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1 Stability investigation of Se- and Te-substituted tetrahedrite

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7

8 DFT (density functional theory) and QTAIM (quantum theory of atoms in molecules)
9 calculations have been performed to investigate the influence of Se and Te substitutions on
10 the stability of tetrahedrite. The formation energies, the laplacian of the electron density, the
11 total and local volume changes and the site charges ones have been determined. The DFT
12 results show that the single atom substitution is the most preferred one and that selenium is
13 preferred for sulphur replacement whereas antimony can be equally replaced by selenium and
14 tellurium. However as selenium substitutes for either sulphur or antimony, QTAIM
15 calculations evidenced large structural and chemical changes in the structures. Additional
16 experimental results, in agreement with QTAIM ones, allow us to conclude that the
17 investigation of alloys stability can not be limited to DFT calculations of formation energies
18 and total volume changes. QTAIM appears as a valuable complementary method to get
19 information on phase stabilities.

20 **Key words:** Cu-Sb-S system; substituted tetrahedrite; phase stability; DFT; QTAIM

21

22 INTRODUCTION

23 Copper antimony chalcogenides have high potentialities as semiconductors for electro-
24 optic devices, thermoelectric devices, optical recording media and sustainable solar cell. As
25 examples we can mention Cu_3SbSe_3 which has enormously drawn attention of the researchers
26 in the thermoelectric field because of its ultra-low lattice thermal conductivity, and the Cu-Sb-
27 S compounds that are modern state-of-the-art thermoelectric materials for midtemperature
28 heat-to-power conversion with the advantage of being environmental friendly. The
29 thermoelectric figure of merit zT for many doped and natural tetrahedrite materials
30 ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) gets close to unity at 450°C ; this value is comparable to that of conventional p-
31 type TE materials. However because of the complexity of the Cu-Sb-S phase diagram around
32 the $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ composition, these materials are always constituted of several phases for
33 which the proportions generally differ from a sample to another one. The large scale use of
34 tetrahedrite for thermoelectric applications necessitates the mastering of the properties and
35 thus the mastering of the material constitution. A way could be to extend the composition
36 range of the tetrahedrite stability. To reach this goal, we investigated the stability of various
37 substituted tetrahedrites in which S atoms were replaced by Se and/or Te ones. This work was
38 mainly carried out by coupled DFT and QTAIM calculations and complemented by some
39 experiments.

40

41 THE Cu-Sb-S SYSTEM

42 Information on the constitutive binary systems Sb-S, Cu-S and Cu-Sb can be found in
43 Ref. 1-6, Ref. 7-8 and Ref. 9-11, respectively. The Sb-S phase diagram only shows one
44 condensed stable binary phase Sb_2S_3 (stibnite) with a congruent melting and two regions of
45 liquid immiscibility. The Cu-S binary system contains three intermediate phases, namely
46 Cu_2S (chalcocite), Cu_9S_5 (digenite) and CuS (covellite) and a solid solution between digenite

47 and chalcocite extending from 83 to 1129°C. Numerous phases have also been identified at
48 low temperatures (<103°C) but considerable uncertainties still remain both on the stability
49 range of the digenite and on the temperatures of phase transitions in the low temperature
50 range. Moreover no studies on the stability of the new minerals as roxbyite ($\text{Cu}_{1.78}\text{S}$), geerite
51 ($\text{Cu}_{1.6}\text{S}$) and spionkopite ($\text{Cu}_{1.4}\text{S}$) have been performed. There are several intermediate phases
52 in the Cu-rich region but only two (δ and η) exist at room temperature.

53 Phase stability and phase relations in the Cu-Sb-S ternary system have been studied by
54 numerous authors.^{3,12-19} There are four compounds in the Cu-Sb-S ternary system, namely
55 CuSbS_2 (chalcostibite), Cu_3SbS_3 (skinnerite), Cu_3SbS_4 (famatinitite), and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$
56 (tetrahedrite). Chalcostibite, CuSbS_2 , forms readily by reaction from the elements and did not
57 show any composition range.³ By contrast, Golovei *et al.*²⁰ found a homogeneity range for
58 CuSbS_2 and a polymorphic transformation. Skinnerite was first reported by Godolikov *et al.*¹⁷
59 who prepared it by sintering Cu_2S and Sb_2S_3 at 480°C and 530°C. It has the ideal composition
60 of Cu_3SbS_3 with a small composition field along the line $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ at 500°C. Karup-Møller
61 *et al.*²¹ have found these ore aggregates crystallized at about 400°C from metal-rich residual
62 magmatic fluids markedly deficient in sulfur. Cu_3SbS_3 is stable in the Cu-Sb-S system in the
63 temperature range 359-607°C. Below 359°C this phase decomposes into a mixture of native
64 antimony, chalcostibite and tetrahedrite,³ but if it is cooled slowly, it decomposes to give a
65 mixture of tetrahedrite, antimony and digenite.²² At 607°C, Cu_3SbS_3 congruently melts.
66 Pfitzner²³ have investigated both the high and low-temperature phases. The high-temperature
67 modification is disordered and stable above 122°C, and is supposed to show high copper ion
68 conductivity or at least a high copper diffusion coefficient. The low-temperature form is
69 ordered and stable below -9°C. Famatinitite, Cu_3SbS_4 , derived from sphalerite, melts
70 congruently at 627°C, and is not known to have any stable polymorph forms.³ The only
71 compound with an extensive composition field in the Cu-Sb-S system is tetrahedrite. The

