Elsevier Editorial System(tm) for Physica C
Manuscript Draft
Manuscript Number: PHYSC-D-09-00727
Title: Synthesis and characterization of $(Bi,Cu)Sr_2(RE,Ca)Cu_2O_z$ (RE: Y or rare-earth element)
Article Type: Special Issue: M^2S IX
Keywords: $(Bi,Cu)Sr_2(RE,Ca)Cu_2O_z$; chemical composition; rare-earth substitution; Ca solubility
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Abstract: Samples with nominal compositions of x=0~0.1 in $(Bi_{(1+3x)/3}Cu_{(2-3x)/3})Sr_2(RE_{1-x}Ca_x)Cu_2O_z$ ((Bi,Cu)-"1-2-1-2"; RE: Y or rare-earth element) were synthesized by a solid-state reaction method and characterized by means of X-ray diffractometry (XRD). It is confirmed that the (Bi,Cu)-"1-2-1-2" forms only when RE=Y, Dy and Ho. Single- or nearly single-phase samples are obtained for x=0~0.05 and the Ca-free composition of this compound is determined to be $(Bi_{1/3}Cu_{2/3})Sr_2RECu_2O_z$. Since ionic radii of Y, Dy and Ho are very close to each other and this seems to be an essential factor for the stability of the (Bi,Cu)-"1-2-1-2".

1. Introduction

Observation of superconductivity at critical temperature (T_c) of 68 K in a Ca-free sample with a nominal composition of $(Bi_{0.5}Cu_{0.5})Sr_2Y_{0.8}Cu_{2.2}O_z$ has been reported for the first time by Ehmann *et al*. [1]. They suggested that the real chemical composition of this compound was $(Bi,Cu)Sr_2(Y,Ca)Cu_2O_z$ and that its idealized crystallographic structure was so-called "1-2-1-2" type characteristically containing (Bi,Cu)O monolayer. It was likely that this compound had a tetragonal unit cell with a space group of P4/mmm having lattice parameters of $a \approx 0.38$ nm and $c \approx 1.17$ nm [1,2]. Real chemical composition of this $(Bi,Cu)Sr_2(Y,Ca)Cu_2O_z$ ((Bi,Cu)-"1-2-1-2"), however, seems to have not yet been made clear especially on the viewpoint of Bi/Cu ratio in the (Bi,Cu)O monolayer and Ca substitution for the Y site. In this study, preparation of single-phase samples with Ca-doping and replacement of the Y sites by some rare-earth species were attempted for the (Bi,Cu)-"1-2-1-2".

2. Experimental

Samples were synthesized by solid-state reaction of commercial reagents of Bi_2O_3, $SrCO_3$, RE_2O_3 (RE: Y, La, Nd, Sm, Eu, Gd, Dy, Ho and Er), $CaCO_3$ and CuO with 3N-up purity. These powders were mixed according to the nominal metallic composition of $(Bi_{1/3+x}Cu_{2/3-x})Sr_2(RE_{1-x}Ca_x)Cu_2O_z$ (x=0~0.1) using an agate mortar. The obtained powder mixtures were calcined at 850˚C for 10 h in air gas mixture. The calcined powders were again pulverized and pelletized, and then finally sintered at 940~1090˚C (according to RE species) for 10 h in air. The obtained black-colored ceramics samples were structurally analyzed by means of X-ray diffractometry (XRD) using CuKα radiation.

3. Results and discussion

3-1. $(Bi,Cu)Sr_2(Y,Ca)Cu_2O_z$

For the case of RE=Y, preliminary XRD results showed that chemical composition of the Ca-free end member of the (Bi,Cu)"1-2-1-2" seemed to be very close to $(Bi_{0.7}Cu_{0.3})Sr_2YCu_2O_z$ and that partial substitution of Ca for Y site did not result in single-phase samples when Bi/Cu ratio in the (Bi,Cu) site was fixed at 0.7/0.3. Therefore, we selected the above mentioned $(Bi_{1/3+x}Cu_{2/3-x})Sr_2(RE_{1-x}Ca_x)Cu_2O_z$ as starting compositions according to the case of $(Pb_{(1+x)/2}Cu_{(1-x)/2})Sr_2(Y_{1-x}Ca_x)Cu_2O_z$ [3] which was isomorphous to the (Bi,Cu)-"1-2-1-2". If valence state of Bi ion was +3, this composition meant that the decrease of positive charge of (Y^{3+},Ca^{2+}) site induced by the Ca substitution was completely compensated by the change in Bi/Cu ratio in the (Bi^{3+},Cu^{2+}) site.

