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# Subsolidus phase relations of the $Y_2O_3$–SrO–CuO system

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The 960 °C subsolidus phase relations of $Y_2O_3$–SrO–CuO system have been determined by X-ray diffraction. The section at room temperature in the $Y_2O_3$–SrO–CuO ternary system can be divided into six three-phase and two-phase regions. In this system, there are five binary compounds: $Y_2SrO_4$, $Y_2Cu_2O_5$, $Sr_2CuO_3$, $SrCuO_2$ and $Sr_{14}Cu_{24}O_{41}$ as well as a solid solution $Y_xSr_{14-x}Cu_{24}O_{41}$ $(0 < x \leqslant 4)$. The structure of the solid solution is discussed. The variation of the lattice parameters of the solid solution with increasing yttrium content has been measured. Electrical resistivity measurements of the solid solution show that there is no superconductive phase in the Y–Sr–Cu–O system.

## 1. Introduction

Since the high-temperature superconductivity was discovered in the La–Ba–Cu–O [1] and Y–Ba–Cu–O [2, 3] systems, much substitutive work has been done. It has been verified that yttrium can be replaced by most rare-earth elements (except Ce, Pr, Pm and Tb) and the superconductivity and basic structure of the superconductive phase can be preserved. Because alkali-earth metals barium and strontium have similar chemical properties and ionic radii, it is significant to study the change in superconductivity and structure when strontium completely replaces barium. Mei *et al.* [4] reported $Y_{0.3}Sr_{0.7}CuO_{4-y}$ with a $T_c$ of about 40 K. Wu *et al.* [5] have reported that in $YSrCuO_{4-y}$ there are two superconductive transitions at 80 and 40 K, corresponding to $YSr_2Cu_3O_7$ (123) and $Y_2SrCu_4O_8$ (214), respectively. Oda *et al.* [6] reported that the tetragonal $YSr_2Cu_3O_7$ exhibited a complete transition in resistance at 81 K. Zhang *et al.* [7] found that a zero resistance was obtained at 90.5 K for $Sr_xY_{1-x}CuO_{3-y}$ ($x = 0.375$–0.5). In contrast, Veal *et al.* [8] reported that samples with the starting composition $YSr_2Cu_3O_7$ were insulating and showed no characteristics of an orthorhombic $YBa_2Cu_3O_7$ phase. In order to search for new superconductive phases, and to identify whether $YSr_2Cu_3O_7$ exists, we investigated the phase relations and the possible superconductive phases in the $Y_2O_3$–SrO–CuO ternary system, more carefully.

## 2. Experimental procedure

The starting materials were $Y_2O_3$ (99.99%), $BaCO_3$ (AR) and CuO(AR). The samples were prepared by solid state reactions. The raw mixture of these materials with different compositions was ground thoroughly, then pressed into pellets, sintered at 930 °C for 24 h in air, then slowly cooled to room temperature. The samples were then reground, repressed into pellets, sintered at 960 °C in air for further 48 h, then slowly cooled in the furnace to room temperature for phase identification or electrical resistivity measurements.

The phase identifications were made with a Guinier–de Wolf monochromatic focusing camera by using $CuK_\alpha$ radiation. Pure silicon powder was added as internal standard for calibration of the lattice parameters. The diffraction data of Sr–Cu oxides and the solid solution $Y_xSr_{14-x}Cu_{24}O_{41}$ $(0 < x < 4)$ were collected using a D/max-RB type X-ray diffractometer with a rotating anode generator (Japanese Rigaku).

Electrical resistivity was determined by the four-probe technique. The mutual-inductance method was adopted to measure the a.c. magnetic susceptibility.

