



## Experimental Phase Equilibria in the Sr-Ca-Cu-O System Under Reduced Oxygen Atmosphere

Ryosuke O. Suzuki\*, Takamichi Ogawa\*,  
Daniel Risold\*, Ludwig J. Gauckler\*\* and Katsutoshi Ono\*

(Received December 18, 1996)

Phase equilibria were studied in the Sr-Ca-Cu-O system by annealing samples at 1153K in Ar-O<sub>2</sub> gas mixtures. The stability ranges of the oxide solid solutions were observed by X-ray diffraction measurements especially at 4 compositions in 12 gas mixtures. 4 sets of invariant 4-phase equilibrium and their oxygen partial pressure,  $P_{O_2}$ , were deduced from the surrounding 3-phase equilibria. The compositions of the related phases were evaluated by combining EDX analysis and the sample compositions. These results are compared with equilibrium calculations based on thermodynamic modelling.

### 1. Introduction

The knowledge of the phase equilibria in the SrO-CaO-CuO-O subsystem is an important guideline for the preparation of the oxide superconductors, because this subsystem contains the solid solutions,  $(\text{Sr,Ca})_2\text{CuO}_3$ ,  $(\text{Sr,Ca})\text{CuO}_2$  and  $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ , which are known as the major secondary phases affecting the superconducting properties of Bi-based high Tc oxide.<sup>1, 2)</sup> It is characteristic of this system that most of the oxides have a wide solubility due to the substitution of Ca for Sr and a better knowledge of the thermodynamic properties of these solid solutions is needed. The phase equilibria in the SrO-CaO-CuO subsystem has been studied by many authors in air and also at a few higher oxygen partial pressure. Data at the lower oxygen partial pressure are however missing, although the highTc oxides are often annealed under the reduced oxygen atmosphere.

In order to predict the equilibrium state in a wide range of temperature, composition, and oxygen partial pressure, it is useful to apply the thermodynamic modelling based on experimental phase diagram and ther-

modynamic data. For example, the thermodynamic properties of the compounds in the systems Sr-Cu-O and Ca-Cu-O were experimentally studied<sup>3, 4)</sup> and optimized thermodynamic descriptions were obtained in combination with other reported data<sup>5, 6)</sup>. For the Sr-Ca-Cu-O system, a thermodynamic description was recently constructed from these ternary assessments and the available experimental data obtained mainly in air and pure oxygen atmosphere.<sup>7)</sup>

The authors reported experimentally that the oxygen atmosphere modified significantly the phase constitution in this subsystem.<sup>8)</sup> The previous work studied the reducing sequence of the phase change in an Ar gas flow, but few quantitative data were obtained in the reduced oxygen atmosphere, and many uncertainties remain. In particular, the compound  $\text{SrCu}_2\text{O}_2$  is known to be stable only in the reduced oxygen atmosphere, but there are few reports concerning the extension of the solubility toward Ca,<sup>7, 8)</sup> and no thermodynamical data on the stability of  $(\text{Sr,Ca})\text{Cu}_2\text{O}_2$  phase.

The purpose of this work was thus to clarify the phase equilibria in the SrO-CaO-CuO-Cu<sub>2</sub>O subsystem

\* Department of Energy Science and Technology, Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto 606-01, Japan

\*\* Non-metallic Materials, Swiss Federal Institute of Technology (ETH-Zürich), Sonneggstr. 5, CH-8092 Zürich, Switzerland

under the reduced oxygen atmosphere experimentally, and to make comparisons with the predicted values.<sup>7)</sup>

## 2. Experimental

Phase equilibria were examined especially at the four compositions listed in **Table 1**. High purity SrCO<sub>3</sub>, CaCO<sub>3</sub> and CuO powder were used as the starting materials. They were calcined in open air with the several intermitting grindings. The calcined temperature was chosen at 1193 K, which is slightly lower than the formation temperature of the infinite-layered oxide (Sr<sub>1</sub>Ca<sub>7</sub>)·Cu<sub>8</sub>O<sub>n</sub>, 1203K.<sup>13)</sup> This is because this oxide hardly decomposes once it was formed. For example, this oxide synthesized at 1223 K did not decomposed completely at 7 temperatures from 1138 K to 1198 K, but it was not formed below 1193 K.

After the equilibration at 1193 K in air, the samples were again annealed at 1153 K in the flow of Ar-O<sub>2</sub> gas mixture. They were annealed for the time ranging from 29 hours to 116 hours with at least two intermitting grindings. Some samples equilibrated in a certain atmosphere were furthermore annealed in another atmosphere. The annealing temperature was regulated within ±3K, and the heating and cooling of the specimens were done in the controlled gas atmosphere.

Pure Ar gas (< 20 ppmO<sub>2</sub>), 90 vol%Ar-10vol% (± 0.27%)O<sub>2</sub>, Ar-5% (±0.03%)O<sub>2</sub>, and Ar-1.0% (±0.03%) O<sub>2</sub> gas sources were served to the gas mixing apparatus. The oxygen concentrations of these gas sources were analysed by the gas chromatography. The mixed gas was blown to the samples and flown out to the open air at an ambient pressure (=P<sup>o</sup> Pa, P<sup>o</sup> = 101325). The oxygen partial pressure, P<sub>O<sub>2</sub></sub>, of thus mixed gas was estimated from the mixing ratio. The four samples listed in **Table 1** were studied in 12 different gas mixtures. Some additional compositions studied previously<sup>8)</sup> were again

annealed in the "pure" Ar and Ar-1.0%O<sub>2</sub> gas.

