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Identification of Anion Sites in BiCuXO (X= Se, S) Heteroanionic Materials

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Heteroanionic materials (HAMs) are inorganic compounds containing more than one anionic species. There has been a significantly increased interest in HAMs owing to the possible arise of new phenomena by combining different anionic characteristics, such as charge, ionic radii, electronegativity, and polarizability, otherwise inaccessible [1,2]. BiCuSeO and BiCuSO are two good representatives of HAMs. They are quintenary compounds with space group P4/nmm, which is isostructural to ZrCuSiAs. BiCuSeO is a new promising thermoelectric material with higher ZT (~1.2) while BiCuSO shows a high Seebeck coefficient (~600μV/K). Both adopt a layered structure formed by fluorite $[Bi_2O_2]^{2+}$ and anti-fluorite $[Cu_2S_2]^{2-}$ or $[Cu_2Se_2]^{2-}$ layers stacked along the c-axis [3]. Precise structural characterization is critical because the position of the anions alters the local atomic and electronic structure. As such, determining both local and global anion bonding is necessary for fundamental understanding of these compounds.

Here, we use Scanning Transmission Electron Microscopy (STEM) to depict a complete picture of the layered structure including identification of the anion positions in BiCuSeO and BiCuSO. The crystals of BiCuSeO and BiCuSO prefer to grow along *a*-axis and *b*-axis (Fig. 1a and Fig. 1b). Therefore, TEM sample preparation becomes challenging as the ground flakes naturally favor the *c*-direction, which makes access to the *a* and *b* axes difficult. To overcome these issues and to access all crystal orientations, samples were prepared by ultramicrotomy. BiCuSeO and BiCuSO single crystals were ground using a mortar and pestle and the micron-sized particles embedded in resin. Then, several sections with 80~90 nm thickness are obtained.

In the high-angle annular dark-field (HAADF) images the contrast is based on scattering amplitude whose sensitivity depends on the scattering power of the relevant atoms, therefore, position of bismuth, copper, and selenium are distinguishable (Figs. 2a and 2c). To identify the positions of lighter atoms: oxygen and sulfur, annular bright-field (ABF) phase-contrast imaging based on wave interference is be preferred, since they have extremely weak scattering (Fig. 2b and Fig. 2d).

Owing to their layered structure, BiCuSeO and BiCuSO show anisotropic electrical and thermal conductivity along in-plane and out-plane directions [4]. Making full use of hydrothermal method, relatively defect-free single crystals can be obtained. Therefore, we can measure their intrinsic properties. The ability to unravel the atomic scale structural information of HAMs is of great importance for improvement of the performance of thermoelectrics, as it can be used to directly corelate their structure to the observe anisotropic properties [5].

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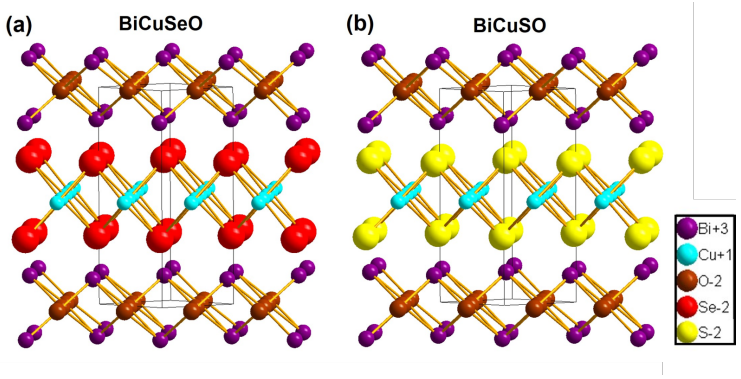

Figure 1. Crystal structure of BiCuSeO(a) and BiCuSO(b), viewed at [110] direction which shows the layered structure.

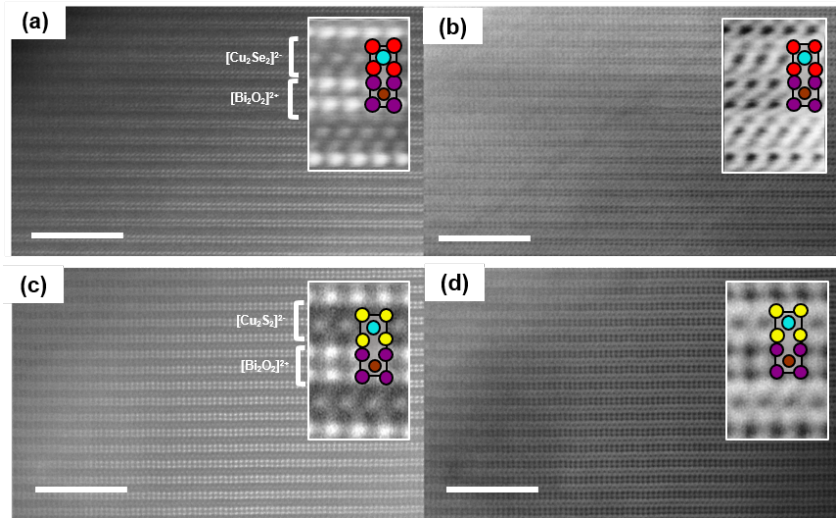

Figure 2. HAADF(a) and ABF(b) image of BiCuSeO along [110] direction, which shows the $[Cu_2Se_2]^{2-}$ and $[Bi_2O_2]^{2+}$ layers. HAADF(c) and ABF(d) image of BiCuSO along [110] direction, which shows the $[Cu_2S_2]^{2-}$ and $[Bi_2O_2]^{2+}$ layers. Scale bars are 5 nm.

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