Structural Study of 90K Superconductor $Gd_1Ba_2Cu_3O_{9-x}$

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90K 초전도체 $Gd_1Ba_2Cu_3O_{9-x}$의 구조에 관한 연구

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요 약

초진도 게시온도 91K이며 87K에서 저항이 완전히 0이 되는 초전도체 $Gd_1Ba_2Cu_3O_{9-x}$를 제조하였다. X선 산란 실험에 의하여 격자상수 a=3.842±0.002Å, b=3.895±0.003Å, c=11.684±0.007Å임이 관측되었다. $Gd_1Ba_2Cu_3O_{9-x}$와 잘 알려진 단상의 Perovskite인 $Y_1Ba_2Cu_3O_{9-x}$의 구조적 유사성을 논하였다. 또한 관측한 X−선 스펙트럼과 단위격자의 여러 면(plane)에서의 산소의 결핍에 따른 영향의 관계에 대해서도 논하였다.

ABSTRACT

$Gd_1Ba_2Cu_3O_{9-x}$ has been found to be a high T_c superconductor with a transition onset at 91 K and zero resistance achieved at 87 K. The structure as determined from x-ray diffraction is orthorhombic, with lattice constants b= 3.842 ± 0.002 Å, b = 3.895 ± 0.003 Å, and c = 11.684 ± 0.007 Å. The structural similarities between the $Gd_1Ba_2Cu_3O_{9-x}$ compound and the well-studied single phase perovskite, $Y_1Ba_2Cu_3O_{9-x}$ are discussed. A correlation between the observed x-ray spectrum and the effect of oxygen deficiencies in several of the unit cell planes is also discussed.

The discovery of high temperature super-conductivity in the La-Ba-Cu-O system with a transition temperature around 30 K [1] and the subsequent discovery in the Y-Ba-Cu-O [2] system of superconductivity around 90 K, has stimulated the search for other high T_c materials.

In this latter system the superconducting phase was quickly identified as $Y_1Ba_2Cu_3O_{9-x}$ [3-6]. The microstructure and crystallography of this compound has been studied by x-ray diffraction [3-6], transmission electron microscopy (7), and neutron diffraction [8, 9]. From the above

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studies, the $Y_1Ba_2Cu_3O_{9-x}$ compound was found to be an oxygen defected perovakite with the Y ion sandwiched between the Ba ions. The replacement of the Y atom with other La series elements also results in 90 K superconductors [10-12]. Most notable in these substitutions is the insensitivity of the transition temperature to the incorporation of magnetic elements. The structure of the unit cell seems to be crucial in preventing the superconducting mechanism from being disrupted by the magnetic ion. In this paper, Gd is substituted for Y in the 1-2-3 compound and the structural and transport properties are studied.

Two standard methods have been used to prepare high T_C superconductors, the solid state reaction method and the coprecipitation method. In the solid state reaction method, samples are prepared quickly by sintering a mixture of the constituent oxides. However the coprecipitation method has the advantage of mixing the constituents on the atomic scale. This method then insures the production of the desired phase and also has the tendency to preserve the stoichiometric ratio throughout the process. The Gd-based samples used in this study were primarily prepared by this method.

In the coprecipitation method, the nitrate forms of the constituents are dissolved in solution and then precipitated out in their carbonate forms through the addition of Na_2CO_3. The remaining powder is repeatedly heated to $900^{\circ}C$ and pulverized to make a solid solution of the 1-2-3 phase. Finally the powder is pressed into pellets and sintered at temperatures between $900^{\circ}C$ and $1000^{\circ}C$ in air atmosphere. However, since the prebaking is done at high temperatures, much of the oxygen in the samples is liberated [13]. Though a degree of oxygen deficiency is needed to form the superconductor, too much deficiency of an oxygen results in a nonsuperconductor. To insure the availability of oxygen,

the sintered pellets are annealed in an atmosphere of 100% oxygen at $500^{\circ}C$ for 12 hours. This annealing time is long enough to make stationary oxygen contented samples during the annealing time. Then the samples are slowly cooled to room temperature, also in the same oxygen atmosphere. More general details of this sample preparation method appears elsewhere. [14]

