Unusual Sn State in the Superconducting Entropy Stabilized Selenide $Ag_{1-x}Sn_{1+x}Se_2$

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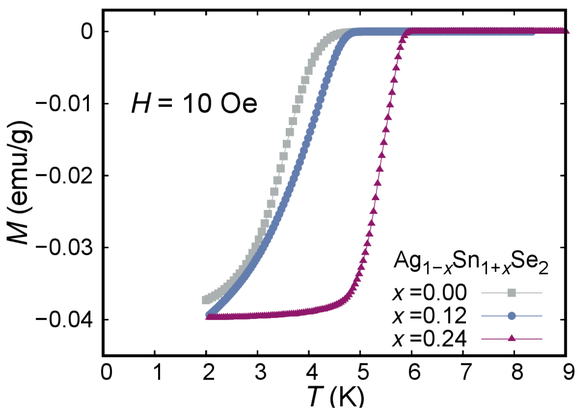
$Ag_{1-x}Sn_{1+x}Se_2$ in Rock-Salt Structure

Crystal Structure and Magnetization

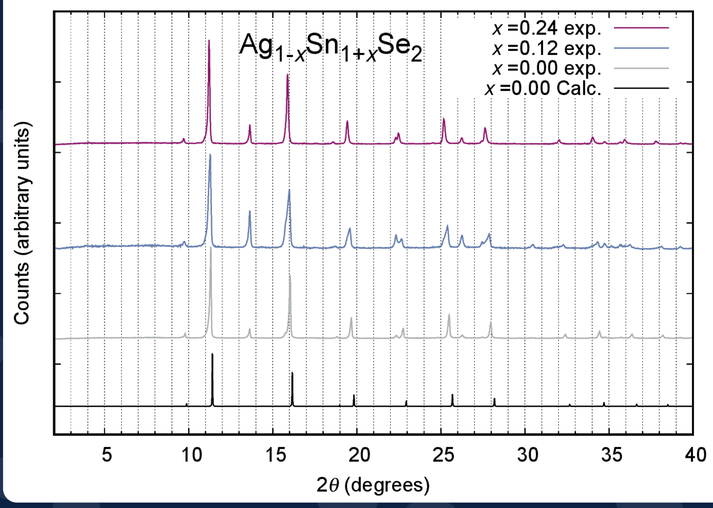
- $Ag_{1-x}Sn_{1+x}Se_2$ crystalize in FCC rocksalt structure for $0 \le x \le 0.24$ [1], while AgSe does not crystalize and SnSe crystalizes in *Pnma*
- $Ag_{0.76}Sn_{1.24}Se_2$ has the highest reported T_c of 6.9 K, and anomalous metallic state observed in AgSnSe2 [2].
- Stability of $Ag_{1-x}Sn_{1+x}Se_2$ in FCC structure may be due to entropy stabilizing the structure. Ag and Sn share the same crystallographic site in a non-ordered fashion. $Ag_{1-x}Sn_{1+x}Se_2$ may fall into Low Entropy Alloys, since only two elements share the site.
- If Ag and Sn sites are disordered, then what are their oxidation states?

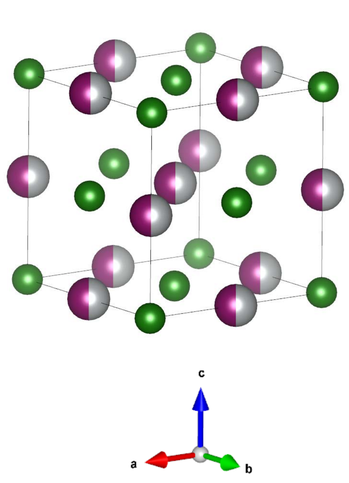


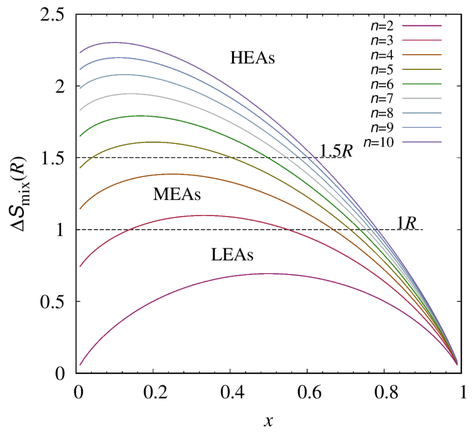
Low Entropy Alloys

Entropy of mixing for alloys with *n* components and concentration *x* for one component. Other components have equivalent concentration [3]

