Transactions of the Materials Research Society of Japan 30[1] 1-4 (2005)

The Dependence of the Lattice Parameters and the Metal Containing Network Positions on Temperature and Oxygen Content in BSCCO2223 High Tc Phase Superconductor

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Three BSCCO2223 samples, which contained different amount of oxygen, were synthesized. The powder X-ray diffraction patterns were meseaured and Rietveld analysis calculations were carried out in the temperature range of 83K to 300K. The c-axis length were in the order of the amounts of the oxygen defects. The variations of z-coordinats of the metal atoms with the oxygen contents were considered at 200K. In the sample, which contained the laregest number of the oxygen defects, showed the larger distances between the Cu atom networks and the Ca atom planes comparering with the distances in the higher oxygen content (x=0.11 oxygen nonstoicheometry) samples, prepared by a conventional solid state reaction. The crystal, made by the solid state method, was worked up to obtain the high purity 2223 by the additional firing. The sample, which must contain the largest amount of oxygen, showed the distance increase between Cu (1) and Ca accompanied with the contradiction of the distances between Ca and Cu (2) , and Sr and Bi.
Key words : BSCCO2223 , Rietveld analysis , lattice constant , metal network position , oxygen content

1. Introduction

Recently several reports were presented in BSCCO2223 system on the effects of oxygen contents and temperature, but the main objects of them were on the Jc [1] or on the electron-phonon interaction [2] and not on the deformation behaviors of crystal structure noticing of the atomic positions. In these several years we have continued the low temperature crystal structural studies on high Tc BSCCO2223. Through these works, it was investigated that the distance between the two BiO planes were rather increased by cooling in some cases and the shrinkage occured mainly among the other layers. [3)4)5)]

In order to complete the theory of ceramics superconductivity, the single crystal X-ray analysis or neutron beam diffraction analysis under low temperature will be required. However, in the case of BSCCO2223 it is very difficult to obtain enough amount of samples for these high precision experiments. In this study, the high purity sample was synthesized by the improvements on the procedures reported by other groups. [6] During the firing, the oxygen content in atmosphere was reduced in order to dicrease the Cu oxidation numbers. Thus, three different oxygen contents samples were produced, then the low temperature X-ray diffraction patterns were measured and the results were analyzed by Rietveld method.

2. Experimental

2. 1 Preparation of the samples

3N commercial grades PbO, Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO powders were used as the raw materials. In order to remove the adsorped water and the other volatile impurities, all of the reagent powders except Bi_2O_3 , were treated at 127 ℃ for 72 hrs. The Bi_2O_3 was heated at 77 ℃ for 72 hrs. The atomic ratio was prepared to be Pb : Bi : Sr : Ca : Cu = 0.34 : 1.84 : 1.81 : 2.03 : 3.06. The procedures of mixing, calcinating and firing were carried out following the method reported by G.Rietveld. [6]

The three different oxygen contents samples obtained were (a) sample A : made by G.Rietveld method ; (b) sample B : fired in N_2 atomosphere in order to decrease the oxidation numbers of Cu ; (c) sample C : produced by the additional firing at higher temperature than the sample A.

Sample A was synthesized as follows. The powders of the raw materials, Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO, were mixed and ground. This powder mixture was calcinated at 800 ℃ for 24hrs, and cooled down to the room temperature. The PbO powder was added to the calcinated mixture, and ground again carefully in the agate mortar. Then it was pressed at 8tons for 5min into the square pellets with a size of 10×10mm and a thickness of 1.5 - 2mm. This compression was repeated two times. After that, it was pressed again by CIP at 200MPa for 10min. The pellet was set in the electric furnace and fired at 850 ℃ for 120hr. Then it was ground again into fine powder and repressed into the same shape pellet. Finally the reproduced pellet was fired again under the same conditions as before. The X-ray diffraction pattern of the sample A showed the trace of the low Tc phase 2212.

Sample B was synthesized in the same procedure as A except the firing, which was carried out in the N_2 atomsphere. Nitrogen was introduced into the furnace and the exhaust gas was analyzed continiously by the oxygen analyser. The minimum value of O_2 content observed was 0.25%.

The pellet of sample A was ground and pressed

for the third time. After that the pellet was fired at 860 ℃ for 120hr. Then the pure 2223 was obtained as sample C, and in the X-ray diffraction pattern of C no impurity peaks appeared.