72 basic structure of minerals of the tetrahedrite group was solved by Pauling and Newman²⁴ and
73 now the widely accepted formula $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ represented its composition. As for the Pauling
74 and Neuman formula, $\text{Cu}_{12+x}\text{Sb}_{4+y}\text{S}_{13}$, where $0 \leq x \leq 1.92$ and $-0.02 \leq y \leq 0.27$, there is no clear
75 evidence so far proving the substitution schemes implied in this formula are correct.²⁴ Cambi
76 and Elli¹⁴ have given an extreme composition range for tetrahedrites going from $4\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$
77 to $3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ (i.e. $\text{Cu}_8\text{Sb}_2\text{S}_7$ to Cu_3SbS_3). Since Skinner *et al.*³ have not managed to prepare
78 a single homogenous phase with the composition $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, they believed that this phase has
79 a stability temperature range below 300°C. These authors also found that the unit cell edges
80 of tetrahedrite decrease with the sulfur content. Tatsuka and Morimoto²⁵ reported the
81 formation of pseudo-tetrahedrite (T'_3) which is stable between 250 and 350°C and is a
82 superlattice of $\text{Cu}_{12+x}\text{Sb}_{4+y}\text{S}_{13}$ (T_3) (lattice parameter of T'_3 is twice that of T_3). Along the
83 Cu_2S - Sb_2S_3 section reported by Chang *et al.*,²⁶ the composition of pseudo-tetrahedrite ranges
84 from Cu_3SbS_3 to $\text{Cu}_{12.39}\text{Sb}_{4.54}\text{S}_{13}$. Below 250°C, a prolonged annealing of T_3 or T'_3 results in
85 a phase mixture consisting of Cu_3SbS_4 , Cu_{2-x}S and Sb. Makowicky and Skinner²⁷ have
86 confirmed that tetrahedrite has two room-temperature phases Cu-poor phase $\text{Cu}_{12.3}\text{Sb}_4\text{S}_{13}$ and
87 Cu-rich phase $\text{Cu}_{13.8}\text{Sb}_4\text{S}_{13}$ produced by a low-temperature exsolution of tetrahedrite
88 $\text{Cu}_{12.59}\text{Sb}_{4.03}\text{S}_{13}$. However when melts, whose compositions lie near that of tetrahedrite, are
89 cooled at the rate of 50-100°C/h, instead of separation of the phase Cu_3SbS_3 , metastable solid
90 tetrahedrite solutions crystallize out and then decompose to phases with a complex structure,
91 which are absent in the phase diagram.²⁸ The crystal structure of stoichiometric tetrahedrite
92 $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ was determined for the first time by Skinner *et al.*³ There is no phase transitions
93 for $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ up to 300°C, and the two exsolution phases $\text{Cu}_{12.3}\text{Sb}_4\text{S}_{13}$ and $\text{Cu}_{13.8}\text{Sb}_4\text{S}_{13}$
94 show a high copper-ion mobility even at room temperature. According to [29] tetrahedrite is
95 stable from $4\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ to Cu_3SbS_3 at 300°C and from $4\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ to $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ at 400°C.
96 Whereas Skinner *et al.*³ reported above 500°C a rapid shrinkage of the composition range for

97 tetrahedrite followed by its decomposition into $\text{Cu}_3\text{Sb}_1\text{S}_4$, Cu_3SbS_3 and Cu_xS (x going from
 98 1.6 to 2) at 543°C , Il'yasheva²⁸ evidenced an incongruent melting for this phase at $574\pm 2^\circ\text{C}$.
 99 All the ternary phases are stable at 500°C .

100 The crystallographic data and the thermodynamic properties of the ternary solid
 101 phases are given in Table 1 and Table 2, respectively.

102

Table I. Crystallographic data of the Cu-Sb-S ternary solid phases

Phase / Name	Crystal system	Space group	Lattice parameters (pm)	Reference
Cu_3SbS_4 /Famatinite	Tetragonal	I-42m	$a=538.5, c=1075.4$	[30]
CuSbS_2 /Chalcostibite	Orthorhombic	Pnma	$a=601.8, b=379.58, c=1449.5$	[32]
$\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ /Tetrahedrite	Cubic	I-43m	$a=1032.4$	[32]
Cu_3SbS_3 /Skinnerite	Monoclinic	$P2_1/c$	$a=781.5, b=1025.2, c=1327.0$	[33]

103

Table II. Thermodynamic properties of the Cu-Sb-S ternary solid phases from Ref. 34

Phase	Temperature	$\Delta_f G^0$ (J/mol of atoms)	$\Delta_f H^0$ (J/mol of atoms)	S^0 (J/K.mol of atoms)
Cu_3SbS_4	25°C	-207500 ± 3900	-200000 ± 6300	298 ± 18
CuSbS_2	25°C	-121400 ± 3400	-119000 ± 3500	148 ± 6.4
Cu_3SbS_3	25°C	-197800 ± 3800	-189300 ± 6500	269.5 ± 13.7

104

105 **SUBSTITUTED TETRAHEDRITE: COMPUTATIONAL PART**

106 **Computational details**

107 The calculations have been performed in the frame of the density-functional theory^{35,36}
108 using the gradient-corrected Perdew–Burke–Ernzerhof (PBE) exchange-correlation
109 functionals.³⁷ All the structures have been relaxed to their equilibrium state and the energy
110 and force thresholds have been fixed to 10^{-7} Ry and 10^{-4} Ry.bohr⁻¹, respectively. The projector
111 augmented wave (PAW) method³⁸ has been used to treat nucleus and core and valence
112 electrons interactions with cutoffs 48 Ry for the energy and 480 Ry for the density. A 4x4x4
113 k-point mesh has been utilized. The Quantum Espresso program package has been used for
114 these calculations.³⁹

115 The analysis of the bonding structure of the alloys has been performed using Bader's
116 quantum theory of atoms in molecule⁴⁰ as implemented in the Critic2 program.⁴¹

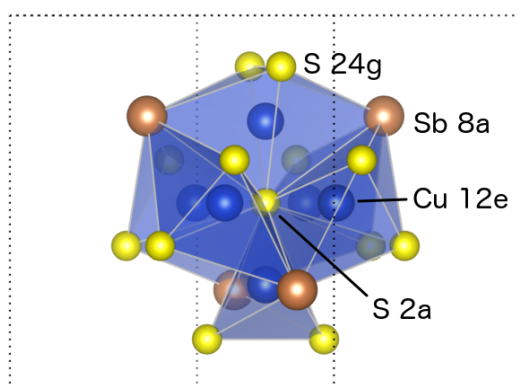
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118 **Crystalline description of the tetrahedrite**