$$\Delta S_{mix} = -R\left[x\ln x + (1-x)\ln\left(\frac{1-x}{n-1}\right)\right]$$



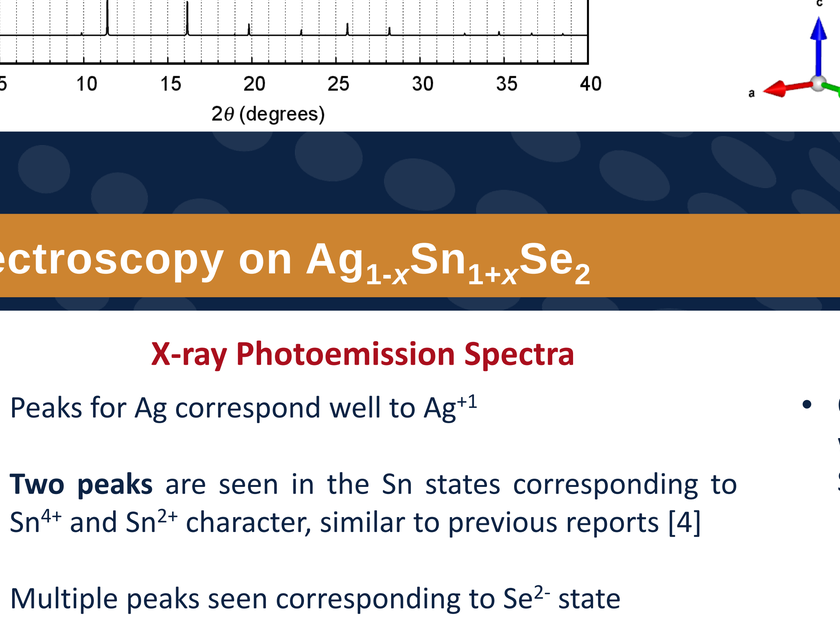




Spectroscopy on $Ag_{1-x}Sn_{1+x}Se_2$

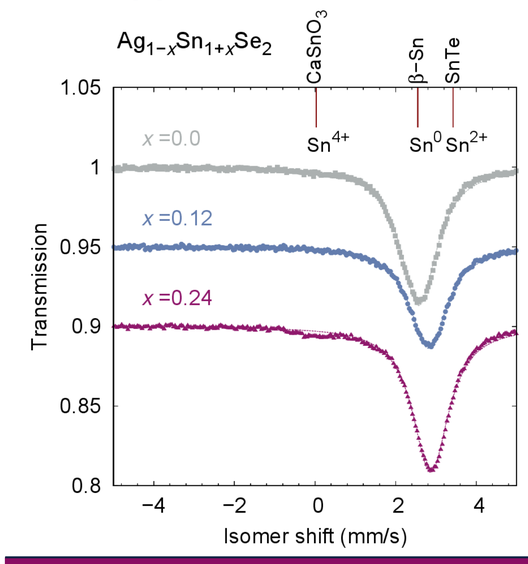
X-ray Photoemission Spectra

- Peaks for Ag correspond well to Ag^{+1}
- **Two peaks** are seen in the Sn states corresponding to Sn^{4+} and Sn^{2+} character, similar to previous reports [4]
- Multiple peaks seen corresponding to Se^{2-} state



