were cooled to room temperature.

Small single crystals suitable for crystal structure investigations were selected from obtained samples. The X-ray intensities data were collected on a KUMA Diffraction KM-4 four-circle diffractometer equipped with a CCD camera, using graphite-monochromatized Mo$K\alpha$ radiation (λ=0.71073 Å). The raw data were treated with the CrysAlis Data Reduction program taking into account an absorption correction. The intensities of the reflections were corrected for Lorentz and polarization factors. The crystal structure was solved by Patterson methods [10] and refined by the full-matrix least-squares method using SHELXL-97 [10]. All results were checked with the PLATON program, and no additional symmetry elements were found [11]. The compositions of all single crystals were confirmed by EDX analysis (EDAX PV9800 microanalyzer).

3. Results and discussion

3.1. Crystal structure of $\mathrm{Ho_{0.67}Cu_2S_2}$, $\mathrm{Yb_{0.80}Cu_{1.60}S_2}$ and $\mathrm{Lu_{0.67}Cu_2S_2}$

The crystal data and the structure refinement details for $\mathrm{Ho_{0.67}Cu_2S_2}$, $\mathrm{Yb_{0.80}Cu_{1.60}S_2}$ and $\mathrm{Lu_{0.67}Cu_2S_2}$ are summarized in Table 1, whereas the refined atomic coordinates and the anisotropic displacement parameters are given in Table 3. Determined lattice parameters are close to those reported in Ref. [4]. Space

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group of higher symmetry ($P\bar{3}m1$) was determined for these compounds when compared with reported in Ref. [4] space group $P\bar{3}$. One position of R, one position of Cu and one position of S were determined. The calculated composition of $Yb_{0.80}Cu_{1.60}S_2$ is slightly different than composition of prepared sample. The positions of Yb and Cu atoms in $Yb_{0.80}Cu_{1.60}S_2$ are partially occupied. The positions of Ho (Lu) atoms are partially occupied and positions of Cu atoms are fully occupied in $Ho_{0.67}Cu_2S_2$ and $Lu_{0.67}Cu_2S_2$. The positions of S atoms are fully occupied for all investigated compounds.

3.2. Crystal structure of $Tm_{1.07}Cu_{0.78}Te_2$ and $LuCuTe_2$

The crystal data and the structure refinement details for $Tm_{1.07}Cu_{0.78}Te_2$ and $LuCuTe_2$ are summarized in Table 2, whereas the refined atomic coordinates and the anisotropic displacement parameters are given in Table 4. Lattice parameters of $Tm_{1.07}Cu_{0.78}Te_2$ and $LuCuTe_2$ are close to those reported in Ref. [7] for the $RCuTe_2$ (R=Tm, Lu). The compounds crystallize in space group $P\bar{3}m1$. Two position of Tm (Lu) were determined for both compounds. One and two positions of Cu were created in the structures of $Tm_{1.07}Cu_{0.78}Te_2$ and $LuCuTe_2$, respectively. One ordered position of Te exists for both structures. The calculated composition of $Tm_{1.07}Cu_{0.78}Te_2$ is slightly different than composition of prepared sample. All positions of Cu are disordered in both structures. One position of Tm is ordered and one position of Tm is disordered in the structure of $Tm_{1.07}Cu_{0.78}Te_2$. All positions of Lu are disordered in $LuCuTe_2$.

3.3. Crystal structure of $TbCu_3S_3$ and $Dy_{1.06}Cu_{2.84}S_3$

The crystal data and the structure refinement details for $TbCu_3S_3$ and $Dy_{1.06}Cu_{2.84}S_3$ are summarized in Table 1, whereas the refined atomic coordinates and the anisotropic displacement parameters are given in Table 3. The crystal structures of the $TbCu_3S_3$ and $Dy_{1.06}Cu_{2.84}S_3$ compounds (space group $R\bar{3}$) are similar. Both compounds crystallizes in larger unit cell than reported in Ref. [4] for RCu_3S_3 (R=Tb, Dy). Two positions of R, one position of Cu and one position of S were determined. The positions of all atoms (except Tb2) are fully occupied in $TbCu_3S_3$. Due to small difference of the composition of the $Dy_{1.06}Cu_{2.84}S_3$ compound from the $DyCu_3S_3$ composition the positions of Dy2 and Cu are defect for it.

3.4. Crystal structure of $ErCu_3S_3$

The crystal data and the structure refinement details for $ErCu_3S_3$ are summarized in Table 1, whereas the refined atomic coordinates and the anisotropic displacement parameters are given in Table 3. The $ErCu_3S_3$ compound (space group $P\bar{3}1c$) crystallizes in larger unit cell than reported in Ref. [4] for $ErCu_3S_3$. Three positions of Er, one position of Cu and one position of S were determined. The positions of Er2 and Er3 are partially occupied. The positions of remaining atoms are fully occupied.

3.5. Crystal structure of $Gd_{0.75}Cu_{1.74}Te_2$

The crystal data and the structure refinement details for $Gd_{0.75}Cu_{1.74}Te_2$ are summarized in Table 2, whereas the refined atomic coordinates and the anisotropic displacement parameters are given in Table 4. Calculated composition of $Gd_{0.75}Cu_{1.74}Te_2$ is slightly different than composition of prepared sample. Observed lattice parameters of $Gd_{0.75}Cu_{1.74}Te_2$ (space group $P\bar{3}1m$) indicate that investigated compound forms superstructure to $GdCuTe_2$ reported in Ref. [7]. Two positions of Gd (one defect), one position of Cu (defect) and one position of Te were determined.

Table 1
Crystal data and structure refinement details of the $TbCu_3S_3$, $Dy_{1.06}Cu_{2.84}S_3$, $Ho_{0.67}Cu_2S_2$, $ErCu_3S_3$, $Yb_{0.80}Cu_{1.60}S_2$, $Lu_{0.67}Cu_2S_2$ compounds.