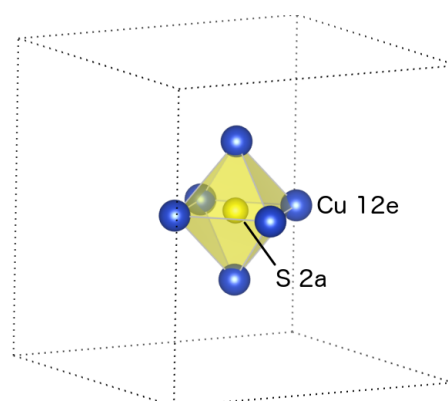
119 The tetrahedrite crystal structure with stoichiometric formula $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ is composed
120 of two formula units and belongs to the body-centered cubic Bravais lattice with group
121 number 217 (I-43m). It contains 29 atoms in the irreducible lattice located at five
122 crystallographic sites. Copper atoms are in the two distinct Wyckoff positions (WP) 12e and
123 12d. Cu 12e is at the centre of a triangle formed by three sulphur atoms (two S in 24g WP and
124 one S in 2a WP) and the assembly constitutes a trigonal plane. If one includes two antimony
125 atoms on either sides of the plane the assembly is a trigonal bipyramid (Fig. 1a). It is noted
126 that the Cu-Sb bond distance of this trigonal bipyramid is rather large with 3.536 Å and the
127 Cu-S ones amount to 2.246 Å and 2.250 Å. It has been reported that, the weak bonding
128 between Cu and Sb leads to soft vibrational modes of Cu having large anisotropic thermal
129 motion, which could explain the low thermal conductivity of the tetrahedrite.^{32,42} Six Cu

130 atoms in 12e WP are located nearby the centre of the lattice forming an octahedron around a
 131 sulphur atom in 2a Wyckoff position (Fig. 1b). The additional six Cu 12e atoms are located at
 132 the cube edges nearby the lattice corners occupied by S 2a atoms. Copper atoms in 12d WP
 133 form a tetrahedral arrangement with four sulphur atoms in 24g WP. They are located on the
 134 cube faces and form a square assembly with three other Cu atoms in 12d WP (Fig. 1c). The
 135 corresponding Cu-Cu distance is as large as 3.650 Å. The Cu-S distances are 2.311 Å and the
 136 S-Cu-S angles amount to 111.5°. As just mentioned the sulphur atoms in the 2a WP are
 137 located both at the corner and at the centre of the cubic lattice, and are at the centre of a
 138 regular octahedron formed with the Cu atoms in 12e WP (Fig. 1b). The Cu-S bond distances
 139 are 2.250 Å. Sulphur atoms occupying the 24g WP form a distorted tetrahedron with their
 140 neighbours, that are one Sb, two Cu 12d and one Cu 12e atoms, with bond distances of 2.452
 141 Å, 2.311 Å and 2.246 Å, respectively (Fig. 1d). The antimony atoms are located in sites 8c
 142 and are surrounded by three sulphur 24g atoms, forming a pyramidal arrangement. As
 143 mentioned above the antimony atoms constitute the apex of a trigonal bipyramid for which Cu
 144 is the centre. It is noted that the height of the pyramid made of Sb and three S atoms is not
 145 aligned with that of the trigonal bipyramid but is tilted by 35.3°. The three Sb-S bond lengths
 146 equal 2.452 Å and the angles are 95.7°.

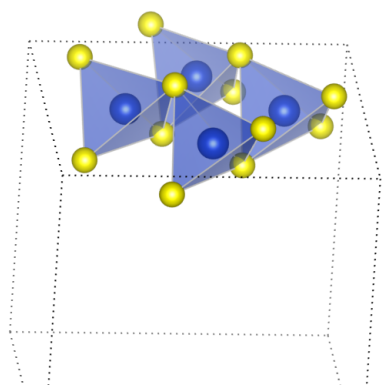
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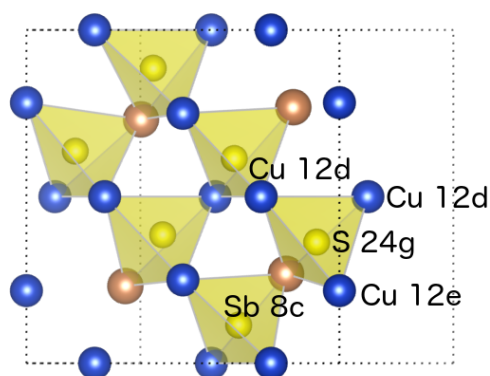
a) Copper 12e at the centre of a trigonal bipyramid with S 2a, S 24g and Sb 8c at the apex.



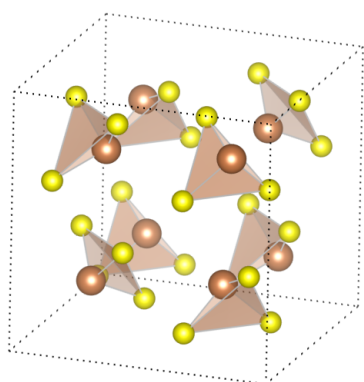
b) Sulphur 2a at the centre of the lattice and at the center of an octahedron formed by six Cu 12e.



c) Copper *12d* arranged in square at the lattice face. They are located at the centre of a tetrahedron with S *24g* at the apex.



d) Sulphur *24g* in the centre of a distorted tetrahedron formed by two Cu *12d* (at the lattice face), one Cu *12e* (at the lattice edge) and one Sb *8c*.



e) Antimony at the apex of a tetrahedron formed with three sulphur *24g* atoms

148 Fig. 1: Structural features of the tetrahedrite. a) Environment of copper in *12e* Wyckoff
 149 position (WP); b) Environment of sulphur in *2a* WP; c) Environment of copper in *12d* WP; d)
 150 Environment of sulphur in *24g* WP; e) Environment of antimony in *8c* WP.

151

152 Procedure

153 The substituting elements considered in this work are Se and Te. The substituted
 154 atoms have been chosen as S and Sb ; S as a chalcogen and Sb since its replacement by Te has
 155 been evidenced in natural tetrahedrite.⁴³ As neither $\text{Cu}_{12}\text{Sb}_4\text{Se}_{13}$ nor $\text{Cu}_{12}\text{Sb}_4\text{Te}_{13}$ have been