The phase and structure responsible for the superconductivity as determined by x-ray diffraction parallels the results from neutron diffraction for $Y_1Ba_2Cu_3O_{9-x}$ [8, 9]. From the similarity of the x-ray diffraction patterns for $Gd_1Ba_2-Cu_3O_{9-x}$ (Figure 1) and $Y_1Ba_2Cu_3O_{9-x}$ it was easily determined that the $Gd_1Ba_2Cu_3O_{9-x}$ compound had the same basic structure. The d-spacings and relative intensity distribution correlated between these two compounds, as well as specific orthorhombic features such as the splitting of the major 206/220/026 peak.
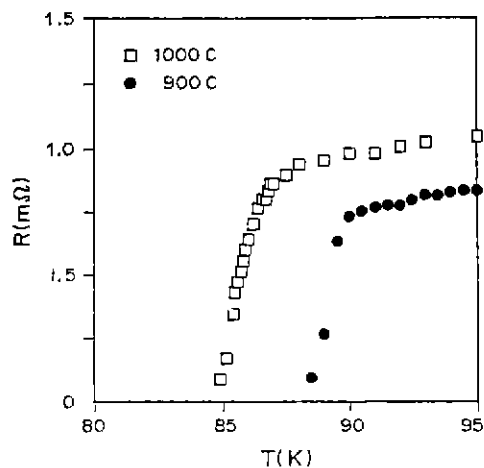

Fig. 1 The resistive transition of $Gd_1Ba_2Cu_3O_{9-x}$ for samples sintering at the temperatures of $900^{\circ}C$ and $1000^{\circ}C$, respectively. Though the sample characteristics are strongly dependent upon the preparation techniques, for these samples the other preparation steps were kept constant.
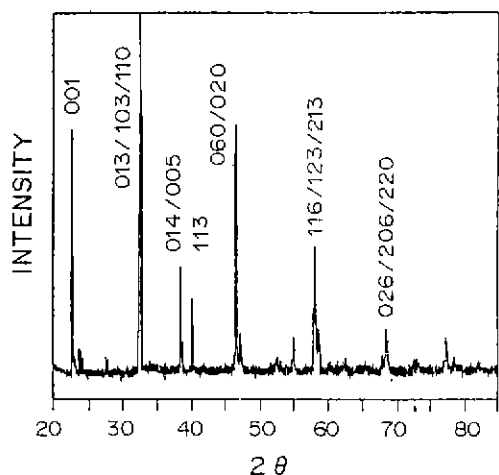
Fig. 2 The x-ray diffraction spectrum of the single phase $Gd_1Ba_2Cu_3O_{9-x}$ compound at room temperature.

From the resistance measurement of the samples it is seen that there are different onset and zero resistance temperatures for samples prepared under different sintering conditions. In Figure 2, it is noted that the sample fired at $900°C$ has a higher zero resistance transition temperature (T_c) 87 K, a leaner transition width, and a lower room temperature resistance than the sample fired at $1000\,°C$ where T_c is 85 K. All other conditions for the preparation of these samples were kept constant. Though it has been shown that the annealing conditions [12] and the rate of cooling [15] have a great effect on the superconducting properties, the present results demonstrate that the sintering temperature is also very important.

For the "K_2NiF_4" structured compound of La-Ba(Sr)-Cu-O, we found that a sintering temperature up to $1150°C$ was possible. However, once a portion of the sample forms an incongruent liquid phase, there is either a reduction in T_c or the sample simply becomes a nonsuperconductor. In the Gd-based sample sintered at $1000°C$ in air atmosphere, we observed that at least part of the sample had melted. This sample had a lower T_c and a higher room temperature resistance. In this case, the reduction in T_c may be attributed to the limitation of oxygen access to the bulk material or the suffocation of the superconducting phase due to the composite interaction of the 1-2-3 phase and the incongruent melted phase.