The phase constitutions were studied by the X-ray diffraction (XRD) measurements of the samples, where CuKα characteristic X-ray was used. The equilibrium state was determined when the X-ray diffraction profiles remained identical after the two annealing periods. The compositions of the equilibrium phases were mainly evaluated from the changes of lattice parameters, which were compiled by Reardon and Hubbard.<sup>9)</sup> For the (Sr,Ca)Cu<sub>2</sub>O<sub>2</sub> solid solution, the compositional dependency reported elsewhere was used.<sup>7)</sup> The secondary electron microscope (SEM) observations and the Electron Dispersive X-ray (EDX) compositional analysis showed a fairly large scattering (8 at% cation at maximum) because of the interferences from the other phases.

## 3. Results

### 3.1 Phase Identification

The experimental phase equilibria at 1193K in air<sup>8)</sup> were again confirmed by the four samples annealed in open air. **Fig.1** shows the nominal compositions studied and the related phase equilibria. The samples at the compositions A and B contained CuO, (Sr,Ca)<sub>2</sub>CuO<sub>3</sub> and (Sr,Ca)<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub>, while the composition D contained (Sr,Ca)CuO<sub>2</sub>, (Sr,Ca)<sub>2</sub>CuO<sub>3</sub> and (Sr,Ca)<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub>. The compositional study for these phases showed a good agreement with the terminal compositions of the solid solutions<sup>8)</sup> shown in **Fig.1**. Although no survey in air was done at 1153 K in this study, the two types of three-phase equilibria (shadowed in **Fig.1**) are certainly valid also at 1153 K in air, because the same phase relations were observed at the lower temperatures than 1193 K.<sup>1, 8, 10-13)</sup>

**Fig.2** shows the portions of the XRD profiles for the composition A. The square root of the diffracted intensities were plotted in **Fig.2** to represent the weak peaks. The volume fractions of the identified phases were evaluated by the integrated intensity and illustrated in **Fig.3**. Due to the overlapping diffraction peaks and the textured structures, the volume fraction analysis contained the fairly large experimental errors. It is, however, useful to extract the phase differences among the samples. Note that the phase constitution in air was obtained for the annealing at 1193 K, but the others at 1153 K.

**Table 1** Nominal Comoposition of the samples.

Composition I.D.	Metallic ratio (%)		
	Sr	Ca	Cu
A	10	29	61
B	11	22	67
C	16	12	72
D	18	32	50

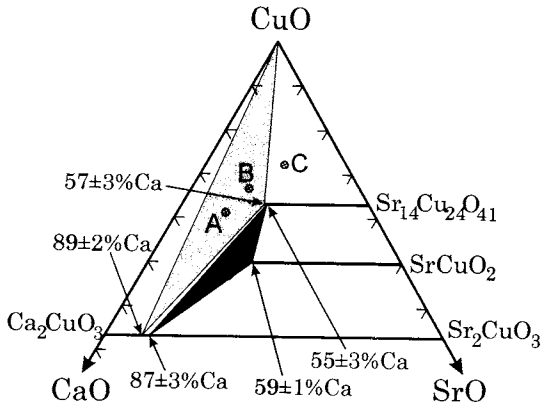


Fig. 1 Phase equilibria in air at 1193 K<sup>8)</sup> and the studied compositions shown as A, B, C and D.

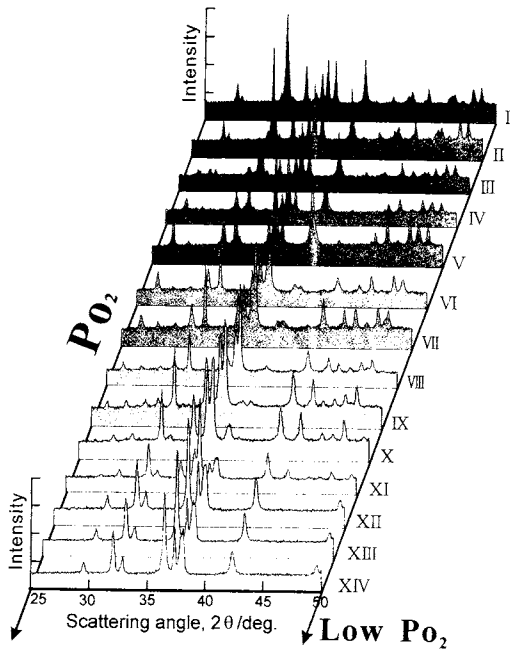


Fig. 2 XRD patterns at the composition A. The abbreviation of the atmosphere is listed in Fig. 3.

The phase changes for the 4 compositions A, B, C and D were studied toward decreasing  $P_{O_2}$ . The phases and their volume fractions identified by XRD were shown in Fig. 3 and Fig. 4. The detected phases were common at these compositions, and the same abbreviation of the phases were applied in Fig. 3 and 4. The Ar gas could not remove oxygen completely from the oxides and it

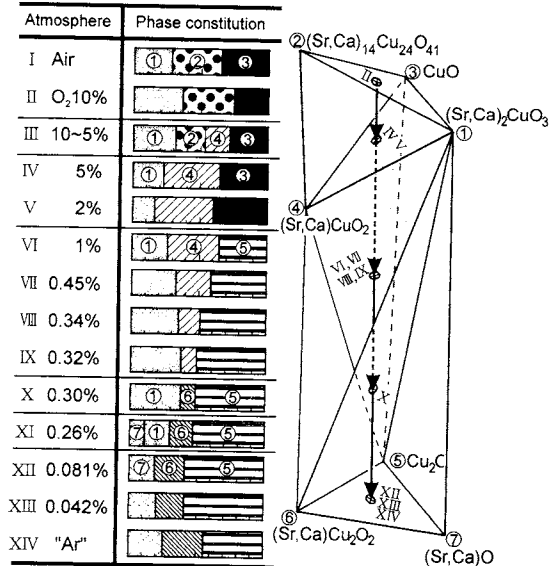


Fig. 3 Phase equilibria under the reduced oxygen atmosphere at the composition A.

