Notes

o.m2.o5 **Structure transformations in fluorinated complex copper oxides.** A.M. Abakumov[1], M.G. Rozova[1], B.Ph. Pavlyuk[1], R.V. Shpanchenko[1], E.V. Antipov[1], J. Hadermann[2], O.I. Lebedev[2], G. Van Tendeloo[2], [1]*Department of Chemistry, Moscow State University, 119899 Moscow, Russia;* [2]*EMAT, University of Antwerp (RUCA), Groenenborgerlaan 171, B-2020 Antwerp, Belgium*

Keywords: fluorination, superconductors, structure.

The soft chemistry technique based on low temperature fluorination by XeF_2 was applied for the preparation of fluorinated cuprates with different structures: $HgBa_2CuO_{4+\delta}$ (Hg-1201), $YBa_2Cu_3O_{6.11}$ (Y-123), $Y_2Ba_4Cu_7O_{14.01}$ (Y-247), La_2CuO_4 (T-phase), $LaHo_{0.75}Sr_{0.25}CuO_{3.9}$ (T*-phase), $La_{6.7}Sr_{1.3}Cu_8O_{19.7}$ and $LaACuGaO_5$ (A=Ca,Sr). The structures of fluorinated phases were studied using X-ray or neutron powder diffraction and high-resolution electron microscopy.

Fluorination of the strongly reduced Hg-1201, phase with T_c=61 K resulted consequently in the increase of T_c up to 97 K, the decrease of T_c and the suppression of superconductivity due to overdoping. Twice the amount of extra anions in comparison with those for the oxygenated Hg-1201 phases with close T_c was found by neutron diffraction. The exchange of extra oxygen for the double amount of fluorine causes an extended shortening of the apical Cu-O bond distances, while the in-plane distances, as well as T_c, do not vary.

The insertion of fluorine in the strongly reduced Y-123 produces the superconducting $YBa_2Cu_3O_6F_2$ phase with T_c=75-94K. Fluorine atoms occupy positions into anion deficient Cu1 layers forming a distorted octahedral coordination of Cu1 atoms. The increase of $CuO_{(apical)}$ distance by 0.5-0.7Å due to Jahn-Teller deformation leads to *c* parameter for the fluorinated phase ranged in 12.8-13.2Å. Similar transformation also takes place in $Y_2Ba_4Cu_7O_{14}$, where the increase of *c* parameter from 51.9Å to 53.5Å was observed.

The sequences of structural changes were found in T and T* phases at different degrees of fluorination. Small amount of fluorine intercalates between the doubled LaO layers in La_2CuO_4 causing the increase of the orthorhombic distortion and the appearance of superconductivity (T_c≈40K). Further fluorine insertion followed by a transformation to tetragonal K_2NiF_4-type structure. At elevated temperatures the fluorination of T and T* materials is accompanied by a redistribution of anions between rocksalt and fluorite-type positions in A_2O_2 blocks resulting in complicated superstructures due to anion ordering and cation displacements.

New fluorine-containing perovskite type tetragonal structures were observed after fluorination of the $La_{6.7}Sr_{1.3}Cu_8O_{19.7}$ and $LaACuGaO_5$ (A=Ca, Sr) phases due to random distribution of oxygen and fluorine atoms between vacant anion sites. Distorted octahedral environment of Cu atoms (in plane $d_{Cu-(O,F)}$ = 1.89Å and apical $d_{Cu-(O,F)}$ = 2.03Å for fluorinated $La_{6.7}Sr_{1.3}Cu_8O_{19.7}$) can be explained by Jahn-Teller effect These compounds do not exhibit superconductivity, possibly due to improper copper oxidation state or common occupations of anion positions in conducting layers by fluorine and oxygen atoms.