156 reported in literature, in order to preclude a too big distorsion of the cell only the substitutions
 157 by one and two atoms per cell have been examined. The investigated compositions are the
 158 following ones : $\text{Cu}_{12}\text{Sb}_4\text{S}_{12.5}\text{Se}_{0.5}$, $\text{Cu}_{12}\text{Sb}_4\text{S}_{12}\text{Se}_1$,
 159 $\text{Cu}_{12}\text{Sb}_{3.5}\text{Se}_{0.5}\text{S}_{13}$, $\text{Cu}_{12}\text{Sb}_3\text{Se}_1\text{S}_{13}$, $\text{Cu}_{12}\text{Sb}_4\text{S}_{12.5}\text{Te}_{0.5}$, $\text{Cu}_{12}\text{Sb}_4\text{S}_{12}\text{Te}_1$, $\text{Cu}_{12}\text{Sb}_{3.5}\text{Te}_{0.5}\text{S}_{13}$,
 160 $\text{Cu}_{12}\text{Sb}_3\text{Te}_1\text{S}_{13}$. The atom replacements on all the crystallographic sites (2a and 24g for S, 8c
 161 for Sb) have been envisaged. For 2 Te or Se atoms substitutions in the case of sulphur, three
 162 possible situations have been considered: 2 atoms at site S 24g, one atom at site S 24g and the
 163 other at site S 2a, and 2 atoms at site S 2a. For 2 Te or Se atoms substitutions in the case of
 164 antimony, since in pure tetrahedrite the eight antimony atoms form a somewhat distorted cube
 165 (hereafter called pseudo-cube) inside the cubic lattice, three possibilities have been
 166 considered: two atoms along the pseudo-cube edge, two atoms along the face diagonal of the
 167 pseudo-cube and 2 atoms along the principal diagonal of the pseudo-cube. The stability of the
 168 phases have been investigated by determining both the formation energies of the alloys using
 169 DFT calculations and the total and local volume changes using QTAIM ones.

170 The formation energies have been determined from the energies E calculated by DFT
 171 according to the following formula:

$$172 \quad \Delta E_f = \frac{E(\text{Cu}_x\text{Sb}_y\text{S}_z\text{X}_t) - xE(\text{Cu}) - yE(\text{Sb}) - zE(\text{S}) - tE(\text{X})}{x+y+z+t} \quad (1)$$

173 Recalling that the number of formula in the unit cell of tetrahedrite is 2, a one-atom sulphur
 174 and antimony substituted tetrahedrite on the one hand and a two-atoms sulphur and antimony
 175 substituted tetrahedrite on the other hand correspond to $\text{Cu}_{12}\text{Sb}_4\text{S}_{12.5}\text{X}_{0.5}$, $\text{Cu}_{12}\text{Sb}_{3.5}\text{X}_{0.5}\text{S}_{13}$, and
 176 $\text{Cu}_{12}\text{Sb}_4\text{S}_{12}\text{X}$, $\text{Cu}_{12}\text{Sb}_3\text{XS}_{13}$, respectively.

177

178

179

180

181 **Results**

182 *Formation energies and total lattice volume changes*

183 **Substitutions of Se and Te for S.** The calculated values are given in Table 3. For a
184 single substitution, both selenium and tellurium atoms prefer occupying site *24g*, the
185 formation energies being -160.7 and -151.6 meV/atom respectively. The substitution at site
186 *2a* is much less favourable by about 8 meV/atom. This preference for the *24g* site has already
187 been experimentally evidenced for Se by Lu et al.⁴⁴ For two Te or Se atoms substitutions as
188 mentioned above three possible situations have been envisaged: two atoms at site S *24g*, one
189 atom at site S *24g* and the other at site S *2a*, and 2 atoms at site S *2a*. For the two former
190 possibilities we observe that for a given substituting atom the energies are very close and
191 actually lie in the error bar that we estimate to be 3-4 meV/atom. The 2-atoms substitution at
192 site *2a* is the least preferential one for both Se and Te. We note that, the substitution with
193 selenium is more preferred than that with tellurium, as the formation reactions pertaining to
194 Se are more exothermic than those pertaining to Te.

195 These results show that whatever the substituting atom (Se or Te), the most favorable
196 situation corresponds to a single atom substitution at site *24g* and that irrespective of the
197 considered site, the replacement of S by Se is the most favorable one.

198

Table III: Formation energies (in meV/atom) and total volume change of the cell (in bohr³) for 1 and 2 atoms Te or Se substitutions for sulphur. Columns 1 and 8 correspond to the ranking w.r.t. formation energies.

	Te substituted for S	ΔE_f	ΔV	ΔE_f	ΔV	Se substituted for S	
1	1 Te for S <i>24g</i>	-151.6	+1.297	-160.7	+0.093	1 Se for S <i>24g</i>	1
2	1 Te for S <i>2a</i>	-144.0	+2.452	-153.1	+0.312	1 Se for S <i>2a</i>	4
3	2 Te for 2 S <i>24g</i>	-136.7	+3.066	-155.5	+0.943	2 Se for 2 S <i>24g</i>	2
4	1 Te for S <i>24g</i> and 1 Te for S <i>2a</i>	-136.2	+3.976	-153.5	+0.685	1 Se for S <i>24g</i> and 1 Se for S <i>2a</i>	3
5	2 Te for 2 S <i>2a</i>	-127.3	+6.200	-144.7	+1.828	2 Se for 2 S <i>2a</i>	5

199

200 The total volume of the substituted structures changes sizeably with respect to that of
201 pristine tetrahedrite as can be seen in Table 3. We observe that, except for 2-Se-atoms
202 substitution, the more energetically favorable the site is, the smaller the volume change. In
203 agreement with the respective atomic volumes of Se and Te atoms, sites substituted with Te
204 are likely to be more affected, as we observe a larger total volume change, than when Se is the
205 substituting element. It appears that, substitutions on site S *2a* induces more drastic changes in
206 the total volume than those on site S *24g*, the volume change being about two to three times
207 as large. As a consequence, the volume increase for 2-atoms substitution at site S *2a* is as
208 large as +6 and nearly +2 Bohr³ for Te and Se, respectively. These results on the volumes are
209 in line with the energetic ones as they can lead to the same inferences as above.

210

211 **Substitutions of Se and Te for Sb.** The calculated values are given in Table 4.
212 Remarkably enough, the formation energies are quite similar, suggesting therefore that both
213 Se and Te may equally substitute for Sb. The most preferred substitution is by far obtained
214 with one Se or Te atom only in place of antimony. The energy difference between the one-
215 atom and two-atoms substitutions is above 20 meV/atom for both Se and Te, the largest
216 energy difference being 23 meV/atom for Se. For two-atoms substitutions, the three
217 configurations, namely two atoms along the pseudo-cube edge, two atoms along the face
218 diagonal of the pseudo-cube and two atoms along the principal diagonal of the pseudo-cube,
219 are energetically undistinguishable since the differences in formation energies lie in the error
220 bar (3-4 meV/atom) ; they spread in the ranges $[-122.2; -123.8]$ meV/atom and $[-120.4; -$
221 $122.5]$ meV/atom for Te and Se, respectively.

