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The Ternary System Eu_2O_3–SrO–CuO: Compounds and Phase Relations

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The subsolidus phase relations of the Eu_2O_3–SrO–CuO ternary system have been investigated by X-ray powder diffraction. All samples were synthesized in air at 950–1000°C. The system can be divided into nine three-phase regions and four two-phase regions. In this system, there exist two solid solutions, $Sr_{14-x}Eu_xCu_{24}O_y$ and $Eu_{1+x}Sr_{2-x}Cu_2O_y$, and one ternary compound, $Eu_{0.8}Sr_{1.2}CuO_{3.4}$. The solid solution $Sr_{14-x}Eu_xCu_{24}O_y$ ($0 \leq x \leq 6$) crystallizes in an orthorhombic unit cell with space group *Fmmm* and lattice constants of $a = 3.950$–3.981 Å, $b = 11.475$–11.298 Å, and $c = 13.401$–12.827 Å. The solid solution $Eu_{1+x}Sr_{2-x}Cu_2O_y$ ($0 \leq x \leq 0.4$) belongs to an orthorhombic system with space group *Immm* and cell parameters $a = 3.761$–3.775 Å, $b = 11.385$–11.252 Å, and $c = 20.019$–20.069 Å. The ternary compound $Eu_{0.8}Sr_{1.2}CuO_{3.4}$ crystallizes in an orthorhombic unit cell with space group *Immm* and lattice constants of $a = 3.713$ Å, $b = 3.787$ Å, and $c = 12.636$ Å. A comparison of the Eu system with reported systems of La, Nd, Ho, and Y indicate that the phase diagrams become complicated with an increase in the lanthanide ion size. © 2001 Academic Press

Key Words: **Eu_2O_3–SrO–CuO; crystal structure; phase diagram.**

INTRODUCTION

A series of R_2O_3–BaO–CuO (R, rare earth) ternary systems has been investigated to clarify the phase relations and to search for new superconductors. These ternary systems include R_2O_3–BaO–CuO (R = La, Y, Gd, Nd, Ho, Dy, Yb,) (1–10) and Pr_6O_{11}–BaO–CuO (11). However, the ternary systems of R_2O_3–SrO–CuO have been investigated less. Only the Nd_2O_3–SrO–CuO system (12–14), the La_2O_3–SrO–CuO system (15, 16), Ho_2O_3–SrO–CuO (25), Y_2O_3–SrO–CuO (26, 27), and $Ln_{2-x}Sr_{1+x}Cu_2O_{6-x/2}$ (Ln = Sm, Eu, Gd) (22) have been reported. In order to find further new compounds, it is necessary to investigate the phase relations of the remaining R_2O_3–SrO–CuO systems. As part of a series of work, here we report the compounds and subsolidus phase relations of the Eu_2O_3–SrO–CuO ternary system.

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EXPERIMENTAL

A series of Eu_2O_3–SrO–CuO samples of different composition were prepared by solid-state reaction of an appropriate mixture of high-purity (> 99.9%) Eu_2O_3, SrO, and CuO. The raw powders with proper compositions were thoroughly mixed, ground, and pressed into pellets, which were sintered at 950–1000°C in air for about 48 h and then slowly cooled in the furnace to room temperature. The above process was repeated for some of the samples until homogeneity was reached. However, we found that the SrO-rich samples were unstable and tended to deliquesce into $SrO \cdot 2H_2O$ in air. Forty-eight samples with different compositions were prepared and their compositions are shown in Fig. 1.

Phase identifications were carried out on a Rigaku Dmax-2400 diffractometer with Cu$K\alpha$ radiation and a graphite monochromator, operating at a step-scan mode with a scanning step of $2\theta = 0.02°$ and a sampling time of 2 s. For the measurement of lattice parameters of the compounds, pure Si was added to the specimens as an internal standard.

RESULTS AND DISCUSSION

According to the results of X-ray diffraction analysis, the subsolidus phase relations of the Eu_2O_3–SrO–CuO system are as shown in Fig. 1. There exist at least two solid solutions, $Sr_{14-x}Eu_xCu_{24}O_y$ and $Eu_{1+x}Sr_{2-x}Cu_2O_y$, and one ternary compound, $Eu_{0.8}Sr_{1.2}CuO_{3.4}$.

