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The ternary system Gd_2O_3–SrO–CuO: compounds and phase relations

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Abstract

The subsolidus phase relations of the Gd_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 ten three-phase regions and two solid solutions. In this system, there exist two solid solutions: $Sr_{14-x}Gd_xCu_{24}O_y$ and $Gd_{1+x}Sr_{2-x}Cu_2O_y$ and one ternary compound: $GdSr_3Cu_2O_y$. The solid solution $Sr_{14-x}Gd_xCu_{24}O_y$ ($0 \leqslant x \leqslant 6.5$) crystallizes in an orthorhombic structure cell with space group *Fmmm* and lattice constants of $a=3.918(1)$–$3.975(1)$ Å, $b=11.466(3)$–$11.282(1)$ Å and $c=13.389(4)$–$12.832(1)$ Å. The solid solution $Gd_{1+x}Sr_{2-x}Cu_2O_y$ ($0 \leqslant x \leqslant 0.3$) belongs to an orthorhombic system with space group *Immm*, lattice constants $a=3.755(1)$–$3.763(1)$ Å, $b=11.354(4)$–$11.257(4)$ Å and $c=20.008(4)$–$20.049(5)$ Å. The ternary compound $(Gd_{0.25}Sr_{0.75})_2CuO_{4-\delta}$ crystallizes in an orthorhombic structure with space group *Immm* and lattice constants of $a=3.7084(3)$ Å, $b=3.7841(4)$ Å and $c=12.6129(9)$ Å.

Keywords: Rare earth compounds; Oxide materials; Crystal structure; X-ray diffraction; Phase diagram

1. Introduction

In order to clarify the phase relations and to search for new superconductors, a series of R_2O_y–BaO–CuO (R=La, Y, Gd, Nd, Ho, Dy, Yb, Pr) ternary systems have been investigated. However, the ternary systems of R_2O_3–SrO–CuO have been less investigated. Results were reported only for the systems Nd_2O_3–SrO–CuO [1–3], La_2O_3–SrO–CuO [4,5], Ho_2O_3–SrO–CuO [6], Y_2O_3–SrO–CuO [7,8] and $Ln_{2-x}Sr_{1+x}Cu_2O_{6-x/2}$ (Ln=Sm, Eu, Gd) [9]. So it is necessary to investigate the phase relations of other R_2O_3–SrO–CuO systems to find further new compounds. As one of a series of investigations on the phase relations of R_2O_3–SrO–CuO systems, we report the compounds and subsolidus phase relations of the Gd_2O_3–SrO–CuO ternary system.

2. Experimental details

A series of Gd_2O_3–SrO–CuO samples of different composition were prepared by solid-state reaction of an appropriate mixture of high purity (>99.9%) Gd_2O_3, SrO and CuO. The raw powders with proper compositions were

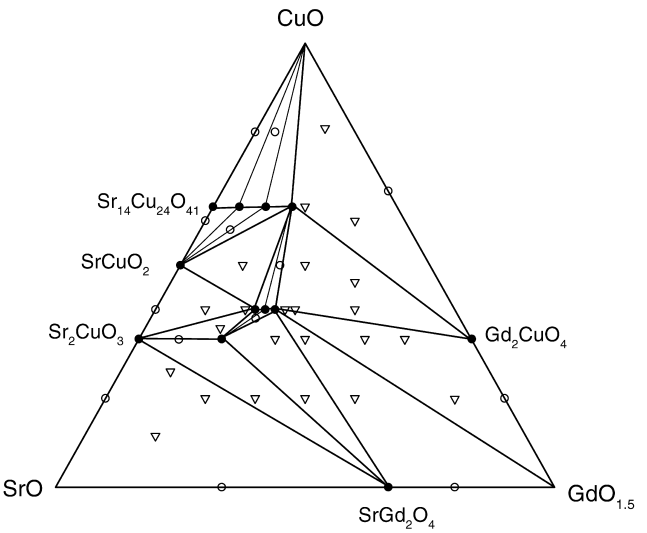

Fig. 1. Subsolidus phase relations of $GdO_{1.5}$–SrO–CuO system derived from samples sintered at 950–1000°C in air: (●) single-phase, (○) two-phase, (△) three-phase.