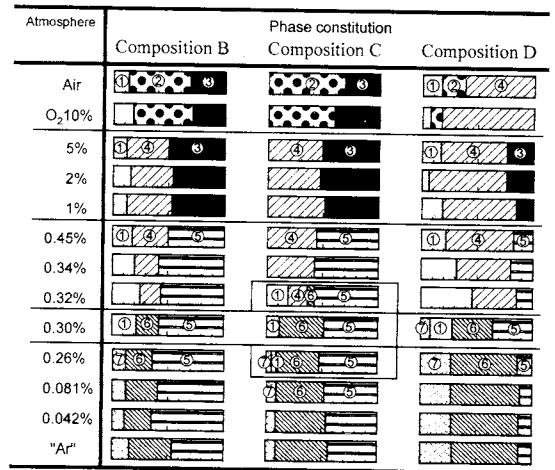


Fig. 4 Phase equilibria under the reduced oxygen atmosphere at the compositions, B, C and D.

produced a steady state, because the "pure" Ar gas contained < 20 ppm oxygen and a faint amount of water vapor.

The sequence of phase change at the composition A is shown three-dimensionally in Fig. 3, considering the compositional tetrahedron of Sr-Ca-Cu-O. The three-phase equilibria confirmed experimentally were shown

as the triangles on which the specimen ID were drawn. The arrows show the reducing sequence for the composition A.

The first difference under the reduced oxygen atmosphere was the appearance of the (Sr,Ca) CuO<sub>2</sub> phase (④). It was found when the samples were annealed in Ar-5%O<sub>2</sub> gas mixture, where the (Sr,Ca)<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub> phase (②) had disappeared. By further decreasing P<sub>O<sub>2</sub></sub>, Cu<sub>2</sub>O (⑤) formed at P<sub>O<sub>2</sub></sub>=0.0045 P°Pa, where CuO (③) had decomposed. The phase (Sr,Ca) Cu<sub>2</sub>O<sub>2</sub> (⑥) was observed at about P<sub>O<sub>2</sub></sub>=0.003 P°Pa, where the phase ④ was no longer observed. CaO (⑦) was detected below P<sub>O<sub>2</sub></sub>=0.0026 P°Pa, where the phase (Sr,Ca)<sub>2</sub>CuO<sub>3</sub> (①) was no longer found. It is interesting that this phase ① for the composition C could be observed only in the narrow P<sub>O<sub>2</sub></sub> range; 0.0032 P°Pa ≥ P<sub>O<sub>2</sub></sub> ≥ 0.0026 P°Pa.

Summarizing the experimental identifications shown in Fig.3 and 4, the phase equilibria detected at the studied four compositions are listed in Table 2. Six sets of 3-phase equilibria confirmed experimentally in the SrO-CaO-CuO-Cu<sub>2</sub>O system.

### 3.2 Composition

The compositions were analyzed especially when the sample contained the three phases. We did not observe any significant changes in the lattice parameters, even if the samples were annealed under the different reduced atmosphere. The compositions analyzed by the lattice parameters were listed in Table 3. Taking account of the scatter of lattice parameters among the previous reports,<sup>9-15)</sup> the estimated error becomes twice larger than the listed values.

The compositions were analyzed by EDX at a few points for a certain phase in the sample which was in the three-phase equilibrium. The average composition from some samples was listed in Table 3. No solubility of Sr nor Ca in both CuO and Cu<sub>2</sub>O was found by EDX analysis. Since all the solid solutions in this system form by substituting Ca by Sr,<sup>1, 7-15)</sup> we assumed the same behaviour for (Sr,Ca)Cu<sub>2</sub>O<sub>2</sub> and neglected the possibility of nonstoichiometry of Cu and O. The chemical formula was taken as (Sr<sub>0.78</sub>Ca<sub>0.22</sub>)Cu<sub>2</sub>O<sub>2</sub>. The substitution of Sr in CaO was hardly confirmed by XRD due to the overlapped peaks and its oxyhydration in air, while 0-15at%Sr was observed by SEM/EDX analysis.

Phase equilibria studied at P<sub>O<sub>2</sub></sub> = 0.01 P°Pa and in the pure Ar gas flow were shown in Fig.5 and Fig.6,

Table 2 Summary of 3 phase and 2 phase equilibria identified.

