VALENT AND CHARGE STATE OF ANTIMONY IONS DOPED IN Bi-CONTAINING HTSC-CERAMICS

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In Bi-containing 2:2:2:3 HTSC-ceramics characterized by increased superconductive transition temperature in comparison with 2:1:4 and 1:2:3 ceramics Bi—O planes give the additional contribution in the states density at the Fermi level together with principal contribution from Cu—O planes. It allows to suppose that Bi-atoms in these systems are not "passive" but perhaps participate in the superconductivity mechanism.

In HTSC-ceramics Bi electronic structure is nearly the same as that of Bi_2O_3 (i.e. the bismuth valence $m \approx 3$, see, for example [1—3]).

Recently Liu Hongbao et al. have reported about superconductivity in Bi—Sr—Ca—Cu—O doped by antimony with $T_c \approx 120\,K$ and $T_c \approx 132\,K$ [4,5]. It is natural to expect that the replacing Bi^{3+} antimony is also in trivalent state.

In this work the X-ray lines shift method (see, for example, [6]) was used to determine the antimony electronic structure in HTSC-ceramic $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_y$ [1)]. The energetical shift of $K_{\alpha 1}$ X-ray line of Sb in $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_7$ concerning metallic Sb with known electronic structure — $Sb^0(5s^25p^3)$ was measured in experiment. The experimental shift $\Delta E_{K\alpha 1} = 173 \pm 5\ meV$ was compared with theoretical shifts calculated within the framework of different modifications of Hartree-Fock method (the analogous procedure is described in [3]). From this comparison the effective charge at the bismuth atoms in $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_y$ was determined ($q_{Sb} \approx 2.0$) and from the charge value the Sb valence was found. The relation $q=im$ was used here, where i-ionicity of the bond in the crystal, m-valence. By assuming that ionicity of the bond in the HTSC oxides is approximately the same as in the antimony oxides (Sb_2O_3 and Sb_2O_5) we get a value $m \approx 4.0$ for the antimony valence in $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_y$. Since in the X-ray lines shift method the average valence of a sample is determined, so the $m \approx 4$ value may also mean a mixture of the Sb tri- and pentavalent ions.

To conclude, it has been revealed that the antimony ions replacing the trivalent bismuth in HTSC-ceramics are in the tetra (or in mixed tri-, penta-) valent state. This state is realized independently of the initial antimony valence at the synthesis. We have synthesized $Bi_{1.9}Sb_{0.1}Sr_2Ca_2Cu_3O_y$ at the Sb_2O_3 and Sb_2O_5 basis. Both syntheses lead to the antimony valent state in ceramics with $m \approx 4.0$ [2)]

References

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