## 3. Results and discussion

The phase diagram in the $Y_2O_3$–SrO binary system has been reported previously [9]. In this system, below 1500 °C only one binary compound, $Y_2SrO_4$, exists. The phase diagram of the $Y_2O_3$–CuO binary system has also been reported [10]. In this system only one binary compound, $Y_2Cu_2O_5$, is formed. According to the JCPDS cards, $Y_2SrO_4$ belongs to an orthorhombic system with $a = 1.00070$ nm, $b = 1.19141$ nm and $c = 0.34098$ nm. Its space group is Pnam (62). $Y_2Cu_2O_5$ belongs to a monoclinic system with space group $P_2(3)$. Its lattice parameters are $a = 1.360$ nm, $b = 0.327$ nm, $c = 1.360$ nm and $\beta = 133.15°$. In the system SrO–CuO, we obtained the following compounds: $Sr_2CuO_3$, $SrCuO_2$ and $Sr_{14}Cu_{24}O_{41}$. The X-ray analysis shows that $Sr_2CuO_3$ belongs to the orthorhombic system, the unit cell is a body centred lattice with $a = 12.708$ nm, $b = 0.3913$ nm and $c = 0.3502$ nm. $SrCuO_2$ belongs to an orthorhombic system with space group Cmcm (63), its lattice parameters are $a = 0.3573$ nm, $b = 1.6333$ nm and $c = 0.3915$ nm, coinciding with those given by Teske *et al.* [11, 12]. The compound $Sr_{14}Cu_{24}O_{41}$ belongs to the orthorhombic system

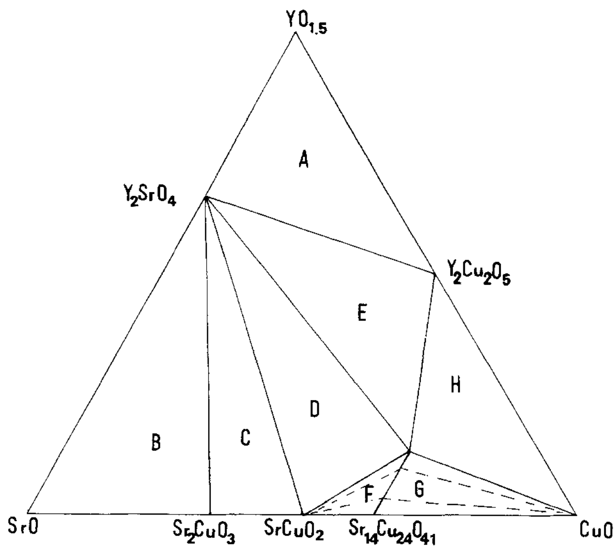


*Figure 1* Subsolidus phase relations of the $Y_2O_3$–SrO–CuO system.

