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Synthesis and characterization of $(Tl_{1-x}M_x)(Ba,Sr)_2Ca_2Cu_3O_z$ (M= Pb, K, Bi) cuprates: The chemical control of high-temperature superconductivity*

Teng-Ming Chen and J. S. Ho.

Department of Applied Chemistry, National Chiao-Tung University, Hsinchu, Taiwan 300

The correlation of dopant stoichiometry and superconducting transition temperature (T_c) of three series of metal-doped $(Tl_{1-x}M_x)(Ba_{0.5}Sr_{1.5})Ca_2Cu_3O_z$ (M= Pb, K, Bi; M-doped Tl-1223) cuprates was investigated. X-ray pure samples were obtained for all phases with $x \leq 0.25$, ≤ 0.25 and 0.60 for M = K, Bi and Pb, respectively. The T_c's of M-doped Tl-1223 phases were found to increase significantly with increasing M content for M = Pb and Bi, whereas that for M = K tends to decrease slightly, as indicated by Meissner effect measurements. The enhancement or suppression of superconductivity (i.e., T_c) of Tl-1223 upon M-doping can not be satisfactorily rationalized without including both empirical oxygen and Tl stoichiometry as well as M content.

1. INTRODUCTION

The thallium-based cuprate superconductor with nominal composition of $(Tl_{0.5}Pb_{0.5})Sr_2(Y_{1-y}Ca_y)_2Cu_3O_9$ (Tl-1223) phase was reported to display high critical temperature (T_c= 124K) [1] and high current density with $J_c > 10^5$ A/cm^2 at 77K by Liu et al.[2] It has also been shown by Matsuda et al. [3] that pinning centers can be introduced into Tl-1223 phases by Ba or/and Pb substitution. However, there have been few systematic studies, with clear understanding of the cation and oxygen compositions, on tuning the electronic structure of Tl-1223 phase by appropriate cation substitution reported. We report the effect of controlled metal (M) substitution for Tl in Tl-1223 phase on the variation of crystal structural and superconducting properties of Tl-1223 phases by simultaneously including empirical Tl, M and oxygen stoichiometry and the formal valence of Cu.

2. EXPERIMENTAL

Three series of $(Tl_{1-x}M_x)(Ba_{0.5}Sr_{1.5})Ca_2Cu_3O_z$ (M= Pb, K, Bi) samples with x = 0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 were prepared according to the method reported elsewhere.[4] The determination of oxygen content of M-doped Tl-1223 phases was performed by a modified iodometric titration method reported by Gopalakrishnan [5]. XRD patterns of the M-doped Tl-1223 samples were measured on a MAC Science MXP-3 diffractometer using Cu K_α radiation with a Ni filter. T_c was measured by a dc SQUID magnetometer (MPMS system, Quantum Design) over the temperature range 120-10K under a field of 2.5 mT.

3. RESULTS AND DISCUSSIONS

The substitution limit of M for Tl in M-doped Tl-1223 was found to be 0.25, 0.6 and 0.25 for phases with M = K, Pb and Bi, respectively, as indicated by XRD data. Impurities such as $Tl(Ba,Sr)_2CaCu_2O_x$ with or without doped M were discovered to coexist with M-doped Tl-1223 phases when the substitution limit was exceeded. The cell dimensions of both Pb- and Bi-doped Tl-1223 phases were found to decrease with increasing dopant content, whereas those of K-doped phases were found to increase with increasing K content. This observation is attributed to the difference in ionic size of six-coordinated M and it can be rationalized by considering the following sequence of ionic radii: $K^+ > Tl^{3+} > Pb^{4+} > Bi^{5+}$.

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The temperature-dependent low-field (25 Oe) magnetization data indicated that all three series of M-doped Tl-1223 were bulk superconductors with x ≤ 0.60, 0.25 and 0.25 for M = Pb, Bi and K, respectively, as indicated by Meissner effect data and represented in Fig. 1. In general, the volume fraction of superconducting phases in these M-doped Tl-1223 was found to first increase to an optimal value and then decrease with increasing dopant content.

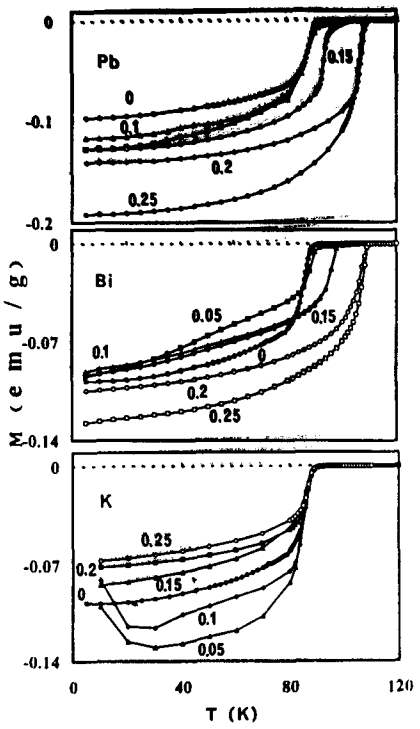

Fig. 1. Field-cooled magnetic susceptibility data for M-doped Tl-1223 phases with M = Pb, Bi and K.

The M-content dependence of T_c is summarized in Fig. 2. T_c of M-doped Tl-1223 phases was found to increase from 93.6K (x = 0) to 112K (x = 0.6), 111K (x = 0.20) for M = Pb, Bi, and deceases down to 91.5K (x=0.25) for M = K, respectively, as the composition of M increases. In general, the substitution of Pb and Bi for Tl in the Tl-1223 phases was considered to be electron-doping, whereas that of K for Tl was considered to be hole-doping. However, the possible rationalization for our observations of T_c variation has been complicated by the difference in oxygen composition from sample to sample and the loss of Tl during sample preparation. Characterizations on the carrier concentration, oxygen composition, crystal structure and magnetization of M-doped Tl-1223 phases are in progress.

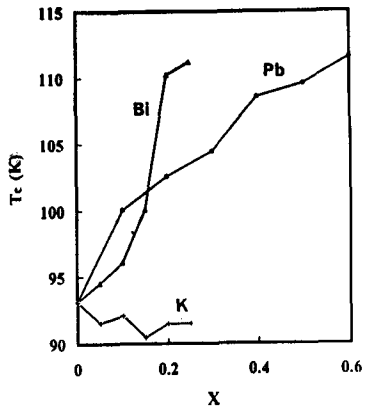

Fig. 2. M-content dependence for M-doped Tl-1223 phases with M = Pb, Bi and K.

4. CONCLUSIONS

The crystal chemistry, variation of T_c and oxygen contents of three series of M-doped Tl-1223 with M = Pb, Bi and K, respectively, were investigated as a function of dopant composition. T_c of Pb- and Bi-doped Tl-1223 phases was found to increase as M content increases, whereas that for K-doped phases was found to decrease slightly with increasing M content. The rationalization should include the valence and composition of M and contents of oxygen and Tl which were found to be difficult to control in sample preparation.

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