Transactions of the Materials Research Society of Japan 28 [2] 349-351 (2003)

Fluorination of $LaBa_2Cu_3O_{6+x}$ Superconductor Prepared by Polymerizable Complex Method.

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Electrochemical fluorination of the $LaBa_2Cu_3O_{6.92}$ (La-123) phase was carried out in the two-electrode cell in the galvanostatic mode using solid state electrolyte. After crystal structure refinement and comparison to the starting non-fluorinated sample it was found that fluorine atoms more likely substitute oxygen atoms in the CuO chains. Such a substitution introduces disorder into the charge reservoir and probably it is responsible for lower holes concentration in the conducting CuO_2 planes, which becomes responsible for the decrease of T_c.

Key words: LaBaCuO, fluorination, sol-gel, superconductivity

1. INTRODUCTION

It is proved that fluorination is an efficient tool of structural modification and hole doping of high-T_c superconductors [1,2]. Common techniques, which use metal fluorides, F_2 or NH_4F as fluorine source, are not always successful for the fluorination of Re-123 with light rear-earth element [3] due to high thermodynamic stability of BaF_2 and ReOF. In the present research we used electrochemical oxidation to carry out fluorine insertion into La-123. Comparison of the crystal structure of the prepared samples was carried out.

2. EXPERIMENTAL

2.1 Synthesis.

Samples of $LaBa_2Cu_3O_{6.92}$ (La-123) were prepared by polymerizable complex method according to the previously described procedure [4]. Electrochemical fluorination was performed at 350°C in solid state using EG&G PAR 273 potentiostat/galvanostat working in two-electrode galvanostatic mode by a constant current of 20 μA. Electrochemical cell was composed of pellets of La-123 and of $Ba_{0.8}La_{0.2}F_{2.2}$ solid electrolyte polished and pressed together by a clamp. The La-123 side of the sandwich was connected as anode, the $Ba_{0.8}La_{0.2}F_{2.2}$ side of the sandwich was connected as cathode. Total charge passed through the cell corresponds to the incorporation of 0.3 F^- per unit cell of $LaBa_2Cu_3O_z$.

2.2 Characterization.

Prepared samples (La-123F) were cut and cross-section was examined by field-emission SEM S-4500 (Hitachi) with EDS detector (accelerating

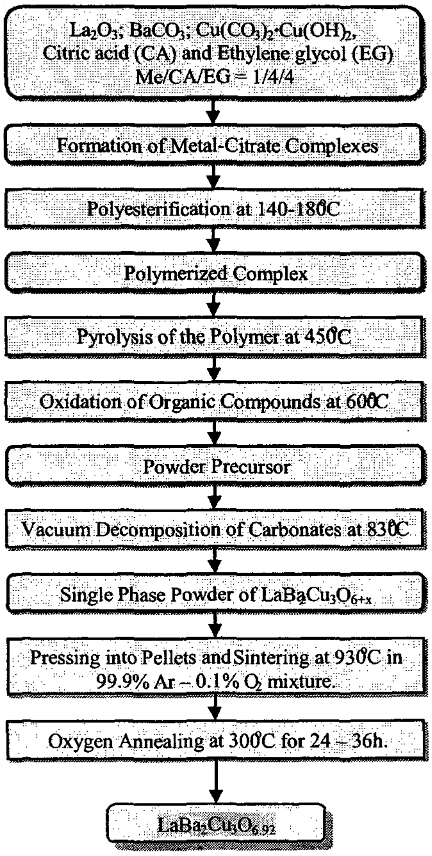

Fig. 1. Flowchart of La-123 synthesis.

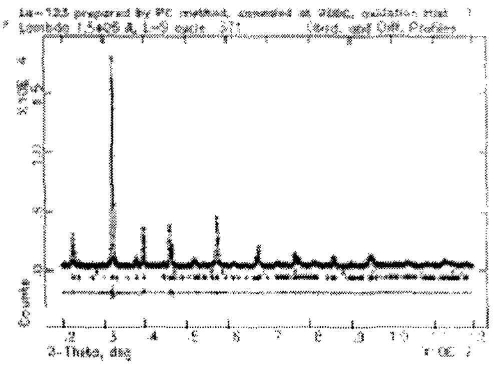

Fig.2 X-ray diffraction pattern of of La-123

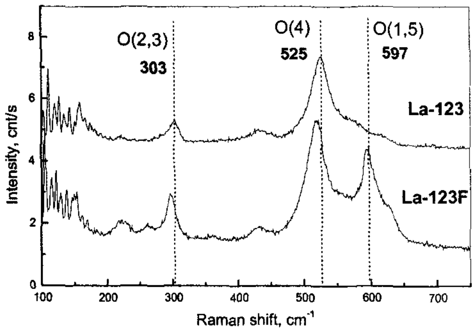

Fig.3 Raman spectra of La-123 before and after fluorination.

voltage 15kV, beam current 10 mA). Raman scattering data were taken by means of Jobin Yvon/Atago Bussan T64000 Raman triple spectrometer (laser power 100mW and wavelength 514.5 nm). XRD data for structural analysis were collected by MacScience Diffractometer using CuK_α radiation. The crystal structure refinement was done by General Structure Analysis System (GSAS). Superconducting properties were studied by SQUID MPMS-5.