1. Binary System

For the binary system Eu_2O_3–CuO, two compounds, Eu_2CuO_4 and $EuCuO_2$, have been reported (17, 18). But under our experimental conditions, only Eu_2CuO_4 was

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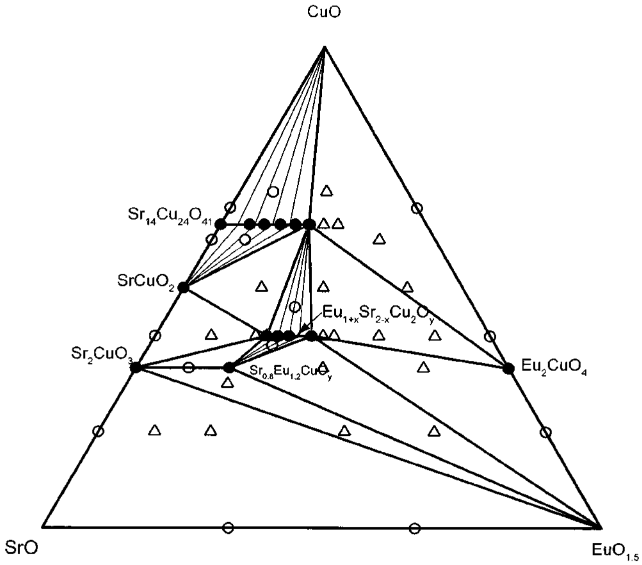

FIG. 1. The subsolidus phase relations of the $EuO_{1.5}$–SrO–CuO system derived from samples sintered at 950–1000°C in air: (●) single phase, (○) binary phases, (△) trinary phases.

identified. It crystallizes in an orthorhombic unit cell with space group *I*4/*mmm*. Its lattice parameters are $a = 3.895$ Å and $c = 11.887$ Å. Our result is in good agreement with the results previously reported (17). In the binary system Eu_2O_3–SrO, no binary compound has been reported, and under our experimental conditions, no binary compound has been found. In the system SrO–CuO, we synthesized three binary compounds Sr_2CuO_3, $SrCuO_2$, and $Sr_{14}Cu_{24}O_{41}$, except $SrCu_2O_3$. This result is in agreement with the result of Chen *et al.* (16) and DeLeeuw *et al.* (14). The compound $Sr_{14}Cu_{24}O_{41}$ has an orthorhombic lattice, space group *Fmmm*, with lattice parameters $a = 11.466$ Å, $b = 13.389$ Å, and $c = 3.918$ Å (19). The compound $SrCuO_2$ cyrstallizes in an orthorhombic lattice, space group *Cmcm*, with $a = 3.562$ Å, $b = 16.32$ Å, and $c = 3.918$ Å (20, 21). The compound Sr_2CuO_3 also belongs to an orthorhombic system with space group *Immm*. Its lattice parameters are $a = 12.68$–12.71 Å, $b = 3.91$–3.913 Å, and $c = 3.48$–3.50 Å (20).

2. Ternary System

In this system, there exist two solid solutions, $Sr_{14-x}Eu_xCu_{24}O_y$ and $Eu_{1+x}Sr_{2-x}Cu_2O_y$, and one ternary compound, $Eu_{0.8}Sr_{1.2}CuO_{3.4}$. Like Ca, Y, Nd, and Ho, Eu can also partially substitute for Sr in $Sr_{14}Cu_{24}O_{41}$ to form a solid solution $Sr_{14-x}Eu_xCu_{24}O_y$. We used the program DICVOL91 (23) to index X-ray powder diffraction data and determine the lattice parameters of the solid solution. According to the results, we find that the solid solution possesses the $Sr_{14}Cu_{24}O_{41}$-type lattice within the solubility limit. The lattice parameters are $a = 3.950$–3.981 Å, $b = 11.475$–11.298 Å, and $c = 13.401$–12.827 Å. Figure 2 shows the variations of lattice constants vs the Eu content for the solid solution. The lattice parameters *b* and *c* decrease with increasing Eu content, same as *V*, while *a* is nearly unchanged. Parameter *c* decreases in a more rapid manner than *b*. From Fig. 2, we find when $x > 6$, the lattice parameters of $Sr_{14-x}Eu_xCu_{24}O_y$ keep constant, and CuO and Eu_2CuO_4 appeared in samples from X-ray diffraction patterns. So we can conclude that the solid solution limit is about $x = 6$. Because Eu has a smaller radius than Sr, we can explain that the unit cell volume will decrease with increasing Eu content. Since the ionic radius of Eu is closer to that of Sr than that of Y, $Sr_{14-x}Eu_xCu_{24}O_y$ has a lager solution limit than $Sr_{14-x}Y_xCu_{24}O_y$ with $x < 1.0$ (24).

