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Reply to the 'Comment on "Insight of the preponderant role of the lattice size in the Sn- based colusite for promoting high power factor"' by E. Guilmeau (J. Mater. Chem. A, 2023, DOI: 10.1039/D2TA03048A)

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Abstract:

Recently, E. Guilmeau submitted a comment (J. Mater. Chem. A, 2023, DOI: 10.1039/D2TA03048A) on our paper on the investigation of the role of the lattice size in the Sn-based colusites for promoting high power factor (J. Mater. Chem. A, 2022, DOI: 10.1039/D2TA01210C), showing a divergent opinion about our experimental as well as theoretical results which evidence a partial relationship between the Seebeck coefficient of Sn-based colusites ($Cu_{26}V_2Sn_6S_{32}$) and the structural cell parameters, regardless of the composition/doping or synthesis approach. We want to address the comments he made in this response.

Discussion/Answer:

We have reported not long ago the first successful Cr incorporation within the bulk Sn-based colusites structure and highlight the role of the lattice in structure.[1] Recently, Guilmeau submitted a comment about our article, where he suggested a misinterpretation of the experimental data from different publications and have not accounted for key aspects of the crystal chemistry in such Sn-based colusites.[2] The author also suggested that our calculation results do not correlate with the experimental observations. In this response, we address all the criticisms and argue that our experimental and theoretical evidence are valid and therefore, that our conclusions remain unchanged. We remind the importance to take in account the global purpose and scope of our current investigation instead of focusing on specific points without considering the other parts of the study.

In our article[1], we claimed that the "*the density of states* [DOS] *peak near the Fermi level appears sharper and stronger when the lattice is larger, which agrees with an overall superior Seebeck coefficient*". The author wrongly stated that: "*If this is correct when varying the cell parameter from 10.74 to 10.90 Å, this statement is erroneous when the cell parameter increases from 10.74 to 10.82 Å.*" However, in Figure 1 (adapted from the Figure 2 in original article[1]), we can clearly observe at $E\text{-}E_{Fermi} \approx -0.15$ eV that the DOS peak becomes gradually sharper and more intense as the lattice parameter increases from 10.74 to 10.82 Å and then from 10.82 to 10.90 Å.

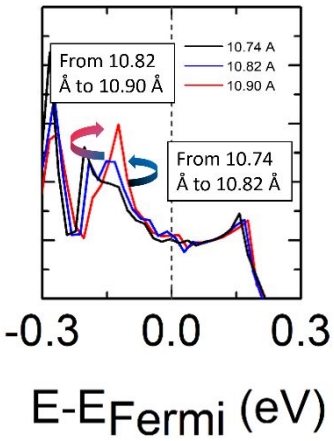

Figure 1. Electronic density of states (DOS) for $Cu_{26}V_2Sn_6S_{32}$ assuming different lattice parameters a (10.74 Å, 10.82 Å, and 10.90 Å) adapted from [1]

This increase in the DOS is directly related to the theoretical prediction of the Seebeck coefficient dependence with the carrier concentration displayed in Figure 7b in our paper.[1] Wherein a subtle Seebeck coefficient enhancement at a fixed carrier concentration can be predicted and agrees with the experimental observation. Therefore, Guilmeau's statement about the fact that the DOS for the cell parameters of 10.74 Å and 10.82 Å are similar and do not induce an effect on the Sn-based colusites Seebeck coefficient appears erroneous.

We do agree with the author that the experimental cell parameters in Sn-based colusites vary generally from around 10.75 Å to 10.83 Å (between the two red lines - Figure 7a.[1]). However, it is noteworthy to mention that the purpose of calculations performed for a cell parameter of 10.90 Å was to extrapolate and confirm the tendency observe in the DOS variation when varying the cell parameters between 10.74 and 10.82 Å, which makes it pertinent in our opinion.