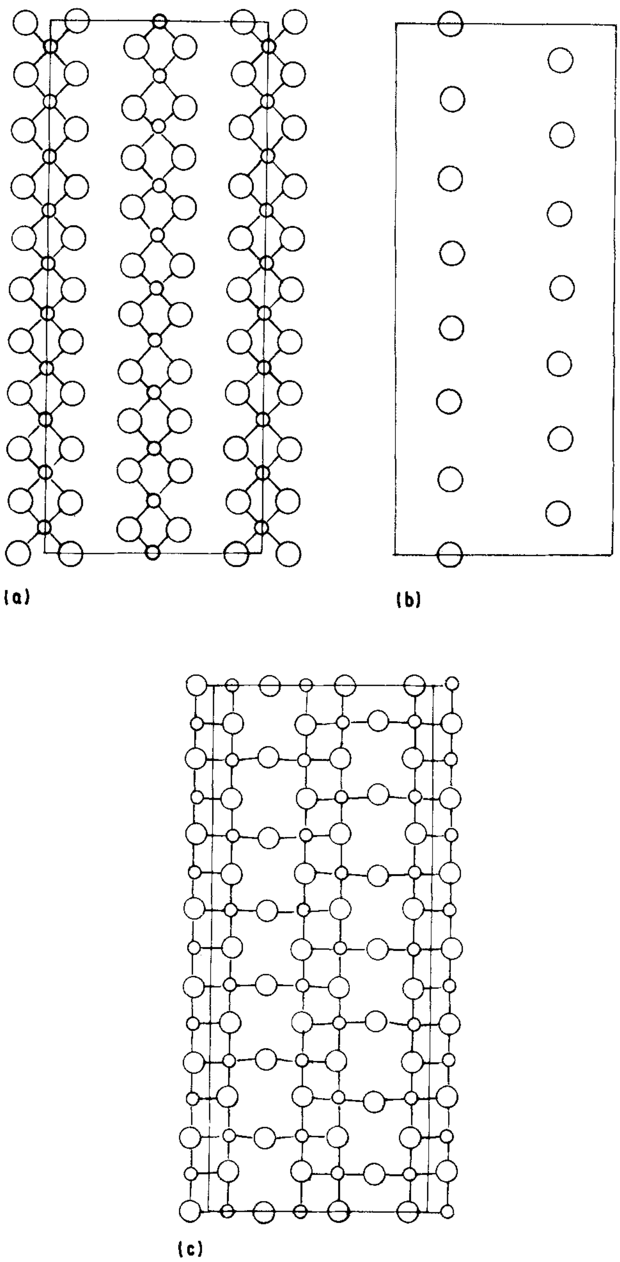


*Figure 2* The structure of $Y_xSr_{14-x}Cu_{24}O_{41}$ ($0 < x \leqslant 4$). The structure can be generated by stacking the layers (a–c) along the *b*-axis by simply aligning the unit cells outlined in the *a–c* plane. (o) Copper and (○) oxygen ions. (a) The infinite $[CuO_{4/2}]$ chains propagating along the *c*-axis. (b) The $[Y_xSr_{14-x}]$ layer residing between the chains and sheets. (c) The $[CuO_{3/3}O_{1/2}]$ sheets. Within the sheets O1 is the triple bridging oxygen; O2 is double bridging.

with $a = 11.470$ nm, $b = 13.402$ nm and $c = 3.939$ nm. The results obtained here are very close to those of McCarron *et al.* [13].

About 90 samples with various compositions of yttrium, strontium and copper were made. From X-ray diffraction measurements, the subsolidus phase relations in the $Y_2O_3$–Sr–CuO system at 960 °C were determined. They are shown in Fig. 1, from which we find that in this system, there is no evidence for the existence of a ternary $YSr_2Cu_3O_7$ oxide. The section at room temperature in the $Y_2O_3$–SrO–CuO system can be divided into the following sections:

(A) $Y_2O_3 + Y_2SrO_4 + Y_2Cu_2O_5$
(B) $Y_2SrO_4 + Sr_2CuO_3 + SrO$
(C) $Y_2SrO_4 + Sr_2CuO_3 + SrCuO_2$
(D) $Y_2SrO_4 + SrCuO_2 + Y_xSr_{14-x}Cu_{24}O_{41}$ $(x = 4)$
(E) $Y_2SrO_4 + Y_2Cu_2O_5 + Y_xSr_{14-x}O_{41} (x = 4)$
(F) $SrCuO_2 + Y_xSr_{14-x}Cu_{24}O_{41} (0 < x < 4)$
(G) $CuO + Y_xSr_{14-x}Cu_{24}O_{41} (0 < x < 4)$
(H) $Y_2Cu_2O_5 + CuO + Y_xSr_{14-x}Cu_{24}O_{41} (x = 4)$