As for the solid solution $Eu_{1+x}Sr_{2-x}Cu_2O_y$, Nguyen *et al.* have reported it (22). Our results are almost agreement with theirs except that $0 \le x \le 0.4$, not $0.1 \le x \le 0.4$. We use the program DICVOL91 (23) to index X-ray powder diffraction

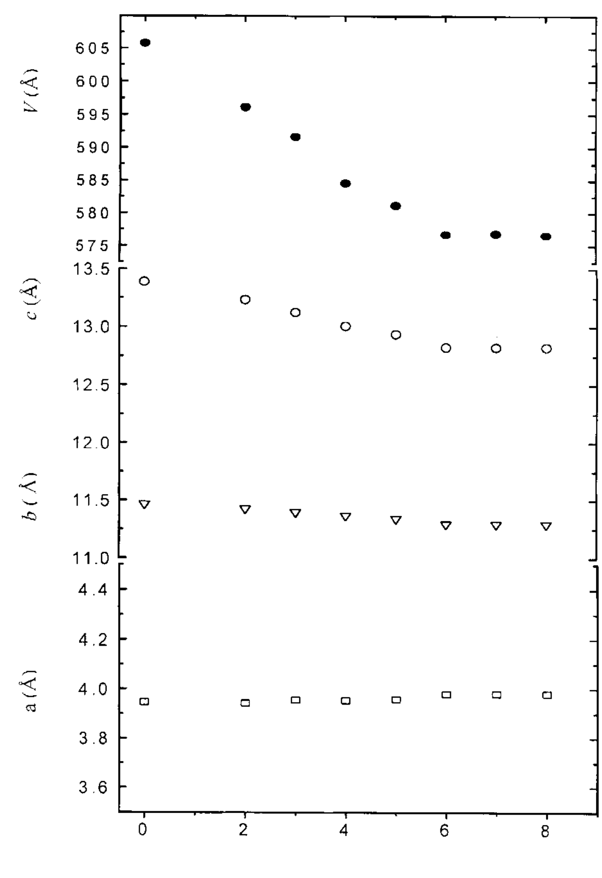

FIG. 2. The variations of lattice constants *a*, *b*, *c* and unit cell volume *V vs x* for $Sr_{14-x}Eu_xCu_{24}O_y$.

TABLE 1
List of *d* Spacings, Diffraction Intensity, and *hkl* for $Eu_{1.1}Sr_{1.9}Cu_2O_y$, $a = 3.770(2)$ Å, $b = 11.334(5)$ Å, $c = 20.035(6)$ Å, Space Group *Immm*, $Z = 6$

No.	h	k	l	d_{calc}	d_{obs}	I_{obs}
1	0	1	5	3.7779	3.779	9
2	1	0	1	3.7050	3.705	13
3	1	1	0	3.5773	3.576	8
4	0	0	6	3.3392	3.341	14
5	0	0	6	2.7458	2.746	100
6	1	0	5	2.6686	2.668	83
7	1	2	5	2.4710	2.472	11
8	1	0	7	2.2796	2.280	15
9	0	1	9	2.1844	2.185	10
10	1	2	7	2.1149	2.115	8
11	1	3	6	2.0847	2.083	23
12	0	0	10	2.0035	2.003	19
13	0	2	10	1.8889	1.889	20
14	2	2	4	1.6845	1.683	9
15	0	0	12	1.6696	1.669	9
16	2	3	3	1.6354	1.639	13
17	0	2	12	1.6015	1.601	22
18	2	3	5	1.5546	1.554	27
19	2	3	7	1.4531	1.453	8
20	1	0	13	1.4266	1.426	9
21	1	3	12	1.4154	1.414	11
22	2	0	10	1.3729	1.374	11
23	2	2	10	1.3343	1.334	10
24	0	1	15	1.3265	1.327	9

