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Phase Relations in the System $BiO_{1.5}$–$YbO_{1.5}$–CuO

X. L. Chen,* F. F. Zhang,† Y. M. Shen,† J. K. Liang,*,‡ W. H. Tang,* and Q. Y. Tu†

*Institute of Physics & Center for Condensed Matter Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, Peoples Republic of China; †Department of Physics, Beijing Normal University, Beijing 100875, Peoples Republic of China; and ‡International Center for Materials Physics, Academia Sinica, Shenyang 110015, Peoples Republic of China

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The subsolidus phase relations for the ternary system, $BiO_{1.5}$–$YbO_{1.5}$–CuO, are investigated by the powder X-ray diffraction method. The system can be divided into six three-phase regions and three two-phase regions. There exist two solid solutions $Bi_{1-x}Yb_xO_{1.5}$ ($0.05 \le x \le 0.35$) and $Yb_{1-x}Bi_xO_{1.5}$ ($x \le 0.02$). The former solution exhibits a tetragonal structure with $0.05 \le x < 0.15$ which is isostructural to β-$BiO_{1.5}$, while a cubic structure with $0.15 \le x \le 0.35$ is isostructural to δ-$BiO_{1.5}$. A new compound with the composition close to $Yb_{12}Bi_{12}CuO_y$ is found. © 1998 Academic Press

INTRODUCTION

The two-dimensional layer $\{Bi_2O_2\}^{2+}$ can be connected by different interlayers to form a variety of layered compounds. The interlayer may consist of individual atoms, as in the Sillén phases, or octahedral and tetrahedral cation oxygens, as in the Aurivillius phases. In addition, substitution of other cations for Bi in the $\{Bi_2O_2\}^{2+}$ layer can result in additional compounds by connecting more interlayers. For details, see the review section of a recent dissertation (1). More complicated interlayers are possible. A typical example is the high T_c superconductors $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ ($n = 1, 2, 3$), where the interlayers are $\{Sr_2Ca_{n-1}Cu_nO_{2n+2}\}$.

The subsolidus phase relations in several ternary systems including $BiO_{3/2}$–$PrO_{11/6}$–CuO (2), $GdO_{3/2}$–$BiO_{3/2}$–CuO (3), and Nd_2O_3–Bi_2O_3–CuO (4) have been studied to search for new layered, Cu-containing compounds. No ternary compounds were found in these systems. In the present study, we have investigated the subsolidus phase relations of the $BiO_{1.5}$–$YbO_{1.5}$–CuO ternary system and the related binary systems. The results are reported here.

EXPERIMENTAL

The specimens were prepared by the solid state reaction of analytically pure $BiO_{1.5}$, $YbO_{1.5}$ and CuO. Before weighing, $YbO_{1.5}$ was preheated at 600°C for 3–4 h to remove the water it absorbed in air. The oxides were weighed on an analytical balance to an accuracy of 0.05 mg, mixed thoroughly in an agate mortar, and pressed into pellets of 12 mm in diameter and 1–2 mm thick. The specimens were then fired for 3–6 days in air. Due to the low melting point (825°C) of $BiO_{1.5}$, the $BiO_{1.5}$-rich specimens were sintered at 750°C, while other specimens were sintered at 800°C. All specimens were cooled in a furnace to room temperature.

The phase identification, determination of lattice parameters and the Rietveld refinement were performed on a STOE/CSS PL/2 X-ray diffractometer with Cu$K\alpha$ radiation (36 kV, 20 mA) at room temperature. All data were collected by step scanning with a step of 0.02° (2θ). The collecting time is 2 s for per step with an angular range from $2\theta = 15$ to 65°. For the Rietveld refinement, the 2θ range is over 100° (5).

