STEM analysis of doping atom positions in η-Cu_6Sn_5

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Environmental concerns have recently resulted in Pb-free Cu-Sn-based solder alloys being commonly used in the electronic device sector. During the soldering process, the intermetallic compound Cu_6Sn_5 spontaneously forms. However, Cu_6Sn_5 is a complex phase which has been found to exist in at least five variants (η', η, η^{6}, η^{8}, η^{4+1}) [1, 2]. The two main crystal structures of Cu_6Sn_5 are the high temperature η phase and the low temperature η' phase. The crystal structure of η phase (P63/mmc) is derived from the NiAs structure, in which Ni and As are replaced by Cu and Sn respectively. Beyond that, 1/5 of the trigonal bipyramidal sites in NiAs structure are randomly occupied by Cu atoms. The two different Wyckoff sites of the former and the latter for Cu are referred to as Cu1 and Cu2, respectively. The η phase is a disordered structure, while the η' phase (C2/c) is an ordered structure.

The transformation from η phase to η' phase is harmful to the stability of electronic devices owing to a significant volume change. However, researchers have found that after being doped with trace elements including Au and Ni, the Cu_6Sn_5 can be stabilized as the η variant, even down to room temperature [3]. In addition, the EPMA composition analysis and the first-principle calculations have shown Au and Ni atoms both occupy the Cu sites in Cu_6Sn_5 although this has not been previously experimentally verified.

In our study, direct evidence was found to show that Au atoms are located on the Cu1 sites in η-Cu_6Sn_5. The stoichiometric $(Cu, Au, Ni)_6Sn_5$ intermetallic used in this experiment was prepared by direct alloying. High-angle annular dark eld (HAADF) imaging, bright field (BF) imaging and atomic-resolution elemental mapping were taken by the aberration-corrected (Cs-corrected) scanning transmission electron microscopy (STEM). The noise in the atomic-resolution elemental mapping images was reduced by using a non-local principle component analysis (NLPCA) process. It is found that the stoichiometric $(Cu, Au, Ni)_6Sn_5$ intermetallic results in the stable η phase. The atomic sites of Cu1 and Sn can be distinguished in atomic-resolution images after being observed from orientation $[2\bar{1}\bar{1}0]$, which is also confirmed by atomic-resolution elemental mapping analysis. Importantly, the distribution of dopant Au atoms was directly shown in the atomic-resolution elemental mapping image after being denoised with Au atoms occupying the Cu1 sites in η-Cu_6Sn_5.

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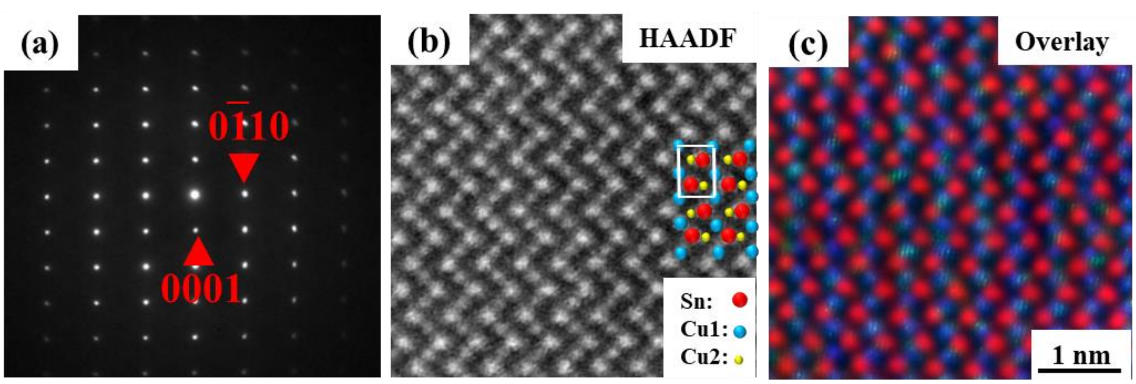

Fig.3. (a) The diffraction pattern, (b) The HAADF image and (c) Noise reduction overlay image of atomic-resolution elemental mapping: Sn(red), Cu(blue), Au(green), Ni(yellow)