

# Synthesis and characterization of (Bi,Cu)Sr<sub>2</sub>(RE,Ca)Cu<sub>2</sub>O<sub>z</sub>

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Abstract: Samples with nominal compositions of  $x=0\sim 0.1$  in  $(\text{Bi}_{(1+3x)/3}\text{Cu}_{(2-3x)/3})\text{Sr}_2(\text{RE}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_z$  ((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  $x=0\sim 0.05$  and the Ca-free composition of this compound is determined to be  $(\text{Bi}_{1/3}\text{Cu}_{2/3})\text{Sr}_2\text{RECu}_2\text{O}_z$ . 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  $(\text{Bi}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{Y}_{0.8}\text{Cu}_{2.2}\text{O}_z$  has been reported for the first time by Ehmann *et al.* [1]. They suggested that the real chemical composition of this compound was  $(\text{Bi,Cu})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_z$  and that its idealized crystallographic structure was so-called "1-2-1-2" type characteristically containing  $(\text{Bi,Cu})\text{O}$  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  $(\text{Bi,Cu})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_z$  ( $(\text{Bi,Cu})$ - "1-2-1-2"), however, seems to have not yet been made clear especially on the viewpoint of Bi/Cu ratio in the  $(\text{Bi,Cu})\text{O}$  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  $(\text{Bi,Cu})$ - "1-2-1-2".

## 2. Experimental

Samples were synthesized by solid-state reaction of commercial reagents of  $\text{Bi}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{RE}_2\text{O}_3$  (RE: Y, La, Nd, Sm, Eu, Gd, Dy, Ho and Er),  $\text{CaCO}_3$  and  $\text{CuO}$  with 3N-up purity. These powders were mixed according to the nominal metallic composition of  $(\text{Bi}_{1/3+x}\text{Cu}_{2/3-x})\text{Sr}_2(\text{RE}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_z$  ( $x=0\sim 0.1$ ) using an agate mortar. The obtained powder mixtures were calcined at  $850^\circ\text{C}$  for 10 h in air gas mixture. The calcined powders were again pulverized and pelletized, and then finally sintered at  $940\sim 1090^\circ\text{C}$  (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  $\text{CuK}\alpha$  radiation.

### 3. Results and discussion

#### 3-1. (Bi,Cu)Sr<sub>2</sub>(Y,Ca)Cu<sub>2</sub>O<sub>z</sub>

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<sub>0.7</sub>Cu<sub>0.3</sub>)Sr<sub>2</sub>YCu<sub>2</sub>O<sub>z</sub> 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<sub>1/3+x</sub>Cu<sub>2/3-x</sub>)Sr<sub>2</sub>(RE<sub>1-x</sub>Ca<sub>x</sub>)Cu<sub>2</sub>O<sub>z</sub> as starting compositions according to the case of (Pb<sub>(1+x)/2</sub>Cu<sub>(1-x)/2</sub>)Sr<sub>2</sub>(Y<sub>1-x</sub>Ca<sub>x</sub>)Cu<sub>2</sub>O<sub>z</sub> [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<sup>3+</sup>,Ca<sup>2+</sup>) site induced by the Ca substitution was completely compensated by the change in Bi/Cu ratio in the (Bi<sup>3+</sup>,Cu<sup>2+</sup>) 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  $965^{\circ}\text{C}$ . 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  $965\sim 970^{\circ}\text{C}$  when sintered in air for 10 h. As shown in Fig. 1, single- or nearly single-phase samples were obtained for  $x=0\sim 0.05$  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<sub>1/3</sub>Cu<sub>2/3</sub>)Sr<sub>2</sub>YCu<sub>2</sub>O<sub>z</sub> 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  $2\theta$  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,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  and  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ . This seems to suggest that fairly 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  $(\text{Bi}_{1/3}\text{Cu}_{2/3})\text{Sr}_2\text{YCu}_2\text{O}_z$  ( $x=0$ ) 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<sub>2</sub>(RE,Ca)Cu<sub>2</sub>O<sub>z</sub> (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  $\text{Y}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Ho}^{3+}$  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  $x=0\sim 0.1$  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  $(\text{Bi}_{1/3+x}\text{Cu}_{2/3-x})\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_z$ , 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  $\text{RE}^{3+}$  ions is likely to be one of the most crucial factors for the stability of this phase.