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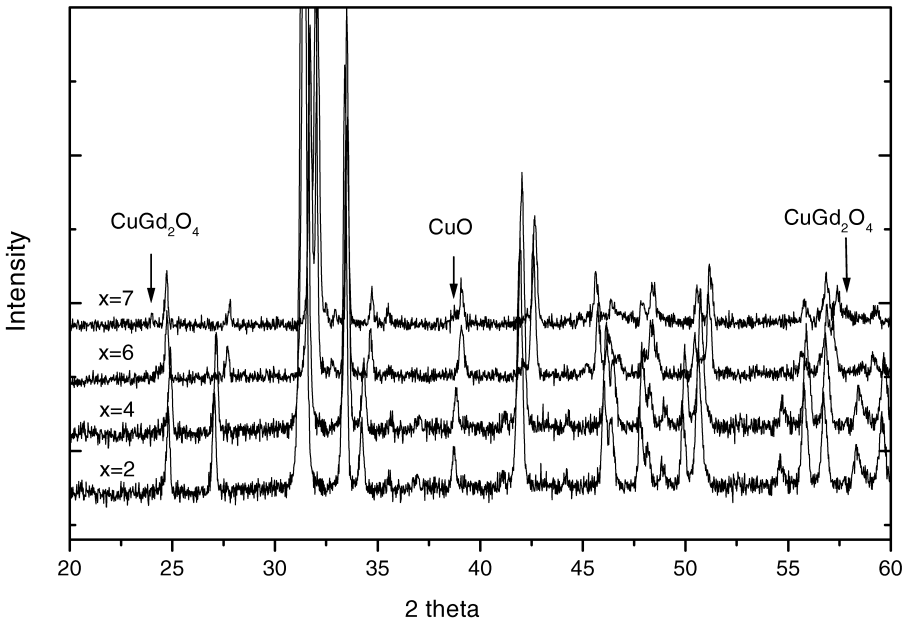

Fig. 2. X-ray diffraction patterns of the solid solution $Sr_{14-x}Gd_xCu_{24}O_y$. At $x>7$, CuO and $CuGd_2O_4$ exist.

Table 1
List[a] of d spacings, diffraction intensity and hkl for $Gd_{1+x}Sr_{2-x}Cu_2O_y$ ($x=0.2$), $a=3.7564(9)$ Å, $b=11.293(3)$ Å, $c=20.034(3)$ Å, space group $Immm$, $Z=6$

