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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 La_2CuO_{4+x} and the $YBa_2Cu_3O_{7-x}$ (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 $Bi_2Sr_2CaCu_2O_{8+x}$ (2212 phase), and Pb-doped $Bi_2Sr_2Ca_2Cu_3O_{10+x}$ (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 Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ 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 affect change in oxygen stoichiometry are done using TGA (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 ^oC 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 La_2CuO_{4+x} and the 123 systems. In a $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_x$ 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 ~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 layers 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.