Figure 1 shows XRD profiles for samples of RE=Y with nominal compositions of x=0, 0.025, 0.05 and 0.075 sintered at 965˚C. Most of the diffraction lines for each sample could be indexed according to the typical "1-2-1-2" structure. For the case of RE=Y, it should be noted that single-phase samples of (Bi,Cu)-"1-2-1-2" were obtained only in a quite narrow temperature range of 965~970˚C when sintered in air for 10 h. As shown in Fig. 1, single- or nearly single-phase samples were obtained for x=0~0.05 while several additional diffraction lines derived from secondary phase(s) clearly appeared in the diffraction patterns for x=0.075 and 0.1.

From these results, it can be concluded that the chemical composition of the Ca-free end member should be just $(Bi_{1/3}Cu_{2/3})Sr_2YCu_2O_z$ or at least quite close to it and that Ca solubility for the Y site seems not to exceed 0.05. The values of lattice constants, a and c, were estimated using 2θ values of respectively (200) and (006) diffraction lines. For all of x, a and c were ranged in 0.3814~0.3818 and 1.171~1.172 nm, respectively, and no systematic change with x were seen probably because of the limitation of experimental accuracy due to too small amount of doped Ca.

In the (Bi,Cu)-"1-2-1-2", the valence state of Bi ion is thought to be in 3+ similarly as in other Bi-containing superconducting cuprates, for example, $Bi_2Sr_2CaCu_2O_8$ and $Bi_2Sr_2Ca_2Cu_3O_{10}$. This seems to suggest that fairy large amount of oxygen deficiency exists in the present (Bi/Cu)-"1-2-1-2". If Bi and Cu ions in the (Bi/Cu)-"1-2-1-2" are respectively in 3+ and in 2+, oxygen content z in $(Bi_{1/3}Cu_{2/3})Sr_2YCu_2O_z$ (x=0) should be ideally 6.67 since Sr and Y ions are in 2+ and in 3+, respectively. This is probably essential for the occurrence of superconductivity in this compound and investigation on this point is now in progress.

3-2. $(Bi,Cu)Sr_2(RE,Ca)Cu_2O_z$ (RE=Dy and Ho)

Attempt was made to synthesize (Bi,Cu)-"1-2-1-2" using several rare-earth species (La, Nd, Sm, Eu, Gd, Dy, Ho and Er) instead of Y, and it was confirmed that (Bi,Cu)-"1-2-1-2" did not form for most of RE species except for Dy and Ho. It should be noted that, in the XRD results, any trace of formation of (Bi,Cu)-"1-2-1-2" was not observed for RE's other than Dy and Ho. Figures 2 and 3 show XRD profiles for samples of RE=Dy and RE=Ho respectively. The ionic radii of Y^{3+}, Dy^{3+} and Ho^{3+} with coordination number of 8 are 1.019, 1.027 and 1.015 nm, respectively [4] and these values are very close to each other. Therefore, it is likely that the ionic radius of RE species is one of the most crucial factors to stabilize (Bi,Cu)-"1-2-1-2" structure. The origin of this phenomenon is not so clear but this is interesting on the viewpoint of crystal chemistry. Single- or nearly single-phase (Bi,Cu)-"1-2-1-2" were obtained for x=0~0.1 as seen in the figures while significant change in lattice parameters with x was not observed similarly as the case of RE=Y.

4. Conclusion

Chemical composition and phase formation of (Bi,Cu)-"1-2-1-2" were investigated. Using nominal composition of $(Bi_{1/3+x}Cu_{2/3-x})Sr_2(Y_{1-x}Ca_x)Cu_2O_z$, nearly single-phase samples were obtained for x up to 0.05. The (Bi,Cu)-"1-2-1-2" was proved to form in very narrow temperature window of 965~970˚C. Using several RE species instead of Y, the (Bi,Cu)-"1-2-1-2" was obtained only for Dy and Ho. Ionic radius of the RE^{3+} ions is likely to be one of the most crucial factors for the stability of this phase.

