Type of presentation: Poster

IT-9-P-3490 Composite crystal structures of M_xCuO_2 cuprates; (M_x = Li_2, $Ca_{.83}$, $Sr_{.73}$, $Ba_{.67}$, $[(Sr/Ca)_2Cu_2O_3]_{1/\sqrt{2}}$, Na)

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The M_xCuO_2 cuprates belong to class of composite crystals consisting of two subsystems[1]: „CuO_2-chains“ and „M_x-cations”. An electron microscopy and diffraction study of a number of rare earth cuprates, is presented (Fig.1.) in relation with the corresponding charge ordering that is induced by variable cation valency and nonstoichiometric composition. Level of cation defficiency and the accompanying self doping affects structure modulation, as well as the average Cu-valency; it can range from Cu+2.30 for $Ca_{.83}CuO_2$, to Cu+2.66 for $Ba_{.67}CuO_2$, and even up to Cu+3.0 for $NaCuO_2$, or down to Cu+2.0 for Li_2CuO_2. In the case of M_x = $Ca_{.83}$, $Sr_{.73}$, $Ba_{.67}$, $[(Sr/Ca)_2Cu_2O_3]1/\sqrt{2}$, the two subsystems are mutually incommensurate and modulated along the “chain” direction, while for the end cases of: M_x = Na, Li_2, the structural unit cells are commensurate (Fig. 2.)

The underlying lattices of these subsystems have common a and b parameters while the ratio c_{Ch}/c_M of their c-parameters along the chain-direction varies with x. For a particular case of $M_x=[(Ca/Sr)_2Cu_2O_3]_{1/\sqrt{2}}$, the so-called “chain-ladder” $(Sr/Ca)_{14}Cu_{24}O_{41}$ compound is well known for its optical and magnetic properties[2],[3]. In this case, the cation subsystem consists of an extended structure: $(Sr/Ca)_2Cu_2O_3$ -“ladders”. The building unit of the ladders is a pair of cations plus a pair of zigzag edge-sharing CuO_4-squares, Fig. 2, that are connected along “rungs”, so that the cLd period is defined by the CuO_4-square diagonal. For the chains, the CuO_4 building units share opposite edges and the c_{Ch} period is equal to the CuO_4-square edge. In the case of “chain-ladder” composite structure, the c_{Ld}/c_{Ch} ratio is found to vary slightly with cation composition, but is always close to $\sqrt{2}$, so that the formula $[(Ca/Sr)_2Cu_2O_3]_xCuO_2$ ($x\approx1/\sqrt{2}$) correctly represents compound's composite structure.

With increasing Ca-substitution the c_{Ld}/c_{Ch} ratio varies from 1.44 for pure $Sr_{14}Cu_{24}O_{41}$, to 1.416 for highly substituted $Sr_{0.6}Ca_{13.4}Cu_{24}O_{41}$. This is accompanied by charge (hole) redistribution between the CuO_2-chains and the Cu_2O_3-ladders[3].

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Acknowledgement: S. Tomić from Zagreb (Croatia), A. Migliori from Bologna (Italy), and G. Van Tendeloo from Antwerp (Belgium) are acknowledged for collacoration and support. Financial support has been received from Croatian Ministry of Sciences, Education and Sport.