RESULTS AND DISCUSSION

In the system $BiO_{1.5}$–CuO, there is only one compound, Bi_2CuO_4. It has a tetragonal structure with lattice parameters $a = 8.498(2)$ Å and $c = 5.814(2)$ Å and space group $P4/ncc$. This result is in good agreement with the previously reported data (ICDD-PDF 42-334).

In the system $YbO_{1.5}$–CuO, there is also only one compound, $Yb_2Cu_2O_5$, which can be indexed based on an orthorhombic cell with lattice parameters $a = 10.712(2)$ Å, $b = 3.424(2)$ Å, and $c = 12.331(3)$ Å. The space group is $Pna2_1$. This result is also in good agreement with the reported one (6).

In the system $BiO_{1.5}$–$YbO_{1.5}$, two solid solutions $Bi_{1-x}Yb_xO_{1.5}$ ($0.05 \le x \le 0.35$) and $Bi_{1-x}Yb_xO_{1.5}$ ($x \ge 0.98$) are identified. Figure 1 shows the subsolidus phase relations in the system $BiO_{1.5}$–$YbO_{1.5}$. No monoclinic phase (7), orthorhombic phase (8), rhombohedral phase (9), or solid solution (10), which were reported in other $BiO_{1.5}$–$RO_{1.5}$ systems, were found in the present system.

The representative X-ray diffraction patterns for the solid solution series $Bi_{1-x}Yb_xO_{1.5}$ ($0.05 \le x \le 0.35$) are shown in Fig. 2. The small peaks at about 25.5° (2θ) are due to K β radiation. The solid solution is isostructural to β-$BiO_{1.5}$

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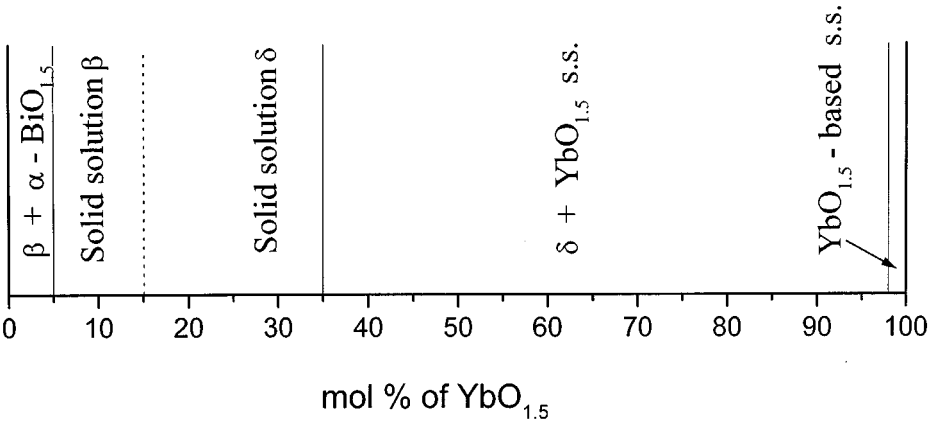

FIG. 1. Subsolidus phase relations in the system $YbO_{1.5}$–$BiO_{1.5}$.

with $0.05 \leq x < 0.15$ and also isostructural to δ-$BiO_{1.5}$ with $0.15 \leq x \leq 0.35$. As an example, $Bi_{0.9}Yb_{0.1}O_{1.5}$ can be indexed based on a tetragonal cell with lattice parameters $a = 7.7731(5)$ Å and $c = 5.6013(4)$ Å. Similar structures were reported for $Bi_{7.5}Y_{0.5}O_{12}$ and $Bi_{7.68}Ti_{0.32}O_{12.16}$ by J. Ducke *et al.* (11). Table 1 shows the X-ray powder diffraction data and the indexed result for $Bi_{0.9}Yb_{0.1}O_{1.5}$ The extinction of the reflections leads exclusively to the space group $P\bar{4}2_1c$. Starting with the initial structural parameter based on β-$BiO_{1.5}$ (12), we refine the structure by the Rietveld method.

