Abstract

This thesis deals with the experimental and theoretical investigations to understand the atomic ordering and site preference of neighboring elements in Cu-rich intermetallic phases. The intermetallic compounds were prepared by the traditional high-temperature solid-state synthesis starting from highly pure constituent elements. Multiple structural characterization methods such as X-ray diffraction, neutron diffraction and energy dispersive X-ray spectroscopy analysis were employed in the experimental portion of this work. To complement the information from synthetic experiments, density functional theory (DFT) based first-principles computational codes such as tight-binding linear muffin-tin orbital employing atomic sphere approximation (TB-LMTO-ASA) and Vienna ab-initio simulation package (VASP), were used for electronic structure calculations.

Unusual atomic ordering and site preference of two neighboring transition metals Cu and Zn in $Cu_6Zn_2Sb_2$ [*P*4/*nmm*; 129] were investigated by combined experimental single crystal X-ray and neutron powder diffraction as well as the first-principles electronic structure calculations. The atomic ordering of Cu and Zn, previously observed in β'-CuZn, was found to persist upon the addition of Sb. The structure is built up by the sequential arrangement of $^{2}_{\infty}[Cu_3Sb]$ slabs and sheets of Zn atoms or as stacking of Cu_2Sb-unit cells interleaved with β'-brass layers along *c*-direction. The specific substitution pattern of Zn to Cu site leads to the observed phase width from $Cu_5Zn_3Sb_2$ to $Cu_6Zn_2Sb_2$.

Ternary Cu-Zn-X (X = Sn, In) compounds adopt the γ-brass structure type and exist in an extended homogeneity range, and obey the Hume-Rothery valence electron concentration rule. X-ray diffraction analyses confirm the site-specific Sn and In substitution in γ-brass structures. γ-Brass type phases with *P*-cell are formed in the Cu-Zn-Sn ternary intermetallics; whereas both *I*- and *P*-cell cubic γ-brass type phases exist for the Cu-Zn-In system.

γ-Brass type phase $Cu_{41}Sn_{11}$ [$F\bar{4}3m$; 216] in the binary Cu-Sn system has been reinvestigated. These structures are constructed by four independent 26-atom γ-clusters and centered at the four high symmetry points of the unit cell. Electronic structure calculation shows that the phase is stabilized by the Hume-Rothery mechanism.

Ternary intermetallic compound Cd_2Cu_3In [$P4_132$; 213] that is an ordered substitution variant of cubic $MgCu_2$ structure type has been uncovered. The unexpected atomic ordering of two neighboring elements Cd and In has been investigated by first-principles DFT calculations, which identify the In-Cu and Cd-Cu bonding effect on the unusual observed ordering of In and Cd in the structure of Cd_2Cu_3In. The structure is described as a three-dimensional network of vertex sharing [Cu_3In] tetrahedra, whereas Cd atoms form a diamond-like network.

Keywords: Intermetallics; Gamma brass; Atomic ordering; Site preference; X-ray diffraction; Electronic structure calculations.