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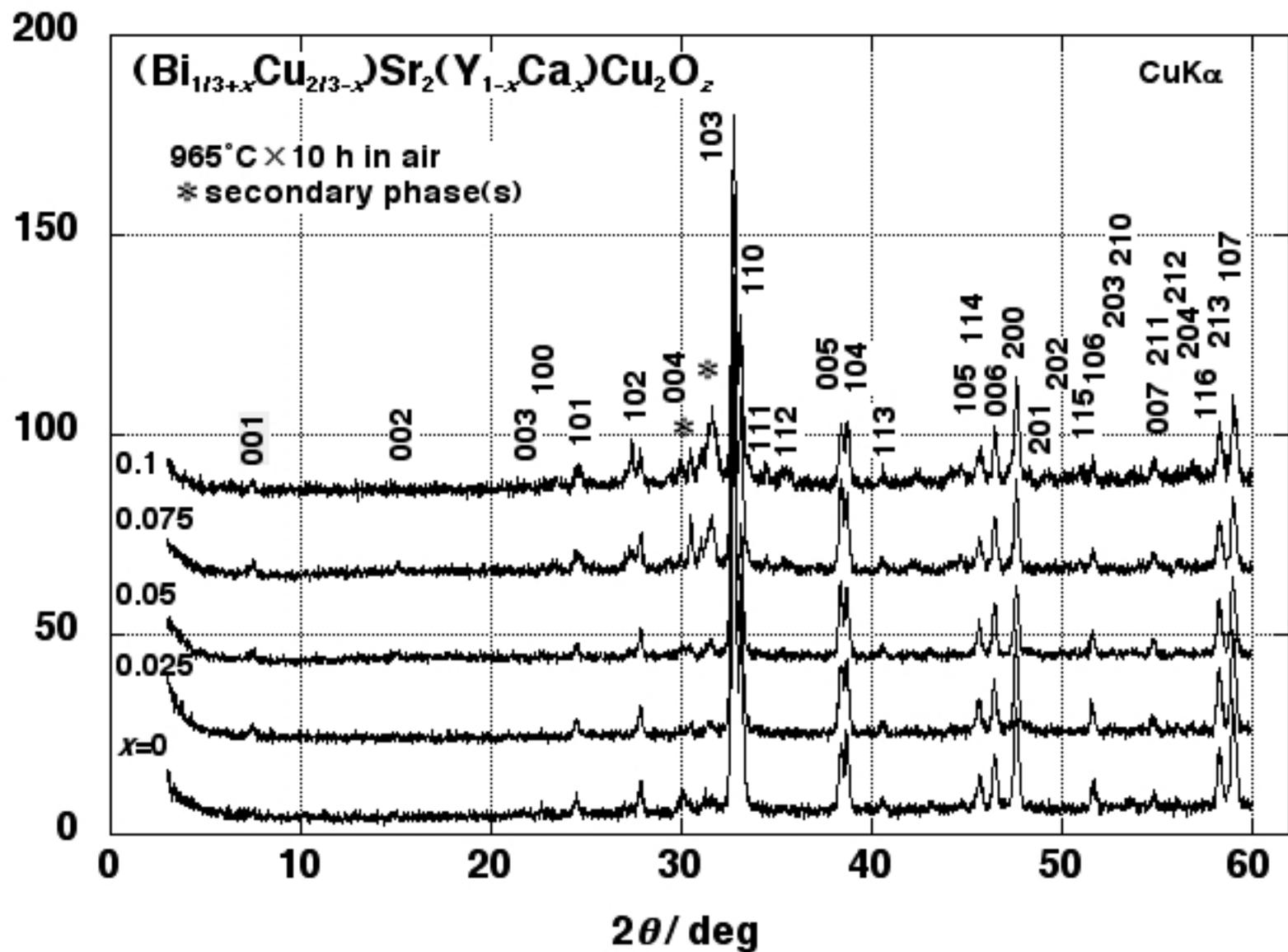
Figure captions