222 Regarding the total volume change of the lattice upon substitutions, it is remarkable
223 that they are all negative irrespective of the substituting atom and configurations. The smallest
224 volume change corresponds to the one-atom substitution. For two-atoms substitutions the
225 situation is contrasted between Se and Te. For Se, the volume changes remain rather small
226 (less than 2 Bohr³). For Te, the two-atoms substitutions at the edge of the pseudo-cube still
227 lead to the modest volume change of -2.6 Bohr³. By contrast, a huge change is observed
228 when two Sb atoms are replaced by Te on the pseudo-cube face and body diagonals.
229 Notwithstanding this observation, the structures are not energetically destabilized as
230 mentioned above.

231

Table IV: Formation energies (in meV/atom) and total volume change of the cell (in bohr³) for 1 and 2 atoms Te or Se substitutions for antimony. Columns 1 and 8 correspond to the ranking w.r.t. formation energies.

	Te substituted for Sb	ΔE_f	ΔV	ΔE_f	ΔV	Se substituted for Sb	
1	1 Te for Sb δc	-144.8	-1.2	-143.4	-1.24	1 Se for Sb δc	1
2	2 Te for 2 Sb δc (pseudo-cube edge)	-123.8	-2.6	-122.5	-1.91	2 Se for 2 Sb δc (pseudo-cube edge)	2
3	2 Te for 2 Sb δc (pseudo-cube diagonal)	-123.6	-26.5	-120.7	-1.71	2 Se for 2 Sb δc (pseudo-cube diagonal)	3
4	2 Te for 2 Sb δc (pseudo-cube face diagonal)	-122.2	-36.1	-120.4	-1.93	2 Se for 2 Sb δc (pseudo-cube face diagonal)	4

232

233 **Partial conclusions.** From the formation energies viewpoint the most favourable
 234 situation corresponds to a single atom substitution, both Te and Se preferring replacing
 235 sulphur at the $24g$ Wyckoff position to sulphur $2a$ and antimony δc ones. Selenium is
 236 preferred for the sulphur substitution whereas tellurium and selenium are equally likely to
 237 replace antimony.

238 The lattice volume change is positive when substitutions occur at the sulphur sites,
 239 whereas it is negative at the antimony ones, the one atom substitution leading in all cases to
 240 the lower volume variation. For two-atoms substitutions, irrespective to the substituted
 241 element and site, Te leads to higher volume changes than Se. One can note that, whereas these
 242 volume variations are extremely large when Te substitutes for Sb, the energetic variations are
 243 quite small.

244

245

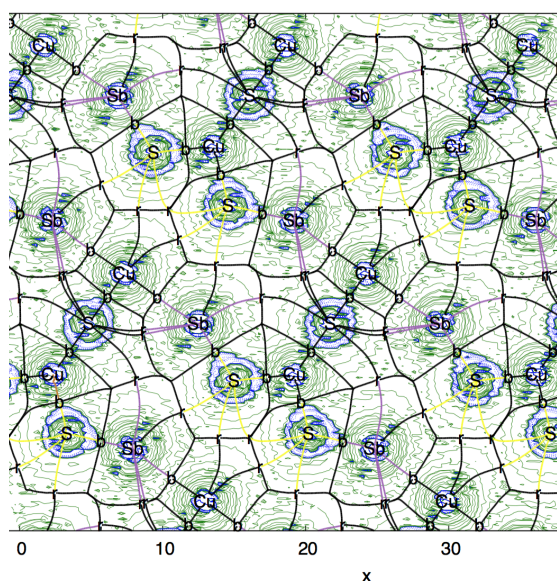
246 *Local volume and atomic charge changes and electron density laplacian*

247 In order to get better insight into the influence of substitutional atoms in the tetrahedrite, the
248 atomic site volume and charge changes and electron density laplacian have been calculated
249 using Bader's theory of atoms in molecules. Only one-atom substitutions are considered here
250 since these lead to the structures bearing highest formation energies and smallest volume
251 changes.

252 **Pure tetrahedrite.** The electron density laplacian of pure tetrahedrite in the (110)
253 plane is depicted in figure 2. This plane contains S *2a* atoms (e.g. sulphur located at abscissa
254 ca. 22), which are bonded to two copper *12e* (at abscissa ca. 20 and 24); the four remaining
255 copper *12e* atoms that complete the octahedra around sulphur ones are located in two planes
256 rotated by 45° from the (110) one and are thus not visible.

257 In the (110) plane, one can see that in agreement with the structure description already
258 reported in literature, Cu *12e* is bonded to two S *24g* atoms and despite the long distance
259 between copper *12e* and antimony atoms (3.536 Å, see above), these atoms are chemically
260 bonded to each other since a bond path is found to connect them and a bond critical point
261 (BCP) is found at the atomic basins boundary. Indeed, in the Bader's description the bonds
262 are characterized by a path connecting two atoms, with b (see Fig. 2) depicting the position of
263 the BCP where the electron density gradient vanishes.

264



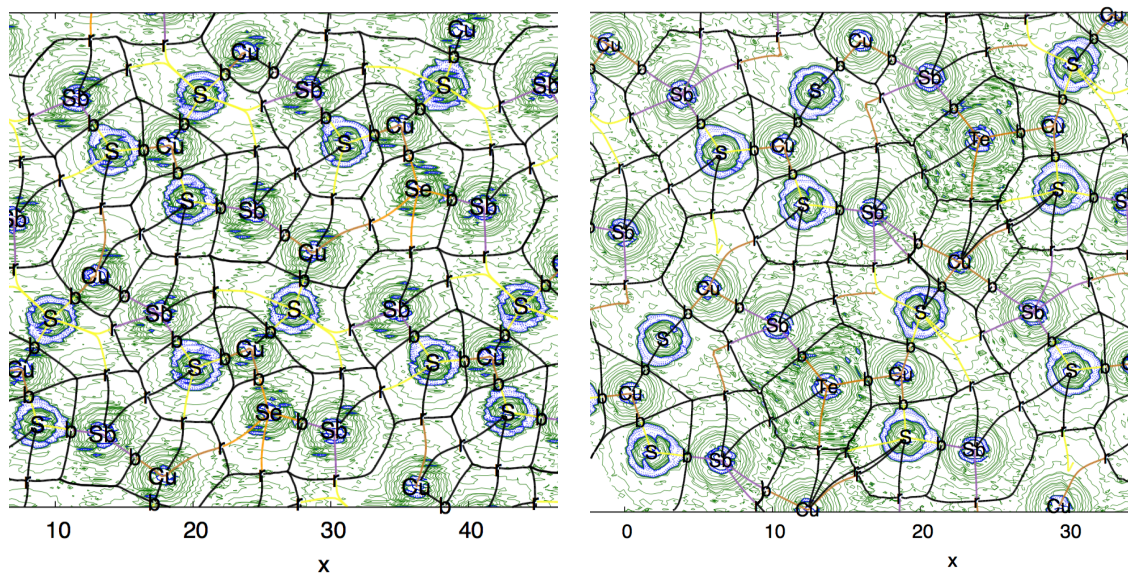
265

266 Fig. 2: Electron density laplacian of pure tetrahedrite. Legend. b: bond critical point; r: ring
 267 critical point; c: cage critical point. Color legend: electron accumulation in blue; electron
 268 depletion in green.

