SUPPLEMENTARY INFORMATION FOR

Understanding the Origin of Disorder in Kesterite-type Chalcogenides $A_2ZnBQ_4$ ($A = Cu, Ag; B = Sn, Ge; Q = S, Se$): the Influence of Inter-layer Interactions.

Panagiotis Mangelis, a Alex Aziz, a Ivan da Silva Gonzalez, b Ricardo Grau-Crespo, a Paz Vaqueiro a and Anthony V. Powell a

a Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, England, United Kingdom
b STFC, Rutherford Appleton Laboratory, ISIS Facility, Didcot OX11 0QX, United Kingdom

S.1: Synthesis Procedure

The optimum synthetic procedure described below was established following exploratory synthesis in which a range of reaction temperatures and times were explored. The conditions presented are those which produce high-purity phases. Cu$_2$ZnSnSe$_4$, Cu$_2$ZnGeSe$_4$ and Cu$_2$ZnSnS$_4$ were prepared by heating the mixtures of elemental powders at 650 °C for 48 hours. The same reaction temperature was used to prepare Cu$_2$ZnGeS$_4$, although the heating time was extended 96 hours. The second firing of selenides was carried out at 800 °C for 96 hours. The synthesis of sulphides, Cu$_2$ZnSnS$_4$ and Cu$_2$ZnGeS$_4$, required a second firing for 96 hours at 850 °C and 700 °C respectively. A heating / cooling rate of 2 °C min$^{-1}$ was applied in each firing of all compounds. For the synthesis of Ag$_2$ZnSnS$_4$ one firing was necessary at 650 °C for 96 hours with a heating / cooling rate of 0.5 °C min$^{-1}$. The corresponding selenide, Ag$_2$ZnSnSe$_4$, was prepared mechanochemically. Stoichiometric amounts of powdered elements were sealed, under an argon atmosphere, into a 25 mL stainless steel jar, together with thirty 6 mm diameter steel balls. The mixture was milled for 4 h at 600 rpm using a Retsch PM100 planetary ball mill and subsequently annealed at 500 °C for 30 min in an evacuated and sealed fused-silica tube.
S.2: Analysis of Powder X-ray Diffraction Data

All materials were initially analysed by powder X-ray diffraction. Rietveld refinements were carried out for all materials in the space groups $I-4$ and $I-42m$. Following the refinement of the scale factor, the background parameters were refined using the reciprocal interpolation function. Subsequently, zero point, lattice parameters, atomic coordinates of the anions and thermal parameters were introduced into the refinement. The peak shape was modelled using a pseudo-Voigt function which mixes Gaussian and Lorentzian functions. Initial refinement of cation site occupancy factors was carried out without constraints, using the idealized fully ordered structural model for each structure type. Site occupancy factors showed no significant deviation from full occupancy and they were subsequently fixed at unity.

S.3 Band structures and band gaps

Table S1 presents the calculated band gaps for all the compositions included in this study, as obtained for the K1 and K2 configurations using the HSE functional, in comparison with available experimental values. The substitution of S with Se tends to decrease the band gap, whereas the substitution of Cu with Ag tends to increase the band gap. These trends are consistent with experiment, as shown in the table. The band gap values calculated for K1 and K2 configurations are similar, except in the Ag-based materials, where only the K1 configuration is relevant due to the high degree of ordering.
Table S1. Band gaps calculated for different compositions of the $A_2BCX_4$ system in the K1 and K2 configurations (eV)

<table>
<thead>
<tr>
<th></th>
<th>K1</th>
<th>K2</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZGS</td>
<td>2.09</td>
<td>2.04</td>
<td>1.88–2.20[1.2]</td>
</tr>
<tr>
<td>CZGSe</td>
<td>1.26</td>
<td>1.17</td>
<td>1.40–1.43[1]</td>
</tr>
<tr>
<td>CZTS</td>
<td>1.49</td>
<td>1.46</td>
<td>1.47 - 1.51 [3-11]</td>
</tr>
<tr>
<td>CZTSe</td>
<td>0.91</td>
<td>0.88</td>
<td>0.97-1.04[12-14]</td>
</tr>
<tr>
<td>AZTS</td>
<td>1.74</td>
<td>1.56</td>
<td>2.00[2]</td>
</tr>
<tr>
<td>AZTSe</td>
<td>1.08</td>
<td>0.92</td>
<td>1.40[15]</td>
</tr>
</tbody>
</table>

Figure S1 Multibank Rietveld refinement for Cu$_2$ZnGeSe$_4$ using powder neutron diffraction data collected at room temperature. Observed (black crosses), refined (red solid lines), difference (lower blue line) profiles. Reflection positions are marked by olive lines.
Figure S2 Multibank Rietveld refinement for Cu$_2$ZnSnS$_4$ using powder neutron diffraction data collected at room temperature. Observed (black crosses), refined (red solid lines), difference (lower blue line) profiles. Reflection positions of the Cu$_2$ZnSnS$_4$ phase are indicated by olive markers, while navy markers denote SnS.
Figure S3 Multibank Rietveld refinement for Cu$_2$ZnSnSe$_4$ using powder neutron diffraction data collected at room temperature. Observed (black crosses), refined (red solid lines), difference (lower blue line) profiles. Reflection positions of the Cu$_2$ZnSnSe$_4$ phase are indicated by olive markers, while navy markers denote SnSe.
Figure S4 Multibank Rietveld refinement for Ag$_2$ZnSnS$_4$ combining powder neutron and X-ray diffraction data collected at room temperature. Observed (black crosses), refined (red solid lines), difference (lower blue line) profiles. Reflection positions are marked by olive lines.
Figure S5 Multibank Rietveld refinement for Ag$_2$ZnSnSe$_4$ combining powder neutron and X-ray diffraction data collected at room temperature. Observed (black crosses), refined (red solid lines), difference (lower blue line) profiles. Reflection positions of Cu$_2$ZnSnSe$_4$ phase are indicated by olive markers, while navy and pink markers denote SnSe and ZnSe respectively.