

## Superstructures of Pb-free and Pb-doped $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ superconducting Phases

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The structures of Bi-2223 and Bi,Pb-2223 were studied by single-crystal XRD. The structures are characterized by incommensurate modulations, however, they can be conveniently described in 5-fold supercells. An additional O atom was found to be inserted in the Bi-O chains, at the level of approximately every 10<sup>th</sup> cation, which defines the translation unit of the modulation wave. A partial substitution of Ca by Bi was also observed in both crystals, and the actual compositions of the crystals were  $\text{Bi}_{2.16}\text{Sr}_2\text{Ca}_{1.84}\text{Cu}_3\text{O}_{10.17}$  (*P222*,  $a = 27.105(4)$ ,  $b = 5.4133(6)$ ,  $c = 37.010(7)$  Å) and  $(\text{Bi}_{1.89}\text{Pb}_{0.22})\text{Sr}_2\text{Ca}_{1.89}\text{Cu}_3\text{O}_{10.18}$  (*Pnnn*,  $a = 26.976(7)$ ,  $b = 5.4130(10)$ ,  $c = 37.042(11)$  Å), respectively. The structures of the  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n+\delta}$  series have a strong 2D character with weak interactions between the BiO layers. In the orthorhombic superstructure of Bi-2223 ( $n = 3$ ), the longitudinal displacement waves of the Bi atoms in two neighboring BiO layers are in phase and, consequently, the transverse waves are out of phase (shifted by 180°). For the monoclinic superstructures of Bi-2212 ( $n = 2$ ) and Bi-2201 ( $n = 1$ ), the phase differences between the transverse waves of the Bi atoms in consecutive slabs are 160 and 72°, respectively. The amplitude of the transverse displacement wave increases with decreasing thickness of the slabs (0.139(7) Å in Bi-2223, 0.156(6) Å in Bi-2212, and 0.310(7) Å in Bi-2201).

**Keywords:** high- $T_c$  superconductor, modulated structure, supercell