EFFECT OF SR ADDITION ON STRUCTURE AND CONDUCTIVITY OF $La_{1-x}Sr_xCuO_{2.5-y}$ PEROVSKITE

Ho-Chieh Yu, Kuan-Zong Fung and Shi-Wei Chuang
Department of Materials Science and Engineering
National Cheng Kung University
Tainan 70101,TAIWAN, Republic of China

ABSTRACT

$La_{1-x}Sr_xCuO_{2.5-y}$ has been recently investigated as a potential superconducting material due to the similarity of its structure and composition compared with $YBa_2Cu_3O_{7-x}$[1].However, this material also exhibits mixed conducting characteristics. In mixed conductors, the aliovalent dopant usually plays an important role on the enhancement of conducting behavior and structural stabilization. Thus, the objective of this work was to study the effect of Sr doping on conductivity and structure stability of the $La_{1-x}Sr_xCuO_{2.5-y}$ using XRD, TEM, AC-impedance spectroscopy. The samples were prepared by conventional ceramic processing. La_2O_3, $SrCO_3$, and CuO were ball-milled in a desired ratio. The powder mixture was then calcined at 800℃ for 24 hours in air. Die-pressed pellets were sintered at 960℃ for 20 hours in air.

The XRD results for samples doped with various amount of SrO, is shown in Fig.1. With the addition of 10% SrO, the powder mixture of La_2O_3 and CuO shows a monoclinic structure after heated at 800℃. With the addition of 15% of SrO, the intensity representing the monoclinic phase significantly reduced. On the contrary, a tetragonal phase was formed. When 20%~30% of Sr was added into La_2O_3 and CuO mixture, only tetragonal phase was observed. This tetragonal phase can be viewed as a $La_{1-x}Sr_xCuO_3$ perovskite with a superstructure due to excessive and ordered oxygen vacancies.However, when the concentration of SrO was increased to 35%, extra reflections from $La_2SrCu_2O_6$ was observed. As more of SrO was added into La_2O_3 and CuO, a Sr-rich phase of $Sr_{0.74}CuO_2$ appeared in addition to the tetragonal phase and $La_2SrCu_2O_6$.

The XRD results indicate that the addition of SrO enhanced the stability of perovskite. Thus, a single tetragonal phase was obtained when X=0.2 or 0.3.The enhancement of Sr addition on the stability of tetragonal perovskite can be rationalized using the following defect reaction:

$$1/2\ O_2 + 2SrO + 2CuO \rightarrow 2Sr_{La}' + 2Cu_{Cu}^{x} + 5O_O^{x} + V_O^{\cdot\cdot}$$

This defect reaction suggests that the incorporation of SrO and CuO into a perovskite lattice in oxygen-rich atmosphere tend to form Cu(Ⅲ) and oxygen vacancy when the formation of oxygen vacancy is favored.

The formation of Cu(Ⅲ) is believed to be the main reason for the stabilization of perovskite. Based on the electroneutrality for a ABO_3 perovskite, divalent cation is not stable in the B-site cation sublattice especially when A site is occupied a trivalent cation such as La^{3+}. When SrO was added into the A-site cation sublattice, Cu(Ⅱ) can be oxidized to Cu(Ⅲ). Thus, the perovskite structure became more stable. As more and more Sr was added , the Cu(Ⅲ) is expected to be saturated under the ambient atmosphere. Thus, Sr-rich phase, $La_2SrCu_2O_6$ and $Sr_{0.74}CuO_2$ were formed. In additions, $LaCuO_3$ perovskite consisting of solely Cu^{3+} as B site ions is not favored either because the tolerance factor estimated is greater than 1.0. This means that Cu^{3+} ion is too small for the octahedral interstice surrounded by oxygen ions.

Fig.2 shows the electrical conductivity plotted as a function of temperature (1/T) for samples doped with various amount of SrO. Without the addition of SrO, the sample exhibited ionic conduction behavior due to the high concentration of oxygen vacancy. With the addition of SrO, the increasing concentration of Cu(Ⅲ) greatly enhanced the electronic conductivity. When the SrO dopant exceed the solubility limit, the SrO-rich second phase suppressed the electronic conduction significantly.

Acknowledgment: This work is supported by Chung-Shan Institute of Science & Technology, Taiwan under the contract # NSC89-2326-D-006-004.

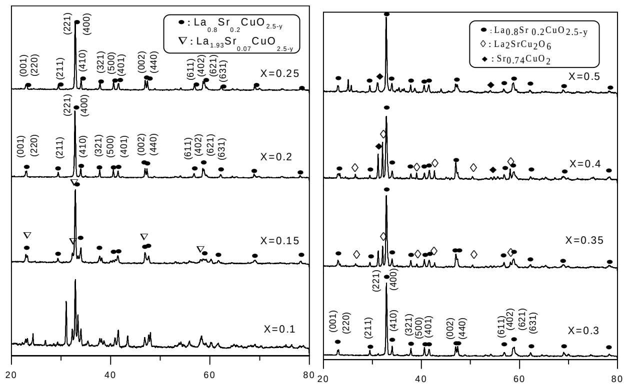

Fig.1 XRD pattern of $La_{1-x}Sr_xCuO_{2.5-y}$, X=0.1~0.5

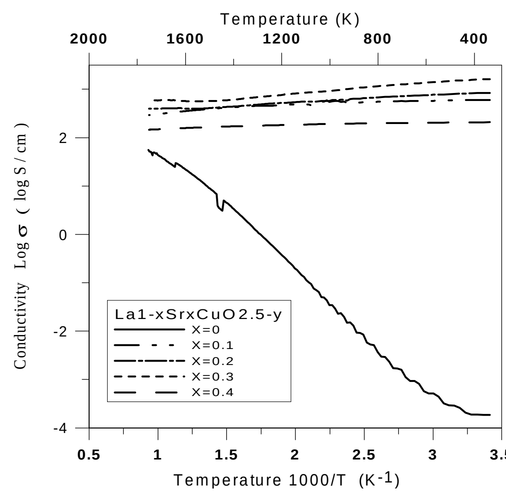

Fig.2 The conductivities of $La_{1-x}Sr_xCuO_{2.5-y}$,X=0.1~0.4, plotted as a function of 1/T (T= 293K to 7073K)

Reference:1.Hervieu, M.; Wang, J.; Provost, J.; Monot, I.; Verbist, K.; Van Tendeloo, G., Physica - C - Superconductivity, Volume: 262, Issue: 3-4, May 20, 1996, pp. 220-226.