Phase equilibria	Composition	Stability range in P <sub>O<sub>2</sub></sub> (P°Pa)
(Sr,Ca) <sub>2</sub> CuO <sub>3</sub> (①) + (Sr,Ca) <sub>14</sub> Cu <sub>24</sub> O <sub>x</sub> (②) + CuO(③)	A, B	0.21 ~ 0.10
(Sr,Ca) <sub>2</sub> CuO <sub>3</sub> (①) + (Sr,Ca) <sub>14</sub> Cu <sub>24</sub> O <sub>x</sub> (②) + (Sr,Ca)CuO <sub>2</sub> (④)	D	0.21 ~ 0.10
(Sr,Ca) <sub>14</sub> Cu <sub>24</sub> O <sub>x</sub> (②) + CuO(③)	C	0.21 ~ 0.10
(Sr,Ca) <sub>2</sub> CuO <sub>3</sub> (①) + (Sr,Ca)CuO <sub>2</sub> (④) + CuO(③)	A	0.05 ~ 0.02
	B, D	0.05 ~ 0.01
(Sr,Ca)CuO <sub>2</sub> (④) + CuO(③)	C	0.05 ~ 0.01
(Sr,Ca) <sub>2</sub> CuO <sub>3</sub> (①) + (Sr,Ca)CuO <sub>2</sub> (④) + Cu <sub>2</sub> O(⑤)	A, B, D	4.5×10 <sup>-3</sup> ~ 3.2×10 <sup>-3</sup>
(Sr,Ca)CuO <sub>2</sub> (④) + Cu <sub>2</sub> O(⑤)	C	4.5×10 <sup>-3</sup> ~ 3.4×10 <sup>-3</sup>
(Sr,Ca) <sub>2</sub> CuO <sub>3</sub> (①) + (Sr,Ca)Cu <sub>2</sub> O <sub>2</sub> (⑥) + Cu <sub>2</sub> O(⑤)	A, B, C	3.0 × 10 <sup>-3</sup>
(Sr,Ca)O(⑦) + (Sr,Ca)Cu <sub>2</sub> O <sub>2</sub> (⑥) + Cu <sub>2</sub> O(⑤)	A, B, D	2.6×10 <sup>-3</sup> ~ "Ar"
	C	8.1×10 <sup>-4</sup> ~ "Ar"

P°=101325. P°Pa = 1 atm. "Ar" = a commercial pure Ar gas (99.995%).

Table 3 Summary of compositional analysis.

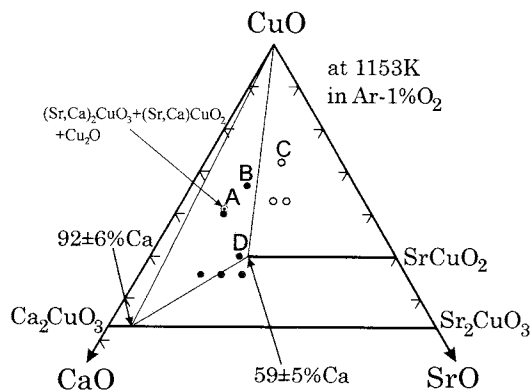
Abbreviations	EDX analysis	XRD analysis	Adapted values after combination with the sample compositions
①	(Sr <sub>0.12±0.01</sub> Ca <sub>0.88±0.01</sub> ) <sub>2</sub> Cu <sub>0.97±0.02</sub> O <sub>x</sub> *1, *4	(Sr <sub>0.1±0.05</sub> Ca <sub>0.9±0.05</sub> ) <sub>2</sub> CuO <sub>3</sub>	(Sr <sub>0.11±0.02</sub> Ca <sub>0.89±0.02</sub> ) <sub>2</sub> CuO <sub>3</sub> *2 (Sr <sub>0.08±0.06</sub> Ca <sub>0.92±0.06</sub> ) <sub>2</sub> CuO <sub>3</sub> *3
②	(Sr <sub>0.40±0.06</sub> Ca <sub>0.60±0.06</sub> ) <sub>14</sub> Cu <sub>23.7±0.07</sub> O <sub>x</sub> *1	(Sr <sub>0.5±0.05</sub> Ca <sub>0.5±0.05</sub> ) <sub>14</sub> Cu <sub>24</sub> O <sub>41</sub>	(Sr <sub>0.43±0.05</sub> Ca <sub>0.57±0.05</sub> ) <sub>14</sub> Cu <sub>24</sub> O <sub>41</sub>
③	CuO	CuO	CuO
④	(Sr <sub>0.41±0.05</sub> Ca <sub>0.59±0.05</sub> ) <sub>2</sub> Cu <sub>0.93±0.06</sub> O <sub>x</sub> *4	(Sr <sub>0.3±0.05</sub> Ca <sub>0.7±0.05</sub> ) CuO <sub>2</sub>	(Sr <sub>0.41±0.05</sub> Ca <sub>0.59±0.05</sub> ) CuO <sub>2</sub>
⑤	Cu <sub>2</sub> O	Cu <sub>2</sub> O	Cu <sub>2</sub> O
⑥	(Sr <sub>0.78±0.06</sub> Ca <sub>0.22±0.06</sub> ) Cu <sub>1.92±0.07</sub> O <sub>x</sub>	(Sr <sub>0.80±0.05</sub> Ca <sub>0.20±0.05</sub> ) Cu <sub>2</sub> O <sub>2</sub>	(Sr <sub>0.78±0.05</sub> Ca <sub>0.22±0.05</sub> ) Cu <sub>2</sub> O <sub>2</sub>
⑦	(Sr <sub>0.93±0.06</sub> Ca <sub>0.07±0.06</sub> )O	CaO	(Sr <sub>0.93±0.05</sub> Ca <sub>0.07±0.05</sub> )O

\*1 : From the specimens for the composition A, which were annealed at P<sub>O<sub>2</sub></sub> = 0.10 P°Pa and in the three phase equilibrium of ①+②+③.