269

270 **Substitutions of Se and Te for S 24g.** As one selenium atom replaces a sulphur 24g
 271 atom, one of the Cu_{12e} -Sb bonds gets broken. This effect is observable as one compares Fig. 2
 272 (at $x=26$) and Fig. 3a (at $x=31$). Important distortions in the structure are also observed,
 273 probably to accommodate the large size of Se: the Cu_{12e} -Se bond distance (2.541 Å) increases
 274 by 13% compared to the Cu_{12e} -S one; Cu 12e moves out of the trigonal plane by about 20%;
 275 the angle Cu_{12e} -S_{2a}-Cu_{12e} of the octahedron height is 150° instead of 180°. One of the Cu_{12e} -
 276 Sb distances shortens by 20% (2.832 Å) while the other enlarges by 10% (3.896 Å) that leads
 277 to the bond breaking.

278



a) Se substitution for S 24g

b) Te substitution for S 24g

279 Fig. 3: Electron density laplacian of substituted tetrahedrite. a) Se substitution for S 24g; b)
 280 Te substitution for S 24g. Legend. b: bond critical point; r: ring critical point; c: cage critical
 281 point. Color legend: electron accumulation in blue; electron depletion in green.

282

Table V: Variation of the atomic charge (in electron charge unit) and atomic sites volume (in bohr³) upon Se substitution for S 24g.

	24g (S)	2a (S)	12e (Cu)	12d (Cu)	8c (Sb)
Δq	+0.01	+0.05	-0.01	-0.01	0
ΔV	+1.15	+5	-2.26	+0.45	-1.31

283

284 The effect of this replacement on the atomic charges and atomic volumes can be seen
 285 in Table 5. Interestingly, sulphur 2a is the most affected atom with a positive change of both
 286 properties; a volume increase as large as +5 bohr³ is observed. The Cu 12e atom to which Se
 287 is bonded is also affected, though in a lower extent and in the opposite way with a decrease of
 288 both the volume and the charge. The site of the antimony atom to which Se is bonded

289 undergoes a volume decrease although its charge remains unchanged. The volume decrease is
 290 about the same in absolute value as the volume increase of the S *24g* site where the
 291 substitution occurs.

292 As Te substitutes for sulphur *24g* the same overall trends are observed as for Se. The
 293 graph of the electron density laplacian (Fig. 3b) shows that one of the Cu_{12e}-Sb is broken
 294 (3.592 Å, +1.2%) while the other one is strengthened (3.181 Å, -10%) and the octahedron
 295 around S *2a* is distorted (the Cu-S-Cu angle is 163°). However, we note that these structural
 296 changes are less drastic than for Se, although the Te substitution is energetically less
 297 favorable than the Se one. The volume change of the site *24g* of sulphur, where the Te
 298 substitution occurs, increases sizably (Table 6) by +3.3 Bohr³ (2.9 times that for Se
 299 substitution) and the volume of the site *12d* (Cu) is almost twice as large as that for the Se
 300 substitution. Only the site *12e* of Cu undergoes a volume decrease of about the same amount
 301 as for Se substitution. These local volume changes explain why the overall volume of the
 302 structure increases (Table 3) as Te substitutes for sulphur.

303 We note finally that the atomic site charges vary in the same way and same extent as
 304 for the Se substitution.

305

Table VI: Variation of the atomic charge (in electron charge unit) and atomic sites volume (in bohr³) upon Te substitution for S *24g*

	24g (S)	2a (S)	12e (Cu)	12d (Cu)	8c (Sb)
Δq	+0.01	+0.04	-0.01	-0.01	-0.01
ΔV	+3.3	+5.6	-2.1	+0.7	+0.2

306

307 **Substitutions of Se and Te for Sb.** The influence of the Se and Te substitutions for
 308 Sb on the electron density laplacian and bonding network of the tetrahedrite is depicted in
 309 figure 4a and 4b, respectively. Interestingly, as Se substitutes Sb a new chemical bond

310 appears between the selenium atom and the sulphur one of the $2a$ site in spite of the large
311 interatomic distance (4.027 Å); The bond is characterized by a bond path between both atoms
312 and a bond critical point located *ca.* $x=24$ (Figure 4a). The Se-S_{2a} interatomic distance is
313 1.156 Å shorter than the Sb-S_{2a} one of the pure tetrahedrite. The appearance of this new bond
314 implies a distortion of the octahedron around the S_{2a} atom; the Cu-S-Cu angle amounts to
315 153.07° and the sulphur atom moves out of the Cu₄ plane by 17.9° in the direction of Se. As
316 to the case of the Te for Sb substitution, the bonding network of the structure is not affected
317 compared to that of the pure tetrahedrite (Figure 4b). Some differences in the atomic charge
318 and volume changes between these two types of substitutions can be observed (Tables 7 and
319 8). First, the atomic charges are barely varying upon Te substitution. By contrast, S_{2a} and Sb
320 undergo significant increase and decrease, respectively, of their charge upon Se substitution,
321 which can be correlated to the appearance of the new bond between these atoms.

