Refinement of the Modulated Structures of Pb-Free and Pb-Doped Bi-2223 HTSC

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Among the members of the high-temperature superconducting Bi-based family $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ (n = 1, 2, 3), the three-layer compound $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (hereafter Bi-2223) is the most attracting one, because of its high critical temperature 110 K, its better transport properties, and its potential industrial applications. However, it is difficult to synthesize the Bi-2223 phase even at the laboratory scale. Partial substitution of Pb for Bi was found to improve the stability, facilitate the synthesis, and enhance the superconducting properties. Due to oxygen off-stoichiometry and differences in the translation periods of the atom layers, the real crystal structures of these compounds are complex and exhibit incommensurate modulations [1]. The superstructures of $Bi_2Sr_2CuO_{6+\delta}$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2201 and Bi-2212, respectively) have been refined on single-crystal diffraction data [2, 3].

We here report refinements of the structures of Pb-free and Pb-doped Bi-2223 phases from single-crystal X-ray diffraction. Single crystals were grown by the Vapor-Assisted Travelling Solvent Floating Zone method [4, 5]. Diffraction data were collected on a Stoe IPDS II diffractometer equipped with Mo $K\alpha$ radiation, a graphite monochromator, and an imaging plate. The structures were refined by the full-matrix least-squares method based on F, using the program package WinCSD [6]. The modulation was found to be approximately commensurate with a vector $q \sim 0.2a^*$. The reflections could be indexed in a satisfactory way in large primitive orthorhombic cells, which correspond to 5-fold supercells of the conventional side-face centered orthorhombic cells.

The average structures were refined in the orthorhombic space group $A2aa$ with cell parameters a = 5.4210(7), b = 5.4133(6) and c = 37.010(7) Å for the Pb-free phase, and a = 5.3952(14), b = 5.4130(10) and c = 37.042(11) Å for the Pb-doped phase. The Bi site was split into two positions, the two partly occupied sites showing the largest difference in the x coordinates, which is in agreement with a modulation along a. The commensurate approximant superstructures were refined in the orthorhombic space group $Pnnn$, using a 5-fold supercell. An additional oxygen site within the BiO layers was identified.

Refinements of the modulated structures were performed in the (3+1)D-superspace group $A2aa(\alpha 00)000$, considering up to 2nd order satellites corresponding to a modulation vector q = (0.2, 0, 0). A longitudinal displacement modulation of the atoms, with increasing magnitude from the CuO_2 to the BiO layers, was confirmed. The transverse displacement modulation showed the largest magnitude for the Cu and Ca atoms.

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