

Comments on superconductivity in $AE_2CuO_{4\pm\delta}$ ($AE = Sr, Ba$)

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Li et al. (1) report on superconductivity ($T_c \sim 73$ K) that emerged in Ba_2CuO_{4-y} (Ba214) synthesized at extremely high pressures (~ 18 GPa). They claim that one of the unique features of this compound is an exceptionally compressed local octahedron. I read this article with great interest. However, I am afraid they stretch things a bit. While they claim the crystal structure of the compound is of the K_2NiF_4 (coined as T) type, as is the case with $(La, Ba)_2CuO_4$, their X-ray powder diffraction data resemble more the Nd_2CuO_4 (coined as T')-type structure (2): In the latter, no local octahedron exists. When lattice parameters are fixed to the reported values ($a = 4.003$ Å and $c = 12.942$ Å), a distinction between T- and T'-Ba214 may not be simple using X-ray diffraction. Nevertheless, the large a/c ratio (~ 0.309) suggests fluorite-structure Ba_2O_2 layers, equivalently T'-Ba214: At the least, Rietveld refinements assuming the T' structure may be worth being considered.

Superconducting $T-Sr_{2-x}Ba_xCuO_{3+\delta}$ (3) (or $Sr_{2-x}Ba_xCuO_{4-\nu}$) (4), where a substantial number of O vacancies exist in the CuO_2 planes, is challenging the notion that the CuO_2 planes are the playground of high- T_c superconductivity. Out-of-plane lattice constants of these materials are smaller than that for T- La_2CuO_4 (5) despite the larger ionic radii of Sr^{2+} and Ba^{2+} compared to La^{3+} . This reduced lattice length stems from the

reduced Jahn–Teller distortions due to the O vacancies in the CuO_2 planes. The material (Ba214) reported by Li et al. (1) may be related to those largely O-deficit $T-Sr_{2-x}Ba_xCuO_{4-\nu}$ cuprates as their Rietveld refinement results (table S1 in supporting information of ref. 1) indicate ($\sim 40\%$ of the oxygen vacancies in the CuO_2 planes). However, the c value (12.942 Å) of the $Ba_2CuO_{4-\nu}$ presented in ref. 1 is far off the extrapolation to $x = 2.0$ in $T-Sr_{2-x}Ba_xCuO_{4-\nu}$ with various x (3): c would be ~ 13.4 Å. This may indicate that the Ba_2O_2 layer does not crystallize in the rock-salt structure as should be in the T structure. Altogether, a formation of a local octahedron in their $Ba_2CuO_{4-\nu}$ remains elusive and the concept of an exceptionally compressed local octahedron may lose its vindicability.

Finally it is worth noting that we have synthesized $Sr_2CuO_{4\pm\delta}$ ($c = 13.55$ Å) (6) and $Ba_2CuO_{4\pm\delta}$ ($c = 14.6$ Å) (7) whose c -axis lattice constants agree well with those expected from the variation of ionic radius [$r_i(La^{3+}) < r_i(Sr^{2+}) < r_i(Ba^{2+})$] and also from the trends derived from the $n \geq 2$ members of $O^{(Sr)}2(n-1)n$ and $O^{(Ba)}2(n-1)n$ homologous series materials in the Sr-Ca-Cu-O (8) and Ba-Ca-Cu-O (9) systems. Also, T_c of ~ 73 K reported by Li et al. (1) roughly coincides with the onset T_c in the resistivity-temperature curves for our T- $Ba_2CuO_{4\pm\delta}$ specimens (7).

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