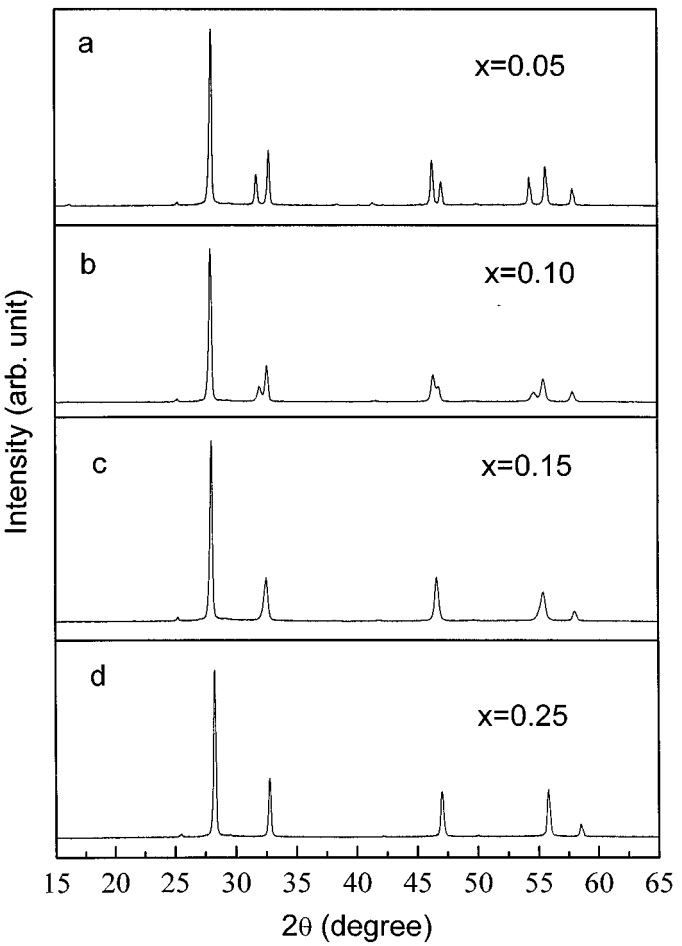

FIG. 2. The X-ray powder diffraction patterns of $Bi_{1-x}Yb_xO_{1.5}$ with Cu$K\alpha$ radiation, (a) $x = 0.05$; (b) $x = 0.10$; (c) $x = 0.15$; (d) $x = 0.25$. The small peaks at about 25.5° (2θ) are due to K β radiation.

The Bi and Yb atoms are put statistically on the site 8(*e*) with the fixed Bi/Yb ratio of 9 : 1. Good agreement between the calculated and the observed diffraction patterns is obtained. The agreement indices R_p, R_{wp}, and s are 10.32%, 13.76%, and 1.891, respectively. The final refined parameters are listed in Table 2. The comparison between refined and observed patterns is presented in Fig. 3.

The solid solution series with $0.15 \leq x \leq 0.35$ exhibits δ-$BiO_{1.5}$ structure, i.e. the CaF_2 structure. Typically, the X-ray powder diffraction data of $Bi_{0.65}Yb_{0.35}O_{1.5}$ (δ phase) and the indexed results are listed in Table 3. Rietveld refinements were performed using the space group $Fm3m$ on the structure. The atomic ratio of Yb and Bi was kept at 35 : 65 and was randomly put at the site of 4(*a*). Initial positions of

TABLE 1
Powder X-Ray Diffraction Data of $Bi_{0.9}Yb_{0.1}O_{1.5}$ with Cu$K\alpha$ Radiation

h k l	$2\theta_{obs}$ (deg)	d_{obs} (Å)	$2\theta_{calc}$ (deg)	I/I_0
1 1 0	16.16	5.48	16.15	1
2 0 1	27.96	3.191	28.00	100
0 0 2	32.02	2.795	32.05	12
2 2 0	32.60	2.747	32.64	25
2 1 2	41.62	2.170	41.50	2
2 2 2	46.36	1.958	46.39	18
4 0 0	46.84	1.940	46.83	12
2 0 3	54.66	1.679	54.68	7
4 2 1	55.44	1.657	55.45	16
4 0 2	57.88	1.593	57.87	7

