Valence of elements in $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ (n=1, 2, 3, 4)

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Abstract: Valence of elements in $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ (n=1, 2, 3, 4) (both argon and oxygen annealed samples) were calculated. The result indicated for both argon and oxygen annealed samples, Hg had the lowest valence for the highest T_c sample. For fixed n, the valence of Cu in oxygen annealed samples was larger than that in argon annealed samples, indicating that oxygen annealed samples produce more carriers than argon annealed samples.

Keywords: Valence, $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ (n=1, 2, 3, 4).

$HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ (n=1, 2, 3, 4) [1] are tetragonal with space group space P4/mmm. For n=1,2,3, nearly single-phase crystals were obtained, while for n=4, the sample was primarily a mixture of the n=3 and 4 phases. These materials also possessed the highest T_c values yet observed for any superconductors. In this paper, the valences of elements in the title compounds were calculated from bond valence sum method [2].

The calculated bond covalency, valences of elements were summarized in **Table 1**. It was found that valences of Hg were a little larger than its normal valence +2.0. We thought this was because the extra oxygen was inserted directly into the HgO layer. The higher valence of Hg and Ba may also indicate that they suffered from a compressive strain. For both argon and oxygen annealed samples, Hg had the lowest valence for the highest T_c sample, suggesting that small valence of Hg was preferred; while for Cu(1), the lowest valence corresponded to the highest T_c only for oxygen annealed samples, for Cu(2), the highest valence corresponded to the highest T_c for both samples. For oxygen with the partial occupancy, the valence was much smaller that its formal valence -2.0 because our results were averaged ones.

It was also interesting to see that within each number n (fixed n), the valence of Cu (including Cu(1) and Cu(2)) in oxygen annealed samples was larger than that in argon annealed samples, independent of oxygen and Hg contents. This revealed that there exist more carrier concentration in oxygen annealed samples than in argon annealed samples. At n = 2, the more carrier concentration in oxygen annealed sample was detrimental to superconductivity because according to experiment [1] T_c in oxygen annealed samples was lower than it was in argon annealed samples. At n = 3,4, more carrier concentration in oxygen annealed samples was preferred for producing higher superconducting temperature. On the other hand, the valence of Hg was influenced by both oxygen and Hg contents. From experiment [1] we knew that for fixed n, the contents of oxygen and Hg for oxygen and argon annealed samples changed only a little for n=2,3,4 and n=3,4 respectively. While at n=2, the oxygen content changed dramatically (0.32 for oxygen annealed sample and 0.21 for argon annealed sample). From our results, we could see that at n=3 and n=4 where oxygen and Hg contents changed only a little, the change of Hg valence was large, while at n = 2, the valence of Hg was almost unchanged. Thus we can deduce that the smaller difference for the valence of Hg at n = 2 was caused by the large difference in oxygen content, that is, if the oxygen content did not show big difference as in the case of n = 3 and n = 4, the valence of Hg could show large difference between oxygen and argon annealed samples.

Table 1. Valences of elements in $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ (n=1, 2, 3, 4).

	$HgBa_2CuO_{4+\delta}$	$HgBa_2CaCu_2O_{6+\delta}$		$HgBa_2Ca_2Cu_3O_{8+\delta}$		$HgBa_2Ca_3Cu_4O_{10+\delta}$	
	Oxygen	Oxygen	Argon	Oxygen	Argon	Oxygen	Argon
T_c	94	122	126	134	124	125	120
Hg	0.99	0.87	0.90	0.83	0.87	0.84	0.82
O(3)	0.1	0.32	0.21	1.0	1.0	1.0	1.0
O(4)	-	-	-	0.24	0.28	0.4	0.47
Hg	2.276	2.229	2.225	2.123	2.259	2.417	2.262
Cu(1)	2.046	2.081	2.068	2.041	2.040	2.102	2.095
Cu(2)	-	-	-	2.095	2.088	2.058	2.048
Ba	2.237	2.223	2.228	2.229	2.196	2.336	2.348
Ca(1)	-	1.994	1.962	1.983	1.969	2.000	1.894
Ca(2)	-	-	-	-	-	1.945	1.964
O(1)	2.224	2.056	2.065	1.928	1.922	2.195	2.108
O(2)	1.746	1.813	1.790	2.076	2.056	1.881	1.859
O(3)	0.856	0.980	0.939	1.801	1.856	1.949	1.955
O(4)	-	-	-	1.014	1.026	1.096	1.287

The structural data are taken from reference 1. T_c, occupancy of Hg, O(3) and O(4) were also listed.

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