3. RESULTS AND DISCUSSION

Initial sample of La-123 was prepared according to the procedure briefly described on Fig.1. The sample became superconducting at 92K. Investigation by XRD did not revile any significant amount of the impurities (Fig. 2), while Raman spectroscopy showed that there is no significant disordering in the Cu-O chains (Fig. 3). Results of X-ray structure refinement (Table I) are in a good agreement with the neutron diffraction studies [5] of La-123 with the similar T_c.

First, fluorination of the prepared ceramic sample was performed at room temperature using liquid electrolyte - KF solution in methanol. Preliminary methanol was dried and dissolved oxygen was eliminated by flow of Ar. Examination of the obtained sample by SEM with EDS displayed that fluorine incorporation took place only within the surface layer due to the low diffusion coefficient at low temperature, and the surface of the grains was heavily etched by the electrolyte.

Table I. Structural parameters of La-123 before and after fluorination (La-123F). Space group Pmmm, La(½,½,½), Ba(½,½,z), Cu(1)(0,0,0), Cu(2)(0,0,z) O(1)(0,½,0), O(2)(0,½,z), O(3)(½,0,z), O(4)(0,0,z), O(5)(½,0,0). Thermal parameters of oxygen were kept constant 1 Å ^{2}.

	Sample La123 (Tc=92K)	**Sample La123F** (Tc=88K)
a, Å	3.89070(12)	3.91311(16)
b, Å	3.93378(21)	3.93672(17)
c, Å	11.8254(6)	11.7830(4)
B (La), Å ^{2}	0.24(5)	0.42(11)
z (Ba)	0.18017(13)	0.17940(17)
B (Ba), Å ^{2}	0.41(5)	1.46(15)
B (Cu(1)), Å ^{2}	0.61(18)	1.14(25)
z (Cu(2))	0.34272(35)	0.3445(5)
B (Cu(2)), Å ^{2}	0.46(10)	1.11(16)
n (O(1))	0.93(2)	0.91(6)
z (O(2))	0.3571(18)	0.3648(25)
z (O(3))	0.3639(16)	0.3716(23)
z (O(4))	0.1562(18)	0.1560(7)
n (O(5))	0.00(2)	0.17(6)
R_{wp}, %	5.44	6.72
R_p, %	4.15	5.30
χ^2	1.769	1.574

Fluorination at elevated temperature using solid-state electrolyte did not produce any significant amount of the impurity phases (Fig. 4). The traces of the degradation were observed only on the surface, which was in the direct contact with the electrolyte. Fluorine could be detected by EDS in the bulk (Fig.5). Raman spectroscopic study (Fig.3) figured out strong disordering in the Cu-O chains. Softening of the disorder-induced mode compared to that for the common La-123 (605cm^{-1}) indicates occupation of chain sites by both oxygen and fluorine atoms. T_c of the fluorinated sample dropped to 88K. X-ray structure analysis was performed using multiple data sets to increase number of parameters required to fit background with substantial diffuse scattering.

Results of structure refinement (Table I) figured out that contraction of the lattice along c direction after fluorination occur mainly due to the decrease of CuO_2-CuO_2 distance, while the thickness of insulating block does not change. It should be pointed out that La-O distance in the fluorinated sample (2.48 and 2.52Å) is much shorter than in the initial La-123 (2.54, 2.58Å) and it is close to the typical La-F distance in LaF_3 and LaOF. This fact supports the idea [6] that F^- occupies conducting planes, which must result in the charge localization on the foreign atom and decrease of T_c. Closer investigation of the delta-F maps shows that oxygen atoms in the chains might be slightly shifted from the ideal positions,

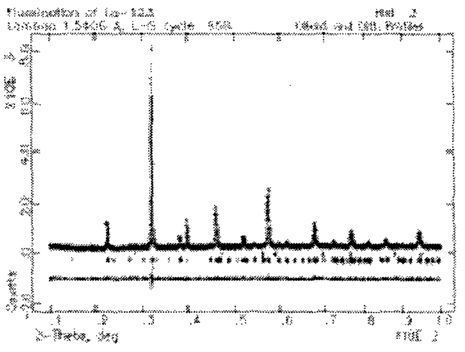

Fig. 4 X-ray diffraction pattern of La-123 after fluorination at 350°C.

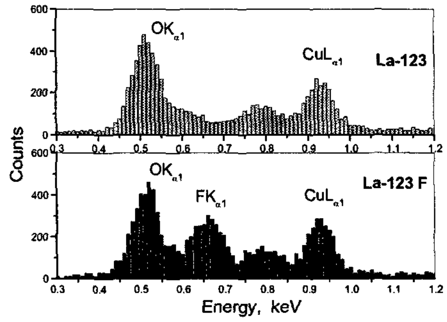

Fig.5 EDS spectra of initial sample of La-123 and sample after fluorination.

which lead to the appearance of Raman-forbidden phonon at 597 cm^{-1} after fluorination. Note, total occupation of the chain oxygen sites determined from refined structural parameters corresponds roughly to the efficiency of the electrochemical process 0.5. To our mind there are two possible faradic processes, which may take place in the La-123 sample upon oxidation - oxidation of divalent copper and oxygen evolution. While in the first case one would expect compensation of the created charge primarily by F^- in vacant position the other process would lead to the replacement of O^{-2} by F^- ions. Unfortunately the data about the process, which can be recorded during a two-electrode galvanostatic oxidation are insufficient for a complete characterization of the electrode process. The XRD results favor the latter process as the prevailing one, however, one cannot exclude a change in the redox composition during annealing following the electrochemical fluorination. More detail study of this phenomenon is currently in progress.

4. REFERENCES

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(Received December 20, 2002; Accepted March 3, 2003)