No.	h k l	d_{calc}	d_{obs}	I_{obs}	No.	h k l	d_{calc}	d_{obs}	I_{obs}
1	0 1 3	5.75	5.75	2	28	0 3 9	1.916	⌈1.915	2
2	0 2 0	5.65	5.65	3	29	1 0 9	1.915	⌊	
3	0 2 2	4.92	4.92	2	30	2 0 0	1.878	1.878	32
4	0 1 5	3.775	3.773	3	31	1 3 8	1.823	1.822	1
5	1 0 1	3.692	3.691	10	32	1 1 10	1.746	1.745	1
6	1 1 0	3.564	3.562	2	33	0 0 12	1.669	1.669	3
7	0 0 6	3.339	3.337	8	34	1 0 11	1.639	⌈1.638	7
8	0 3 3	3.279	3.278	1	35	0 2 12	1.638	⌊	
9	1 1 4	2.904	2.903	2	36	2 0 6	1.600	1.599	17
10	0 2 6	2.874	2.872	1	37	2 3 5	1.550	1.550	34
11	0 4 0	2.823	2.823	1	38	2 4 4	1.492	1.493	3
12	1 0 5	2.740	2.739	100	39	2 3 7	1.449	1.449	3
13	1 3 0	2.659	2.657	72	40	2 1 9	1.424	1.423	5
14	0 0 8	2.504	2.503	1	41	1 3 12	1.413	1.414	3
15	0 4 4	2.459	2.458	7	42	2 0 10	1.370	1.370	10
16	1 3 4	2.348	2.347	1	43	1 1 14	1.328	1.328	7
17	0 3 7	2.278	⌈2.276	10	44	0 3 15	1.259	⌈1.258	3
18	1 0 7	2.276	⌊		45	1 0 15	1.258	⌊	
19	0 5 1	2.244	⌈2.243	9	46	2 0 12	1.248	1.248	3
20	1 4 1	2.243	⌊		47	2 6 6	1.235	⌈	
21	0 1 9	2.184	2.183	4	48	2 3 11	1.235	1.235	5
22	0 4 6	2.155	2.155	2	49	3 1 2	1.235	⌊	
23	1 2 7	2.111	2.111	2	50	3 0 5	1.195	1.195	4
24	1 3 6	2.080	2.080	21	51	3 3 0	1.188	1.188	5
25	0 0 10	2.003	2.002	14	52	1 0 17	1.124	⌈1.124	3
26	0 5 5	1.967	⌈1.966	4	53	3 2 7	1.124	⌊	
27	1 4 5	1.966	⌊		54	2 6 10	1.107	1.107	2
					55	3 3 10	1.022	1.022	4

[a] Figure of merit: $M(23)=15.1$, $F(23)=15.8$.

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. Forty-five samples with different compositions were prepared and their compositions are shown in Fig. 1.

Phase identifications were carried out on a Rigaku Rint-2400 diffractometer with Cu Kα 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.

3. Results and discussion

According to the results of X-ray diffraction analysis, the subsolidus phase relations of the Gd_2O_3–SrO–CuO system are shown in Fig. 1. There exist two solid solutions, $Sr_{14-x}Gd_xCu_{24}O_y$ and $Gd_{1+x}Sr_{2-x}Cu_2O_y$ and one ternary compound, $(Gd_{0.25}Sr_{0.75})_2CuO_{4-\delta}$.

For the binary system Gd_2O_3–CuO, three compounds, Gd_2CuO_4, $Gd_{1.726}CuO_4$ and $GdCu_2O_4$ have been reported [10–13]. But under our experimental conditions, only Gd_2CuO_4 was identified. It crystallizes in an orthorhombic unit cell with space group *I4/mmm*. Its lattice parameters are $a=3.894$ and $c=11.883$ Å. Our result is in good agreement with the results previously reported [10,11]. In the binary system Gd_2O_3–SrO, two binary compound $SrGd_2O_4$ and $SrGd_4O_7$ have been reported [14]. Only $SrGd_2O_4$ was found under our experimental conditions. In the system SrO–CuO, we synthesized three binary compounds Sr_2CuO_3, $SrCuO_2$ and $Sr_{14}Cu_{24}O_{41}$, but did not find $SrCu_2O_3$. This result agrees with the result of Chen et al. [5] and DeLeeuw et al. [3]. 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 [15]. The compound $SrCuO_2$ crystallizes in an orthorhombic lattice, space group *Cmcm*, with $a=3.562$ Å, $b=16.32$ Å and $c=3.918$ Å [16,17]. 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, $b=3.910$–3.913 Å and $c=3.48$–3.50 Å [16,18].

In this system, there exist two solid solutions, $Sr_{14-x}Gd_xCu_{24}O_y$ and $Gd_{1+x}Sr_{2-x}Cu_2O_y$ and one ternary compound, $(Gd_{0.25}Sr_{0.75})_2CuO_{4-\delta}$. Like Ca, Y, Nd and Ho, Gd can partially substitute for Sr in $Sr_{14}Cu_{24}O_{41}$ to form the solid solution $Sr_{14-x}Gd_xCu_{24}O_y$. X-ray diffraction patterns of the selected solid solution members of $Sr_{14-x}Gd_xCu_{24}O_y$ are shown in Fig. 2. We used program DICVOL91 [19] to index the X-ray powder diffraction data and determine the lattice parameters. Fig. 3 shows the linear variations of lattice constants vs. the Gd content for the solid solution. The lattice parameters *b*, *c* and *V*