The lattice constants were determined from the x-ray d-spacings by assuming the 1-2-3 structure. The calculated results of the lattice constant are a = 3.842 ± 0.002 Å, b = 3.895 ± 0.003 Å, c = 11.684 ± 0.007 Å. An accurate fit to the observed x-ray intensities is proposed by the movement of the Ba and Cu atoms from "ideal" positions in the unit cell. The atoms may move as a result of oxygen deficiencies.

Based on the x-ray theory, a computer program was written that would present an x-ray spectrum from the inputs of the lattice parameters and atomic positions. A strict assumption of the atomic positions in the perovskite cell (called the "ideal" positions) however could not account for the intensities in the observed pattern. Trying to account for the discrepancies by altering the level of oxygen occupancy that is assumed, only changed the calculated intensities by a few percent. (Table 1) No definite conclusion as to the position and amount of the oxygen deficiencies could be drawn based only upon the "ideal" assumption.

However when we depart from a strict interpretation of the atomic positions in the cell a better correlation between the calculated and observed intensities is obtained. (Table 2). Thus the computer program was altered to allow for the movements of other atoms in the cell which may be caused by structural distortions due to the oxygen deficiencies. Since the Gd atom assumes a symmetric position in the unit cell, it is unlikely that this atom will move much due to the oxygen deficiencies around it. The move-

ment of the Ba atom which is a large x-ray scatterer, and the Cu atoms which have less scattering power but still significantly more than the O atoms, should result in large changes in the x-ray intensities. The program was do-looped to allow for changes in ths Ba and Cu atomic positions which would produce a calculated x-ray spectrum that was near the observed spectrum. The statistical variable S that was used to evaluated each atomic position was where $I_{exp}(I_{the})$ is experimental(theoretical) intensity.

This statistical variable S was minimized in a do loop from the computer program to find out the best position of the Ba, Cu atoms.

Once all of the atomic positions inside of the unit cell were determined, the integrated intensity of the each Bragg line was calculated. Then, to determine the correlation between oxygen deficiencies and the intensity variation, we assumed various oxygen deficiency conditions on each plane in the unit cell.

The oxygen deficiency effect on the intensity spectrum was calculated for several of the unit cell planes. Much greater agreement between the observed and calculated spectrum occurs when the atoms are moved from strict "ideal" positions (Table 1) to more "real" positions (Table 2). It is noted, however, that the discrepancy function S is actually a slowly varying function near the minimum point. Also, S does not change much for each different assumption of the oxygen deficiency situation. Thus the exact position of the Ba and Cu atoms are hard to determine. We mainly considered oxygen deficiency situations that corresponded to the observed value of the oxygen deficiency (x near 2) for these perovskite compounds. The best fit occurs for the case where there is an oxygen atom missing from the Gd plane and one missing from the outer Cu planes. This situation is also the conclusion from neutron

scattering for $Y_1Ba_2Cu_3O_{9-x}$ [8, 9]. As a result of these oxygen defects, the calculated Ba position moves from 1/6 to 1/6 + 0.016 while the Cu atoms move from 1/3 to 1/3 + 0.052. However, as noted above, the Cu atom position change could basically be anywhere between 0.030 to 0.055, since S changes little near the minimum point. The values for the atomic positional changes compare reasonably with the values of .020 and .022 obtained by neutron scattering for the Ba and Cu movements in $Y_1Ba_2Cu_3O_{9-x}$. We must note that the difference in the discrepancy function between all of the assumed oxygen deficiency situations is minimal, so that a definite conclusion as to which one is correct cannot be made. This is again the result of the low scattering power of the oxygen atoms in the x-ray measurement. In normal situations, neutron scattering could solve this problem, however the large absorption associated with the Gd atom prevents this from being done on this sample.

Particular attention is drawn to the 014/005 line. When the calculation assumes strict positions for the Ba and Cu atoms in the unit cell, the intensity of this line is almost zero. This is primarily the result of the assumed body-centered position of the Ba atom. Experimentally, the 014/005 line is one of the most prominent in the spectrum. This has been shown to be true for other 1-2-3 superconductors as well, namely Er [16], Ho [17], La [18, 19], and Y [3]. Much of the discrepancy is resolved when the calculation assumes the movements of the Ba and Cu atoms as described above. Thus the 014/005 line is a sensitive indicator of these atomic movements.