Empirical formula	$TbCu_3S_3$	$Dy_{1.06}Cu_{2.84}S_3$	$Ho_{0.67}Cu_2S_2$	$ErCu_3S_3$	$Yb_{0.80}Cu_{1.60}S_2$	$Lu_{0.67}Cu_2S_2$
Formula weight	445.72	447.75	301.70	454.06	304.22	308.43
Space group	$R\bar{3}$ (No. 146)	$R\bar{3}$ (No. 146)	$P\bar{3}m1$ (No. 164)	$P\bar{3}1c$ (No. 163)	$P\bar{3}m1$ (No. 164)	$P\bar{3}m1$ (No. 164)
Unit cell dimensions	a=6.747(1) Å	a=6.723(2) Å	a=3.8860(5) Å	a=6.7070(9) Å	a=3.8660(5) Å	a=3.869(1) Å
	c=19.170(5) Å	c=19.069(6) Å	c=6.385(1) Å	c=12.675(3) Å	c=6.272(1) Å	c=6.326(1) Å
Volume	755.9(3) Å^3	746.5(4) Å^3	83.50(2) Å^3	493.7(1) Å^3	81.18(2) Å^3	82.03(2) Å^3
Number of formula units per unit cell	6	6	1	4	1	1
Calculated density	5.875 g/cm^3	5.976 g/cm^3	6.000 g/cm^3	6.108 g/cm^3	6.223 g/cm^3	6.244 g/cm^3
Absorption coefficient	27.415 mm^{-1}	28.687 mm^{-1}	29.327 mm^{-1}	30.650 mm^{-1}	34.283 mm^{-1}	33.856 mm^{-1}
F(000)	1200	1199	135	812	134	138
Crystal color	Red	Red	Red	Red	Red	Red
Crystal size	0.10 × 0.05 × 0.04 mm	0.09 × 0.04 × 0.03 mm	0.08 × 0.05 × 0.04 mm	0.10 × 0.05 × 0.03 mm	0.11 × 0.05 × 0.05 mm	0.10 × 0.05 × 0.04 mm
Θ range for data collection	3.19–26.32	3.20–27.44	6.39–27.41	3.21–26.72	3.25–27.78	3.22–27.75
Index ranges	$-8 \le h \le 8$	$-8 \le h \le 8$	$-4 \le h \le 5$	$-8 \le h \le 8$	$-3 \le h \le 5$	$-5 \le h \le 5$
	$-8 \le k \le 8$	$-8 \le k \le 8$	$-5 \le k \le 4$	$-8 \le k \le 8$	$-5 \le k \le 4$	$-5 \le k \le 5$
	$-23 \le l \le 23$	$-24 \le l \le 24$	$-8 \le l \le 7$	$-15 \le l \le 16$	$-8 \le l \le 8$	$-8 \le l \le 8$
Reflections collected	3149	3134	783	3149	1013	1025
Independent reflections	348 [R(int.)=0.0489]	383 [R(int.)=0.0772]	92 [R(int.)=0.0761]	350 [R(int.)=0.0570]	99 [R(int.)=0.1258]	98 [R(int.)=0.0315]
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Data/restraints/parameters	348/0/25	383/0/25	92/0/10	350/0/26	99/0/10	98/0/10
Goodness-of-fit on F^2	1.152	1.101	1.260	1.295	1.152	1.234
Final R indices [$I > 2\sigma(I)$]	$R1$=0.0380, $wR2$=0.1008	$R1$=0.0344, $wR2$=0.0992	$R1$=0.0430, $wR2$=0.1028	$R1$=0.0351, $wR2$=0.0947	$R1$=0.0384, $wR2$=0.0891	$R1$=0.0191, $wR2$=0.0421
R indices (all data)	$R1$=0.0384, $wR2$=0.1011	$R1$=0.0383, $wR2$=0.1012	$R1$=0.0439, $wR2$=0.1030	$R1$=0.0435, $wR2$=0.0989	$R1$=0.0384, $wR2$=0.0891	$R1$=0.0195, $wR2$=0.0422
Extinction coefficient	0.0027(3)	0.0002(1)	–	0.0025(4)	–	0.060(8)
Largest diff. peak and hole (e/Å^3)	1.767 and −0.911	1.159 and −1.963	2.826 and −1.279	2.687 and −2.951	1.654 and −1.859	1.343 and −0.995

Table 2
Crystal data and structure refinement details of the $Gd_{0.75}Cu_{1.74}Te_2$, $TbCuTe_2$, $DyCuTe_2$, $Tm_{1.07}Cu_{0.78}Te_2$, $LuCuTe_2$ compounds.