References

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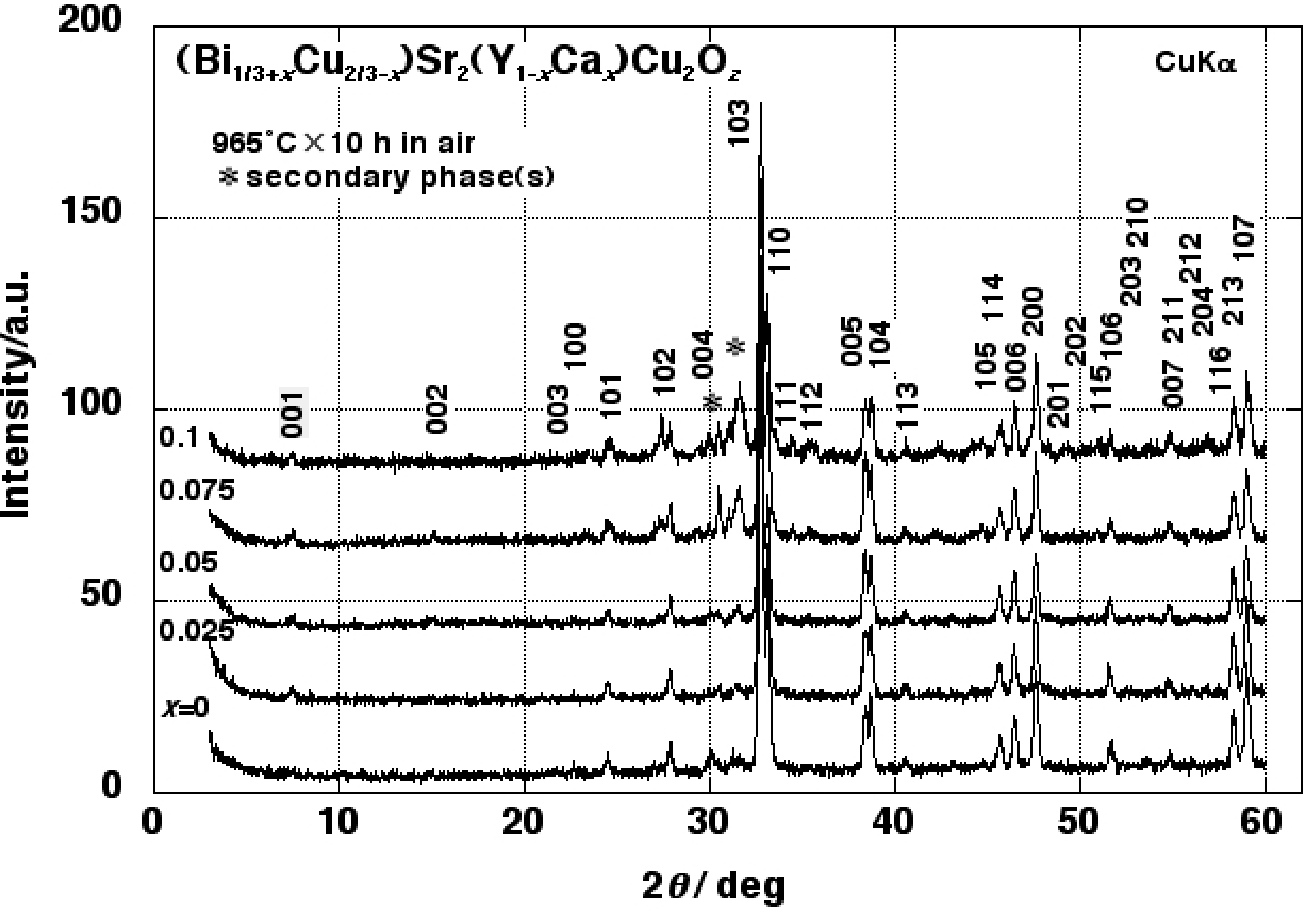
Figure captions

