Zeitschrift für Kristallographie 185, A2 (1988) – P15 5.2.TU

Lanthanum substitution in $YBa_2Cu_3O_{9-\delta}$

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$YBa_2Cu_3O_{9-\delta}$ exhibits four crystallographically different metal sites which are candidates for substitution by lanthanoids. The difference in site preference of the lanthanoids is critically dependent on their size and valence state, and a selectivity of big lanthanoids for the Y/Ba sites was found.

In attempts to substitute one quarter of Y with La (Nd), 50% of the La (but only 8% of the Nd) preffered the Ba site and the shift in composition made the samples impure due to formation of the $BaCuO_2$ phase. When analogous substitution of the Ba site was attempted, all of the La introduced entered this site, whereas only 44% of the Nd did.

A more detailed study of the La for Ba substitution shows that the maximum oxygen content at 100 kPa O_2 and 340°C increases almost linearily with the degree of substitution up to $Y(Ba_{0.5}La_{0.5})_2Cu_3O_{7.35}$. The increased La for Ba substitution favours occupational disorder in the crystal structure. At room temperature, the symmetry shifts from orthorhombic to tetragonal at a substitution level of 14% La and the X-ray powder diffraction pattern corresponds to cubic perovskite for 50% substitution. Interesting temperature induced changes are found for $Y(Ba_{0.85}La_{0.15})_2Cu_3O_{7.1}$ which is tetragonal at room temperature. The structure transforms to orthorhombic at 690 K in air, but converts back to tetragonal upon further heating to 940 K. This behaviour is due to temperature induced changes in the oxygen content, leading to redistribution over O(1) and O(5) sites when the total occupancy of these sites departs significantly from 1:

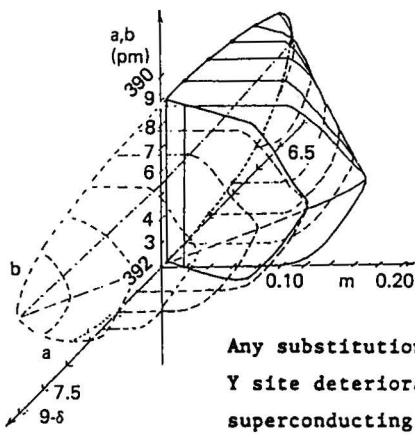

Fig.1: $Y(Ba_{1-m}La_m)_2Cu_3O_{9-\delta}$; Room temperature orthorhombic lattice parameters a and b for various degree of La for Ba substitution and various oxygen content up to saturation limit for 100 kPa and 340°C. Hypothetical course above this limit.

Any substitution which does not exclusively concern the Y site deteriorates progressively the high temperature superconducting properties.