	$Gd_{0.75}Cu_{1.74}Te_2$	$TbCuTe_2$	$DyCuTe_2$	$Tm_{1.07}Cu_{0.78}Te_2$	$LuCuTe_2$
Empirical formula	$Gd_{0.75}Cu_{1.74}Te_2$	$TbCuTe_2$	$DyCuTe_2$	$Tm_{1.07}Cu_{0.78}Te_2$	$LuCuTe_2$
Formula weight	483.70	477.66	481.24	487.67	493.71
Space group	$P\bar{3}m1$ (no. 162)	$P\bar{3}m1$ (no. 164)	$P\bar{3}m1$ (no. 164)	$P\bar{3}m1$ (no. 164)	$P\bar{3}m1$ (no. 164)
Unit cell dimensions	$a=7.478(1)$ Å	$a=8.629(1)$ Å	$a=8.619(1)$ Å	$a=4.2610(6)$ Å	$a=4.2600(6)$ Å
	$c=7.015(1)$ Å	$c=13.856(3)$ Å	$c=13.857(3)$ Å	$c=6.904(1)$ Å	$c=6.905(1)$ Å
Volume	$339.7(1)$ Å³	$893.6(3)$ Å³	$891.5(3)$ Å³	$108.56(3)$ Å³	$108.52(3)$ Å³
Number of formula units per unit cell	3	8	8	1	1
Calculated density	7.093 g/cm³	7.101 g/cm³	7.171 g/cm³	7.460 g/cm³	7.555 g/cm³
Absorption coefficient	31.400 mm⁻¹	33.035 mm⁻¹	34.011 mm⁻¹	38.137 mm⁻¹	40.453 mm⁻¹
F(000)	607	1584	1592	202	204
Crystal color	Black	Black	Black	Black	Black
Crystal size	0.08 × 0.07 × 0.03 mm³	0.05 × 0.03 × 0.02 mm³	0.08 × 0.07 × 0.03 mm³	0.07 × 0.04 × 0.04 mm³	0.09 × 0.06 × 0.04 mm³
Θ range for data collection	3.15–27.47	2.73–27.48	3.10–27.47	5.53–27.04	2.95–27.04
Index ranges	$-9 \le h \le 9$ $-9 \le k \le 9$ $-9 \le l \le 9$	$-11 \le h \le 10$ $-11 \le k \le 9$ $-11 \le l \le 9$	$-11 \le h \le 11$ $-11 \le k \le 11$ $-17 \le l \le 17$	$-5 \le h \le 5$ $-5 \le k \le 5$ $-8 \le l \le 8$	$-5 \le h \le 5$ $-5 \le k \le 5$ $-8 \le l \le 8$
Reflections collected	3567	12,057	9410	1316	1126
Independent reflections	305 [R(int.)=0.0636]	830 [R(int.)=0.0846]	824 [R(int.)=0.1062]	116 [R(int.)=0.1060]	116 [R(int.)=0.1134]
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Data/restraints/parameters	305/0/19	830/0/44	824/0/44	116/0/11	116/0/16
Goodness-of-fit on F^2	1.223	1.184	1.252	1.216	1.245
Final R indices [$I > 2\sigma(I)$]	R1=0.0401, wR2=0.1004	R1=0.0573, wR2=0.1523	R1=0.0589, wR2=0.2015	R1=0.0399, wR2=0.0910	R1=0.0472, wR2=0.1245
R indices (all data)	R1=0.0415, wR2=0.1016	R1=0.0899, wR2=0.1717	R1=0.0805, wR2=0.2166	R1=0.0412, wR2=0.0917	R1=0.0509, wR2=0.1279
Extinction coefficient	0.008(1)	0.00033(8)	0.0002(1)	–	–
Largest diff. peak and hole (e/Å³)	3.509 and −1.352	3.447 and −5.044	5.200 and −5.503	3.536 and −1.626	2.234 and −2.515

3.6. Crystal structure of $TbCuTe_2$ and $DyCuTe_2$

The crystal data and the structure refinement details for $TbCuTe_2$ and $DyCuTe_2$ are summarized in Table 2, whereas the refined atomic coordinates and the anisotropic displacement parameters are given in Table 4. The crystal structures of the $TbCuTe_2$ and $DyCuTe_2$ compounds (space group $P\bar{3}m1$) are similar and form superstructures to those reported in Ref. [7]. Two fully occupied positions of Tb (Dy), three positions of Cu (two of them are partially occupied) and four fully occupied positions of Te were determined for both compounds.

3.7. Crystallographic aspects of the $\sim RCu_3S_3$ and $\sim RCuTe_2$ (R=Gd–Lu) compounds

The relevant interatomic distances and the coordination numbers of the R and Cu atoms for the investigated compounds are listed in Tables 5–10. All distances are close to the sum of the respective ionic radii [12]. Overall, the crystal structures of the $\sim RCu_3S_3$ and $\sim RCuTe_2$ (R=Gd–Lu) compounds are built in similar way. The sulfur (tellurium) atoms are stacked in a close packed arrangement with the layers in the sequence AB. The R atoms are distributed over octahedral interstices, whereas Cu atoms are located in tetrahedral interstices. For the RCu_3S_3 ($R_{2/3}Cu_2S_2$) composition, one third of octahedral interstices are filled by R atoms and a half of tetrahedral interstices are occupied by Cu atoms. For the $RCuTe_2$ composition, 1/2 of octahedral interstices are filled by R atoms and 1/4 of tetrahedral interstices are occupied by Cu atoms. All investigated compounds are distributed between the compositions $R_{2/3}Cu_2X_2$–$RCuX_2$.

The $Ho_{0.67}Cu_2S_2$, $Yb_{0.80}Cu_{1.60}S_2$ and $Lu_{0.67}Cu_2S_2$ compounds (Fig. 1) crystallize in $CaAl_2Si_2$ structure type (space group $P\bar{3}m1$) similar to $Er_{0.85}Cu_{1.45}S_2$ [8] and $RCuSe_2$ (R—Gd–Lu) [9]. The R atoms occupy every second layer of octahedra. The layers of tetrahedra filled by Cu atoms are located between the layers of octahedra. The structure of $Tm_{1.07}Cu_{0.78}Te_2$ (Fig. 1b) is derived from the structure of aforementioned $Ho_{0.67}Cu_2S_2$ compound. Second position of R atoms (Tm2) exists in $Tm_{1.07}Cu_{0.78}Te_2$ when compared with one position of R (Ho) in the structure of $Ho_{0.67}Cu_2S_2$. The Tm atoms (Tm1 and Tm2) are distributed over two layers of octahedra in the structure of the $Tm_{1.07}Cu_{0.78}Te_2$ compound. The Cu atoms occupy tetrahedra in $Tm_{1.07}Cu_{0.78}Te_2$ similar to structure of $Ho_{0.67}Cu_2S_2$. Additional disorder of the Cu atoms is observed in the structure of $LuCuTe_2$ (Fig. 1c). Two positions of R atoms (Lu1 and Lu2) exist in the structure of $LuCuTe_2$ similar to the above mentioned structure of $Tm_{1.07}Cu_{0.78}Te_2$. One additional position of Cu (Cu2) exists in $LuCuTe_2$ when compared with one position of Cu in $Tm_{1.07}Cu_{0.78}Te_2$. The Lu atoms are distributed over all octahedral positions and Cu atoms are distributed over all tetrahedral positions in $LuCuTe_2$.