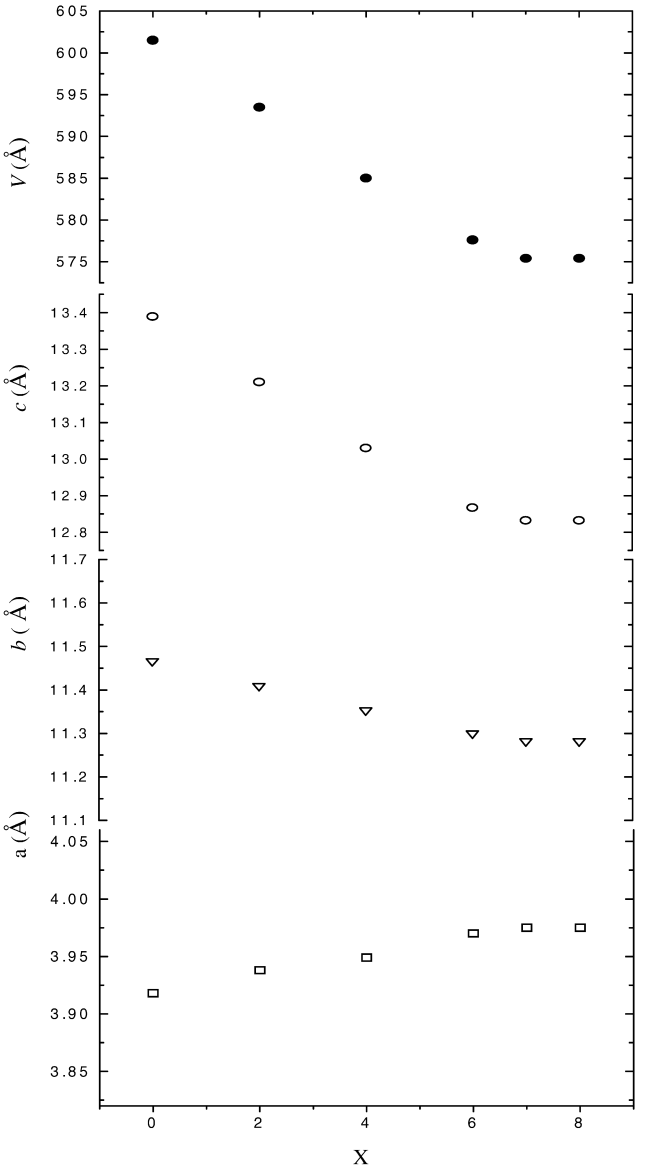

Fig. 3. Variations of the lattice constants *a*, *b*, *c* and unit cell volume *V* vs. *x* for $Sr_{14-x}Gd_xCu_{24}O_y$.

decrease with increasing Gd content, while *a* lightly increases. The parameter *c* decreases in a more rapid manner than *b*. From Figs. 2 and 3, we find that when $x>6.5$, the lattice parameters of $Sr_{14-x}Gd_xCu_{24}O_y$ remain constant and other phases appear. This means that the samples with $x>7$ are three phase. According to the lattice constants in the single phase and three-phase regions, we can conclude that solid solution limit is about $x=6.5$. Among the $Sr_{14-x}Ln_xCu_{24}O_y$ 14–24 lanthanide analogs, one has $x=5$ for the Y system and $x=7$ for the Nd system, but *x* is only equal to 4 for the La system. So it is difficult to explain the solid solution limit in view of the difference between Ln^{3+} and Sr^{2+}.