TABLE 2
Refined Structural Parameters of $Bi_{0.90}Yb_{0.10}O_{1.5}$[a]

Atom	Site	*X*	*Y*	*Z*	Occupancy	*B* (Å^2)
Bi	8(e)	0.0063(4)	0.2486(4)	0.2389(5)	0.90	1.74(3)
Yb	8(e)	0.0063(4)	0.2486(4)	0.2389(5)	0.10	1.74(3)
O1	8(e)	0.291(6)	0.269(6)	0.005(3)	1.0	9.1(4)
O2	4(d)	0	0.5	0.41(1)	1.0	6.0(5)

[a] Crystal structure data: $a = 7.7731(5)$ Å, $c = 5.6013(4)$ Å, space group $P\bar{4}2_1c$, $R_p = 10.32\%$, $R_{wp} = 12.88\%$, $R_{exp} = 7.275\%$.

TABLE 3
Powder X-Ray Diffraction Data of $Bi_{0.65}Yb_{0.35}O_{1.5}$ with Cu$K\alpha$ Radiation

h k l	$2\theta_{obs}$ (deg)	d_{obs} (deg)	$2\theta_{calc}$ (deg)	I/I_0
1 1 1	28.50	3.132	28.498	100
2 0 0	33.02	2.7127	33.024	45
2 2 0	47.40	1.9179	47.399	40
3 1 1	56.24	1.6356	56.240	35
2 2 2	58.98	1.5660	58.980	9

oxygen atoms was set at 8(*e*) (0.25, 0.25, 0.25) and the occupancy factor was set as 0.75 (=6/8). It was found that the refinement of the oxygen position at 32(*f*) (*x*, *x*, *x*) can further decrease R_{wp}. This results in $x = 0.30(1)$. A similar situation was observed at δ-$BiO_{1.5}$ (13). Table 4 gives the structural parameters of the final refinement. The result of the final Rietveld refinement is plotted in Fig. 4. Satisfactory refinement was achieved with $R_p = 10.01\%$, $R_{wp} = 12.88\%$, and $s = 1.596$. The temperature factors *B* are 3.30(6) and 9.7(5) Å^2 for (Yb, Bi) and O atoms, respectively. These values are quite large. Similar results were observed in δ-Bi_2O_3, where the temperature factors are 6.4 and 13.7 Å^2 for Bi and O, respectively (13). This can be attributed to the disorder of oxygen atoms.

The solid solution $Bi_{1-x}Yb_xO_{1.5}$ ($0.05 \le x \le 0.35$) undergoes a phase transition from tetragonal to cubic with increasing $YbO_{1.5}$. The values of the lattice parameters of β and δ in the different specimens are listed in Table 5. Since it is evident that the cell parameters of β are related to that of δ by the relations $a_t = \sqrt{2}c_t \approx \sqrt{2}a_c$, in Fig. 5, we plot the variation of $a_t/\sqrt{2}$, c_t, and a_c vs $YbO_{1.5}$ content. It can be seen that c_t decreases and $a_t/\sqrt{2}$ increases with increasing $YbO_{1.5}$ content, *x*. When $YbO_{1.5}$ content reaches 0.15, $a_t/\sqrt{2}$ is equal to c_t. The structure transforms from tetragonal to cubic. This is a displacement phase transition resulting from order to disorder of the atoms. There is no two-phase region between β and δ. With $x > 0.35$, c_t is essentially unchanged and δ and $YO_{1.5}$-based solid solution coexist, suggesting the solubility for δ is $x = 0.35$.