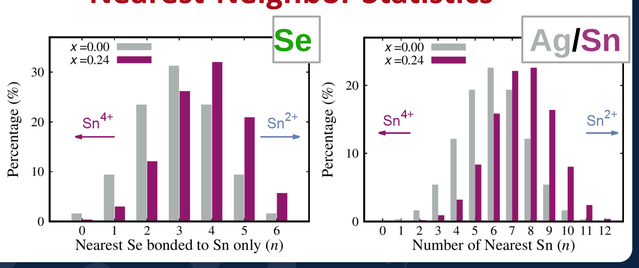
Mössbauer Spectra

- Only one peak seen Mössbauer spectra, which corresponds to previously observed Sn^{3+} state [5]



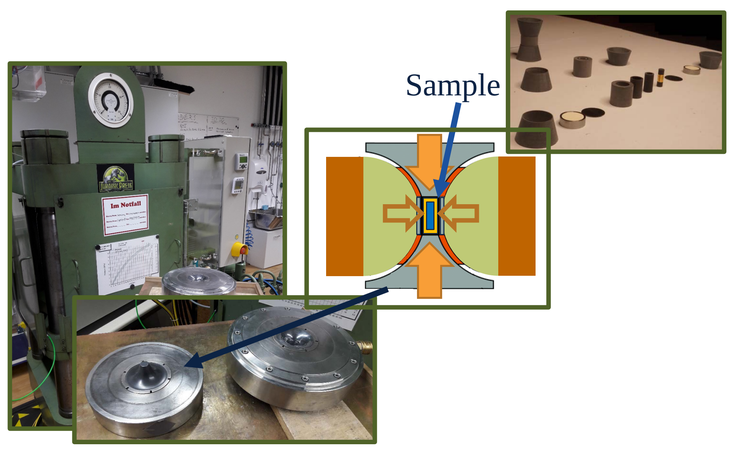
	IS(mm/s) vs BaSnO3	Width(mm/s)
$AgSnSe_2$	2.59	1.09
$Ag_{0.88}Sn_{1.12}Se_2$	2.83	1.10
$Ag_{0.76}Sn_{1.24}Se_2$	2.88	1.08

Nearest-Neighbor Statistics



High Pressure Synthesis

Solid state syntheses of $Ag_{1-x}Sn_{1+x}Se_2$ have been carried out at **~6 GPa** and **600 ° C**. A Belt-type press (**bottom**) allow the synthesis of samples with volumes of more than ≈100 mm^3.

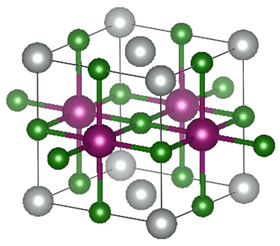


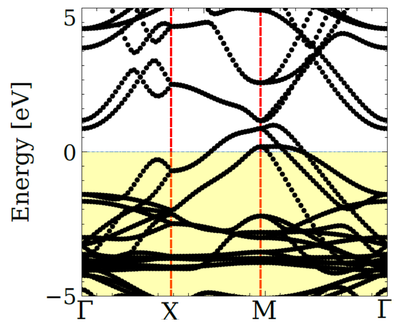
Band Calculations

Calculations, AgSe and SnSe in Rock-salt structure. SnSe predicted as TI [6]

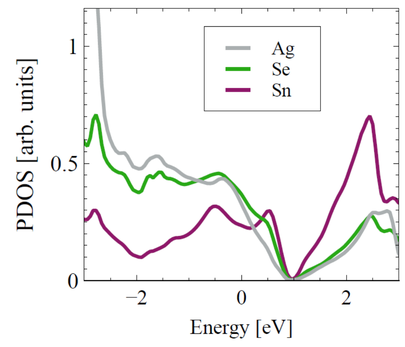
$AgSnSe_2$

Band calculation for ordered AgSnSe2





Contribution from all three elements near the Fermi level, which is consistent with metallic behaviour



Acknowledgements and References

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6. Y. Sun, et al., *Phys. Rev. B* **88**, 235122 (2013).

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