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

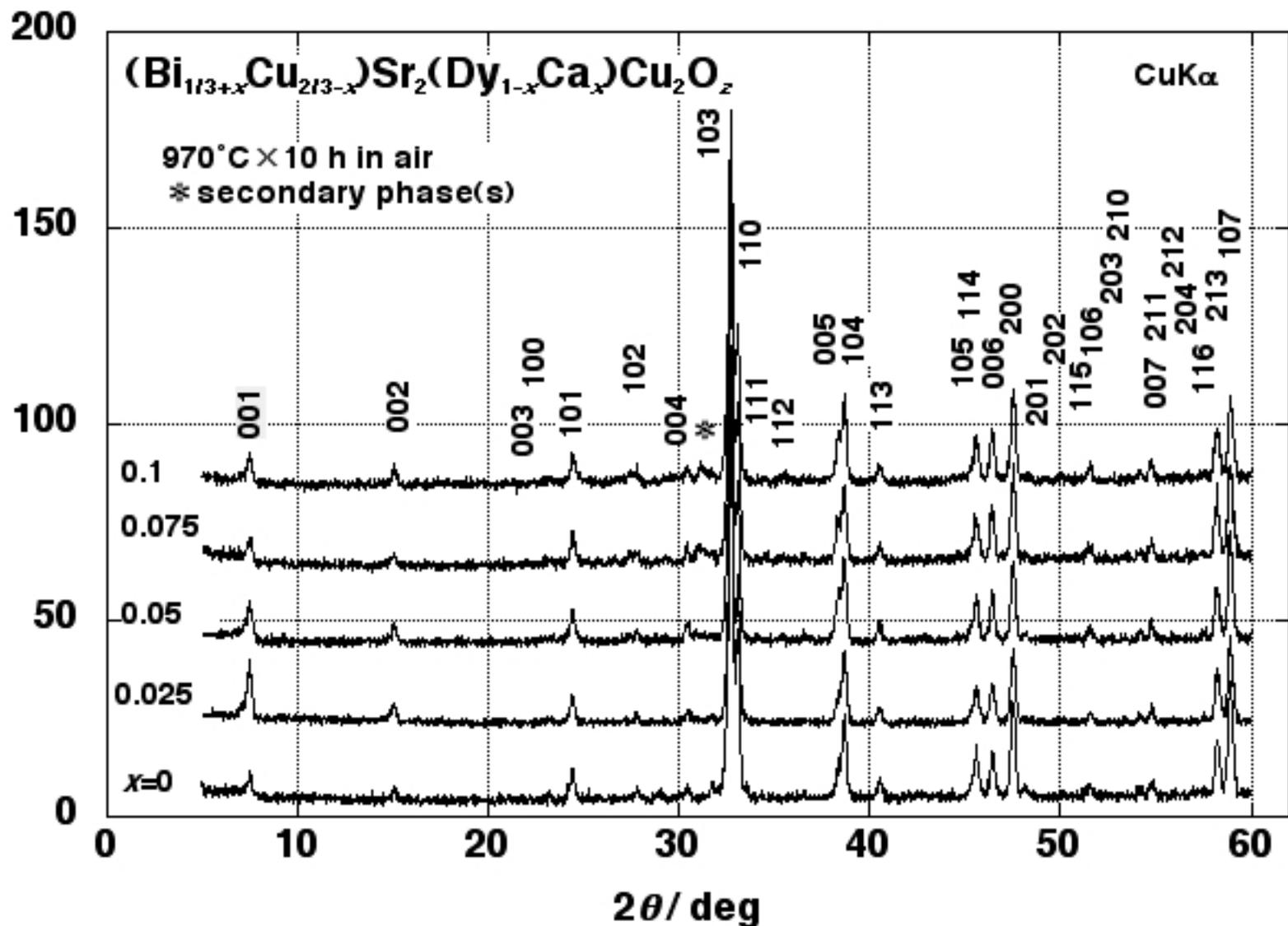
Fig. 2. XRD profiles for samples of RE=Dy.

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

Intensity/a.u.



Intensity/a.u.



Intensity/a.u.