It must also be noted that the exact values of the intensity distribution changes from sample to sample. We believe that this is due to different oxygen occupancy situations in these samples (and hence different atomic placements)

Table 1. Experimental and calculated intensities for $Gd_1Ba_2Cu_3O_{9-x}$ assume no Ba, Cu movement

HKL	2	D(OBS)	D(CALC)	A	B	C	D	E	F
001	7.643	11.557	11.6842	8	0	3	2	0	1
003/010	22.872	3.885	3.8954	84	10	12	10	12	11
100	23.205	3.830	3.8415	5	5	5	6	5	7
013	32.569	2.747	2.7542	46	51	48	54	48	58
103/110	32.790	2.729	2.7350	100	100	100	100	100	100
014/005 104	38.549	2.334	2.3369	34	0.0	0.1	0.1	0.1	0.1
113	40.339	2.234	2.2384	27	23	18	21	18	19
020/006	46.641	1.946	1.9477	79	32	28	31	28	29
200	47.383	1.917	1.9208	13	15	13	15	13	14
016/023 106/120	52.616	1.738	1.7395	5	5	5	5	5	6
203/210	53.277	1.718	1.7227	5	2	3	2	3	3
116/123	58.194	1.584	1.5865	40	35	35	35	35	35
213	58.599	1.574	1.5755	11	17	16	18	16	19
026	68.000	1.378	1.3770	3	9	8	8	8	8
206/220	68.366	1.372	1.3675	15	17	15	16	15	15

Oxygen Deficiency (plane location)	...	None	Cu	Gd	Gd,Cu	Ba
Oxygen Deficiency (# 0 missing)	...	0	2	1	1,1	2
Discrepancy Function Smin	...	0.223	0.220	0.229	0.223	0.238
Movement of Ba Position (c units)	...	0	0	0	0	0
Movement of Cu Position (c units)	...	0	0	0	0	0

Lattice constants used: a = 3.842 ± 0.002 Å

b = 3.895 ± 0.003 Å

c = 11.684 ± 0.007 Å

A : Experimentally observed intensity.

B : Calculated intensity assuming 100% oxygen occupancy in the unit cell (x≈0).

C : Calculated intensity assuming a total oxygen deficiency in the outer Cu planes, i.e. 2 oxygen atoms are removed (x=2).

D : Calculated intensity assuming a total oxygen deficiency in the Gd plane, i.e. 1 oxygen atom is removed (x=1).

E : Calculated intensity assuming a total oxygen deficiency in the Gd plane and a selected removal of one of the oxygen atoms in the outer Cu plane (x≈2).

F : Calculated intensity assuming a total oxygen deficiency in the Ba planes, i.e. 2 oxygen atoms are moved (x=2).

Table 2. Experimental and calculated intensities for $Gd_1Ba_2Cu_3O_{9-x}$ calculated the Ba, Cu movement

HKL	2	A	B	C	D	E1	E2	G
001	7.643	8	8	11	8	9	7	13
003/010	22.872	84	11	12	13	17	13	14
100	23.205	5	5	5	7	5	5	8
013	32.569	46	46	46	46	41	43	52
103/110	32.790	100	100	100	100	100	100	100
014/005	38.549							
104		34	13	3	23	12	14	7
113	40.339	27	26	19	27	27	20	27
020/006	46.641	79	28	26	25	23	24	25
200	47.383	13	17	14	17	15	14	16
016/023	52.616							
106/120		5	5	5	8	12	5	12
203/210	53.277	5	3	3	3	4	3	3
116/123	58.194	40	25	31	20	22	25	25
213	58.599	11	16	16	15	14	15	17
026	68.000	3	5	6	3	4	4	5
206/220	68.366	15	14	14	13	12	13	13