The crystal structure of the $TbCu_3S_3$ and $Dy_{1.06}Cu_{2.84}S_3$ compounds (Fig. 2a) represents a distinctive $\sqrt{3}a \times \sqrt{3}a \times 3c$ superstructure to the compounds with $CaAl_2Si_2$ structure type. The crystal structure of the $ErCu_3S_3$ compound (Fig. 2b) is $\sqrt{3}a \times \sqrt{3}a \times 2c$ superstructure and crystal structure of $Gd_{0.75}Cu_{1.74}Te_2$ (Fig. 2c) is $\sqrt{3}a \times \sqrt{3}a \times 1c$ superstructure to the compounds with $CaAl_2Si_2$ structure type. Separate layers of the R-centered octahedra and Cu–centered tetrahedra along c axis are observed in the structures of the $Gd_{0.75}Cu_{1.74}Te_2$, $ErCu_3S_3$ and $TbCu_3S_3$ ($Dy_{1.06}Cu_{2.84}S_3$) compounds. These structures represent $a \times b \times nc$ series ($n=1$, 2 ,3, …, $a(b) \sim 3.9(4.3)$ Å, $c \sim 6.3(7.0)$ Å for compounds with S or Te). The compounds $Gd_{0.75}Cu_{1.74}Te_2$, $ErCu_3S_3$ and $TbCu_3S_3$ ($Dy_{1.06}Cu_{2.84}S_3$) are realized for $n=1$, 2 and 3, respectively. The ordering of the positions of the R atoms is observed during the formation of superstructures.

Table 3
Atomic coordinates and anisotropic displacement factors for $TbCu_3S_3$, $Dy_{1.06}Cu_{2.84}S_3$, $Ho_{0.67}Cu_2S_2$, $ErCu_3S_3$, $Yb_{0.80}Cu_{1.60}S_2$, $Lu_{0.67}Cu_2S_2$.

Atom	Position	x/a	y/b	z/c	Occupancy	U_{eq}, Å^2	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$TbCu_3S_3$												
Tb1	3a	0	0	0	1	0.0106(4)	0.0105(5)	0.0105(5)	0.0109(6)	0	0	0.0053(2)
Tb2	6c	0	0	0.33304(6)	0.50	0.0155(4)	0.0148(5)	0.0148(5)	0.0171(8)	0	0	0.0074(3)
Cu	18f	0.9999(1)	0.3319(1)	0.12322(7)	1	0.0216(4)	0.0213(7)	0.0211(7)	0.0224(8)	−0.0015(4)	0.0003(4)	0.0107(5)
S	18f	0.3317(3)	0.3326(3)	0.08315(13)	1	0.0122(5)	0.011(1)	0.011(1)	0.013(1)	0.0000(7)	−0.0005(6)	0.0060(8)
$Dy_{1.06}Cu_{2.84}S_3$												
Dy1	3a	0	0	0	1	0.0120(4)	0.0089(4)	0.0089(4)	0.0181(6)	0	0	0.0045(2)
Dy2	6c	0	0	0.33309(6)	0.56	0.0125(4)	0.0105(5)	0.0105(5)	0.0166(7)	0	0	0.0052(2)
Cu	18f	0.9998(1)	0.3320(1)	0.12350(7)	0.94	0.0182(4)	0.0178(6)	0.0175(6)	0.0196(7)	−0.0010(4)	0.0002(4)	0.0090(5)
S	18f	0.3316(3)	0.3322(3)	0.08277(12)	1	0.0110(5)	0.0093(9)	0.0086(9)	0.0148(10)	−0.0013(7)	−0.0010(7)	0.0041(7)
$Ho_{0.67}Cu_2S_2$												
Ho	1a	0	0	0	0.67	0.0147(7)	0.0115(8)	0.0115(8)	0.0210(12)	0	0	0.0057(4)
Cu	2d	1/3	2/3	0.6292(5)	1	0.0239(9)	0.020(1)	0.020(1)	0.030(1)	0	0	0.0104(6)
S	2d	1/3	2/3	0.248(1)	1	0.015(1)	0.014(1)	0.014(1)	0.017(2)	0	0	0.0070(8)
$ErCu_3S_3$												
Er1	2c	1/3	2/3	1/4	1	0.0084(4)	0.0080(5)	0.0080(5)	0.0092(6)	0	0	0.0040(2)
Er2	2d	1/3	2/3	3/4	0.22	0.0078(9)	0.007(1)	0.007(1)	0.009(1)	0	0	0.0035(6)
Er3	2a	0	0	1/4	0.78	0.0065(4)	0.0064(5)	0.0064(5)	0.0068(7)	0	0	0.0032(3)
Cu	12i	0.3335(2)	0.3322(2)	0.5647(1)	1	0.0174(4)	0.0162(7)	0.0172(7)	0.0184(7)	0.0013(5)	−0.0008(5)	0.0081(6)
S	12i	0.9964(4)	0.3311(4)	0.6270(1)	1	0.0091(5)	0.008(1)	0.009(1)	0.009(1)	0.0005(8)	0.0011(7)	0.0049(9)
$Yb_{0.80}Cu_{1.60}S_2$												
Yb	1a	0	0	0	0.80	0.0149(5)	0.0110(6)	0.0110(6)	0.0227(8)	0	0	0.0055(3)
Cu	2d	1/3	2/3	0.3755(6)	0.80	0.0183(9)	0.017(1)	0.017(1)	0.020(1)	0	0	0.0086(6)
S1	2d	1/3	2/3	0.755(1)	1	0.0088(9)	0.004(1)	0.004(1)	0.017(2)	0	0	0.0022(7)
$Lu_{0.67}Cu_2S_2$												
Lu	1a	0	0	0	0.67	0.0101(4)	0.0097(4)	0.0097(4)	0.0108(5)	0	0	0.0049(2)
Cu	2d	1/3	2/3	0.6279(2)	1	0.0220(4)	0.0210(5)	0.0210(5)	0.0238(7)	0	0	0.0105(3)
S	2d	1/3	2/3	0.2432(4)	1	0.0101(5)	0.0097(7)	0.0097(7)	0.011(1)	0	0	0.0049(4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.
The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+\cdots+2hka^*b^*U_{12}]$.

