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XAFS analysis of Cu-doped $SnSe_2$ nanostructured thermoelectric materials

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1 Introduction

Tin diselenide ($SnSe_2$) – an n-type semiconductor with a hexagonal, layered, crystal structure – has gained attention as a potential sustainable thermoelectric (TE) material, which can convert directly between a temperature difference and an electric current. $SnSe_2$ represents one of the few n-type TE materials which is both sustainable – avoiding the use of the rare Te, or the toxic Pb – and has shown a relatively high dimensionless thermoelectric figure of merit, *ZT* value, when doped with halogens such as Cl and Br.[1,2]

Cu has also been reported as a potential promising dopant for $SnSe_2$ – with relatively small amounts leading to significant increases in the carrier concentration, n, and thus electrical conductivity. However, there are contradicting reports as to the mechanism and effect of Cu doping. One reported a significantly increased n at low temperatures, but the mechanism was not clarified.[3] Another report suggested that Cu atoms intercalate between the layers of the $SnSe_2$ crystal structure and that ionization of these atoms leads to electron donation, but only at high temperatures.[4]

Given the important potential that Cu doping has in improving the TE properties of $SnSe_2$, in this study we synthesized $SnSe_2$ nanosheets (NSs) with ($SnSe_2$:Cu) and without ($SnSe_2$) Cu doping. The NSs were investigated using XAFS measurement to provide insights into the location and effects of the Cu doping. The NSs were also sintered into pellets to measure the TE properties of the material.

2 Experiment

$SnSe_2$ and $SnSe_2$:Cu NSs were synthesised using a wet chemical method previously reported.[5] The source of Cu doping was an impurity in the Sn precursor, Sn (IV) acetate, while the Cu-free $SnSe_2$ NSs were synthesised by changing the Sn precursor to SnF_4.

The NSs were mixed with boron nitride and hand pressed for 5 minutes to form pellets for the measurements of XAFS. XANES and EXAFS measurements were performed for both the Sn and Se *K*-edges in transmission mode at BL-NW10A of the PF-AR facility.

To check the TE properties, $SnSe_2$:Cu NSs were sintered into a pellet by hot press and measurement was conducted using Light Flash Analysis (LFA) and a ZEM-3. The carrier concentration was measured using the Hall measurement method in a Physical Properties Measurement System.

3 Results and Discussion

$SnSe_2$:Cu demonstrated a significantly increased Hall carrier concentration, n_H, over the reported value for undoped, bulk $SnSe_2$[6] – with a value of 1.2×10^{19} cm^{-3} compared with 2.3×10^{18} cm^{-3} for bulk $SnSe_2$ at approximately 300 K. Indicating that the presence of Cu is capable of increasing the value of n_H even at room temperature.

XANES and EXAFS spectra of the Se *K*-edge for both the $SnSe_2$ and $SnSe_2$:Cu samples, showed no significant difference, indicating that the presence of Cu has no significant effect on the Se atoms.

The Sn K-edge spectra, on the other hand, showed some key differences. As shown by the XANES spectra and its first derivative in Fig. 1a, the edge jump energy of $SnSe_2$:Cu was slightly reduced, indicating that some Sn atoms have been reduced from Sn^{4+} to Sn^{2+} in order to maintain charge neutrality of the lattice due to the inclusion of Cu^+ ions.

The k^3-weighted EXAFS oscillations for the Sn k-edge were plotted and their Fourier transforms (FT) are shown as the dotted lines in Fig. 1b. The two sample's data was also fitted using FEFF calculations and the results are shown by the solid lines in Fig. 1b. The main peak represents the Sn-Se bond, while the second largest peak represents the Sn-Sn path. The significant increase in the Sn-Se peak intensity indicated the increase of the coordination number of the Sn atoms. The FEFF calculation results also showed that, while the Sn-Se bond length was not significantly changed, the Sn-Sn interatomic distance was slightly decreased – from 3.844 Å for $SnSe_2$ to 3.819 Å for $SnSe_2$:Cu.

