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LETTER TO THE EDITOR

The interrelationship of Cu effective charge and superconductivity in the T′-type $Gd_{1.85-x}Pr_xCe_{0.15}CuO_y$ system

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Abstract. The lattice oxygen content (y) is measured and the effective charge (n) on Cu is calculated for the T′-type $Gd_{1.85-x}Pr_xCe_{0.15}CuO_y$ $0.0 \leqslant x \leqslant 1.85$ compounds. It is found that the superconductive response (T_c onset) of the samples is related to n. Whenever $n \leqslant 1.87$ (± 0.01), the compounds are superconducting. The optimum T_c is seen for $n \sim 1.79$ which is in good agreement with the values of n ($1.77 \leqslant n \leqslant 1.84$) calculated from the reported y in different optimum T_c T′-cuprates. This brings out a universality in the interrelationship between n and T_c.

In high temperature cuprate superconducting (SC) systems, the content of ordered lattice oxygen manifests the important role it plays in affecting the value of critical temperature (T_c) in a given compound [1–7]. It is now almost an accepted view that a critical level of carrier doping of Cu–O planes, via charge transfer, is essential, besides other factors, for a layered cuprate to exhibit superconductivity [8–14]. The band structure calculations also clearly show the important role played by oxygen content and aliovalent ion doping in understanding the superconductivity of the layered cuprates [15, 16]. Experimental findings have shown that in T′-type Ln_2CuO_4 (Ln = lanthanide) compounds, a critical level of carrier (electron) doping for the onset of superconductivity could not be achieved merely by any extent of tetravalent Ce or Th ion substitution. A reduction annealing step is mandatory to generate sufficient additional electron carriers through oxygen vacancy creation [17–19]. Further, experiments have shown that in T′-type $Ln_{2-x}Ce_xCuO_y$ (Ln = Pr, Nd, Sm, Eu, Gd), the higher Ce^{4+} content ($x \geqslant 0.18$) and/or the smaller radius Gd^{3+} ion have led to enough lattice compression [20, 21] to make reduction process (Ar, N_2 or He annealing) somewhat ineffective to generate adequate additional carriers and, therefore, $Gd_{1.85}Ce_{0.15}CuO_y$ and $Nd_{2-x}Ce_xCuO_y$ ($x \geqslant 0.18$) compounds have failed to exhibit superconductivity [5, 20, 22]. Hall effect data on the above T′-compositions are very scanty and mutually at too large variance to bring out any definitive view on the sign and the density of majority carriers [17, 23–29]. An alternative indirect way to visualize carrier concentration is to calculate the effective charge (n) on Cu in [13] layered cuprates, by determining the lattice oxygen content.

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Recently, it has been reported [22] that T′-type $Nd_{2-x}Ce_xCuO_y$, $x < 0.18$ (NCCO) and $Nd_{1.82-x}A_xCe_{0.18}CuO_y$, A = Ca, Sr or Ba, $0.6 \leqslant x \leqslant 0.18$ (NACCO) compounds exhibit superconductivity whenever the effective charge (n) on Cu is $\leqslant$1.88 ($\pm$0.01). This is an important observation and merits further validation. Since in argon annealed T′-type $Ln_{1.85}Ce_{0.15}CuO_y$, T_c is found to depend on the choice of the lanthanide ion [30], unlike the Ln(or Y)$Ba_2Cu_3O_7$ system wherein T_c has been nearly independent of the Ln ion (except Pr), it is, therefore, desirable to see if the onset of superconductivity criterion of $n \leqslant 1.88$ holds good for the other compounds in the electron doped T′-type system. For this, a $Gd_{1.85-x}Pr_xCe_{0.15}CuO_y$, $0 \leqslant x \leqslant 1.85$ (Gd(Pr)214) system wherein the smaller Gd ion is progressively replaced by a larger Pr ion, affecting lattice volume, is investigated.

The polycrystalline samples of $Gd_{1.85-x}Pr_xCe_{0.15}CuO_y$, $x = 0.0$, 1.10, 1.35 and 1.85 were carefully prepared by the solid state reaction route. The details are given elsewhere [31]. The samples were checked for single phase formation by XRD (Philips, PW1820) and EDAX (Kevex, system 8000). No impurity phases were detected. For all the compositions, the SEM (JEOL, JSM6100) photo-micrographs showed well developed and closely packed grains without any impurity phases. A typical SEM micrograph is shown in figure 1. The T_c onset was determined by temperature dependent ac susceptibility (χ–T) measurements using an APD system in conjunction with an E.G.&G. model 5208 two-phase lock-in analyser. Only the reduced samples, except $x = 0$, exhibited superconductivity [31, 32]. In the reduced (Ar annealed) samples, as seen from the x-ray absorption near edge structure (XANES), Pr was in the 3+ state and Ce predominantly 4+. Further, in the oxygenated samples a weak but clear signature of Pr^{4+} (< 5%) along with predominant 3+ peak was present in the Pr L_3 edge [33].