The solubility of $BiO_{1.5}$ in $YbO_{1.5}$ is very small. It is difficult to determine the solid solution region accurately by only using the lattice parameteric method because the small differences between the lattice parameters of the specimens. Figure 6 shows that the peaks of solid solution δ (indicated by arrows) disappear when $YbO_{1.5}$ content reaches 0.98. A previous study (14) revealed that the monoclinic $BiO_{1.5}$ has little or no solid solution for various cations. So in the present system, the solid solution should be less than 2%.

In light of the ionic radius of lanthanide elements, Iwahara *et al.* (15) reported that the crystal structure of the solid solutions in $BiO_{1.5}$–$RO_{1.5}$ systems varies with the atomic number, from the rhombohedral phase for R^{3+} with large radii to the fcc phase for R^{3+} with small radii. For a compound containing R^{3+} cations with a radius of

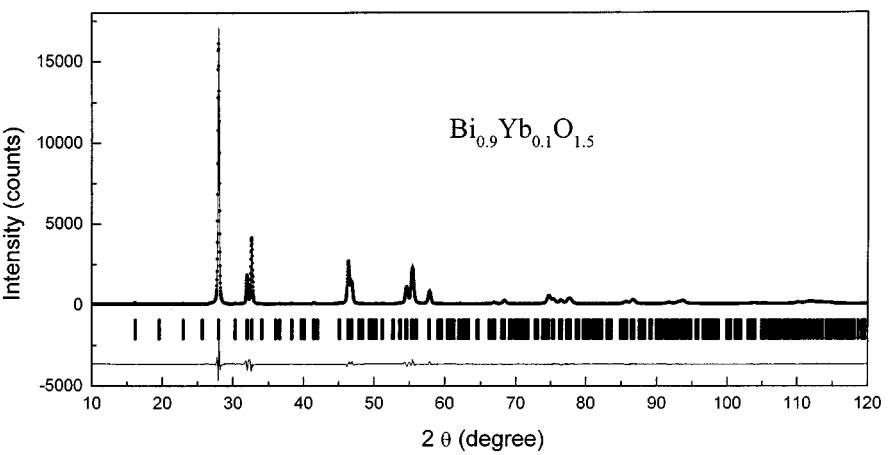

FIG. 3. The Rietveld refinement result of $Bi_{0.9}Yb_{0.1}O_{1.5}$. Small points represent the experimental data, and solid lines, the calculated patterns. The vertical bars indicate the positions of the diffraction peaks. The solid line at the bottom is the difference between the experimental and calculated data.

TABLE 4
Refined Structural Parameters of $Bi_{0.65}Yb_{0.35}O_{1.5}$[a]

Atom	Site	*X*	*Y*	*Z*	Occupancy	*B* (Å^2)
Bi	4(a)	0	0	0	0.65	3.30(6)
Yb	4(a)	0	0	0	0.35	3.30(6)
O	32(f)	0.30(1)	0.30(1)	0.30(1)	0.1875	9.7(5)

[a] Crystal structure data: $a = 5.4201(2)$ Å, space group $Fm3m$, $R_p = 10.01\%$, $R_{wp} = 12.88\%$, $R_{exp} = 8.07\%$.

TABLE 5
Lattice Parameters of Solid Solutions β and δ

	$YbO_{1.5}$ content	*a* (Å)	*c* (Å)
β	0.05	7.718(2)	5.626(2)
	0.10	7.754(4)	5.581(4)
	0.15	7.780(8)	5.501(8)
δ	0.20	5.4884(5)	
	0.25	5.4617(7)	
	0.30	5.4372(8)	
	0.35	5.4202(1)	
	0.40	5.4184(1)[a]	
	0.50	5.424(1)[a]	
	0.70	5.4166(3)[a]	
	0.95	5.420(1)[a]	

[a] The lattice parameters of beyond the solubility which essentially do not change with $YbO_{1.5}$ content.

medium size one anticipates that both fcc and rhombohedral phases exist, depending on its composition. This inference has been verified experimentally. In our experiment, only the fcc phase occurred in the $BiO_{1.5}$–$YbO_{1.5}$ system because the radius of Yb is small.

