

# Phononic and thermodynamic properties of the sulvanite compounds: A first-principles study



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## ABSTRACT

We have calculated the phononic and thermodynamic properties of the sulvanite family:  $\text{Cu}_3\text{TMX}_4$  (TM = V, Nb, Ta; X = S, Se) using first-principles phonon calculations within the Density Functional Theory and the quasi-harmonic approximation. General trends in the phonon dispersion relation, the partial density of states, the thermal expansion and the heat capacity at constant pressure are discussed for these compounds. Our calculated frequencies at  $\Gamma$  are in good agreement with the available experimental Raman spectra, especially for the high-frequency  $A_1$  and  $F_2^d$  modes. Finally, at low-temperature when Se replaces S, it is observed that the broad peak of the heat capacity is almost a factor of two larger.

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## 1. Introduction

The family of ternary compounds named sulvanites  $\text{Cu}_3\text{TMX}_4$  (TM = V, Nb, Ta; X = S, Se) have gained attention due to their blend of interesting properties such as good ionic conductivity, p-type transparent conductivity, lattice constants similar to silicon making possible the growth of hetero-epitaxial thin films on Si substrates and band gap range [1–4]. In spite of that, the sulvanite compounds have not been studied intensively and theoretical research is quite scarce [5–7]. Regarding the vibronic and thermodynamic properties of these indirect gap polar covalent semiconductors [6,7], there is not a comprehensive study of those. Up to date, the authors know only about two previous investigations related with the vibrational properties of the sulvanite compounds, in particular  $\text{Cu}_3\text{TMS}_4$ , one of these were carried out using reflectivity and Raman scattering in the infrared region [8], this experimental investigation revealed that exist some modes with a high degree of anharmonicity due, apparently, to configurational disorder in the Cu sites. The other research was a micro-Raman study [9], where basically the results obtained by the previous investigation were confirmed [8].

In this work we present theoretical results of the phononic and thermodynamic properties of the sulvanite compounds calculated by first-principles Density Functional Theory (DFT) and the quasi-harmonic approximation (QHA). General trends of the phononic structure are discussed employing the dispersion relation and the partial density of states (PDOS), the obtained frequencies at  $\Gamma$  are compared with the available experimental Raman spectra, and finally thermodynamic properties are analysed using the thermal expansion and the heat capacity at constant pressure.

## 2. Method of calculation

In this work all total energies, ionic forces and stress tensor components were performed within the first-principles DFT framework which has proven to be one of the most accurate methods for the computation of the electronic structure of solids [10,11]. The projector augmented wave (PAW) method [12] was used to approximate the electron–ion interaction and the generalised gradient approximation (GGA-PBEsol) [13] for the exchange–correlation functional as it is implemented in the VASP code [14,15]. The PAW atomic reference configurations are the same used in previous studies of these compounds [5,6]. A cut-off energy of 498 eV is used for the plane waves expansion of the kinetic energy, where the total energy was converged to 1 meV/unit cell. All structural parameters for each calculated volume have been optimised by simultaneously minimising all atomic forces and stress tensor

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components via the conjugate gradient algorithm. The Brillouin zone was sampled by  $4 \times 4 \times 4$   $\mathbf{k}$ -mesh according to the Monkhorst–Pack scheme with a Gaussian broadening of 0.01 eV for cell relaxation, with this mesh the ionic forces are converged to 0.1 meV/Å. For the calculation of the total energy and the equation of state (EOS) the tetrahedron method including Blöchl corrections [16] was used, with a  $\Gamma$ -centred  $10 \times 10 \times 10$   $\mathbf{k}$ -mesh.