Nguyen et al. [9] have been reported a solid solution of the type $Gd_{1+x}Sr_{2-x}Cu_2O_y$. Our results are almost in agreement with theirs. X-ray diffraction patterns of select-

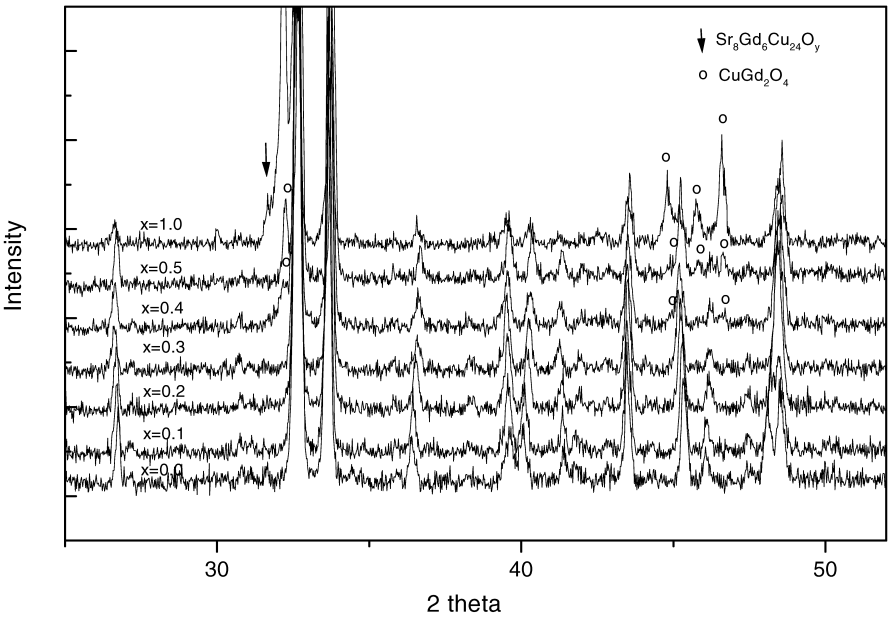

Fig. 4. X-ray diffraction patterns of the solid solution $Gd_{1+x}Sr_{2-x}Cu_2O_y$. At $x>0.3$, Gd_2CuO_4 exists but $Sr_{7.5}Gd_{6.5}Cu_{24}O_{41}$ not obviously. At $x=1.0$, a significant amount of $Sr_{7.5}Gd_{6.5}Cu_{24}O_{41}$ and $CuGd_2O_4$ is evident.

ed solid solution members of $Gd_{1+x}Sr_{2-x}Cu_2O_y$ are shown in Fig. 4. We used the program DICVOL91 [19] to the index X-ray powder diffraction data. The results obtained for $x=0$ are listed in Table 1. We find that the solid solution has an orthorhombic lattice, with cell parameters $a=3.755(1)$–$3.763(1)$ Å, $b=11.354(4)$–$11.257(4)$ Å and $c=20.008(4)$–20.049 (5) Å. Fig. 5 shows the variations of the lattice constants *vs.* the Gd content for the solid solution $Gd_{1+x}Sr_{2-x}Cu_2O_y$. From Figs. 4 and 5, we find that when $x>3$, the lattice parameters of the solid solution remain constant and other phase appear. So we can conclude that the solid solution limit is about $x=6.5$.

Another compound we identified in this study is $(Gd_{0.25}Sr_{0.75})_2CuO_{4-\delta}$. Listed in Table2 are the diffraction data for $(Gd_{0.25}Sr_{0.75})_2CuO_{4-\delta}$. Because the diffraction lines with indices $h+k+l=2n+1$ are systematically extinct, the possible space groups are *Immm*, *I222*, $I2_12_12_1$ and *Imm2*. According to the diffraction data and the results of Ref. [5], 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*, and the parameters $a=3.7084(3)$ Å, $b=3.7841(4)$ Å and $c=12.6129(9)$ Å.