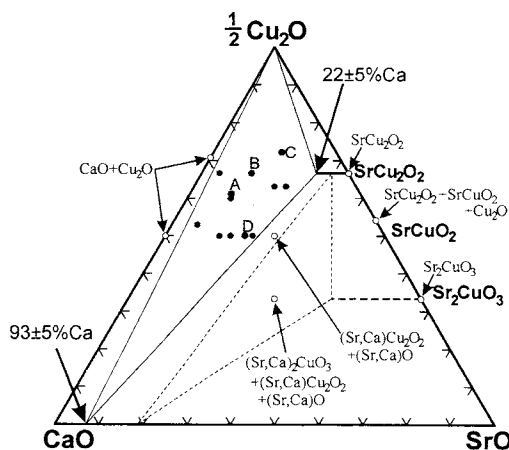
\*2 : In case of the equilibrium with ②.

\*3 : In case of the equilibria without ②.

\*4 : From the specimens whose phase equilibria were ①+③+④.



**Fig. 5** Phase equilibria at 1153 K in Ar-1%O<sub>2</sub> gas and studied compositions. The open, closed and shaded circles shows that the identified phases were CuO + (Sr,Ca) CuO<sub>2</sub>, CuO + (Sr,Ca) CuO<sub>2</sub> + (Sr,Ca)<sub>2</sub>CuO<sub>3</sub>, and (Sr,Ca) CuO<sub>2</sub> + (Sr,Ca)<sub>2</sub>CuO<sub>3</sub>, respectively.



**Fig. 6** Phase equilibria in "pure Ar" gas at 1153 K. The identified phases at the composition of the closed circles were Cu<sub>2</sub>O + (Sr,Ca) Cu<sub>2</sub>O<sub>2</sub> + (Sr,Ca) CaO.

respectively. The three-phase equilibrium of ①+④+③ in Fig. 5 and that of ⑦+⑥+⑤ in Fig. 6 were determined by considering both the compositional studies and the constraint of the specimens' compositions. The compositional evaluation errors were narrower by the requirements that the observed phase equilibria should be satisfied at the sample compositions. The previous study, for example, neglected the solubility of Sr in CaO be-

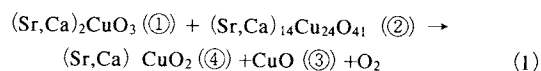
cause of less compositions studied.<sup>8)</sup> Table 3 showed thus estimated compositions for the 7 phases.

## 4. Discussion

### 4.1 PO<sub>2</sub> for Invariant Equilibria

According to the phase rule of the thermodynamics, the equilibrium with the four condensed phases can be established only at a fixed  $P_{O_2}$  because we fixed the annealing temperature in the four component system. Therefore, the coexistence of four condensed phases could be hardly observed in this work. The four-phase equilibrium at a certain temperature can be shown as a tetrahedron in the compositional three-dimensional space, and the four flat surfaces of the tetrahedron correspond to the three-phase equilibria. Four sets of the four phase equilibria could be deduced by combining the surrounding three phase equilibria as the following way. Their  $P_{O_2}$  are listed in Table 4.

The three phase equilibria of ①+②+③ and ①+②+④ were found in air or in 10%O<sub>2</sub> for the compositions, A, B and D. These two equilibria changed commonly to the three phase equilibrium of ①+④+③ in the sequence of reducing procedure from 10%O<sub>2</sub> to 5%O<sub>2</sub>. We can therefore conclude on the existence of the four phase equilibria of ①+②+④+③ at a fixed  $P_{O_2}$  in the range of 0.10 P<sup>°</sup>Pa to 0.05 P<sup>°</sup>Pa, which was estimated here at 0.08 ± 0.02 P<sup>°</sup>Pa. The chemical reaction can be written as,



where the coefficients were omitted.

Thermodynamic study in the Sr-Cu-O ternary system showed  $P_{O_2} = 0.051$  P<sup>°</sup>Pa for the three phase equilibrium of SrCuO<sub>2</sub> + Sr<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub> + CuO.<sup>3)</sup> The undetected three phase equilibrium of (Sr,Ca)CuO<sub>2</sub>(④) + (Sr,Ca)<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub>(②) + CuO(③) will be, therefore, found at  $P_{O_2}$  range of 0.08 ± 0.02 P<sup>°</sup>Pa and 0.051 P<sup>°</sup>Pa.

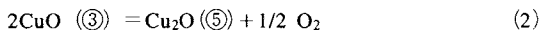
Another four phase equilibrium ①+④+③+⑤ can be deduced at a certain  $P_{O_2}$  between 0.02 P<sup>°</sup>Pa and 0.0045 P<sup>°</sup>Pa, considering that the samples at the four studied compositions changed the three-phase equilibrium from ①+④+③ to ①+④+⑤ by lowering  $P_{O_2}$ . This evaluation of  $P_{O_2}$  range can be narrowed as  $< 1.0 (\pm 0.03) \times 10^{-2}$  P<sup>°</sup>Pa, because the other samples shown in Fig. 5 were still the phase equilibria of ①+④+③. Since the solubility of Sr and Ca in both CuO and Cu<sub>2</sub>O is