Phonon calculations have been performed using the force constants direct method [17], to extract the complete set of Hellmann–Feynman forces we have used  $2 \times 2 \times 2$  supercells (64 atoms) and ionic displacements of 0.01 Å (the number of independent displacements are reduced by using the point symmetry of the Wyckoff positions) for all six compounds. Long-range macroscopic electric field effects due to the displacements of ions in polar semiconductors splits longitudinal and transverse frequencies of the infrared active optical modes, this can be considered into the dynamical matrix by a non-analytical contribution depending on the Born effective charge (BEC) tensors and the high-frequency dielectric tensor ( $\epsilon_\infty$ ). In the present calculation we have calculated the BEC tensors and  $\epsilon_\infty$  using Density Functional Perturbation Theory (DFPT) as implemented in the VASP code [18]. Phonon dispersion relations and PDOS were calculated from the force constants using the PHONOPY code [19,20]. The thermodynamic properties were calculated within the QHA, for each compound we have calculated a set of eight volumes and then the energies are fitted to the universal EOS for solids [21].

### 3. Results and discussion

The refinements [22–25] of the crystal structure of the sulvanite compounds show that their crystal structure are characterised by a simple cubic lattice which pertains to the space group  $P43m$ , with one formula unit per primitive cell. The point groups  $D_{2d}$ ,  $T_d$  and  $C_{3v}$  are associated to the Wyckoff positions  $3d$  ( $\frac{1}{2}, 0, 0$ ) Cu,  $1a$  (0,0,0) TM and  $4e$  ( $u, u, u$ ) X, respectively. Each cation is tetrahedrally coordinated by four S (Se) ions, whereas each anion is coordinated by one TM ion, which is its only first-nearest neighbour, and three Cu ions. In a previous work [5], we calculated the EOS and equilibrium volumes for all these compounds with different local and semi-local exchange–correlation functionals, it was concluded that semi-local functionals perform quite well, with a mean absolute relative error of 1.1% for the equilibrium volumes. We have used for this work the set of optimised structures obtained with PBEsol from that study [5].

#### 3.1. Phononic properties

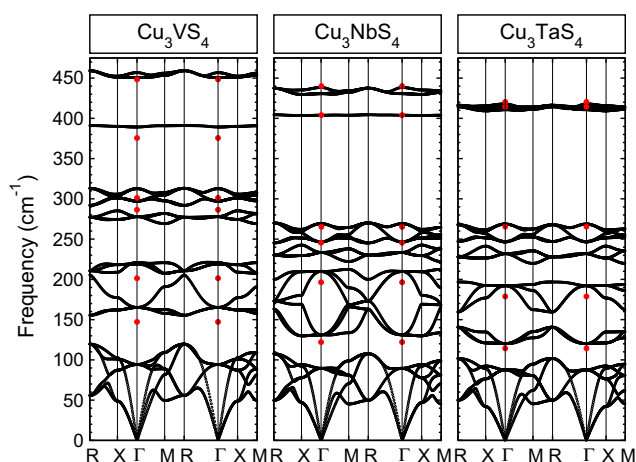
The sulvanite primitive cell contains eight atoms; therefore the phonon spectrum contains 3 acoustic and 21 optical branches.  $T_d$  is the point group of the sulvanite compounds, it contains 5 irreducible representations: 2 one-dimensional ( $A_1, A_2$ ), 1 two-dimensional ( $E$ ), and 2 three-dimensional ( $F_1, F_2$ ); the mechanical, acoustic and optical representations are given by  $\Gamma_{\text{mec}} = A_1 \oplus E \oplus 2F_1 \oplus 5F_2$ ,  $\Gamma_{\text{acu}} = F_2$  and  $\Gamma_{\text{opt}} = A_1 \oplus E \oplus 4F_2$ , respectively. In Table 1 we summarise the infrared (IR) and Raman active modes for each element. The sulvanites are polar covalent

**Table 1**  
IR and Raman active modes decomposition (point group  $T_d$ ) for  $\text{Cu}_3\text{TMX}_4$  (TM = V, Nb, Ta, X = S, Se).