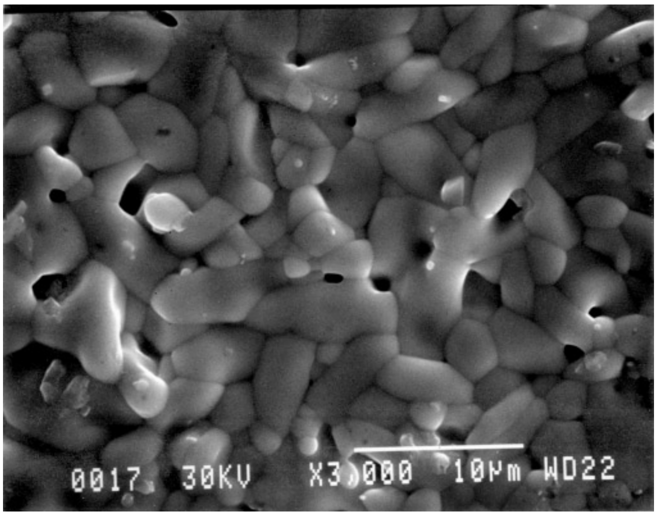

Figure 1. Typical scanning electron micrograph of $Gd_{1.85}Ce_{0.15}CuO_y$ sample.

To calculate the effective charge (n) on Cu, a knowledge of lattice oxygen content (y) in the above samples is essential. With the knowledge of valence state of Pr being 3+ in the reduced samples, it has been now possible to estimate lattice oxygen content with assertion. We have estimated, by the iodometric titration method [34], the oxygen content (y) per formula unit for the reduced and the well oxygenated $Gd_{1.85-x}Pr_xCe_{0.15}CuO_y$, $0.0 \leqslant x \leqslant 1.85$ samples. From the estimated values of y, given in table 1, it is clearly seen that y progressively decreases in the reduced samples with increasing Pr content (x). This indicates that incorporation of a bigger

Pr ion ($r = 1.126$ Å, coordination number (CN) = 8) for the smaller Gd ion ($r = 1.053$ Å, CN = 8) [35], leading to lattice expansion (∼5%) for $x = 0.0$ to $x = 1.85$ [31], facilitates oxygen vacancy creation on reduction. This, in turn, induces additional electron carriers in the system and makes Gd(Pr)214 superconducting whenever $n \leqslant 1.87 \pm 0.01$ (table 1).

Table 1. Estimated values of oxygen content (y) (by iodometry), effective charge (n) on Cu and T_c(onset) for $Gd_{1.85-x}Pr_xCe_{0.15}CuO_y$, $0 \leqslant x \leqslant 1.85$ compounds for the reduced (argon annealed) and the oxygenated conditions.

x	Annealing atmosphere	$y \pm 0.005$	$n^a \pm 0.01$	T_c (K)
0.00	Argon	2.01	1.95	non-SC
0.00	Oxygen	4.05	1.97	non-SC
1.10	Argon	4.01	1.87	6.5
1.10	oxygen	4.07	1.99	non-SC
1.35	Argon	3.98	1.81	17.0
1.35	oxygen	4.07	1.99	non-SC
1.85	Argon	3.97	1.79	21.0
1.85	Oxygen	4.08	2.01	non-SC

[a] Calculated assigning formal valence states 3^+ to Gd and Pr, 4^+ to Ce and 2^- to oxygen.

Though the superconductivity is induced around $n \sim 1.87$, the optimum T_c is found in the vicinity of $n \sim 1.79$ as has also been seen earlier in NCCO and NACCO T′-type compounds [22]. $n = 1.79$ (±0.01) for optimum T_c is, remarkably, in good agreement with the values of n ($1.77 \leqslant n \leqslant 1.84$) calculated from the values of y, reported by others [11, 36–40], for the optimum T_c in various T′-type cuprates. Significantly, these n values seem to provide some universality to the finding that T′-type cuprates exhibit superconductivity for $n \leqslant 1.88$ (±0.01).

From the present studies it is concluded that the T′-type cuprates exhibit superconductivity whenever the effective charge (n) on Cu is ⩽1.88 and, for optimum T_c, $n \sim 1.79$.

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