The subsolidus phase relations for the ternary system, $BiO_{1.5}$–$YbO_{1.5}$–CuO, which consists of six three-phase regions and three two-phase regions, are shown in Fig. 7:

1. $CuO + Bi_2CuO_4 + Yb_2Cu_2O_5$
2. $Bi_2CuO_4 + \alpha$-$BiO_{1.5}$ + solid solution β
3. Bi_2CuO_4 + solid solution β
4. Bi_2CuO_4 + solid solution δ
5. Bi_2CuO_4 + solid solution $\delta + Yb_{12}Bi_{12}CuO_y$
6. $Bi_2CuO_4 + Yb_2Cu_2O_5 + Yb_{12}Bi_{12}CuO_y$
7. $Yb_2Cu_2O_5 + YbO_{1.5} + Yb_{12}Bi_{12}CuO_y$
8. solid solution $\delta + YbO_{1.5} + Yb_{12}Bi_{12}CuO_y$
9. $Yb_2Cu_2O_5 + YbO_{1.5}$

A new ternary compound with the composition close to $Yb_{12}Bi_{12}CuO_y$, was identified. The reaction of formation of this phase is very sluggish. Figure 8 shows that the XRD pattern of this compound of a sample annealed for 1 week at 875°C. Its powder diffraction data are listed in Table 6. Attempts to index its diffraction pattern failed because some weak diffraction peaks which cannot be indexed are always present. Further structural characterization of this compound is underway.

CONCLUSION

We obtained the following results after present investigation on the system $BiO_{1.5}$–$YbO_{1.5}$–CuO:

1. In the binary system $BiO_{1.5}$–$YbO_{1.5}$, there exist two solid solution series, $Bi_{1-x}Yb_xO_{1.5}$ with $0.15 \le x \le 0.35$ and $Yb_{1-x}Bi_xO_{1.5}$ with $x \le 0.02$. For the former solution, it is isostructural to β-$BiO_{1.5}$ with $0 \le x < 0.15$ and isostructural to δ-$BiO_{1.5}$ with $0.15 \le x \le 0.35$.
2. There is only one ternary compound $Yb_{12}Bi_{12}CuO_y$ in the system $BiO_{1.5}$–$YbO_{1.5}$–CuO.

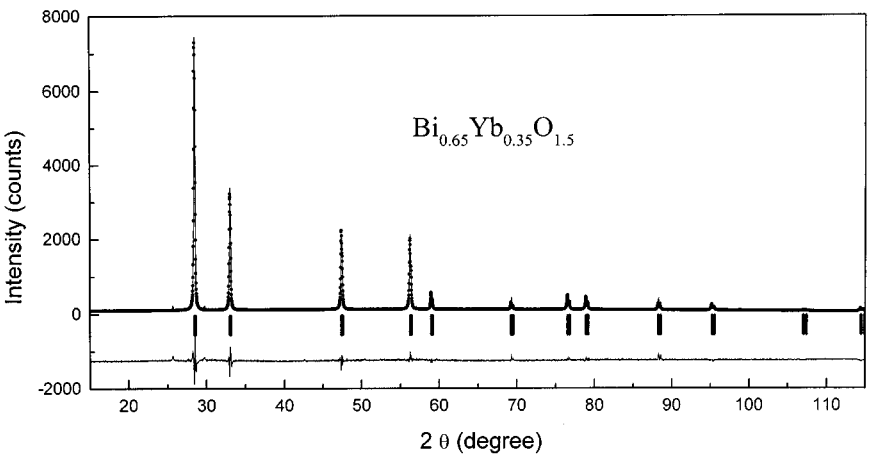

FIG. 4. The Rietveld refinement pattern of $Bi_{0.65}Yb_{0.35}O_{1.5}$. Small points represent the experimental data, and solid lines, the calculated patterns. The vertical bars indicate the positions of the diffraction peaks. The solid line at the bottom is the difference between the experimental and calculated data.