The second point is that the author suggested that in our article we did not consider the sulphur volatilisation or initial (that is, self) stoichiometry deviation which might impact the lattice parameter as well as the formation of disorder phenomena, such as mixed cationic occupancy (antisite), and/or interstitial positions in the Sn-based colusites and its effect in the transport properties. We must remind the author that this statement was clearly discussed in our article[1] on page 10709: "*Such dilatation/contraction of the lattice can be first provided by the substitution/doping of an impurity element. ... lattice variation despite an apparently similar composition."* We would like to point out that we do not contest or ignore the Sn-based colusites literature which evidences that the composition/disorder effect influences the transport properties, especially the Seebeck coefficient, mostly due to the carrier tuning.[3-6] However, our findings still revealed a striking insight related to the lattice size effect and its role in the Sn-based colusites. We did not claim that it is the main parameter which fully controls the Seebeck coefficient but

shown for the first time, that a relationship exists and can "contribute" to it. We insist on the word "contribution" considering that the Sn-based colusites and more broadly the sulfide-based thermoelectric materials will be always strongly affected by their respective off-stoichiometry and induces the carrier tuning created by the sulphur deficiency. For example, in our article Figure 7a.[1], discrepancies are visible in the Seebeck values for a fixed lattice parameter, which obviously infers that the other contribution such as the composition and disorder effect play their roles as extensively reported in the literature.[3-6] However, the quantification of this phenomenon evolves large instruments (neutron diffraction, transmission electronic microscopy) not always accessible. Moreover, they are not accurate or are too local to be quantifiable or valuable for a systematic investigation.

Later, the author suggested that "*to establish a careful comparison relationship between the Seebeck coefficient with the cell parameter imposes to compare what is comparable*" and quotes: "*The fact that the increase of Seebeck coefficient with the cell parameter is not a structural or band structure effect, but a composition effect…*" before discussed a comparison with his work on the isostructural Ge-based colusite.[7-8] He advanced an assumption which appeared erroneous. It turns out that the Ge-based and Sn-based colusites are NOT comparable due to their dissociating structural and transport properties. The Ge-based colusites is characterized by a significantly lower lattice parameter (≈ 10.62 Å) compared to the Sn-based one (≈ 10.78 Å). This induces several structural and electronic structure differences compared to the Sn-based colusites. For example, the absence of exsolution process and a better electrical conductivity due to a Fermi level deeper inside the valence band in the case of the Ge-based colusites. This fact is even more pronounced in the case of a full occupancy by a group-6 element in the T site ($Cu_{26}T_2Ge_6S_{32}$, T = Cr, Mo, W). This specific structural occupancy can be only obtainable with the Ge-based colusites and tunes significantly the band structure of the Ge-based colusites as the author evidenced it in their previous study is therefore no comparable with the Sn-based colusites.[7] In our article, we insist that the comparison must be made only between the Sn-based colusites to keep our conclusion valid.

Finally, Guilmeau notified that our discussion about the maximum and average *PF* (Figure 8 in our article[1]) is erroneous. We read: "*The average PF value obtained by Kamińska et al. is about 0.95 mW m^{-1} K^{-2}, which is indeed about 35% higher than the value of 0.7 mW m^{-1} K^{-2} published in $Cu_{25}ZnV_2Sn_6S_{32}$. However, the authors omitted to consider in their figure and discussion the average PF value of 0.85 mW m^{-1} K^{-2} achieved by Guélou et al., i.e. very close to the maximum value of 0.95 mW m^{-1} K^{-2} reported by Kamińska et al. and obviously within experimental uncertainty (estimated to be about 11% for the power factor).*" We can first confirm that our statement mentioned in our article[1] is still valid. We demonstrated the highest PF_{max} = 1.2 mW m^{-1} K^{-2} at 700K as well as the average *PF*, PF_{ave} = 0.95 mW m^{-1} K^{-2} between 300 K – 700 K, so far obtained on Sn-based colusites. We agree that the current report of the average *PF* value of 0.80 mW m^{-1} K^{-2} (recalculated from another work[9]) achieved by Guélou *et al.* is worth to be included and we are thankful to the author for that. However, it remains that the difference between our respective performance is obvious and comparable to most of the reported enhancements on other thermoelectric materials within the state-of-the-art, even considering the experimental uncertainty.

In resume, the author of this comment[2] valuably wants to remind the importance of the composition and disorder in the Sn-based colusites to their contribution to thermoelectric properties. He displayed his opinion that, in the current material we reported on,[1] all the electrical properties are dominated only by the subtle influence of the composition and specific

order/disorder phenomena which is so far, the only interpretation reported in the literature. In our current study, we would like to highlight a novel finding which evidences that the control of the lattice parameters constitutes also a key point in the Sn-based colusites that plays a non-negligible role for obtaining a novel doping opportunity as well as can slightly contribute to influence the overall Seebeck coefficient, together with the composition and other doping effect. Certainly, further investigation should be performed in order to create a material specification and quantify each contribution for creating a synergic effect in Sn-based colusites.

Conflict of interest

The author declares no conflict of interest.

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