Table 4
Atomic coordinates and anisotropic displacement factors for $Gd_{0.75}Cu_{1.74}Te_2$, $TbCuTe_2$, $DyCuTe_2$, $Tm_{1.07}Cu_{0.78}Te_2$, $LuCuTe_2$.

Atom	Position	x/a	y/b	z/c	Occupancy	U_{eq}, Å^2	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$Gd_{0.75}Cu_{1.74}Te_2$												
Gd1	2c	1/3	2/3	0	1	0.0167(4)	0.0158(5)	0.0158(5)	0.0185(7)	0	0	0.0079(3)
Gd2	1a	0	0	0	0.26	0.024(1)	0.026(2)	0.026(2)	0.020(3)	0	0	0.013(1)
Cu	6k	0.3565(4)	0	0.3720(4)	0.87	0.0319(8)	0.026(1)	0.034(1)	0.037(1)	0	0.0002(9)	0.0172(8)
Te	6k	0.6811(1)	0	0.2522(1)	1	0.0194(4)	0.0200(5)	0.0160(6)	0.0206(6)	0	−0.0053(3)	0.0080(3)
$TbCuTe_2$												
Tb1	2c	0	0	0.2605(1)	1	0.0308(7)	0.0347(9)	0.0347(9)	0.022(1)	0	0	0.0174(5)
Tb2	12j	0.50286(6)	0.49714(6)	0.24595(8)	1	0.0109(4)	0.0094(6)	0.0094(6)	0.0149(6)	−0.0012(2)	0.0012(2)	0.0054(5)
Cu1	2d	1/3	2/3	−0.0719(3)	1	0.014(1)	0.015(1)	0.015(1)	0.012(2)	0	0	0.0080(3)
Cu2	12j	0.6682(5)	0.8341(2)	−0.4290(3)	0.77	0.020(1)	0.013(2)	0.018(2)	0.028(2)	−0.0016(8)	−0.003(1)	0.006(1)
Cu3	12j	0.340(2)	0.170(1)	−0.0713(9)	0.23	0.035(4)	0.046(9)	0.046(7)	0.012(6)	0.007(3)	0.015(6)	0.023(5)
Te1	2d	1/3	2/3	0.1210(1)	1	0.0141(7)	0.0151(9)	0.0151(9)	0.012(1)	0	0	0.0076(5)
Te2	12j	0.1715(1)	0.3431(1)	0.3802(1)	1	0.0128(5)	0.0128(7)	0.0121(9)	0.0131(8)	0.0002(6)	0.0001(3)	0.0061(4)
Te3	12j	0.3238(1)	0.16193(9)	0.1182(1)	1	0.0139(5)	0.0087(8)	0.0157(7)	0.0148(8)	−0.0003(3)	−0.0007(6)	0.0043(4)
Te4	2d	2/3	1/3	0.3830(1)	1	0.0151(7)	0.0148(9)	0.0148(9)	0.015(1)	0	0	0.0074(5)
$DyCuTe_2$												
Dy1	2c	0	0	0.2600(1)	1	0.0267(6)	0.0272(8)	0.0272(8)	0.025(1)	0	0	0.0136(4)
Dy2	12j	0.50311(6)	0.49689(6)	0.24616(7)	1	0.0122(5)	0.0097(6)	0.0097(6)	0.0186(7)	−0.0012(1)	0.0012(1)	0.0058(4)
Cu1	2d	1/3	2/3	0.9293(3)	1	0.020(1)	0.021(1)	0.021(1)	0.020(2)	0	0	0.0106(8)
Cu2	12j	0.6682(4)	0.8341(2)	−0.4299(3)	0.72	0.018(1)	0.012(1)	0.015(1)	0.027(2)	−0.0024(7)	−0.0048(15)	0.0063(9)
Cu3	12j	0.338(1)	0.1692(8)	−0.0705(8)	0.28	0.044(3)	0.062(8)	0.056(5)	0.016(6)	0.009(3)	0.018(5)	0.031(4)
Te1	2d	1/3	2/3	0.1215(1)	1	0.0140(7)	0.0149(8)	0.0149(8)	0.012(1)	0	0	0.0074(4)
Te2	12j	0.17138(8)	0.3427(1)	0.3797(1)	1	0.0129(5)	0.0119(7)	0.0115(8)	0.0151(9)	0.0005(5)	0.0002(3)	0.0057(4)
Te3	12j	0.3241(1)	0.16208(8)	0.1187(1)	1	0.0134(5)	0.0079(8)	0.0146(7)	0.0156(9)	−0.0005(3)	−0.0010(5)	0.0040(4)
Te4	2d	2/3	1/3	0.3826(1)	1	0.0146(7)	0.0137(8)	0.0137(8)	0.016(1)	0	0	0.0068(4)
$Tm_{1.07}Cu_{0.78}Te_2$												
Tm1	1a	0	0	0	1	0.0183(6)	0.0125(7)	0.0125(7)	0.030(1)	0	0	0.0062(3)
Tm2	1b	0	0	1/2	0.07	0.038(7)	0.03(1)	0.03(1)	0.03(1)	0	0	0.019(5)
Cu	2d	1/3	2/3	0.637(1)	0.39	0.021(2)	0.020(3)	0.020(3)	0.023(5)	0	0	0.010(1)
Te	2d	1/3	2/3	0.2571(2)	1	0.0142(6)	0.0127(7)	0.0127(7)	0.017(1)	0	0	0.0063(3)
$LuCuTe_2$												
Lu1	1a	0	0	0	0.765(7)	0.0210(9)	0.015(1)	0.015(1)	0.031(1)	0	0	0.0079(5)
Lu2	1b	0	0	1/2	0.235(7)	0.025(2)	0.023(3)	0.023(3)	0.029(5)	0	0	0.011(1)
Cu1	2d	2/3	1/3	0.371(2)	0.31(1)	0.049(5)	0.058(7)	0.058(7)	0.03(1)	0	0	0.029(4)
Cu2	2d	2/3	1/3	0.096(7)	0.19(1)	0.08(1)	0.07(1)	0.07(1)	0.10(3)	0	0	0.036(8)
Te	2d	1/3	2/3	0.2554(3)	1	0.0220(8)	0.0177(9)	0.0177(9)	0.030(1)	0	0	0.0089(4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.
The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+\cdots+2hka^*b^*U_{12}]$.

