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I. Introduction (literature review)

I.1 Wurtzite-kesterite and wurtzite-stannite ($I_2-II-IV-VI_4$ compounds)

Accordingly to literature [1,2], different crystal structure types are discussed for $I_2-II-IV-VI_4$ quaternary semiconductors ($I=Cu,Ag$; $II=Zn,Cd$; $IV=Si,Ge,Sn$; $VI=S,Se$). Such as, the kesterite and stannite-type structure which belong to the tetragonal crystal system, as well as in the wurtz-kesterite or wurtz-stannite type structure which belong to the monoclinic and orthorhombic crystal system (see figure for the case of CZTS,Se compounds 1).

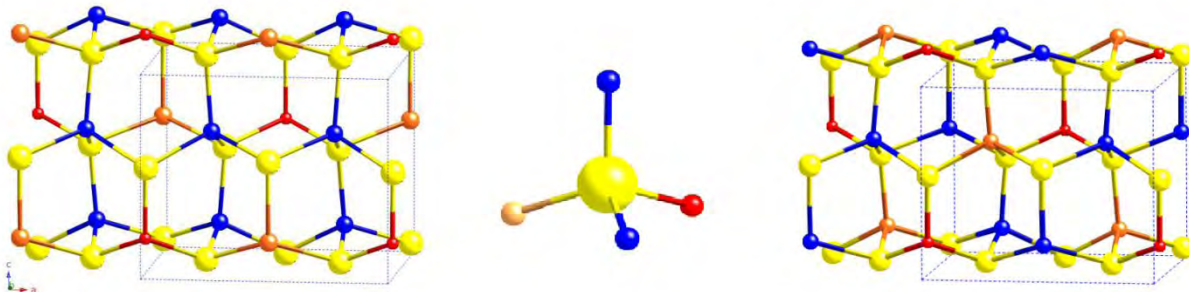


Figure 1. Orthorhombic wurtz-stannite (left) and monoclinic wurtz-kesterite (right) the structural motif is presented in the middle. Colors represent blue: Cu, orange: Zn, Sn: red and yellow: S or Se.

The wurtz-stannite and wurtz-kesterite type structure can be derived from the wurtzite type structure in a similar way as the kesterite and stannite type structure is derived from the sphalerite type structure, that is, by doubling the unit cell of the wurtzite type structure in the direction of the crystallographic c axis and introducing three different cations in an ordered way. The wurtz-stannite type structure can be described as an orthorhombic superstructure of the wurtzite type structure with unit cell dimension $a_{or} \sim 2a_w$, $b_{or} \sim \sqrt{3}a_w$ and $c_{or} \sim c_w$ (where subscripts or and w represent orthorhombic and wurtzite respectively) [2].



Space groups, Wyckoff position and site occupancies for each structure types for $A_2^I B^{II} C^{IV} X_4^{VI}$ compounds are described below:

- Kesterite structure, space group $I\bar{4}$, Wyckoff position and site occupancies 2a: (0,0,0) occupied by A^I , 2c: (0,1/2,1/4) occupied by A^I , 2d: (0,1/2,3/4) occupied by B^{II} , 2b: (1/2,1/2,0) occupied by C^{IV} , 8i (x,y,z) occupied by X^{VI} .
- Stannite structure, space group $I\bar{4}2m$, Wyckoff position and site occupancies 2a: (0,0,0) occupied by B^{II} , 4d: (0,1/2,1/4) occupied by A^I , 2b: (1,2,1/2,0) occupied by C^{IV} and 8g: (x,x,z) occupied by X^{VI} .
- Wurtz – stannite structure, space group $Pmn2_1$, Wyckoff position and site occupancies 2a: (0,y,z) occupied by B^{II} , 4b: (x,y,z) occupied by A^I , 2a (0,y,z) occupied by C^{IV} , 2a (0,y,z) occupied by X^{VI} (2 different position occur), 4b: (x,y,z) occupied by X^{VI} .
- Wurtz – kesterite structure, space group Pc , Wyckoff position and site occupancies 2a: (x,y,z) occupied by A^I (4 different position occur), 2a: (x,y,z) occupied by B^{II} (2 different positions occur), 2a: (x,y,z) occupied by C^{IV} (2 different positions occur), 2a: (x,y,z) occupied by X^{VI} (8 different positions occur).

Theoretical studies from S.Chen *et al.* [1] reported two fundamental structures with a 16-atom primitive unit cell: the wurtzite-kesterite and the wurtzite-stannite structure, which correspond to the zinc-blende derived kesterite and stannite structure, respectively. The first-principles total-energy calculations show that the energy stability between the zinc-blende and wurtzite derived structures exhibits a clear dependence on the cation size difference and the ionicity of the $I_2-II-IV-VI_4$ compounds. Generally speaking, quaternary semiconductors with small and strongly ionic elements, for example

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$\text{Ag}_2\text{ZnGeS}_4$, prefer the wurtz-kesterite structure, whereas $\text{Cu}_2\text{CdSiS}_4$ prefers the wurtz-stannite structure. Since for this report we further focus on $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ compounds only, the wurtz-kesterite and wurtz-stannite structure are no longer discussed.