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**Comment on “Insight of the preponderant role of the lattice size in the Sn- based colusite for promoting high power factor”** by P. Kamińska, C. Bourgès, R. Chetty, D. Gutiérrez-Del-Río, P. Śpiewak, W. Świążkowski, T. Nishimura, T. Mori, *J. Mater. Chem. A*, 2022, 10, 10701

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### **Abstract**

The recent paper published by Kamińska *et al.* (Kamińska *et al.*, *J. Mater. Chem. A*, 2022, **10**, 10701–10714) suggests that the Seebeck coefficient of Sn-based colusites ( $\text{Cu}_{26}\text{T}_2\text{Sn}_6\text{S}_{32}$  with  $T = \text{V, Nb, Ta}$ ) increases with the cell parameter, regardless of the composition/doping or synthesis approach. Multiple lines of evidence disprove this assumption, but are consistent with a composition/disorder effect. This imposes a significant revision of the understanding of the relationship between the structure and thermoelectric properties in this family. Furthermore, the authors claimed to have reached a record power factor ( $PF$ ) and an increase of 35 % compared to state-of-the-art Sn-based colusites. However, a careful comparison with previously published data show that they omitted to consider in their comparison some already published  $PF$  values so the peak value achieved remains comparable to the best reported values within experimental uncertainty.

### **Broader context**

The past few years have seen a renewed interest in thermoelectric sulfides as the earth-abundance of sulphur is one critical aspect to encourage the large-scale production of thermoelectric devices with a potentially meaningful impact on mitigating climate change. Following reports of excellent properties in ternary and quaternary sulfides, the performance of cost-efficient sulfides has become closer to that of well-established state-of-the-art materials such as selenides, tellurides, clathrates, skutterudites, Zintl phases, silicides

etc...with ZT values now reaching unity.<sup>1,2</sup> Synthetic derivatives of the natural quaternary sulfide colusite have been especially studied since 2014, now reaching thermoelectric performances on par with current state-of-the-art sulfides.<sup>3</sup>

## Discussion

In their recent article, Kamińska *et al.*<sup>4</sup> report that Sn-based colusites can reach high power factor values of around 1.1-1.2 mW m<sup>-1</sup> K<sup>-2</sup> at 700 K and claim that the increase of the Seebeck coefficient (and power factor) in Sn-based colusites is directly linked to the increase of the cell parameter (**Figure 1**, left). “*The evident tendency to promote a globally larger Seebeck for a larger lattice parameter and reversely is highlighted, regardless of the composition/doping or synthesis approach*”. This conclusion is mainly based on data taken from the literature and on calculations results assuming that “*the density of states peak near the Fermi level appears sharper and stronger when the lattice is larger, which agrees with an overall superior Seebeck coefficient*”. However, Kamińska *et al.* misinterpreted the experimental data from different publications and have not accounted for key aspects of the crystal chemistry in such Sn-based colusites. Moreover, their calculation results do not correlate with the experimental observations.

According to their theoretical calculations, Kamińska *et al.* claimed that the “*the density of states peak near the Fermi level appears sharper and stronger when the lattice is larger, which agrees with an overall superior Seebeck coefficient*”. 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. Obviously, the density of states (DOS) for the cell parameters of 10.74 Å and 10.82 Å, are similar and the calculated Seebeck coefficient and carrier concentration, respectively,  $2.92 \times 10^{21}$  cm<sup>-3</sup> and  $2.90 \times 10^{21}$  cm<sup>-3</sup>, are comparable. Importantly, it must be noted that the experimental cell parameter in Sn-based colusites can vary from around 10.76 Å to 10.83 Å between the two red lines, calling into questions the pertinence of calculations performed for a cell parameter of 10.90 Å. In addition, the theory does not fit with the experiment. Experimental values of the Seebeck coefficient (see Figure 7 in Ref. 1) increases drastically from around 25 μV K<sup>-1</sup> to 100 μV K<sup>-1</sup> (*i.e.* by a factor 4) when the cell parameter increases from 10.76 Å to 10.83 Å; however, as mentioned above, their calculated Seebeck coefficient remains constant for such lattice parameters. The density of states near the Fermi level calculated for the cell parameters of 10.74 and 10.82 Å are

remarkably identical. Moreover, the experimental Seebeck coefficient tends to decrease when the cell parameter increases above 10.84 Å, which is in disagreement with their theoretical calculations. This behaviour has not been discussed by the authors. The conclusion and sentence, “*the density of states peak near the Fermi level appears sharper and stronger when the lattice is larger, which agrees with an overall superior Seebeck coefficient*”, is thus erroneous.