For the compound $Sr_{14}Cu_{24}O_{41}$, $Sr^{2+}$ can be partially replaced by $Y^{3+}$ to form solid solution $Y_xSr_{14-x}Cu_{24}O_{41}$ ($0 < x \leqslant 4$). The layered structure of $Sr_{14}Cu_{24}O_{41}$ shows that the structure includes both Cu–O planes and chains separated by strontium, and the copper ion in both structural elements is located at the centre of the squares of oxygen lying parallel to the *a–c* plane [13]. Furthermore, X-ray analysis shows that the solid solutions $Y_xSr_{14-x}Cu_{24}O_{41}$ ($0 < x \leqslant 4$) and $Sr_{14}Cu_{24}O_{41}$ have isomorphous structure. In the solid solution $Y_xSr_{14-x}Cu_{24}O_{41}$ ($0 < x \leqslant 4$), $Y^{3+}$ occupies the same site as that of $Sr^{2+}$ in $Sr_{14}Cu_{24}O_{41}$. The elements of the structure in $Y_xSr_{14-x}Cu_{24}O_{41} (0 < x \leqslant 4)$ are depicted in Fig. 2. Because the $Y^{3+}$ ionic radius is less than that of the $Sr^{2+}$ ion, replacing $Sr^{2+}$ by $Y^{3+}$ must change the lattice parameters. When the yttrium content increases, the variation in lattice parameters in $Y_xSr_{14-x}Cu_{24}O_{41}$ ($0 < x \leqslant 4$) is as shown in Fig. 3. Because the structure is layered, the substitution directly affects the layer stacking axis (*b*-axis), while it has a lesser effect on the *a–c* plane parameters. The parameters of $Y_4Sr_{10}Cu_{24}O_{41}$ are $a = 1.1360$ nm, $b = 1.2950$ nm and $c = 0.3938$ nm.

Preliminary electrical resistivity measurements showed that $Sr_{14}Cu_{24}O_{41}$ is a semiconductor and $Y_xSr_{14-x}Cu_{24}O_{41}$ ($0 < x \leqslant 4$) gradually becomes an insulator as the yttrium content increases. It is interesting to compare $Y_xSr_{14-x}Cu_{24}O_{41} (0 < x \leqslant 4)$ with $YBa_2Cu_3O_{7-y}$. Structurally, they are layered and have as their basic squares planar copper atoms bound to oxygen. The square planar units are arranged so as to form both Cu–O chains and Cu–O planes. The difference between them appears to be in the mode of linkage of the square planar copper oxygen

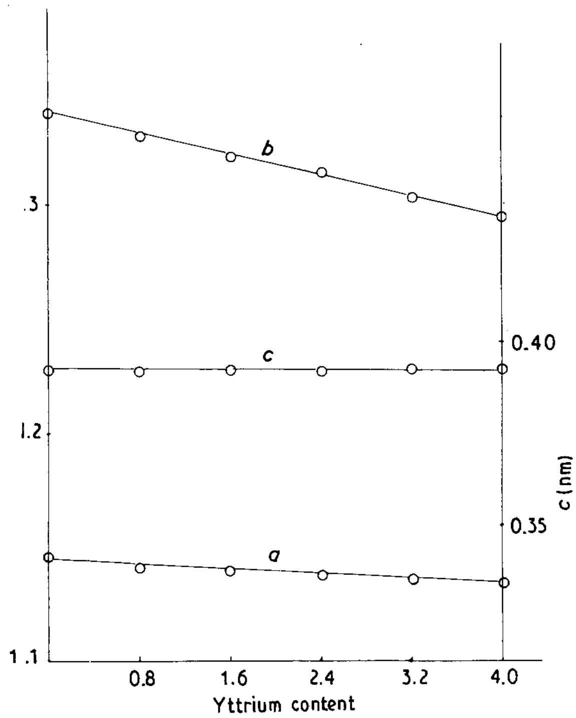


*Figure 3* Variation of the lattice parameters with yttrium content.

units: edge-shared in $Y_xSr_{14-x}Cu_{24}O_{41}$ ($0 < x \leqslant 4$), corner-shared in $YBa_2Cu_3O_{7-y}$. In addition, in $Y_xSr_{14-x}Cu_{24}O_{41}$ ($0 < x \leqslant 4$), there is no continuous corner-shared $CuO_2$ network, as there is in $YBa_2Cu_3O_{7-y}$, i.e. there is no true $CuO_2$ plane in this compound, therefore it does not exhibit superconductivity.

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