2. 2 X-ray Diffraction Measurements

Rigaku RINT2500 equipped with a liquid nitrogen cooling system was used throughout the experiments. X-ray diffraction intensities of sample A and B were meseared by step-scanning in the range of 10° to 75°, with the step interval of 0.02°, and the samplig time of 1.20 sec., using CuKα radiation with 50KV 300mA. For the sample C the same radiation source condition was used, in the range of 12° to 85°, with 0.024° of the step width, and 5.0sec sampling time. The temperature was controlled at room temperature, 200K, 150K, 120K, 110K, 100K and 83K for sample A and B, and for sample C it was controlled at roon temperature, 200K, 123K, 110K, 100K and 90K.

In the sampling operation of the powder X-ray diffraction, especially on a ceramics superconductor several proposals were reported, in order to avoid, the severe orientations of the crystals, although none of them is entirely perfect. [7] In this work, for sample A and B, the grease was placed at the bottom of the holder and then it was covered by the specimen powder. By this technique the orientation was prevented almost completely, but the flatness of the sample surfaces was not perfect, because it could not be pressed strongly. As the specimen film was rather thin, it was hard to obtain the enough diffraction intensities. Farthermore the copper peaks from the holder can not be avoided and then the data of the diffraction intensities in the range of 42.00 ° - 43.00 ° and 50.00 ° - 51.00 ° were ignored in the calculation of the analysis.

Sample C powder was dispersed into the cellulose cemedain. After the mixture was solidified, it was ground so as to obtain fine isotropic grains. By this technique the sample could be pressed down well to the bottom of the holder, and sufficient intensities were obtained. However, the high back ground and broadening of the peak, caused by the adsorption and the scattering of the beam, could not be avoided. And even by this treatment, the Cu peak exhibitions were not completely disappeared so that the following three 2θ regions 42.86 ° - 44.03 °, 50.12 ° - 51.71 °, and 73.80° - 75.53° were ignored in calculations. In the case of sample B, the appearance of the impurities peaks, the main of which was the 2212 phase accompanied by several other unknown compounds, could not be avoided. In spite of the effort to analyze the X-ray patterns of B as the two component systems of 2223 and 2212, no reasonably converged results were obtained. Then sample B pattern was analyzed as the 2223 single phase system ignoring the 16 2θ regions caused by impurities.

2. 3 Rietveld analysis

The analysis by the Rietveld method was carried out by means of the RIETAN97β program. [8] The crystal structure determination on BSCCO2223 was first performed by Kijima et al. [9] In this work, at the innitiation of the calculations the results of thier report were applied as the starting install parameters.

The important problem is the distance variations among the network planes composed of the metal or the metal oxides. Considering the scattering powers and the number of the atoms contained, the reflection from the Bi(Pb) planes affects the most on the diffraction patterns. Referring to the previous reports 3)4)5), c-parameter of Bi must be around 0.042. Then the install data was varied every 0.0005 from 0.048 to 0.037. The results of the calculations with the install data range from 0.0451 to 0.0420 showed the converged value 0.0431 - 0.0430. These procedures were repeated for every experimental conditions. R values resulted from the calculations were as follows ; Rwp of sample A (8.24 - 6.11), B (10.09 - 9.21), C(5.15 - 4.19) : RI of sample A(4.74 - 2.69), B(4.42 - 3.95), C(5.68 - 4.97) : RF of sample A (3.51 - 1.78), B (3.12 - 2.66), C (3.10 - 2.64).

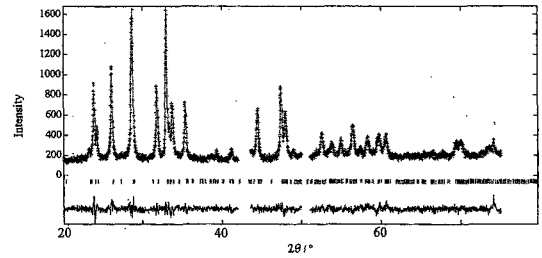

Fig.1 Rietveld refinement paterns for the sample A (200K). Rwp=7.98, Rp=6.23, Re=6.20, Ri=2.35, Rf=1.65

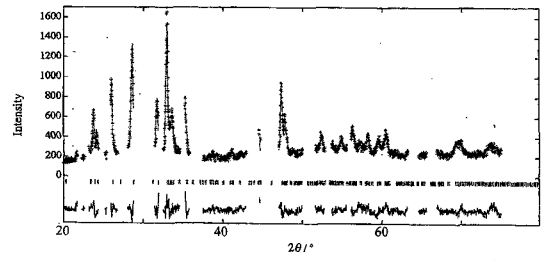

Fig.2 Rietveld refinement paterns for the sample B (200K). Rwp=9.13, Rp=7.21, Re=5.63, Ri=4.19, Rf=2.95