In their figure 7, the authors plotted Seebeck coefficients versus cell parameters taken from different series of Sn-based colusite samples. They notably mention that “*The evident tendency to promote a globally larger Seebeck for a larger lattice parameter and reversely is highlighted, regardless of the composition/doping or synthesis approach*”. However, the authors misinterpreted the data and simply forgot that the cell parameter in Sn-based colusites is mainly affected by disorder phenomena induced by sulphur volatilisation or initial (that is, self) stoichiometry deviation. Disorder phenomena, such as mixed cationic occupancy (antisite), and/or interstitial positions, have been well described in such Sn-based colusites, and are known to increase the cell parameter. The structure being fully or partially disordered, the cell parameter is expanded. This has been addressed and clearly demonstrated in different papers,<sup>5-8</sup> whose conclusions have been summarised in a recent review.<sup>3</sup> In 1994, P.G. Spry *et al.* first observed such disorder phenomena in natural colusites.<sup>9</sup> Those stoichiometric deviations and disorder, induced by sulphur volatilisation in synthetic colusites, reduce the carrier concentration by electron doping and increase the Seebeck coefficient. In summary, the increase of the Seebeck coefficient with the cell parameter is not a structural or DOS effect, but a composition/disorder effect that affects the hole concentration.

To establish a careful comparison relationship between the Seebeck coefficient with the cell parameter imposes to compare what is comparable. In other words, it imposes that the crystal structure is well ordered and that stoichiometric deviation does not occur or is limited. The fact that the increase of Seebeck coefficient with the cell parameter is not a structural or band structure effect, but a composition effect, is further supported by the results published on the isostructural  $\text{Cu}_{26}\text{Cr}_2\text{Ge}_6\text{S}_{32}$ ,  $\text{Cu}_{26}\text{Mo}_2\text{Ge}_6\text{S}_{32}$  and  $\text{Cu}_{26}\text{W}_2\text{Ge}_6\text{S}_{32}$  phases (well crystallised, non-disordered, and prepared in the same conditions) where an opposite trend is observed.<sup>10</sup> Indeed, the  $\text{Cu}_{26}\text{Cr}_2\text{Ge}_6\text{S}_{32}$  phase has a larger Seebeck coefficient compared to the  $\text{Cu}_{26}\text{Mo}_2\text{Ge}_6\text{S}_{32}$  and  $\text{Cu}_{26}\text{W}_2\text{Ge}_6\text{S}_{32}$  phases, while it exhibits a lower cell parameter (Figure 1, right). A stronger argument is the observation of constant or even slightly decreasing Seebeck

coefficient in the series  $\text{Cu}_{26}\text{Cr}_{2-x}\text{Mo}_x\text{Ge}_6\text{S}_{32}$  and  $\text{Cu}_{26}\text{Cr}_{2-x}\text{W}_x\text{Ge}_6\text{S}_{32}$ , when the cell parameter increases with the Mo or W content ( $x$ ) (Figure 1, right).<sup>11</sup> Similarly, in  $\text{Cu}_{26}\text{V}_2\text{Ge}_6\text{S}_{32}$  and  $\text{Cu}_{26}\text{V}_2\text{Sn}_6\text{S}_{32}$  (also well-crystallised, non-disordered, and prepared in the same conditions), the cell parameter is significantly lower in  $\text{Cu}_{26}\text{V}_2\text{Ge}_6\text{S}_{32}$  than in  $\text{Cu}_{26}\text{V}_2\text{Sn}_6\text{S}_{32}$ , while their Seebeck coefficients are comparable (Figure 1, right).<sup>5,10</sup> Moreover, the series  $\text{Cu}_{26-x}\text{Nb}_2\text{Sn}_{6+x}\text{S}_{32-6}$  (Ref. 59 in Figure 1, left) exhibits an opposite trend with a negative slope of the Seebeck coefficient versus cell parameter.<sup>7</sup> This behaviour is not addressed by Kamińska *et al.*<sup>4</sup> while it is logically linked to a change of composition (Cu/Sn ratio). In summary, those opposite behaviours clearly demonstrate that the main statement and conclusion proposed by Kamińska *et al.* in their article are erroneous.