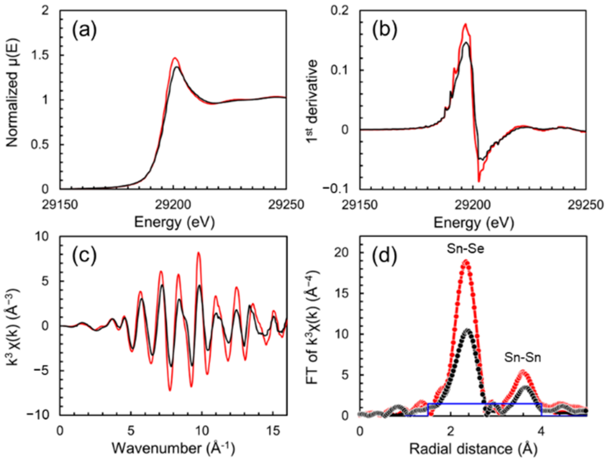

Fig. 1: XAFS measurement results for the Sn *K*-edge of $SnSe_2$ (black) and $SnSe_2$:Cu (red) NSs. (a) XANES spectra; (b) First derivative of (a); (b) k^3-weighted EXAFS oscillations; (d) FT of (c), where dotted lines are the raw data, solid lines show the fitting results by FEFF calculation, and the calculation window is shown in blue.

From these results we can conclude that Cu^+ ions mostly likely enter the crystal structure of $SnSe_2$, not by substituting Sn, but by intercalating between the layers, at a distance from a Sn atom which is close to the Sn-Se bond length (Fig 2). The result of this is the attraction of the nearby Se^{2-} ions, which move slightly towards Cu^+, but maintain the same distance to the Sn atom (Fig 2a). The neighbouring Sn then shifts towards the space vacated by the moving Se atoms, shortening the distance between the two Sn atoms (Fig 2b). The presence of Cu^+ ions also likely causes the reduction of Sn^{4+} to Sn^{2+} to maintain charge neutrality of the lattice.

Finally, a DFT calculation was performed for a 1×1×1 cell of $SnSe_2$ (Fig 2c) and a 2×2×2 supercell of $SnSe_2$:Cu containing a single Cu^+ ion intercalated between the layers of the crystal structure (Fig. 2d). The results confirmed that in that position, the Cu^+ ion has a significant contribution to the density of states (DOS) of the valence band of $SnSe_2$, pushing the Fermi level into the conduction band and thus resulting in an increased carrier concentration.

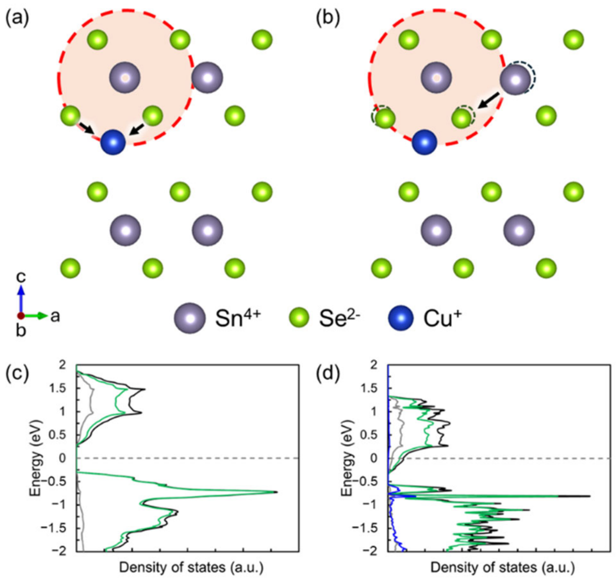

Fig. 2: (a), (b) schematic image showing the entry of Cu^+ ions into the crystal structure of $SnSe_2$. (c), (d) DFT total DOS calculations for (c) $SnSe_2$ and (d) $SnSe_2$:Cu. Black, green, gray, and blue represent the total DOS and contributions from Se^{2-}, Sn^{4+} and Cu^+, respectively.

4 Conclusions

Through XAFS analysis and DFT calculation, we were able to identify the location of the Cu^+ dopant ions in the n-type TE material $SnSe_2$ and gain new insights into the mechanism by which Cu doping can increase the carrier concentration, which will be of significant use in further development of this and other TE materials.

References

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