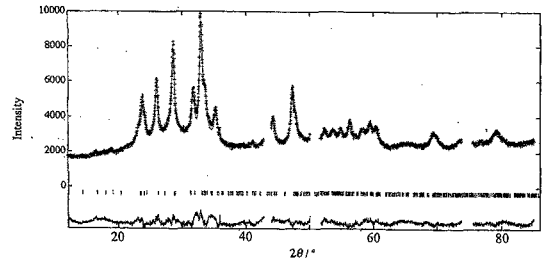

Fig.3 Rietveld refinement paterns for the sample C (200K). Rwp=4.19, Rp=3.38, Re=1.84, Ri=4.95, Rf=2.77

The typical examples of the analyzed patterns were showen in Fig.1,2,3.

3. Results and Discussions

The contradiction behaviors of c-axis length with the temperature decrease on every samples were exhibited in Fig.4. By cooling from the room temperature to 120K c-axis length decreased rapidly and almost linearly in all of the sample A, B and C. In the low temperature range, around Tc, the contractivility of A and B were remarkably reduced. In these deviations from the linearity of lattice parameters, it seemed likely that there were the infinitesimal positions around 100K and 110K in sample A and sample B respectively. On the other hand c-axis of sample C whose shrinkage was almost linear for the whole temperature range, was steeply contracted in the range from 120K to 90K. The shrinking displacements of c-axis between the room temperature and the lowest were 0.136(4)Å(0.37%), 0.142(8)Å(0.38%), 0.150(8)Å(0.41%) in A, B and C respectively. The largest contradiction was observed in the sample C comparing with A and B. There are also the shrinkages of around 0.3% along the a- and b-axis for all of the samples, but the atomic positions in x-y planes are restricted to the special points of symmetry. Then the atomic parameter refinments by Rietveld analysis along these axis were not carried out.

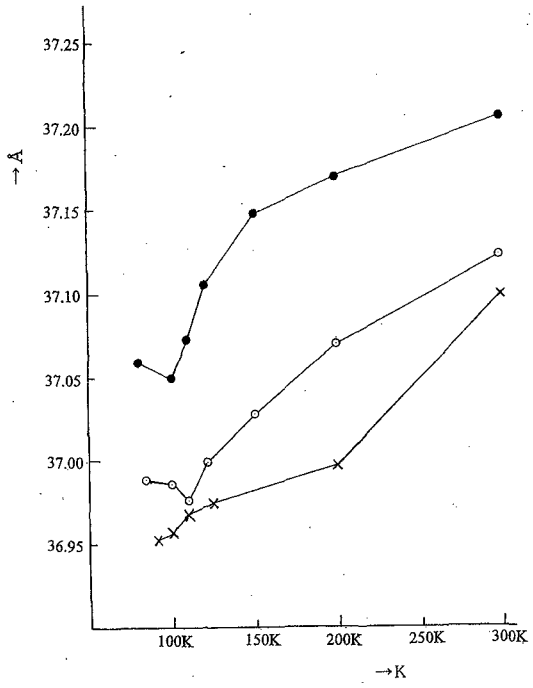

Fig.4 Dependence of the c-axis length of the sample A(○), sample B(●) and sample C(×).

It is worthy to notice that the length of the c-axis was arranged in order of B, A and C. Mainly because of the easiness to obtain the pure sample, YBCO has become the object of more than a thousand of investigations, and the precise oxygen content analysis was performed and the crystal structural data were reported in detail. [10] In the case of BSCCO2223, the firing process by the atomosphere of reduced oxygen content yielded many impurities so it is hard to expect to high accuracy analysis as in YBCO case. [10] In this study the Cu oxidation numbers were determined by means of the iodine titration resulting 2.33 for A and 2.07 for B. [11][12] The oxygen contents were calculated by the electric neutrality condition methods on sample A and sample B and the results were 10.11 and 9.72 respectively. Assuming the ideal composition was $Bi_2Sr_2Ca_2Cu_3O_{10+x}$, as far as this analytical technique concerned, it means that the oxygen contents were almost saturated in sample A (nonstoichiometry x=0.11). [12] But it must be reasonable that the Cu atom in sample C shows the larger oxidation number than that of sample A, because of the additional firing precedure. Thus the amount of the oxygen defects in the crystal of A, B and C must be in the order of B, A and C. The relationships between the oxygen defects contents and the c-axis length of BSCCO2223 were identical with the results of investigations on YBCO [10] and reference 2).

