Functionalized TaS_2 for thermoelectric applications: an ab-initio investigation

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INTRODUCTION

Thermoelectricity (TE) is a very promising field of research where wasted heat is converted into electricity through the Seebeck effect. The TE efficiency is closely connected to the dimensionless figure of merit ZT that can be written as (1)

$$ZT = \frac{\sigma S^2}{k} T \tag{1}$$

ZT depends on the electrical conductivity (σ), the Seebeck coefficient (S) and inversely on the thermal conductivity (k). Therefore, efficient TE materials should have high σ and S, and low k. In this scenario, many efforts are currently ongoing to optimize ZT by increasing S and and/or by reducing k.

Among different strategies, 2D materials show promising features for TE applications due to their relatively high electronic conduction properties [1]. However, 2D materials still exhibit large thermal conductivities, hindering their possible TE applications. For this reason, great efforts have been recently devoted to reduce their thermal conductivity. A recent experimental study [2] showed that the 2D TaS_2 functionalization with specific covalently-bonded organic side-chains (CBOSs) leads to a drastic thermal conductivity reduction without affecting the electronic properties. However, the role of the CBOSs in affecting k has not fully yet been clarified. The focus of this work is to investigate this system by proposing a model that comprehensively explains the reduction of thermal conductivity.

METHODS

All the calculations have been performed by means of first principles DFT calculations using the Quantum Espresso package[3]. The characterization of the vibrational and thermal properties has been performed by means of the Alamode package[4]. The thermal conductivity is obtained using the Boltzmann Transport Equation within the Relaxation Time Approximation (BTE-RTA).

CONCLUSIONS

The calculations showed a dramatic TaS_2 thermal conductivity reduction upon the CBOS functionalization. We attribute such a significant reduction to i) the increase of the TaS_2 inter-layer separation and ii) the role of CBOSs as thermal energy-sinks. We finally explore the use of longer and/or chemically different CBOSs to further reduce the thermal conductivity of 2D materials therofre increasing the overall ZT.

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REFERENCES

[1] J. Wu et al. *erspectives on Thermoelectricity in Layered and 2D Materials*, advanced electronic materials, (2018).
[2] S. Wang et al. *Organic covalent modification to improve thermoelectric properties of TaS_2,*, nature communication, (2022).
[3] P.Giannozzi et al., Condens.Matter 21, (2009).
[4] T. Tadano et al., Condens.Matter 26 , (2014).

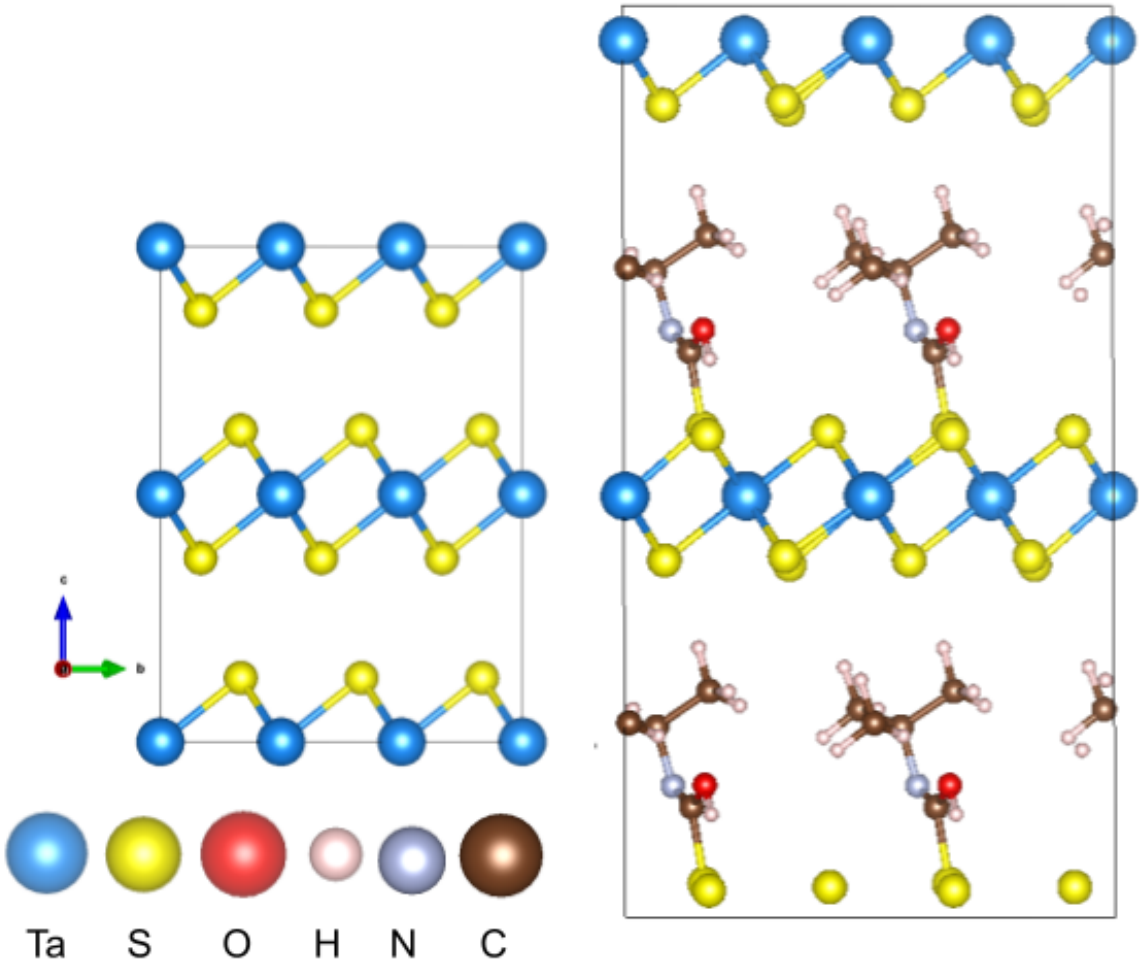

Fig. 1. Left: pristine 2D structure of TaS_2.
Right: CBOSs-functionalized TaS_2 structure