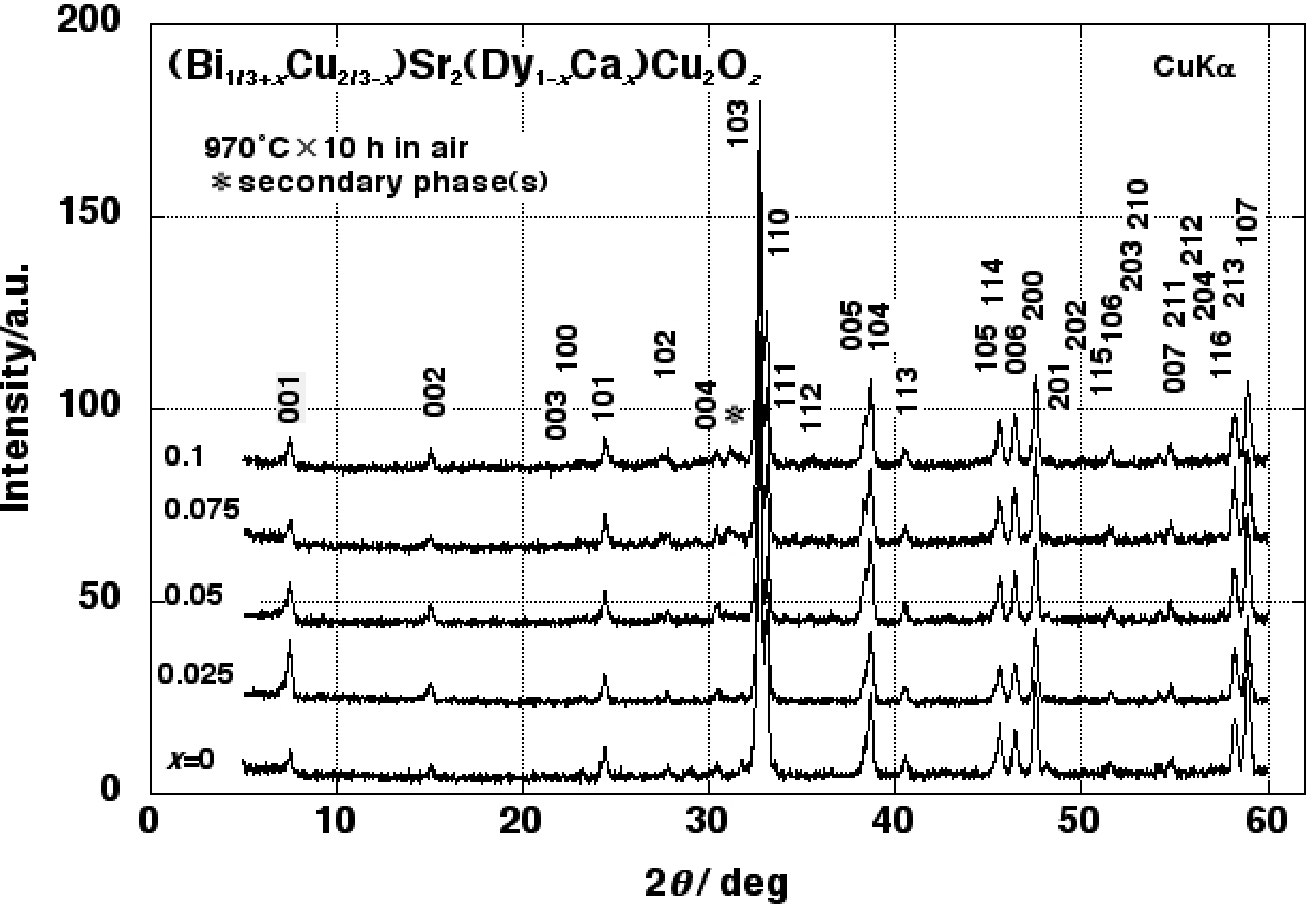
Fig. 1. XRD profiles for samples of RE=Y.

Fig. 2. XRD profiles for samples of RE=Dy.

Fig. 3. XRD profiles for samples of RE=Ho.



(Bi1/3+xCu2/3-x)Sr2(Y1-xCax)Cu2Oz
CuKα
965˚C×10 h in air
* secondary phase(s)
Intensity/a.u.
2θ / deg
x=0
0.025
0.05
0.075
0.1
001
002
003
100
101
102
004
103
110
111
112
005
104
113
105
114
006
200
201
202
115
106
203
210
007
211
116
204
212
213
107
0
50
100
150
200
0
10
20
30
40
50
60