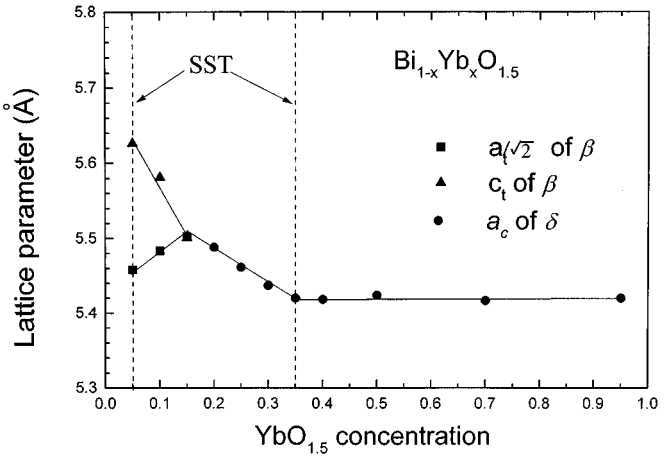

FIG. 5. The variation of lattice parameters vs the $YbO_{1.5}$ content for $Bi_{1-x}Yb_xO_{1.5}$. SST = solid solution limit.

TABLE 6
Powder Diffraction Data of the Compound $Yb_{12}Bi_{12}CuO_y$, $\lambda = 1.5405$ Å

$2\theta_{obs}$ (deg)	d_{obs} (Å)	Intensity
21.65	4.10	5
21.92	4.05	4
22.72	3.91	6
24.02	3.705	10
24.32	3.660	8
27.56	3.236	60
28.58	3.123	100
30.16	2.963	45
33.00	2.714	30
33.34	2.687	35
34.68	2.586	6
37.24	2.414	4
41.20	2.191	4
43.42	2.084	5
44.30	2.045	5
45.28	2.003	7
46.26	1.963	16
47.22	1.925	14
47.98	1.896	12
48.06	1.892	12
49.40	1.845	16
49.70	1.834	14
50.91	1.794	6
53.08	1.725	4
55.32	1.661	9
55.70	1.650	9
56.98	1.616	14
57.42	1.605	7
58.16	1.586	6
58.62	1.575	7
59.30	1.558	9
62.76	1.481	5
63.74	1.460	3