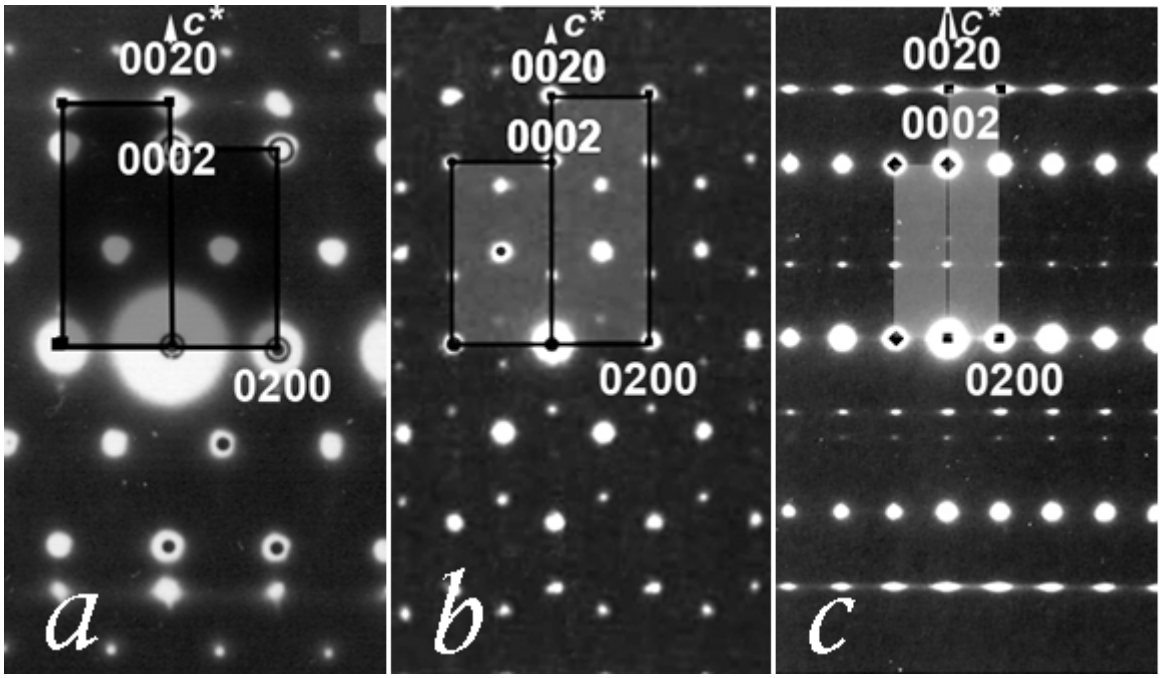

Fig. 1: EDP of M_xCuO_2 composite crystals for M_x= $Ca_{.83}$ (a), $Sr_{.73}$ (b), $[Sr/Ca_2Cu_2O_3]_{1/\sqrt{2}}$ (c), along the [1000] zones perpendicular to the "CuO_2-chains". Indexing in 4-D crystallography notation; the third index is for the "chain-", the fourth one for the "cation-sublattice". Two subsystem unit cells are indicated; mismatch corresponds to: $(1-x)c^*_{Ch}$.

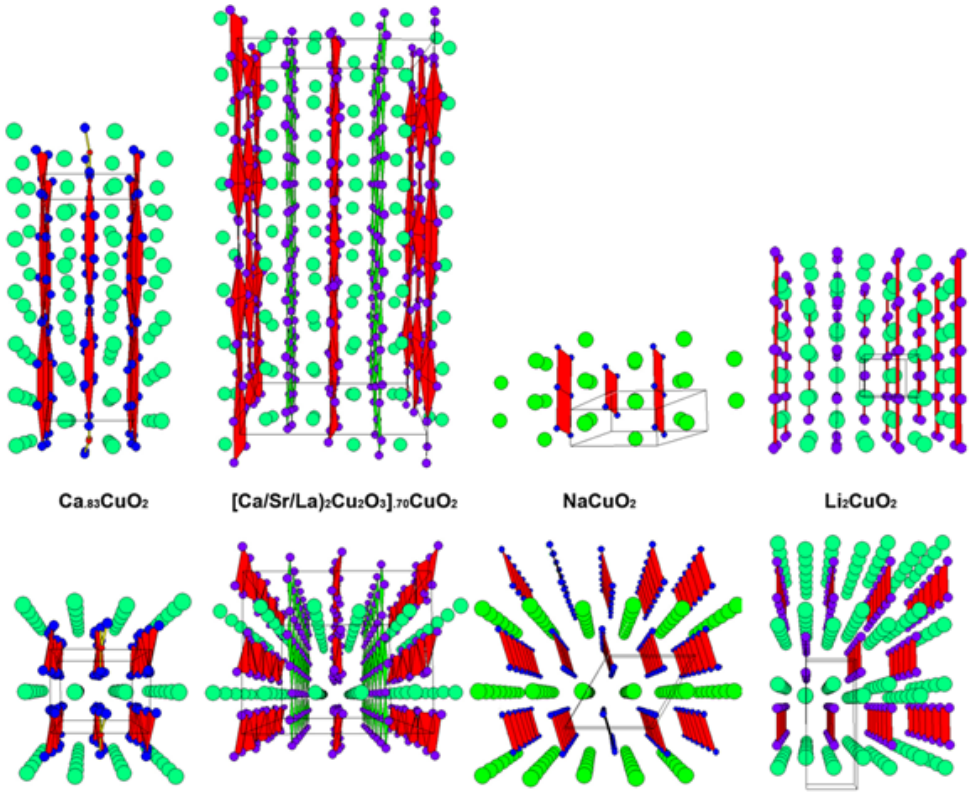

Fig. 2: Schematic representtion of the composite crystal structures of $Ca_{.83}CuO_2$, $(Sr/Ca/La)_{14}Cu_{24}O_{41}$, (with incommensurate "$CuO_2$-chain" modulation), and $NaCuO_2$, Li_2CuO_2 (with commensurate superlattices); in top view (up), and front view (down).