By comparing the system $GdO_{1.5}$–SrO–CuO system with other $RO_{1.5}$–SrO–CuO (R=La, Nd, Ho and Y)

Table 2
List[a] of *d* spacings, diffraction intensity and *hkl* for $(Gd_{0.25}Sr_{0.75})_2CuO_{4-\delta}$, $a=3.7084(3)$ Å, $b=3.7841(4)$ Å, $c=12.6129(9)$ Å, space group *Immm*, $Z=2$

No.	*h k l*	d_{calc}	d_{obs}	I_{obs}	No.	*h k l*	d_{calc}	d_{obs}	I_{obs}
1	0 0 2	6.31	6.31	11	19	2 1 3	1.548	1.548	32
2	0 1 1	3.625	3.626	14	20	0 2 6	1.406	1.406	13
3	1 0 1	3.557	3.556	12	21	1 2 5	1.401	1.401	10
4	0 0 4	3.153	3.154	22	22	2 0 6	1.391	⌈1.391	18
5	0 1 3	2.813	2.812	61	23	2 1 5	1.390	⌊	
6	1 0 3	2.781	2.780	84	24	1 1 8	1.355	1.355	12
7	1 1 0	2.648	2.648	100	25	2 2 0	1.324	1.324	16
8	0 0 6	2.102	2.102	36	26	1 2 7	1.231	⌈1.231	10
9	1 0 5	2.086	2.085	18	27	3 0 1	1.230	⌊	
10	1 1 4	2.028	2.028	38	28	2 1 7	1.223	⌈1.222	15
11	0 2 0	1.892	1.892	29	29	2 2 4	1.221	⌊	
12	2 0 0	1.854	1.854	30	30	0 3 3	1.208	1.208	10
13	1 1 6	1.646	1.646	38	31	2 0 8	1.201	1.201	8
14	0 2 4	1.622	⌈1.622	16	32	1 3 0	1.194	1.194	12
15	1 0 7	1.621	⌊		33	3 0 3	1.186	1.186	13
16	2 0 4	1.598	1.599	15	34	3 1 0	1.175	1.175	15
17	0 0 8	1.577	1.577	9	35	1 1 10	1.120	1.120	14
18	1 2 3	1.564	1.564	31	36	1 3 6	1.038	1.038	7

[a] Figure of merit: $M(33)=33.3$, $F(33)=26.7$.