Table 5
Interatomic distances (δ, Å) and coordination numbers (C.N.) of the R and Cu atoms in the $Ho_{0.67}Cu_2S_2$, $Yb_{0.80}Cu_{1.60}S_2$ and $Lu_{0.67}Cu_2S_2$ compounds.

Atoms		δ, Å			C.N.
		$Ho_{0.67}Cu_2S_2$	$Yb_{0.80}Cu_{1.60}S_2$	$Lu_{0.67}Cu_2S_2$	
R	−6S	2.747(4)	2.707(3)	2.712(1)	6
Cu	−3S	2.376(2)	2.379(2)	2.378(1)	4
	−1S	2.432(7)	2.386(7)	2.433(3)	

Table 6
Interatomic distances (δ, Å) and coordination numbers (C.N.) of the R and Cu atoms in the $Tm_{1.07}Cu_{0.78}Te_2$ and $LuCuTe_2$ compounds.

Atoms		δ, Å		C.N.
		$Tm_{1.07}Cu_{0.78}Te_2$	$LuCuTe_2$	
$R1$	−6Te	3.033(1)	3.026(1)	6
$R2$	−6Te	2.977(1)	2.983(1)	6
Cu(Cu1)	−3Te	2.566(3)	2.585(5)	4
	−1Te	2.623(9)	2.582(1)	
Cu2	−1Te	–	2.42(5)	4
	−3Te	–	2.70(2)	

Table 7
Interatomic distances (δ, Å) and coordination numbers (C.N.) of the R and Cu atoms in the $TbCu_3S_3$ and $Dy_{1.06}Cu_{2.84}S_3$ compounds.

Atoms		δ, Å		C.N.
		$TbCu_3S_3$	$Dy_{1.06}Cu_{2.84}S_3$	
$R1$	−6S	2.750(2)	2.733(2)	6
$R2$	−6S	2.760(2)	2.745(2)	6
Cu	−1S	2.365(2)	2.362(2)	4
	−1S	2.372(2)	2.366(2)	
	−1S	2.393(2)	2.389(2)	
	−1S	2.434(3)	2.423(3)	

Table 8
Interatomic distances (δ, Å) and coordination numbers (C.N.) of the R and Cu atoms in the $ErCu_3S_3$ compound.

Atoms		δ, Å	C.N.
Er1	−6S	2.712(2)	6
Er2	−6S	2.742(2)	6
Er3	−6S	2.723(2)	6
Cu	−1S	2.344(2)	4
	−1S	2.377(2)	
	−1S	2.391(2)	
	−1S	2.431(3)	

Table 9
Interatomic distances (δ, Å) and coordination numbers (C.N.) of the R and Cu atoms in the $Gd_{0.75}Cu_{1.74}Te_2$ compound.

Atoms		δ, Å	C.N.
Gd1	−6Te	3.1027(9)	6
Gd2	−6Te	2.969(1)	6
Cu	−1Te	2.569(3)	4
	−1Te	2.651(3)	
	−2Te	2.672(2)	

Table 10
Interatomic distances (δ, Å) and coordination numbers (C.N.) of the R and Cu atoms in the $TbCuTe_2$ and $DyCuTe_2$ compounds.

Atoms		δ, Å		C.N.
		$TbCuTe_2$	$DyCuTe_2$	
$Tb1$	−3Te2	3.054(1)	3.048(1)	6
	−3Te3	3.121(2)	3.112(1)	
$Tb2$	−1Te1	3.068(1)	3.067(1)	6
	−2Te3	3.068(1)	3.061(1)	
	−1Te4	3.098(1)	3.088(1)	
	−2Te2	3.099(1)	3.093(1)	
$Cu1$	−3Te3	2.641(1)	2.641(1)	4
	−1Te1	2.673(5)	2.664(5)	
$Cu2$	−1Te4	2.583(4)	2.584(3)	4
	−2Te2	2.612(2)	2.612(1)	
	−1Te2	2.643(4)	2.639(4)	
$Cu3$	−1Te1	2.53(1)	2.55(1)	4
	−2Te3	2.568(9)	2.563(8)	
	−1Te3	2.62(1)	2.62(1)	

trigonal one of $CaAl_2Si_2$. Selenium atoms in the structure of $ScCuSe_2$ are also stacked in a close-packed arrangement with layers in the sequence AB and the similar occupation of the octahedral and tetrahedral interstices of Sc and Cu atoms respectively was observed. Additional ordering of the positions of the Cu atoms and vacancies are observed in $ScCuSe_2$ when compared with $CaAl_2Si_2$ structure type.

