EFFECT OF OXYGEN STOICHIOMETRY ON T_c OF Bi-BASED SUPERCONDUCTORS

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The role of oxygen stoichiometry on T_c is relatively well established on La₂CuO_{4+x} and the YBa₂Cu₃O_{7-x} (123) superconductors[1,2], as compared to the Bi-based superconductors. In this paper we will present results of our investigations on the effects of oxygen stoichiometry on the transition temperature T_c of Bi₂Sr₂CaCu₂O_{8+x} (2212 phase), and Pb-doped Bi₂Sr₂Ca₂Cu₃O_{10+x} (2223 phase). We show that the effects of oxygen stoichiometry on T_c of these two phases are very different. These results might be helpful in understanding the mechanism of superconductivity in the Bi-based superconductors.

The 2212 and 2223 phases of Bi-based superconductors were synthesized using appropriate amounts of analytical grade Bi2O3, PbO, SrCO3, CaCO3 and CuO by the solid state reaction method. Some details of the method to produce the 2212 phase with excess oxygen has been recently reported[3]. Experiments on the thermal cycling of the annealed samples to change in oxygen stoichiometry are done using TGA affect (Thermogravimetric Analysis) technique which allows us to monitor weight changes of ~ 0.01%, followed by magnetic and resistivity studies to observe changes in T_c and superconductivity. In Fig.1, we present recent results on the change in T_c for the 2212 phase vs weight change produced by thermal cycling (heating in air to different temperatures up to 850 $^{\rm O}C$ and cooling in air or Ar)[3]. An increase of T_c from 70 to 95 K for 2212 phase corresponding to weight loss of 0.16% is observed. This is opposite to the effect of oxygen stoichiometry on T_c for the La₂CuO_{4+x} and the 123 systems. In a Bi1.6Pb0.4Sr2Ca3Cu4O_x sample, consisting of mainly 2223 phase with small amount of 2212 phase, it is observed that as T_c of the 2212 phase increases from 70 K to above 90 K with weight loss of $\sim 0.2\%$, the T_C of the 2223 phase decreases from 110 K to 106 K. This leads us to infer that excess oxygen resides in different locations in the two phases, viz. Bi-O double layers in the 2212 phase, triple Cu-O layers in addition to Bi-O double lavers in the 2223 phase.

In a recent paper, Hybertsen and Mattheiss[4] have used band structure calculations on the idealized (2212) structure to show that excess oxygen can reduce the metallic conductivity of the Bi-O layers, suppressing T_c . However the actual structure of the 2212 phase differs from the idealized structure and we have no proof that excess oxygen resides in the double Bi-O layers of the 2212 phase. Experiments planned for the near future may determine the location of excess oxygen in the Bi-based systems. These results will also be presented.