Oxygen Deficiency (Plane Location)	None	Cu	Gd	Gd,Cu	Gd,Cu	Ba
	B	C	D	E1	E2	F
Oxygen Deficiency (# 0 missing)	0	2	1	1,1	1,1	2
Discrepancy Function Smin	0.202	0.216	0.200	0.208	0.211	0.224
Movement of Ba Position (c units)	0.021	0.011	0.028	0.016	0.022	0.011
Movement of Cu Position (c units)	0.037	0.015	0.048	0.052	0.034	0.047

Lattice constance used: a = 3.842 ± 0.002 Å
b = 3.895 ± 0.003 Å
c = 11.684 ± 0.007 Å

A : Experimentally observed intensity.

B : Calculated intensity assuming 100% oxygen occupancy in the unit cell (x=0).

C : Calculated intensity assuming a total oxygen deficiency in the outer Cu planes, i.e. 2 oxygen atoms are removed (x=2).

D : Calculated intensity assuming a total oxygen deficiency in the Gd plane, i.e. 1 oxygen atom is removed (x=1).

E : Calculated intensity assuming a total oxygen deficiency in the Gd plane and a selected removal of one of the oxygen atoms in the outer Cu plane (x=2).

F : Calculated intensity assuming a total oxygen deficiency in the Ba planes, i.e. 2 oxygen atoms are removed (x=2).

and the presence of other "impurity" phases in small but varying amounts. Though the best single-phased sample was chosen for the data presented in this study, the results for the atomic placements may be different for other samples for these reasons.

In summary, $Gd_1Ba_2Cu_3O_{9-x}$ has been prepared in single phase form. The onset of the resistive transistion is 91 K with zero resistance obtained at 87 K. The structure as determined from x-ray analysis is very similar to that of $Y_1Ba_2Cu_3O_{9-x}$, i.e. a triplet unit cell with stacked ordering of the Ba, Gd, and Ba atoms. Refinement of the Ba and Cu positions to the x-ray spectrum has been calculated. The oxygen deficiencies are located in the Gd plane and the outer Cu planes for x=2.

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REFERENCES

1. "Possible High T_C Superconductivity in the Ba-La-Cu-O System." J. G. Bednorz and K. A. Muller, Z. Phys. B, **64**, 189-193 (1986).

2. "Superconductivity at 93K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure." M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J Huang, Y. O. Wang, and C. W. Chu, Phys. Rev. Lett. 58, 908-910 (1987).

3. "Crystallography and microstructure of $Y_1Ba_2Cu_3O_{9-x}$, a Perovskite-based superconducting Oxide." R. Beyers, G. Lim, E. M. Engler and R. J. Savoy, T. M. Shaw, T. R. Dinger, W. J. Gallagher and R. L. Sandstrom, Appl. Phys. Lett. 50, 1918-1920 (1987).

4. "Superconductivity above 90K in the compound $YBa_2Cu_3O_x$; structural, transport, and magnetic properties." P. M. Grant, R. B. Beyers, E. M. Engler, G. Lim, S.S.P. Parkin, M. L. Ramirez, V. Y. Lee, A. Nazzal, J. E. Vazquez and R. J. Savoy Phys. Rev. B, 35, 7242-7244 (1987).

5. "Bulk superconductivity at 91K in single-phase oxygen-deficient Perovskite $Ba_2YCu_3-O_{9-\delta}$." R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. 58, 1676-1679 (1987).

6. "Room-temperature structure of the 90K bulk superconductor $YBa_2Cu_3O_{8-x}$." Y. Le Page, W. R. McKinnon, J. M. Tarascon, L. H. Greene, G. W. Hull, and D. M. Hwang, Phys. Rev. B, 35, 7245-7248 (1987).

7. "Identification and preparation of single phase 90K oxide superconductor and structural determination by lattice imaging." W. J. Gallagher, R. L. Sandstrom, T. R. Dinger, T. M. Shaw, and D. A. Chance, *Solid State Commun.* 63(2), 147-150 (1987).