The compounds of the R_2X_3–Cu_2X (R–rare earth, X–S, Se, Te) systems can be divided into two main subgroups:

(1) the compounds formed rare earth elements with larger ionic radii (La–Nd, Sm, Gd, Tb).
(2) the compounds formed rare earth elements with smaller ionic radii (Gd–Lu).

The surroundings of the rare earth and Cu atoms should be simply explained according to principles described by Pauling [14]. Each Cu atom is surrounded by four X atoms formed tetrahedron in the structures of the compounds of both subgroups. Each rare earth atom with larger ionic radii (first subgroup) is surrounded by 7X atoms formed mono-capped trigonal prism. Each rare earth atoms with smaller ionic radii (second subgroup) is surrounded by 6X atoms formed octahedron. The compounds of the first subgroup crystallize with the $LaCuS_2$ type of structure (space group $P2_1/c$). These compounds are realized at the composition $RCuX_2$ (X–S, Se) [15–19]. The crystal structures of the compounds of the second subgroup are realized according to following principles: the X atoms are stacked in a close packed arrangement, whereas the R atoms are distributed over octahedral interstices and Cu atoms are located in tetrahedral interstices. The crystal structure of earlier reported $RCuS_2$ (R—Y, Dy–Lu) compounds (space group $Pnma$) [20,21] should be described in similar
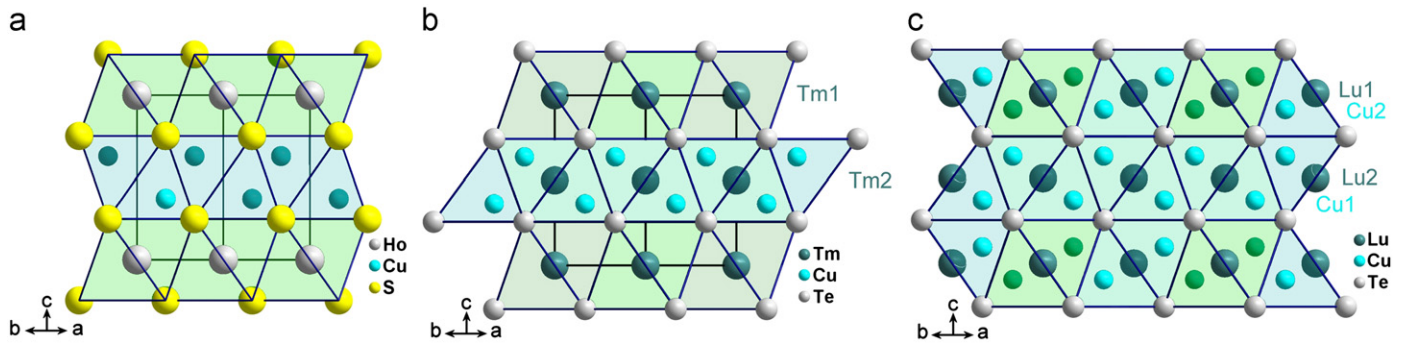
The crystal structure of the $TbCuTe_2$ and $DyCuTe_2$ compounds (Fig. 3a) represents a distinctive $2a \times 2a \times 2c$ superstructure to the compounds with $CaAl_2Si_2$ structure type. Separate layers of the R-centered octahedra and Cu-centered tetrahedra along c axis are observed in the structure of these compounds. The ordering of the positions of the Cu atoms is observed during the formation of superstructures.

The crystal structure of the $ScCuSe_2$ compound ($C2/m$) has been recently investigated in Ref. [13] (Fig. 3b). This compound forms also a superstructure to the compounds with $CaAl_2Si_2$ structure type. A unit cell of $ScCuSe_2$ is eight times larger than

Fig. 1. The packing of R-centered octahedra and Cu-centered tetrahedra in the structures of $Ho_{0.67}Cu_2S_2$ (a), $Tm_{1.07}Cu_{0.78}Te_2$ (b) and $LuCuTe_2$ (c).
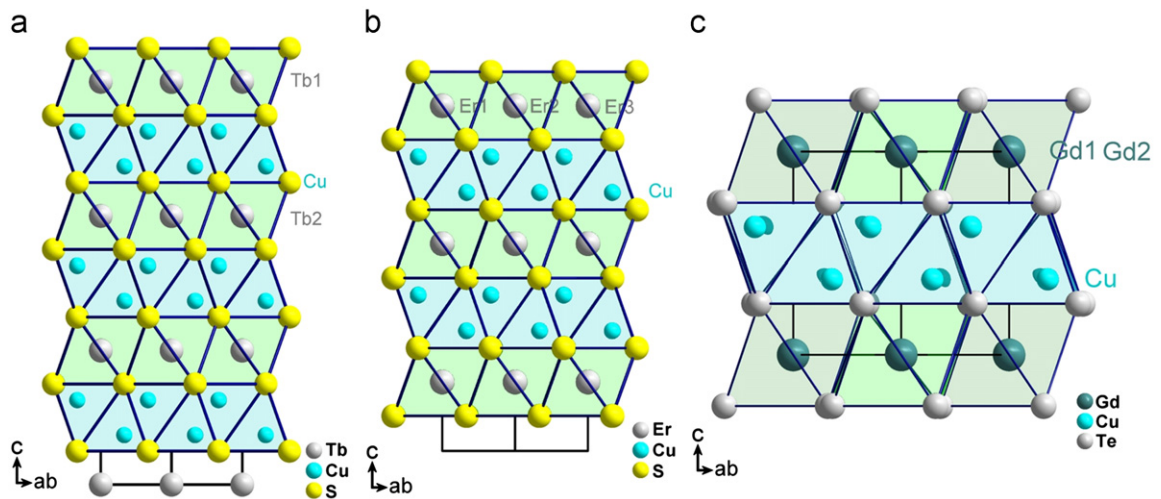