data. As an example, results for $Eu_{1.1}Sr_{1.9}Cu_2O_y$ ($x = 0.1$) are listed in Table 1. $Eu_{1.1}Sr_{1.9}Cu_2O_y$ belongs to an orthorhombic system. According to the results of (11–16, 22), the space group of $Eu_{1.1}Sr_{1.9}Cu_2O_y$ is *Immm*. Figure 3 shows the variations of lattice constants *vs* the Eu content for the solid solution $Eu_{1+x}Sr_{2-x}Cu_2O_y$. According to Fig. 3 and the phase purity check, we can conclude that the solid solution limit is about $x = 0.4$. The solid solution has an orthorhombic lattice with cell parameters $a = 3.761$–3.775 Å, $b = 11.385$–11.252 Å, and $c = 20.019$–20.069 Å.

Another compound we identified in this study is $Eu_{0.8}Sr_{1.2}CuO_{3.4}$. This compound might be a member of narrow solid solution $Eu_{2-x}Sr_xCuO_y$. But the solid solution is too narrow for us to determine its limit. Listed in Table 2 are the diffraction data for $Eu_{0.8}Sr_{1.2}CuO_{3.4}$. Because the diffraction lines with indices $h + k + l = 2n + 1$ are systematically extinct, the possible space groups are *Immm*, *I*222, $I2_12_12_1$, and *Imm*2. According to the diffraction data and the results of (16), it has the same space group as $Nd_{2-x}Sr_xCuO_{4-y}$. So it can be indexed as an orthorhombic pattern with space group *Immm*, parameters $a = 3.713$ Å, $b = 3.787$ Å, and $c = 12.636$ Å.

3. *A Comparison with SrO–$RO_{1.5}$–CuO (R = La, Nd, Ho, and Y)*

In order to analyze the difference between the $EuO_{1.5}$–SrO–CuO system and other $RO_{1.5}$–SrO–CuO (R = La, Nd, Ho, and Y) systems, we compared our results with these systems. We found that the ionic size of R^{3+} is a dominant factor for determining the phase relations of different $RO_{1.5}$–SrO–CuO systems. Diagrams become complicated with an increase in the lanthanide ion size. The ionic size of Y^{3+} is the smallest in these five ions when there is the same coordination, and in the Y system, only one solid solution, $Sr_{14-x}Y_xCu_{24}O_{41}$, is found (26, 27). In the Ho system there are one solid solution, $Sr_{14-x}Ho_xCu_{24}O_{41}$, and one ternary compound, $SrHo_2CuO_5$. In the Eu system, there exist two solid solutions, $Sr_{14-x}Eu_xCu_{24}O_y$ and $Eu_{1+x}Sr_{2-x}Cu_2O_y$, and one ternary compound, $Eu_{0.8}Sr_{1.2}CuO_{3.4}$. In the Nd system there are three solid solutions, $Sr_{2-x}Nd_{1+x}Cu_2O_y$, $Sr_xNd_{2-x}CuO_y$, and