**Table 4** Summary of 4 phase equilibria and their oxygen partial pressure ( $P_{O_2}$ ) at 1153 K.

Phase Equilibria	Composition	Stability in $P_{O_2}$ (P°Pa)		
		Observed	Estimated	Calculated
(Sr,Ca) <sub>2</sub> CuO <sub>3</sub> (①) + (Sr,Ca) <sub>14</sub> Cu <sub>24</sub> O <sub>41</sub> (②) + (Sr,Ca)CuO <sub>2</sub> (④) + CuO(③)	A, B, D	0.10 ~ 0.05	0.08±0.02	0.12
(Sr,Ca) <sub>2</sub> CuO <sub>3</sub> (①) + (Sr,Ca)CuO <sub>2</sub> (④) + CuO(③) + Cu <sub>2</sub> O(⑤)	A	0.02 ~ 0.01	0.0099	0.0099
	B, D	0.01 ~ 0.0045		
(Sr,Ca) <sub>2</sub> CuO <sub>3</sub> (①) + (Sr,Ca)CuO <sub>2</sub> (④) + (Sr,Ca)Cu <sub>2</sub> O <sub>2</sub> (⑥) + Cu <sub>2</sub> O(⑤)	A, B, C	3.2×10 <sup>-3</sup> ~ 3.0×10 <sup>-3</sup>	3.1±0.2 ×10 <sup>-3</sup>	0.23×10 <sup>-3</sup>
	C	3.2×10 <sup>-3</sup>		
(Sr,Ca)O(⑦) + (Sr,Ca) <sub>2</sub> CuO <sub>3</sub> (①) + (Sr,Ca)Cu <sub>2</sub> O <sub>2</sub> (⑥) + Cu <sub>2</sub> O(⑤)	A, C	2.6×10 <sup>-4</sup>	2.8±0.25 ×10 <sup>-3</sup>	0.20×10 <sup>-3</sup>
	B	3.0×10 <sup>-3</sup>		
		~ 2.6×10 <sup>-3</sup>		
	D	3.0×10 <sup>-3</sup>		

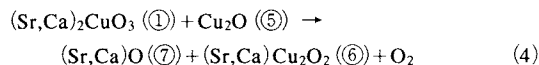
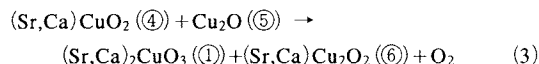
$P^{\circ}=101325$ ,  $P^{\circ}Pa = 1$  atm.

negligible, this invariant equilibrium can be represented by the reaction



of the Cu-O binary system. The  $P_{O_2}$  for ①+④+③+⑤ was, therefore, evaluated as 0.0099 P°Pa, which is the value assessed for the binary equilibrium CuO-Cu<sub>2</sub>O.<sup>16)</sup> The previous work succeeded to construct this equilibrium ①+④+③+⑤ artificially by annealing the mixture of 4 compositions, Ca<sub>2</sub>CuO<sub>3</sub>, (Sr<sub>0.5</sub>Ca<sub>0.5</sub>)CuO<sub>2</sub>, CuO and Cu<sub>2</sub>O, together with the CuO + Cu<sub>2</sub>O powder mixture placed separately.<sup>8)</sup>

In the similar way, the other two four-phase equilibria were found as shown in Table 3. Their chemical reactions are written as,



respectively. Accompanying with the above reactions, the three-phase equilibria of ④+⑤+⑥, ①+④+⑥, ①+⑤+⑦ and ①+⑥+⑦ may be found. The last set was partially detected as shown in Fig. 6, but the others were not observed in this study. This is because they can exist at the narrow  $P_{O_2}$  range and because they locate in the unstudied compositional area. These three-phase equilibria are also expected from the thermodynamic calculations.<sup>7)</sup>

## 4.2 Compositions for Invariant Equilibria

The volume fractions of the phases in the three-phase equilibria changed corresponding to  $P_{O_2}$  as shown in Fig. 3 and Fig. 4. This indicated that the metallic compositions or oxygen concentration of the related three phases are not constant. A slight compositional change was observed by the analysis of the lattice parameters, however there was no clear systematic relationship with  $P_{O_2}$ . For the simplicity, the equilibrium compositions in the three-phase equilibrium were fixed, and it was assumed that the three-phase equilibria could be shown as the flat triangles in 3 dimensional compositional space. These triangles were illustrated in Fig. 3 for the composition A.

The invariant four phase equilibrium can be illustrated as the tetrahedron in the compositional space. Six set of three-phase equilibria confirmed experimentally can be shown as the surfaces of the four-phase tetrahedrons. The vertex compositions of the tetrahedrons are therefore the same of the three-phase equilibria. Thus the compositions of the four phase equilibria were analyzed and summarized in Fig. 7.

The vertex of ① for the tetrahedron of ①+②+③+④ (Fig.7(e)) was taken as (Sr<sub>0.11</sub>±0.02Ca<sub>0.89</sub>±0.02)<sub>2</sub>CuO<sub>3</sub>, while the vertex of ① for the tetrahedron of ①+③+④+⑤ (Fig.7(d)) was taken as (Sr<sub>0.08</sub>±0.06Ca<sub>0.92</sub>±0.06)<sub>2</sub>CuO<sub>3</sub>. The two surfaces of the former tetrahedron required to fit with the three-phase equilibria in air, while the latter should fit with the three-phase equilibria at  $P_{O_2} = 0.01$  P°Pa. This compositional discrepancy may be within the experimental errors, but it is also possible to consider that the three-phase equilibrium of ①+③+④ can change its equilibrium compositions under the reduced oxygen atmosphere.