$(Bi_{1/3+x}Cu_{2/3-x})Sr_2(Dy_{1-x}Ca_x)Cu_2O_z$
CuKα
970°C × 10 h in air
* secondary phase(s)
Intensity/a.u.
2θ / deg
0
50
100
150
200
10
20
30
40
50
60
0.1
0.075
0.05
0.025
x=0
001
002
003
100
101
102
004
*
103
110
111
112
005
104
113
105
114
006
200
201
202
115
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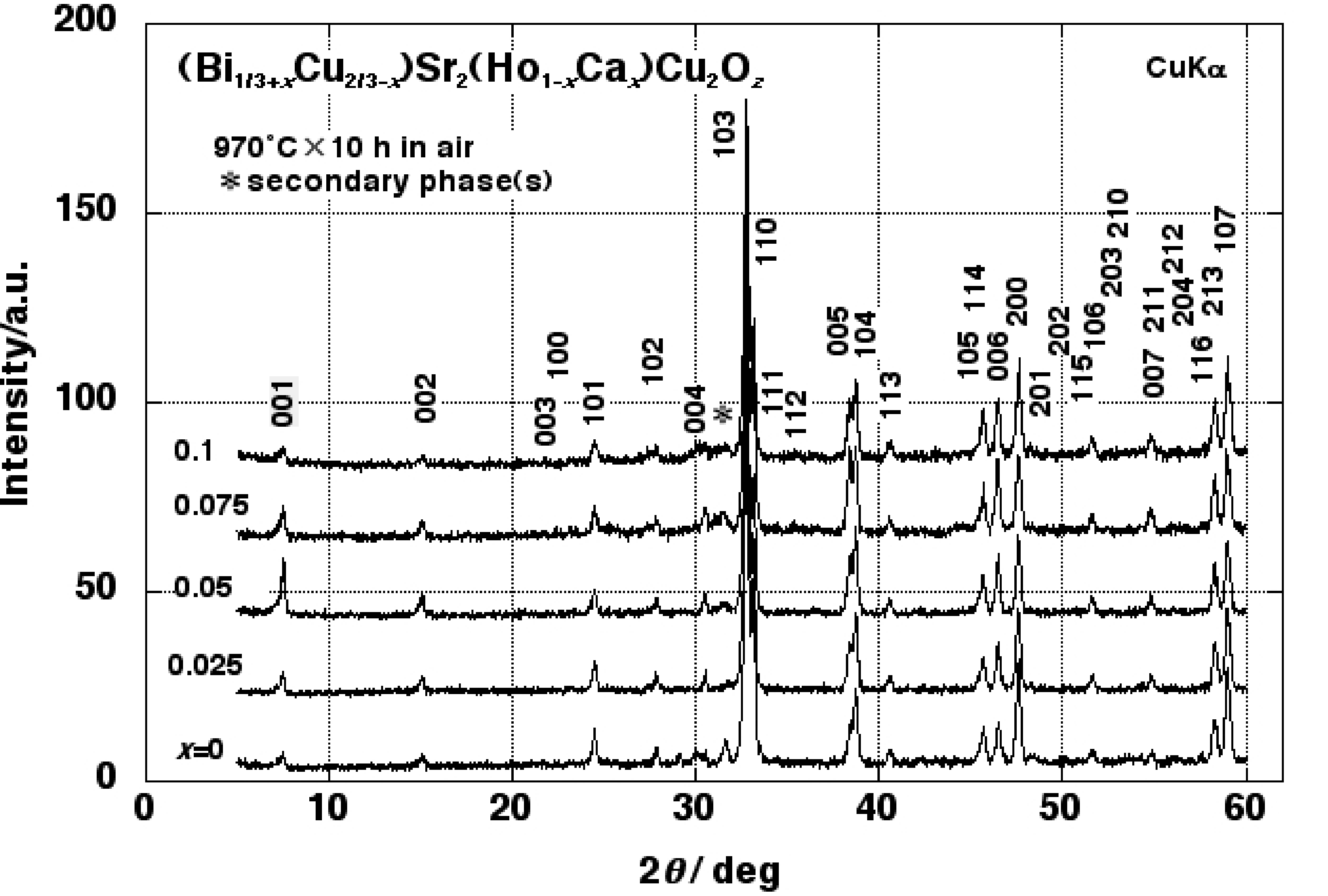
212
204
116
213
107



$(Bi_{1/3+x}Cu_{2/3-x})Sr_2(Ho_{1-x}Ca_x)Cu_2O_z$
CuKα
970°C × 10 h in air
* secondary phase(s)
Intensity/a.u.
2θ / deg
0.1
0.075
0.05
0.025
x=0
001
002
003
100
101
102
004
103
110
111
112
005
104
113
105
114
006
200
201
202
115
106
203
210
007
211
204
212
116
213
107
0
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150
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0
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