Fig. 2. The packing of R-centered octahedra and Cu-centered tetrahedra in the structures of $TbCu_3S_3$ (a), $ErCu_3S_3$ (b) and $Gd_{0.75}Cu_{1.74}Te_2$ (c).
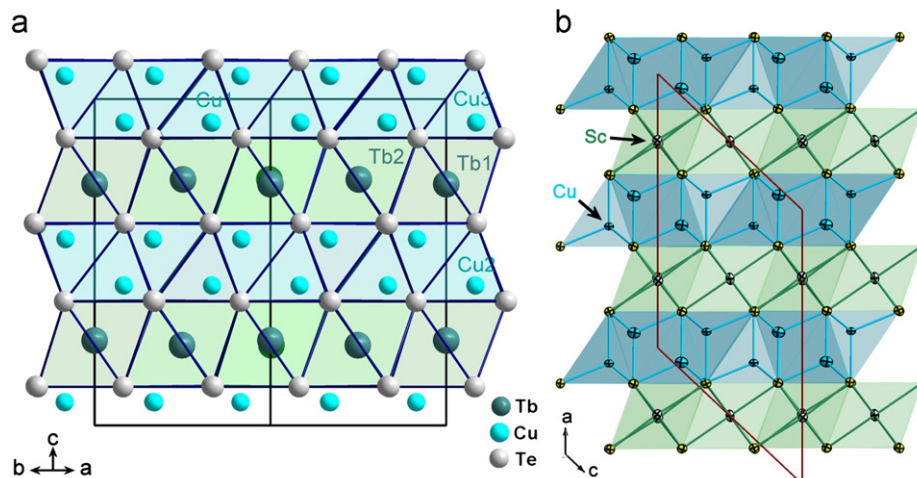

Fig. 3. The packing of Tb-centered octahedra and Cu-centered tetrahedra in the structure of $TbCuTe_2$ (a) and Sc-centered octahedra and Cu-centered tetrahedra in the structure of $ScCuSe_2$ [13] (b).

way. The S atoms are stacked in a close packed arrangement with the layers in the sequence AB. A half of octahedral interstices are filled by R atoms and 1/4 of tetrahedral interstices are occupied by Cu atoms. Similar principles are realized in the structure of the $R_7Cu_3Te_{12}$ (R—Y, Tb–Tm) compounds (space group $R\bar{3}m$) [22,23]. The close packed Te layers in …$hhcc$… stacking exists in the crystal structure of the $R_7Cu_3Te_{12}$ (R=Tb, Dy, Ho, Er and Tm)

compounds. The R atoms occupy 7/12 of octahedral interstices, whereas the Cu atoms occupy 1/8 of tetrahedral interstices.

As it was described above all investigated in present work compounds are distributed between the compositions $R_{2/3}Cu_2X_2$–$RCuX_2$. For the compounds with the simplest $CaAl_2Si_2$ structure type (space group $P\bar{3}m1$) one position of R(1a Wyckoff position) and one position of Cu(2d Wyckoff position) exist. The position of

R is ordered and the position of Cu is disordered at the composition $RCuX_2$. The position of R is disordered and the position of Cu is ordered at the composition $R_{2/3}Cu_2X_2$. The positions of both atoms are disordered at the intermediate compositions.

The formation of superstructures with ordering of the metal and vacancy positions was observed earlier (see for example Zr_5Te_6 [24], Ni_3Te_2 [25], Cu_4Al_3 [26,27]). In the case of the studied compounds the formation of the particular superstructure is connected with the ordering of the positions of R and Cu atoms. The following possibilities are observed:

(1) *The compounds with the composition $RCuX_2$.* The position of R is ordered and the position of Cu is disordered for the compounds of $CaAl_2Si_2$ structure type (for example, $RCuSe_2$ (R–Gd–Lu) [9]). All positions of R are ordered and two of three positions of Cu are disordered in the structure of $TbCuTe_2$ and $DyCuTe_2$.

(2) *The compounds with the composition $R_{2/3}Cu_2X_2$.* The position of R is disordered, whereas the position of Cu is ordered for the compounds of $CaAl_2Si_2$ structure type (for example, $Lu_{0.67}Cu_2S_2$ [present work]). One of three positions of Er and one position of Cu are ordered in the structure of $ErCu_3S_3$. Also, one of two positions of Tb and one position of Cu are ordered in the structure of $TbCu_3S_3$.

(3) *The compounds with the intermediate composition.* The positions of R and Cu are disordered for the compounds of $CaAl_2Si_2$ structure type (for example $Yb_{0.80}Cu_{1.60}S_2$ [present work]). One of two positions of Gd and one position of Cu are disordered in $Gd_{0.75}Cu_{1.74}Te_2$. In the same manner the crystal structure of $Dy_{1.06}Cu_{2.84}S_3$ is formed.

Supplementary information

Further details of the crystal-structure investigation(s) may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number(s) CSD-423552 ($TbCu_3S_3$), CSD-423551 ($Dy_{1.06}Cu_{2.84}S_3$), CSD-423550 ($Ho_{0.67}Cu_2S_2$), CSD-423553 ($ErCu_3S_3$), CSD-423549 ($Yb_{0.80}Cu_{1.60}S_2$), CSD-423548 ($Lu_{0.67}Cu_2S_2$), CSD-423544 ($Gd_{0.75}Cu_{1.74}Te_2$), CSD-423554 ($TbCuTe_2$), CSD-423545 ($DyCuTe_2$), CSD-423546 ($Tm_{1.07}Cu_{0.78}Te_2$), CSD-423547 ($LuCuTe_2$), (http://www.fiz-karlsruhe.de/).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.12.004.

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