## 4.3 Comparison with the optimized database

The following calculations were obtained from the optimized thermodynamic description of the Sr-Ca-Cu-O system,<sup>7)</sup> which was based on those of the ternaries Sr-Cu-O and Ca-Cu-O<sup>5, 6)</sup> and experimental data in air and higher  $P_{O_2}$ .

A calculated isothermal section at 1153K and 10 Pa O<sub>2</sub> is shown in Fig. 8. These conditions were estimated to be close to those of the isothermal section studied in the pure Ar gas atmosphere shown in Fig. 6. A calculation of the fraction of phases as a function of the oxygen partial pressure at the composition of sam-

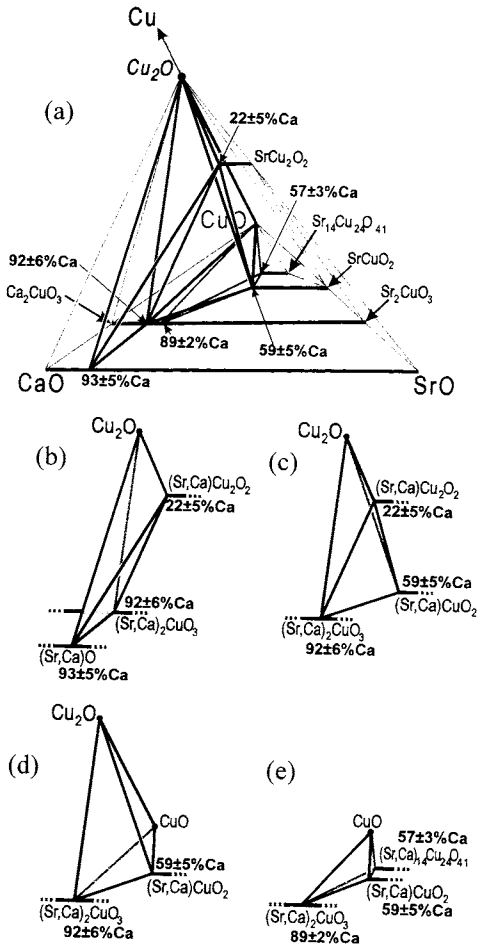


Fig.7 4 sets of 4-phase equilibria ((b)-(e)) and their locations in the compositional tetrahedron (a).

ple A is shown in Fig. 9. The general features of the calculated phase evolution agree relatively well with the experimental observations. For example, the drastic decrease in the fraction of the phase (Sr,Ca)CuO<sub>2</sub> below 1%O<sub>2</sub> can be clearly seen in both the experimental and the calculated figures. Some discrepancies are however found concerning the invariant reactions at lower P<sub>O<sub>2</sub></sub>. The calculated P<sub>O<sub>2</sub></sub> values of the 4-phase invariant equilibria at 1153 K are included in Table 4. The equilibria ①+④+⑤+⑥ and ①+⑤+⑥+⑦ are observed at higher P<sub>O<sub>2</sub></sub> than expected from the thermodynamic computation. Some changes in the model description have therefore been tested to account for the new experimental results.

The thermodynamic properties of (Sr,Ca)Cu<sub>2</sub>O<sub>2</sub> are

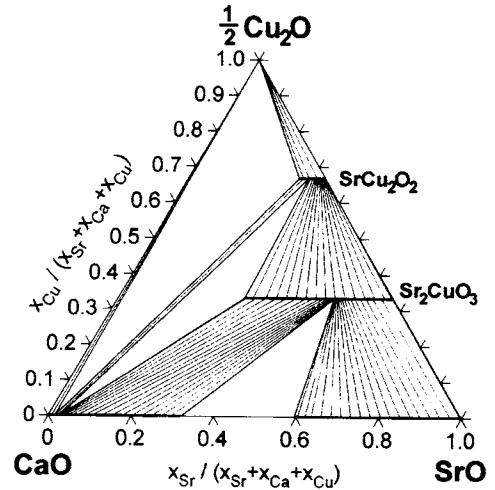


Fig.8 Isothermal section calculated at 1153 K, P<sub>O<sub>2</sub></sub> = 10 Pa, using the thermodynamic description in Ref.7.

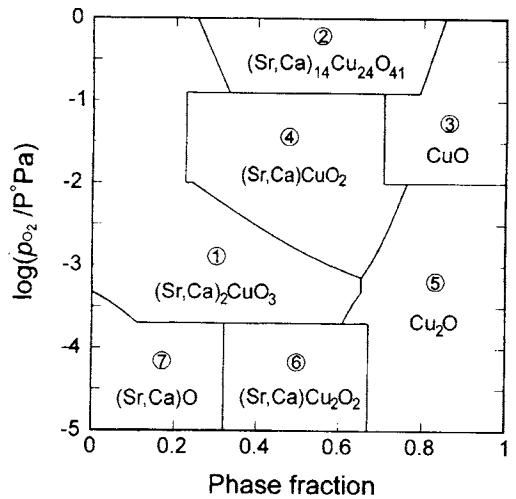


Fig.9 Phase fraction calculated at 1153 K for the composition A, using the thermodynamic description in Ref.7.

probably the less known among those of the phases involved in the equilibria ①+④+⑤+⑥ and ①+⑤+⑥+⑦. It may be assumed that the stability of this phase is underestimated by the above calculations, which would explain the discrepancies shown in Table 4. (Sr,Ca)Cu<sub>2</sub>O<sub>2</sub> was described in Ref.7 as an ideal solution due to the lack of any data, thus a different compositional dependence of the Gibbs energy was studied here. It appeared

that only a Sr-Ca interaction parameter much larger than that for any other (Sr, Ca) -solid solutions could lead to a closer fit of both the solubility data and the  $P_{O_2}$  values. The Gibbs energy of (Sr,Ca)Cu<sub>2</sub>O<sub>2</sub> would show a minimum at a concentration of 10 to 20 %Ca and influence the phase relations in consequence. This large interaction parameter cannot be justified at the moment. Further experimental data, especially on the equilibria involving (Sr,Ca)Cu<sub>2</sub>O<sub>2</sub>, (Sr,Ca)CuO<sub>2</sub>, and Cu<sub>2</sub>O at Ca-poor compositions may then give an important clue to this problem.