Element	Mechanical representation	IR	Raman
Cu	$F_1 \oplus 2F_2$	$F_2$	$F_2$
TM	$F_2$	$F_2$	$F_2$
X	$E \oplus A_1 \oplus F_1 \oplus 2F_2$	$F_2$	$A_1, E, F_2$

semiconductors which have also a partly ionic character as it is revealed by the electron localisation function [5,6], therefore the dispersion curves show a LO/TO splitting of the infrared active optical modes ( $F_2$ ) at the  $\Gamma$ -point, which is determined by the BEC and the electronic part of the dielectric constant  $\epsilon_\infty$  (see Supplemental material). In Figs. 1 and 2 we show the calculated phonon dispersion relation including the LO/TO splitting for  $\text{Cu}_3\text{TMS}_4$  and  $\text{Cu}_3\text{TMSe}_4$ , respectively, and Figs. 3 and 4 display the PDOS. Tables 2 and 3 present the calculated phonon frequencies at the  $\Gamma$ -point compared with the available experimental Raman spectra for  $\text{Cu}_3\text{TMS}_4$  and  $\text{Cu}_3\text{TMSe}_4$ , respectively.

The phonon spectrum can be divided into three frequency regions: low or acoustical ( $0$ – $120$   $\text{cm}^{-1}$  and  $0$ – $90$   $\text{cm}^{-1}$  for  $\text{Cu}_3\text{TMS}_4$  and  $\text{Cu}_3\text{TMSe}_4$ , respectively), medium ( $120$ – $320$   $\text{cm}^{-1}$  and  $90$ – $225$   $\text{cm}^{-1}$ ) and high ( $320$ – $460$   $\text{cm}^{-1}$  and  $225$ – $360$   $\text{cm}^{-1}$ ). The acoustic branches are built up from states of all ions; in the case of  $\text{Cu}_3\text{TMS}_4$  the contribution of Cu-states are the most significant, whereas the contribution of TM-states are the less important, these states show a substantial increment along the heavy masses of the TM cations being comparable the contribution of the anion states and Ta-states. For  $\text{Cu}_3\text{TMSe}_4$  the acoustic branches are made up mainly from Cu and Se-states in the same proportion, in contrast the contribution of TM-states display the same trend of the previous compounds. The medium region has 17 branches labelled by the irreducible representations at  $\Gamma$  as  $F_1^a, F_2^a, F_2^b, F_1^b, F_2^c$  and  $E$ , we have ordered them by increasing frequency fashion in Tables 2 and 3. The  $F_1^a$  branches are built up mainly from Cu-states and some contribution of TM and S-states for  $\text{Cu}_3\text{TMS}_4$ , contrary the  $F_1^a$  branches for  $\text{Cu}_3\text{TMSe}_4$  are built up from Cu and Se-states almost equally and the contribution of Nb and Ta-states become also significant. The remaining branches of the medium region are made up from S-states for the most part, a small contribution of Cu-states and a negligible contribution of the TM-states for  $\text{Cu}_3\text{TMS}_4$ . On the other hand, in  $\text{Cu}_3\text{TMSe}_4$  these branches are made up from Cu and Se-states evenly, this is due to their similar masses; and the contribution of TM-states continue to be insignificant. The high frequency region has 4 branches labelled as  $A_1$  and  $F_2^d$ , it is observed a gap between this set of branches that becomes smaller when the masses of TM cations increase, and this gap is completely closed for  $\text{Cu}_3\text{TaS}_4$  where the  $A_1$  and  $F_2^d$  branches merge due to the large mass of Ta. The no degenerated  $A_1$  branch it built up from S-states almost entirely for  $\text{Cu}_3\text{VS}_4$  and  $\text{Cu}_3\text{NbS}_4$ , whereas for the remaining compounds there is a contribution of Cu-states.



**Fig. 1.** Calculated phonon dispersion relation for  $\text{Cu}_3\text{VS}_4$ ,  $\text{Cu}_3\text{NbS}_4$ ,  $\text{Cu}_3\text{TaS}_4$ . Red circles denote experimental Raman data [8]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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