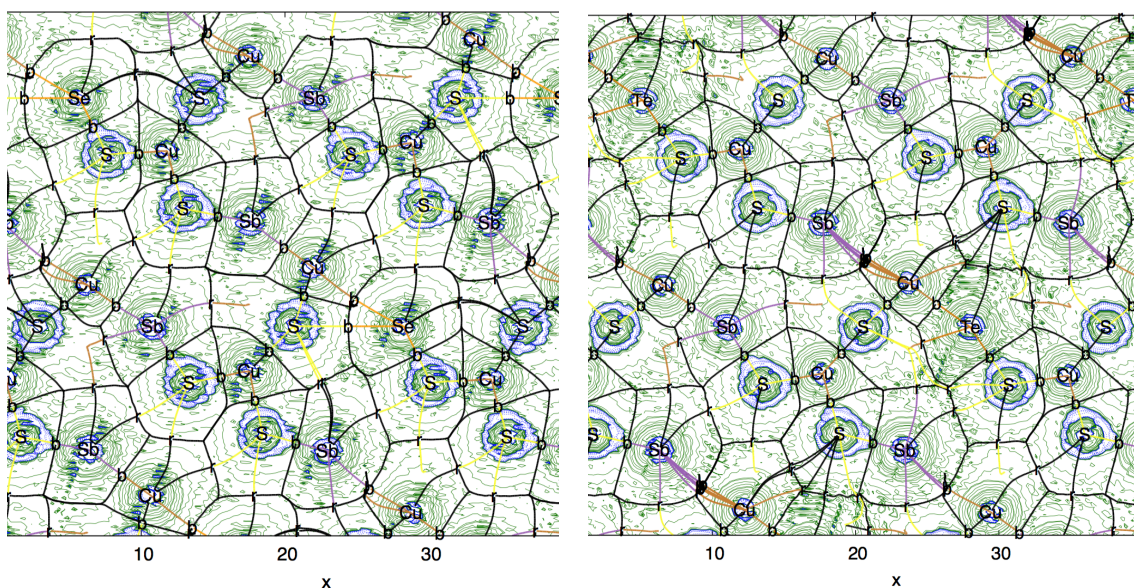
322 The volumes are affected in various ways. For both Se and Te substitutions, the
323 volume of S_{2a} increases drastically by up to 5 and 7 Bohr³, respectively, and that of Cu_{12e}
324 (bonded to S_{2a}) decreases by 2.5 Bohr³, on average. The Cu_{12d} atoms being far from the
325 substitution site, their volumes are not affected. As to the substituted site Sb, the volume
326 decreases (increases) drastically (slightly) when Se (Te) is the substituting atom, these
327 variations being in line with the differences in atomic sizes between Sb, Se and Te. Since the
328 substitution at the Sb site is energetically equally plausible by Se and Te, we can infer that the
329 total contributions to the formation energy of the various structural, electronic and bonding
330 changes occurring in the structures are comparable.

331

332

333

334



a) Se substitution for Sb δc

b) Te substitution for Sb δc

335 Fig. 4: Electron density laplacian of substituted tetrahedrite. a) Se substitution for Sb δc ; b)

336 Te substitution for Sb δc . Legend. b: bond critical point; r: ring critical point; c: cage critical

337 point. Color legend: electron accumulation in blue; electron depletion in green.

338

Table VII: Variation of the atomic charge (in electron charge unit) and atomic sites volume (in bohr³) upon Se substitution for Sb δc .

	24g (S)	2a (S)	12e (Cu)	12d (Cu)	8c (Sb)
Δq	+0.03	+0.05	-0.01	0	-0.06
ΔV	-0.90	+5.1	-2.32	0	-4.07

339

340

341

342

343

Table VIII: Variation of the atomic charge (in electron charge unit) and atomic sites volume (in bohr³) upon Te substitution for Sb 8c.

	24g (S)	2a (S)	12e (Cu)	12d (Cu)	8c (Sb)
Δq	+0.01	+0.01	0	+0.01	-0.02
ΔV	+0.60	+7.2	-2.7	-0.2	+0.6

344

345 **Partial conclusions.** Irrespective of both the substituting and the substituted atoms,
 346 the atomic charge changes are quite weak on all sites, the maximum being 0.06 electron
 347 charge unit. When substitution occurs on the S_{24g} site, irrespective of the substituting atom,
 348 charge change is only noticeable on the S_{2a} site. When substitution occurs on the Sb_{8c} site, the
 349 largest charge change occurs on this site while being weaker as Te substitutes for Sb.

350 Regarding the local volume changes, the S_{2a} site is the most impacted by both S_{24g} and
 351 Sb replacements. In all cases, the volume of the site S_{2a} increases. One can see that the volume
 352 of the site Cu_{12e}, which is adjacent to the site S_{2a}, decreases, though to a lesser extent. As one
 353 could expect, the impact of the substitution on the local volume changes is weaker when the
 354 site of interest is far from the substituted one (e.g. volume of the Cu_{12d} site when the
 355 replacement is on the Sb site).

356 The electron density laplacian shows few or even no chemical and structural
 357 modifications when Te substitutes for S_{24g} or Sb, respectively. In the case of Se, bigger
 358 structural distortions have been evidenced with the breaking of a Cu_{12e}-Sb bond when the
 359 substitution occurs on S_{24g} site and the formation of a Se-S_{2a} one when the substitution occurs
 360 on Sb site.

361

362

363 **SUBSTITUTED TETRAHEDRITE: EXPERIMENTAL PART**

364 DFT calculations of formation energies and total volume changes showed that : i) the
365 most favourable situation corresponds to a single atom substitution, ii) selenium is preferred
366 for the sulphur substitution whereas tellurium and selenium are equally likely to replace
367 antimony, whereas QTAIM calculations evidenced larger structural and chemical distortions
368 when Se is the substituting element irrespective of the substituted site. Since these results
369 seem inconsistent, we experimentally investigated the following compositions:
370 $\text{Cu}_{12}\text{Sb}_{3.5}\text{Se}_{0.5}\text{S}_{13}$, $\text{Cu}_{12}\text{Sb}_4\text{S}_{12.5}\text{Te}_{0.5}$ and $\text{Cu}_{12}\text{Sb}_{3.5}\text{Se}_{0.5}\text{S}_{12.5}\text{Te}_{0.5}$. We have not investigated
371 $\text{Cu}_{12}\text{Sb}_{3.5}\text{Te}_{0.5}\text{S}_{13}$ and $\text{Cu}_{12}\text{Sb}_4\text{S}_{12.5}\text{Se}_{0.5}$ as these works were already done by Bouyrie et al.⁴⁵
372 and Lu et al.⁴⁴, respectively, and the authors found single-phased materials with a tetrahedrite
373 structure.