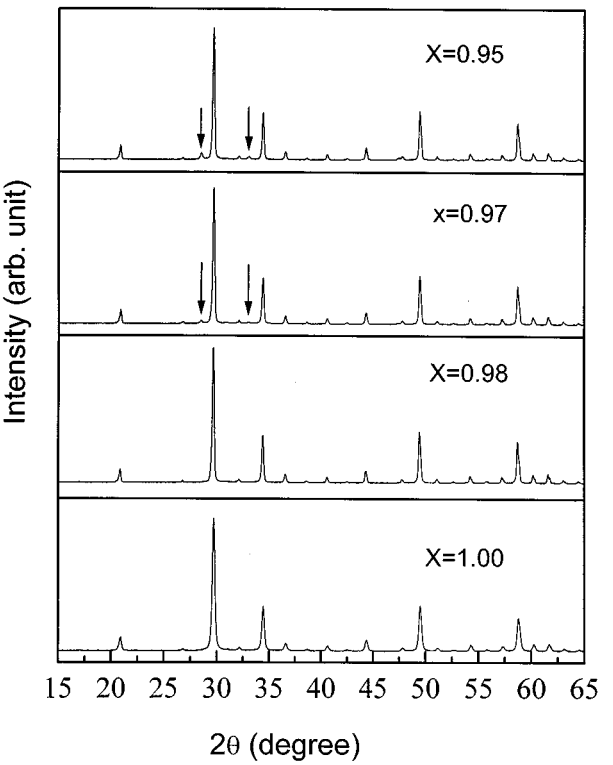

FIG. 6. The powder X-ray diffraction patterns of $Bi_{1-x}Yb_xO_{1.5}$ with Cu$K\alpha$ radiation, (a) $x = 0.95$; (b) $x = 0.97$; (c) $x = 0.98$; (d) $x = 1.00$. The arrows indicate the diffraction peaks of solid solution $Bi_{1-x}Yb_xO_{1.5}$ with $x = 0.35$.

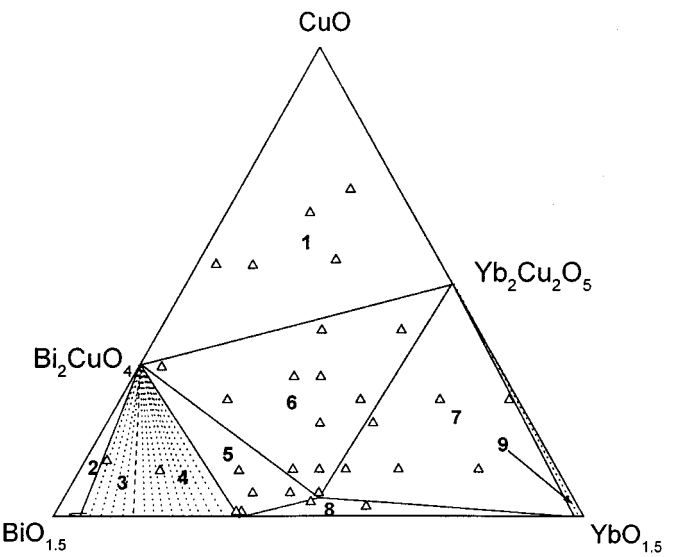

FIG. 7. Subsolidus phase relations in the ternary system $BiO_{1.5}$–$YbO_{1.5}$–CuO.

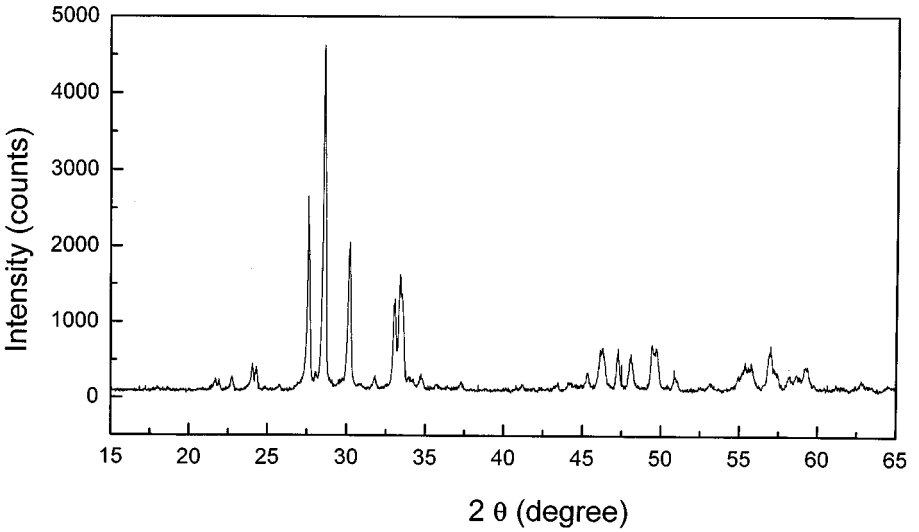

FIG. 8. The X-ray powder diffraction patterns of $Bi_{12}Yb_{12}CuO_y$ with Cu$K\alpha$ radiation.

ACKNOWLEDGMENT

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