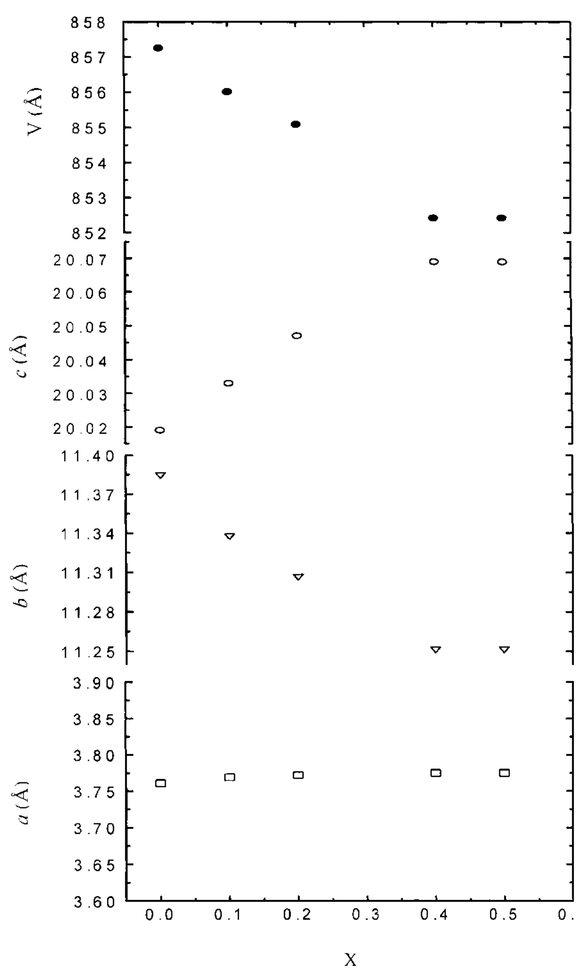

FIG. 3. The variations of lattice constants *a*, *b*, *c* and unit cell volume *V vs x* for $Eu_{1+x}Sr_{2-x}Cu_2O_y$.

TABLE 2
List of *d* Spacings, Diffraction Intensity, and *hkl* for $Eu_{0.8}Sr_{1.2}CuO_y$, $a = 3.7124(7)$ Å, $b = 3.787(8)$ Å, $c = 12.636(6)$ Å, Space Group *Immm*, $Z = 1$

No.	h	k	l	d_{calc}	d_{obs}	I_{obs}	No.	h	k	l	d_{calc}	d_{obs}	I_{obs}
1	0	0	2	6.3180	6.34	9	25	2	2	0	1.3255	1.325	13
2	0	1	1	3.6276	3.633	14	26	0	1	9	1.3164	1.317	8
3	1	0	1	3.5619	3.565	11	27	0	0	10	1.2636	1.262	7
4	0	0	4	3.1590	3.162	20	28	1	2	7	1.2324	1.233	8
5	0	1	3	2.8161	2.819	85	29	2	2	4	1.2223	1.223	9
6	1	0	3	2.7850	2.786	87	30	0	2	8	1.2129	1.213	9
7	1	1	0	2.6510	2.651	700	31	0	3	3	1.2092	1.209	9
8	1	1	2	2.4446	2.439	8	32	2	0	8	1.2029	1.202	9
9	0	0	6	2.1060	2.105	32							
10	0	1	5	2.1021									
11	1	0	5	2.0891	2.089	16	35	3	1	0	1.1763	1.176	9
12	1	1	4	2.0307	2.031	32	36	1	1	10	1.1407	1.140	9
13	0	2	0	1.8935	1.894	27	37	2	2	6	1.1218	1.122	10
14	2	0	0	1.8562	1.856	24	38	1	3	4	1.1178	1.118	9
15	1	2	1	1.6719	1.672	8	39	3	1	4	1.1023	1.103	9
16	1	1	6	1.6490	1.649	28	40	0	1	11	1.0993	1.099	10
17	1	0	7	1.6234	1.623	14	41	1	2	9	1.0791	1.079	8
18	2	0	4	1.6004	1.601	10	42	2	1	9	1.0738	1.073	8
19	0	0	8	1.5795	1.579	10	43	1	3	6	1.0394	1.039	9
20	1	2	3	1.5659	1.566	25	44	3	1	6	1.0269	1.027	9
21	2	1	3	1.5498	1.550	23	45	2	2	8	1.0154	1.015	9
22	0	2	6	1.4081	1.408	13	46	3	2	3	1.0059	1.005	9
23	2	1	5	1.3914	1.392	15	47	1	2	11	0.9495	0.949	9
24	1	1	8	1.3569	1.357	11	48	2	1	11	0.9458	0.946	9

$Sr_{14-x}La_xCu_{24}O_{41}$ and one compound, $SrNd_2Cu_2O_6$ (16). The ionic size of La^{3+} is the largest in these five ions. In the La system there are five ternary solid solution series, $Sr_{14-x}La_xCu_{24}O_{41}$, $La_{2-x}Sr_{1+x}Cu_2O_{6+\delta}$, $La_{1+x}Sr_{2-x}Cu_2O_{5.5+\delta}$, $La_{8-x}Sr_xCu_8O_{20-\delta}$, and $(La, Sr)_2CuO_{4-\delta}$ (22).

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