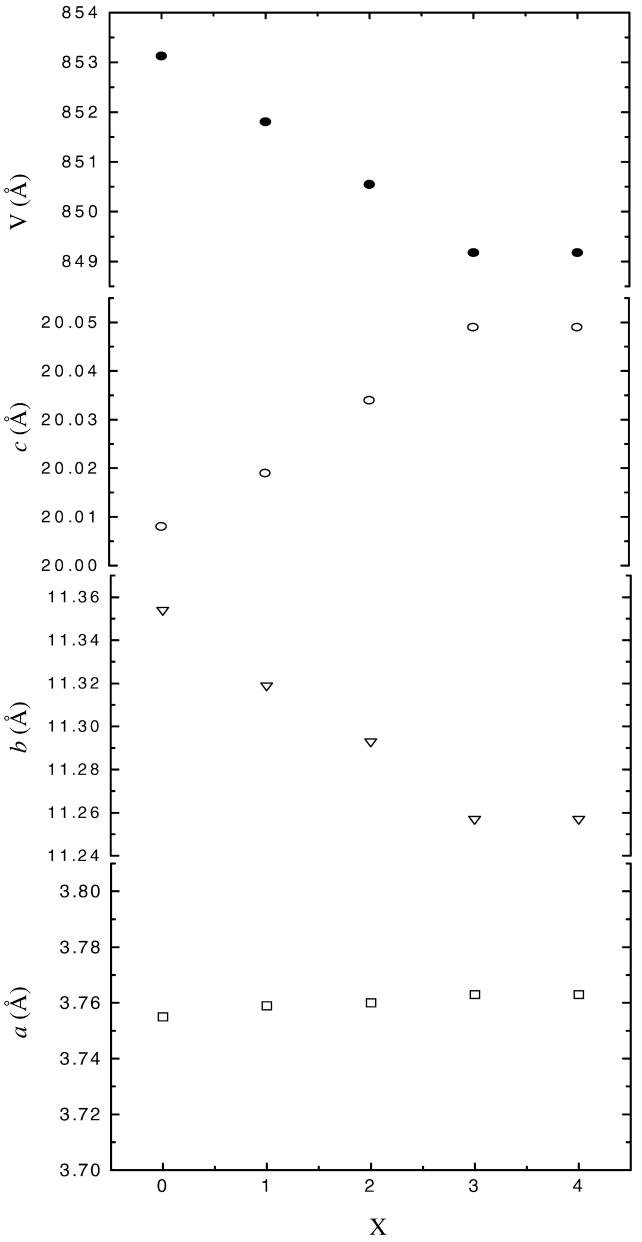

Fig. 5. Variations of the lattice constants *a*, *b*, *c* and unit cell volume *V* vs. *x* for $Gd_{1+x}Sr_{2-x}Cu_2O_y$.

systems, we found that the ionic radius of R^{3+} is a dominant factor for determining the phase relations in the different $RO_{1.5}$–SrO–CuO systems. The diagrams become more complicated with increasing lanthanide ion radius. The ionic radius of Y^{3+} is the smallest of these five ions for the same coordination and only in the Y system, one solid solution, $Sr_{14-x}Y_xCu_{24}O_{41}$ is found [7,8]. In the Ho system one finds one solid solution, $Sr_{14-x}Ho_xCu_{24}O_{41}$ and one ternary compound $SrHo_2CuO_5$ [6]. In the Gd system, there exist two solid solutions, $Sr_{14-x}Gd_xCu_{24}O_y$ and $Gd_{1+x}Sr_{2-x}Cu_2O_y$ and one ternary compound, $(Gd_{0.25}Sr_{0.75})_2CuO_{4-\delta}$. 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 $Sr_{14-x}Nd_xCu_{24}O_{41}$ and one compound, $SrNd_2Cu_2O_6$ [5]. The ionic radius of La^{3+} is the largest among these five ions and is closest to the ionic radius of Sr^{2+}. In 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 $(La, Sr)_2CuO_{4-\delta}$ [4,5].

4. Conclusions

In conclusion, we have synthesized samples of the Gd_2O_3–SrO–CuO ternary system in air at 950–1000°C. The subsolidus phase relations of the Gd_2O_3–SrO–CuO ternary system have been investigated by X-ray powder diffraction. The system can be divided into ten three-phase regions and two solid solutions. In this system, there exist two solid solutions: $Sr_{14-x}Gd_xCu_{24}O_y$ and $Gd_{1+x}Sr_{2-x}Cu_2O_y$ and one ternary compound: $GdSr_3Cu_2O_y$. The solid solution $Sr_{14-x}Gd_xCu_{24}O_y$ ($0 \leqslant x \leqslant 6.5$) crystallizes in an orthorhombic unit cell with space group *Fmmm* and lattice constants of $a = 3.918(1)$–$3.975(1)$ Å, $b = 11.466(3)$–$11.282(1)$ Å and $c = 13.389(4)$–$12.832(1)$ Å. The solid solution $Gd_{1+x}Sr_{2-x}Cu_2O_y$ ($0 \leqslant x \leqslant 0.3$) belongs to an orthorhombic system with space group *Immm*, lattice constants $a = 3.755(1)$–$3.763(1)$ Å, $b = 11.354(4)$–$11.257(4)$ Å and $c = 20.008(4)$–$20.049(5)$ Å. The ternary compound $(Gd_{0.25}Sr_{0.75})_2CuO_{4-\delta}$ crystallizes in an orthorhombic structure with space group *Immm* and lattice constants of $a = 3.7084(3)$ Å, $b = 3.7841(4)$ Å and $c = 12.6129(9)$ Å. By comparing the $GdO_{1.5}$–SrO–CuO system with other $RO_{1.5}$–SrO–CuO (R = La, Nd, Ho and Y) systems, we found that the larger the lanthanide ion radius, the more complicated the corresponding phase diagram.

Acknowledgements

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