### 5. Conclusions

The stability ranges for the oxides were observed at 4 compositions in the reduced oxygen atmosphere, and the phase equilibria at  $P_{O_2}=0.01$  P°Pa and in "pure" Ar gas were studied. Six sets of 3-phase equilibria could be confirmed experimentally, and the equilibrium compositions for the related phases were analyzed by the lattice parameters, EDX analysis and the compositional constraints. Four sets of the invariant 4-phase equilibrium and their equilibrium oxygen partial pressures were deduced from the reducing sequences and the surrounding 3-phase equilibria. A comparison of these results with thermodynamic calculations generally showed a good agreement, but revealed a large discrepancy in the value of the oxygen partial pressures of two invariant reactions.

The present results offer essential data to improve the model description of the Sr-Ca-Cu-O system, and have pointed out the need for further experimental studies concerning the thermodynamic properties of the phase (Sr, Ca)Cu<sub>2</sub>O<sub>2</sub>.

### Acknowledgements

The authors thank to Mr. T. Unesaki for EDX analysis, Mr. T. Mimura for his experimental assistance, and Dr. R. Müller, Mr. H. Nishiura and Dr. B. Hallstedt for their helpful discussions.

### References

1) R. O. Suzuki, S. Kambara, H. Tsuchida, K. Shimizu and K. Ono, in T. Ishiguro and K. Kajimura (Ed.); Adv. in Superconductivity II (Proc. of 2nd Intern. Symp. on Superconductivity, ISS'89), Springer-Verlag, Tokyo, p.235(1989).

2) R. Müller, Th. Schweizer, P. Bohac, R. O. Suzuki and L. J. Gauckler, *Physica C* **203**, 299 (1992).  
 3) R. O. Suzuki, P. Bohac, and L. J. Gauckler, *J. Am. Ceram. Soc.* **75**, 2833(1992).  
 4) R. O. Suzuki, P. Bohac, and L. J. Gauckler, *J. Am. Ceram. Soc.* **77**, 41 (1994).  
 5) D. Risold, B. Hallstedt, and L. J. Gauckler, *J. Am. Ceram. Soc.* **78**, 2655 (1995).  
 6) D. Risold, B. Hallstedt, and L. J. Gauckler, *J. Am. Ceram. Soc.* **80**, 527 (1997).  
 7) D. Risold, B. Hallstedt, and L. J. Gauckler, *J. Am. Ceram. Soc.* **80**, 537 (1997).  
 8) R. O. Suzuki, K. Ono, and L. J. Gauckler, in K. Yamafuji and T. Morishita (Ed.), Adv. in Superconductivity VII (Proc. of 7th Intern. Symp. on Superconductivity, ISS'94), Springer-Verlag, Tokyo, p.357 (1995).  
 9) B. J. Reardon and C. R. Hubbard, *Powder Diffraction*, **7**, 142 (1992).  
 10) M. Vallino, D. Mazza, F. Abbattista, C. Brisi and M. L-Borlera, *Mater. Chem. Phys.* **22**, 523 (1989).  
 11) J. Liang, Z. Chen, F. Wu and S.Xie, *Solid State Comm.* **75**, 247 (1990).  
 12) S. G. Popov, Y. Y. Skolis, F. M. Putilina, L. I. Khramtsova, *Russ. J. Inorg. Chem.* **37**, 1340(1992).  
 13) A. S. Kosmynin, B. V. Slobodin, V. L. Balashov, A. A. Fotiev, I. K. Garkushin, G. E. Sheter and A. S. Trunin, *Russ. J. Inorg. Chem.* **37**, 970(1992).  
 14) R. S. Roth, C. J. Rawn, J. J. Ritter and B. P. Burton, *J. Amer. Ceram. Soc.* **72**, 1545(1989).  
 15) C. Krüger, W. Reichelt, A. Almes, U. König, H. Oppenmann and H. Scheler, *J. Solid State Chem.* **96**, 67(1992).  
 16) B. Hallstedt, D. Risold, and L. J. Gauckler, *J. Phase Equilibria* **15**, 483(1994).

### 要 旨

酸化物超伝導体に関係するSr-Ca-Cu-O系の相平衡関係を1153 KでAr-O<sub>2</sub>混合ガスを用いて試料を焼鈍することにより調査した。酸化物は広い範囲で固溶体を形成したが、その酸素分圧に対する安定領域を粉末X線回折法で、12種類のガス雰囲気、4組成で調べた。実験的に得た3相平衡関係から新たに4種の不偏系4相平衡とその平衡酸素分圧を導出した。また関係する相の組成をEDXによる組成分析と試料組成から評価した。これらの実験結果を熱力学モデルに基づく平衡計算の結果と比較して検討した。