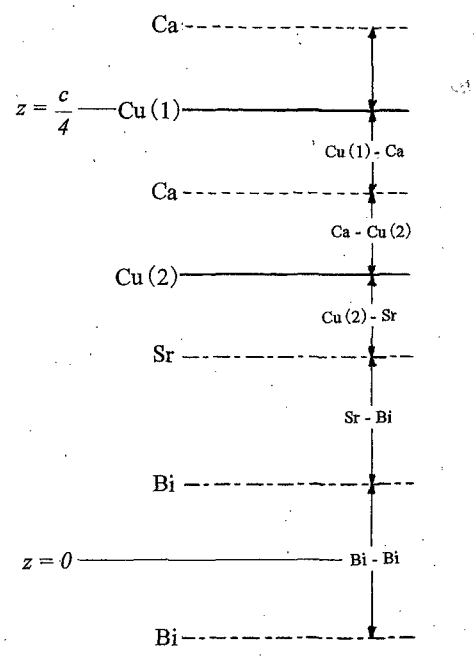

Fig.5 Schematic figure of metal or metal oxide planes in BSCCO2223 crystal, from z=0 to z=c/4.

Though the precise determinations of the atomic positions are rather distressing, taking notice to the large reflection powers of the heavy atoms, it can be expected that the displacements over 0.005 Å and 0.01 Å in the lattice parameter and the metal atom positions respectively may be considered as significant, in these calculations, .

The variations of distances among the metal atoms along the c-axis were sensitive to the oxygen contents, and the effects of temperature on them were relatively slight, so the oxygen contents effects

on them at 200K were under consideration in this study. The arrangements of metal atom planes along the c-axis were schematically showen in Fig.5, from z=0 to z=c/4. The distances of separation (Å) for each samples were tabulated in Table I.

Taking notice the differences of each distance from the sample B to sample A, it was remarkable that Cu(1)-Ca and Ca-Cu(2) were reduced 0.052 Å and 0.023 Å respectively, and this contradictions were accompanied by increase of Cu(2)-Sr and Sr-Bi, 0.015 Å and 0.056 Å rsapectively.

	sample B	sample A	sample C
Cu(1)-Ca	1.691	1.639	1.781
Ca-Cu(2)	1.674	1.651	1.576
Cu(2)-Sr	1.692	1.707	1.689
Sr-Bi	2.644	2.700	2.616
Bi-Bi	3.184	3.143	3.177

Table I. Distances between the ajacent metal or metal oxides planes along the c-axis (Å)

The addition of oxygen at this stage, B to A, resulted the bonding strength increase among these networks which contain copper atoms. The displacements of the distances from sample A to sample C, remarkable reduction was observed at Ca-Cu(2) 0.075 Å, at Sr-Bi 0.084 Å, and at Cu(2) -Sr 0.019 Å. The large expansion appeared at Cu(1)-Ca(a) 0.142 Å, and this behavior was accompanied by the increase of the distance Bi-Bi 0.034 Å.

These variations of distances resulting from the oxygen contents must correspond to the order of the affinities of the metal atoms to the oxygen in BSCCO2223 crystal.

4. Conclusions

By the effort of making the high densitiy powder pellets followed by the firing of higher temperature and longer than the procedures reported, very pure specimens of BSCCO2223 was obtained. According to this procedure the specimens of three grades oxygen contents by the firing under specially controlled atmosphere were synthesized. The X-ray diffraction patterns of them were measured under the temperature range from room temperature to 83K, then Rietveld analyses were carried out. The length of the longest c-axis was in order of the oxygen defects. Concerning with the dependence on temperature, c-axis contradicted almost linearly with cooling in the perfect crystal, but in the sample with many defects the contradiction coefficients decreased remarkably around Tc and the displacement behaviors of the metal or metal oxides planes were complicated including partial expansions.

In the imperfect crystal, the positions of the Ca planes were most sensitive to the temperature change and to the oxygen contents.

5. Ackowlagements

The authers like to ackowlage to Mr.Yoshizawa and Mr.Matsubara and our colleages who accumulated many fundamental data on the sample preparation, X-ray diffraction mesearments and Rietveld analysis. We also thank to Mr. Masuda and Mrs.Oki for the achievments of iodine titration and other chemical analysis. We like to extend oue appreciation to Mr,Imura in Mitsubishi Chem. Ltd. for his friendry discussions on the Rietveld analysis.

6. References

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(Received December 23, 2004; Accepted January 31, 2005)