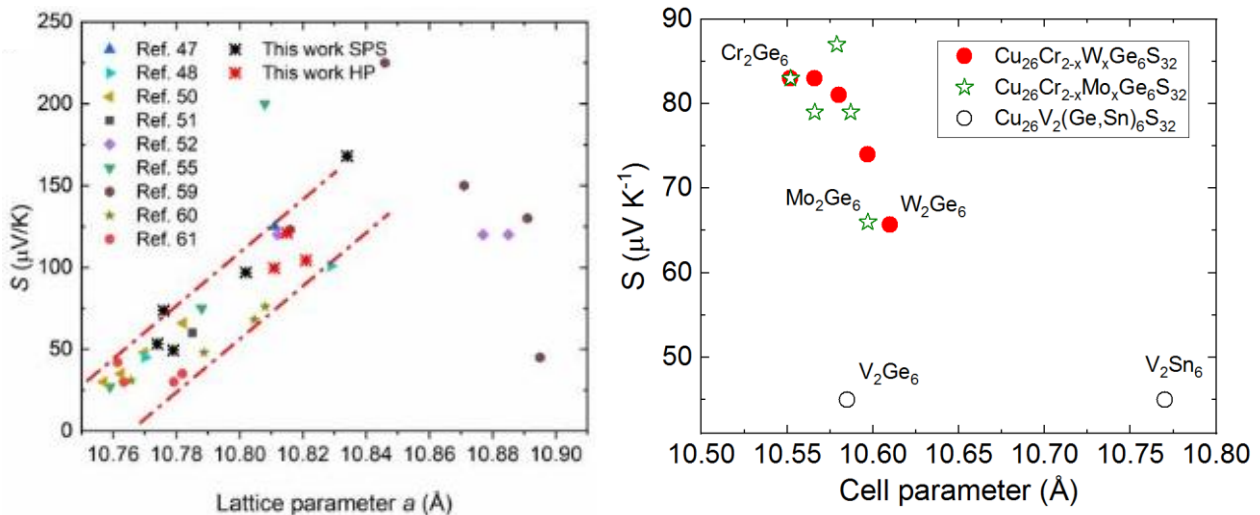


Figure 1. Seebeck coefficient as a function of cell parameter from Kamińska *et al.* (left) and in three different series of isostructural colusite phases (right).

On the top of this, the Figure 8 and associated text, published by Kamińska *et al.*,<sup>4</sup> is also partially erroneous: "It is noteworthy to mention that the obtained maximum  $PF$  ( $PF_{max}$ ) values constitute a record in the Sn-based colusite at 700 K as well as an increase of more than 35 % of the average  $PF$  highly valuable in these cost-efficient sulfide compounds." The average  $PF$  value obtained by Kamińska *et al.* is about  $0.95 \text{ mW m}^{-1} \text{ K}^{-2}$ , which is indeed about 35% higher than the value of  $0.7 \text{ mW m}^{-1} \text{ K}^{-2}$  published in  $\text{Cu}_{25}\text{ZnV}_2\text{Sn}_6\text{S}_{32}$ . However, the authors omitted to consider in their figure and discussion the average  $PF$  value of  $0.85 \text{ mW m}^{-1} \text{ K}^{-2}$  achieved by Guélou *et al.*,<sup>3,12</sup> *i.e.* very close to the maximum value of  $0.95 \text{ mW}$

$\text{m}^{-1} \text{K}^{-2}$  reported by Kamińska *et al.* and obviously within experimental uncertainty (estimated to be about 11% for the power factor).

In conclusion, the aim of the present comment was to draw attention on the crystal chemistry of thermoelectric sulfides which requires detailed investigations to understand the close relationships between crystal structures, chemical compositions and transport properties. It clearly emphasizes that careful comparisons, taking into account all the aspects of crystal chemistry, should be systematically performed in order to elucidate the subtle influence of order/disorder phenomena on the electrical properties of these materials.

## CONFLICTS OF INTEREST

The author declares no conflict of interest.

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None

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