Uncovering the element-specific interatomic distances throughout the Cu(Br,I) alloy system

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Copper(I) iodide (CuI) is both a transparent and p-type semiconductor with various applications, e.g. in diodes, solar cells, blue and UV LEDs and thin film transistors. [1][2] Next to various other forms of doping and alloying, anion substitution with bromide can be used to tune the free hole concentration in functional layers, enabling optimized performance of active devices.[3]

To understand the change of material properties with different alloying compositions, it is vital to investigate not only the crystal structure, but the displacement of the atoms in their local environment within the crystal lattice. In consequence, X-ray absorption spectroscopy was used at the Cu, Br and I K-edges to determine the fine structure of $CuBr_{1-x}I_x$ samples. The samples investigated had anion compositions x varying from 0 to 1 and were realized by solid state synthesis of crystalline powders or by pulsed laser deposition.[4]

The absorption spectra at the Cu K-edge - both in the near-edge and extended region - prove the formation of copper oxides, primarily in the powder samples. The thin films had been capped with an Al_2O_3 layer in situ, as an approach to prevent further post-deposition oxidation. The analysis of the extended fine structure at the I and Br K-edges reveals a nonlinear change of the average Cu-Br and Cu-I bond lengths with composition x with consistent results for powder and thin film samples. This bond length dependence is different from that observed for group III-V and group II-VI zincblende alloys,[5] which show a linear dependence on the composition. Comparison to the bond length change in $RbBr_{1-x}I_{x,}$[6] crystallising in the rock salt structure, shows similarities that may identify this bond length bowing as a characteristic feature of group I-VII alloys.

Unlike the first nearest neighbour bond lengths, the distances between second and third nearest neighbouring atoms in the $CuBr_{1-x}I_x$ samples are consistent with previous findings for other zincblende alloys. The respective interatomic distances vary linearly with composition. Furthermore, the distances between third nearest neighbours coincide for both types of absorbing atom and follow the virtual crystal approximation. This indicates that the lattice distortions seen on a local scale due to alloy-induced lattice mismatch average out at distances larger than the second nearest neighbour shell.

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