374

375 **Synthesis and characterization**

376 The three aforementioned ternary and quaternary alloys have been prepared by mixing
377 their constitutive elements with high purity grade in required proportion in evacuated ($\sim 10^{-2}$
378 Pa) sealed silica ampoules. The mixture was heated up to 680 °C and maintained at this
379 temperature for 8 h. In order to get the equilibrium state, the samples have been quenched
380 from melt in cold water and annealed at 400°C for about 150 h. The constitutive phases of the
381 samples were evidenced by X-ray powder diffraction using a Bruker D8 Advance
382 diffractometer with Cu-K α radiation in the 2θ range from 5° to 80° and their proportion were
383 evaluated by Rietveld refinement.

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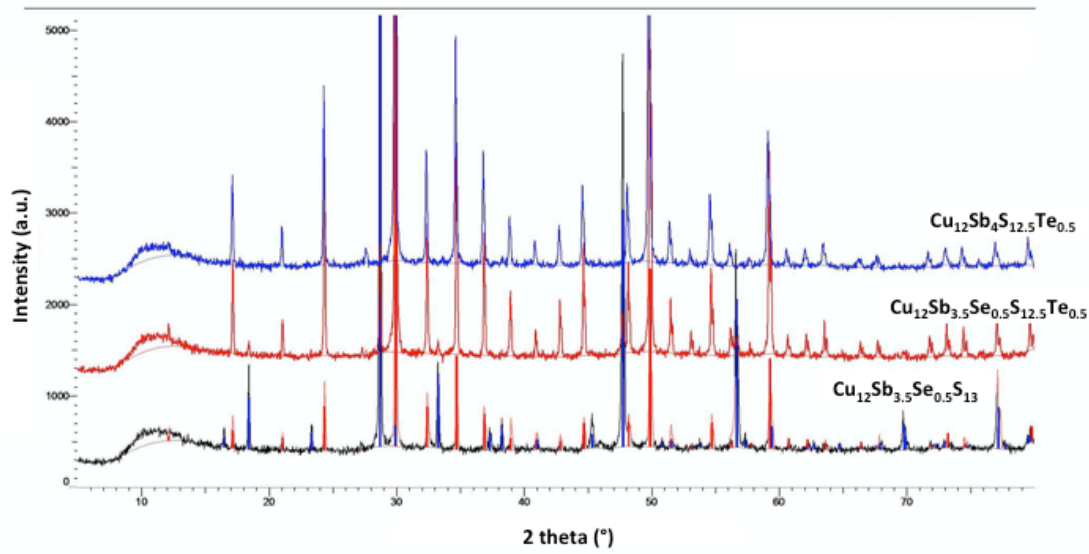
387

388 **Results**

389 The X-ray diffraction patterns for the three investigated samples are given in Figure 5
390 and the constitution of the alloys with the percentage of each phase determined by Rietveld
391 refinement are given in Table 9.

392 When one Te atom is substituted for a S one, the alloy is constituted of one phase only
393 which crystallizes in a tetrahedrite structure. As expected the lattice parameter of this phase (a
394 = 1036.1 pm) is larger than that of the pure sulphur tetrahedrite ($a=1032.4$ pm, see above).
395 When one Se atom is substituted for a Sb one, the alloy is constituted of two phases in an
396 equivalent ratio. One of these phases crystallizes in a tetrahedrite structure with a lattice
397 parameter $a= 1034.3$ pm, the other one crystallizes in a famatinite structure with the lattice
398 parameters $a=539.0$ pm and $c=1076.1$ pm which are larger than those of the pure sulphur
399 famatinite ($a=538.5$ pm and $c=1075.4$ pm, see above). When one Se atom is substituted for a
400 Sb one and one Te is substituted for a S one, the alloy is mainly constituted (95%) of a
401 tetrahedrite phase, the secondary phase (5%) crystallizing in a famatinite structure.

402 The whole results show that in spite of low formation energies and high volume
403 changes, alloys containing a tellurium atom at a sulphur site stabilize the tetrahedrite
404 structure. This statement is in agreement with the QTAIM calculations, which find lower
405 structural and chemical distortions when Te is the substituting element.



406

407 Fig. 5: X-ray diffraction patterns of $\text{Cu}_{12}\text{Sb}_4\text{S}_{12.5}\text{Te}_{0.5}$, $\text{Cu}_{12}\text{Sb}_{3.5}\text{Se}_{0.5}\text{S}_{12.5}\text{Te}_{0.5}$ and

408 $\text{Cu}_{12}\text{Sb}_{3.5}\text{Se}_{0.5}\text{S}_{13}$ alloys

409

Table IX: Constitution of the $\text{Cu}_{12}\text{Sb}_4\text{S}_{12.5}\text{Te}_{0.5}$, $\text{Cu}_{12}\text{Sb}_{3.5}\text{Se}_{0.5}\text{S}_{13}$ and $\text{Cu}_{12}\text{Sb}_{3.5}\text{Se}_{0.5}\text{S}_{12.5}\text{Te}_{0.5}$ samples and percentage of each phase determined by X-Ray diffraction measurements and Rietveld refinement.

Sample composition	Sample constitution (%)	
	Tetraedrite	Famatinite
$\text{Cu}_{12}\text{Sb}_4\text{S}_{12.5}\text{Te}_{0.5}$	100	0
$\text{Cu}_{12}\text{Sb}_{3.5}\text{Se}_{0.5}\text{S}_{13}$	45	55
$\text{Cu}_{12}\text{Sb}_{3.5}\text{Se}_{0.5}\text{S}_{12.5}\text{Te}_{0.5}$	95	5

410

411 CONCLUSION

412 In this work, we investigated Se and Te substitutions in tetrahedrite by coupling DFT

413 and QTAIM calculations. DFT calculations of formation energies and total volume changes

414 showed that the most favourable situation corresponds to a single atom substitution and that

415 selenium is preferred for the sulphur substitution whereas tellurium and selenium are equally
416 likely to replace antimony. By contrast, QTAIM calculations evidenced irrespective of the
417 substituted site, larger structural and chemical distortions when Se is the substituting element.
418 In order to clarify these inconsistencies, we experimentally investigated three alloys and
419 found that by contrast to a Se substitution for Sb, a Te substitution for S stabilizes the
420 tetrahedrite structure. This investigation shows that a DFT calculation of formation energies
421 and total volume changes is not sufficient to put forward conclusions on alloys stability. By
422 giving chemical and structural information on a compound, in addition of being a good
423 method to explain the structure-properties relationships, QTAIM appears as a valuable
424 method to get information on phase stabilities.

425

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434

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