8. "Structure of the single-phase high-temperature superconductor $YBa_2Cu_3O_{7-x}$." M.A. Beno, L. Soderholm, D.W. Capone II, D. G. Hinks, J. D. Jorgensen, Ivan K. Schuller, C. U. Segre, and K. Zhang, Appl. Phys. Lett. 51, 57-59, (1987).

9. "Oxygen ordering in the crystal structure of the 93K superconductor $YBa_2Cu_3O_7$ using powder neutron diffraction at 298 and 79.5K." J. E. Greedan, A. O'Reilly and C. V. Stager, Phys. Rev. B, 35, 8770-8773 (1987).

10. "Superconductivity above 90K in the

square-planar compound system ABa_2Cu_3-O_{6+x} with A = Y, La, Nd, Sm, Eu, Gd, Ho, Er, and Lu." P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Foster, and C. W. Chu, Phys. Rev. Lett. 58, 1891-1894 (1987).

11. "New superconducting cuprite Perovskite." "D. W. Murphy, S. Sunshine, R. B. van Dover, R. J. Cava, B. Batlogg, S. M. Zahurak, and L. F. Schneemeyer, Phys. Rev. Lett. 58, 1888-1890 (1987).

12. "Oxygen and rare-earth doping of the 90K superconducting Perovskite $YBa_2Cu_3O_{7-x}$." J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Mull and E. M. Vogel, Phys. Rev. B, 36, 226-234 (1987).

13. "The development of High T_C Ceramic Superconductors: An Introduction." D. R. Clarke, Advanced Ceramic Materials, 2, 273-292 (1987).

14. "Practical preparation of Copper Oxide superconductors." Xiao-Dong Chen, Sang Young Lee, John P. Golben, Sung-Ik Lee, R. D. McMihael, Yi Song, Tae W. Noh, and J. R. Gaines, Rev. Sci. Instrum. 58 1565-1571 (1987)

15. "Structural phase transition in YBa_2Cu_3-$O_{7-\delta}$· the role of dimensionality for high temperature superconductivity." Ivan K. Schuller, D. G. Hinks, M. A. Beno, D. W. Capone II, L. Soderholm, J.-P. Locquet, Y. Bruynseraede, C. U. Segre, and K. Zhang, Solid State Commun. 63(5), 385-388 (1987).

16. "Superconductivity of the single-phase compound $Er_1Ba_2Cu_3O_{9-\delta}$: Transport and structural properties." John P. Golben, Sung-Ik Lee, Sang Young Lee, Yi Song, Tae W. Noh, Xiao-Dong Chen, J. R. Gaines and Rodney T. Tettenhorst, Phys. Rev. B, 35 8075-8708 (1987).

17. "Transport and structural properties of the $Ho_1Ba_2Cu_3O_{9-\delta}$ superconductor." Sung-Ik Lee, John P. Golben, Yi Song, Sang Young Lee, Tae W. Noh, Xiao-Dong Chen, Joe Testa, J. R. Gaines and Rodney T. Tettenhorst, Appl. Phys. Lett. 51 282-284 (1987).

18. "The Effect of Structural Changes on the Superconducting Transition Temperature of $La_1Ba_2Cu_3O_{9-\delta}$" Sung-Ik Lee, John P. Golben, Sang Young Lee, Xiao-Dong Chen, Yi Song, Tae W. Noh, R. D. McMichael, Yue Cao, Joe Testa, Fulin Zuo, J. R. Gaines, A. J. Epstein, D. L. Cox, J. C. Garland, T. R. Lemberger, R. Sooryakumar, Bruce R. Patton, and Rodney T. Tettenhorst, *High Temperature Superconductors*, Materials Research Society Extended Abstract, 53-58 (April, 1987).

19. "Effect of structural changes on the zero-resistance transition temperature La_1Ba_2-$Cu_3O_{9-\delta}$." Sung-Ik Lee, John P. Golben, Sang Young Lee, Xiao-Dong Chen, Yi Song, Tae W. Noh, R. D. McMichael, J. R. Gaines, D. L. Cox, and Bruce R. Patton, Phys. Rev. B, 36, 2417-2420 (1987).