

Synthesis and Properties of Compounds in the System $\text{Sr}_2\text{CuO}_3\text{-Ca}_2\text{CuO}_3$

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The ternary compounds Ca_2CuO_3 , Sr_2CuO_3 , and their solid solution $\text{Sr}_{2-x}\text{Ca}_x\text{CuO}_3$ have been prepared by the decomposition of coprecipitated oxalates and/or by conventional solid state reaction. Both reaction methods are compared. The obtained compounds crystallize in the orthorhombic system. The lattice constants were determined, and the formation of solid solution crystals over the whole range of composition was obtained. The compounds were characterized concerning their thermal stability and their decomposition in moist air. Thermogravimetric, X ray, and vapor pressure measurements show that the compounds are of a very slight variation in oxygen stoichiometry. First measurements of the specific heat and IR spectra are discussed. © 1992 Academic Press, Inc.

Introduction

The worldwide search for new superconducting materials has led, besides the discovery of new more complicated compounds, to intensive studies on coexisting phases in these systems, especially on other copper containing compounds. Most of these investigations are dedicated to phase equilibria and structural questions. Understanding of binary phase diagrams of the type MeO-CuO ($\text{Me} = \text{Ca}, \text{Sr}, \text{Ba}$) plays an important role for the formation mechanism of superconducting phases, the growth of single crystals, the search for new reaction methods involving complex oxide precursors (1, 2), and the question of superconductivity itself. We decided to study the compounds Sr_2CuO_3 , Ca_2CuO_3 , and their solid solution crystals in order to understand their

role in the formation of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ and their possible use as complex precursors.

Experimental

The material was prepared either by solid state reaction of stoichiometric amounts of SrCO_3 , CaCO_3 , and CuO or decomposition of a mixture of coprecipitated oxalates. Using a planet mill (Pulverisette 5, Fritzsches GmbH), the powders for the solid state reaction were ball milled in agate mortar with dry *n*-heptane. After they were dried, the powders, of an average size of 2-4 μm , were treated thermally as described in the following. Coprecipitation of the metal oxalates was carried out as described earlier (3) using the effect of adding organic solvents to reduce solubility and particle size of the pre-

cipitate (4). The obtained light blue powders, of an average particle size of $3\ \mu\text{m}$, consisted of a mixture of the individual metal oxalates. This follows from IR spectroscopic and X-ray investigations.

REM photographs confirm the particle size, measured by a laser particle size analyzer (Analysette 22, Fritsch GmbH).

Determination of lattice constants was carried out by Rietveld refinement of experimental data obtained by powder diffraction measurements with monochromatized $\text{CuK}\alpha$ radiation. Thermoanalytical investigations concerning thermal stability and specific heat measurements were accomplished using Netzsch equipment (STA 409 and DSC 404).

Results

The compounds Sr_2CuO_3 and Ca_2CuO_3 first were prepared and their structure was determined by investigation of single crystal X-ray data by Teske and Müller-Buschbaum (5, 6). The compounds have orthorhombic structure and are isotypic. They reported the compounds to be stable in dry air, but to hydrolyze in water and to be easily solved in acids. Roth *et al.* (7, 8) investigated phase equilibria in the systems CaO-CuO , SrO-CuO , and SrO-CaO-CuO . They pointed out that unit cell dimensions of $\text{Sr}_{2-x}\text{Ca}_x\text{CuO}_3$ solid solution crystals follow roughly linear trends with composition. But their determined lattice constants for $\text{Sr}_{1.00}\text{Ca}_{1.00}\text{CuO}_3$ do not correspond exactly to this composition, if they are compared to the known values of Ca_2CuO_3 and Sr_2CuO_3 (5, 6). Our detailed study on this problem is based on Rietveld refinement of powder diffraction data. Obtained R_{wp} (weighed pattern) factors are in the range of 0.04–0.07. The specimens were prepared by thermal decomposition of the corresponding oxalate mixtures at 900°C for 16 hr. This method led to phase pure products, while the application of solid state reaction was not success-

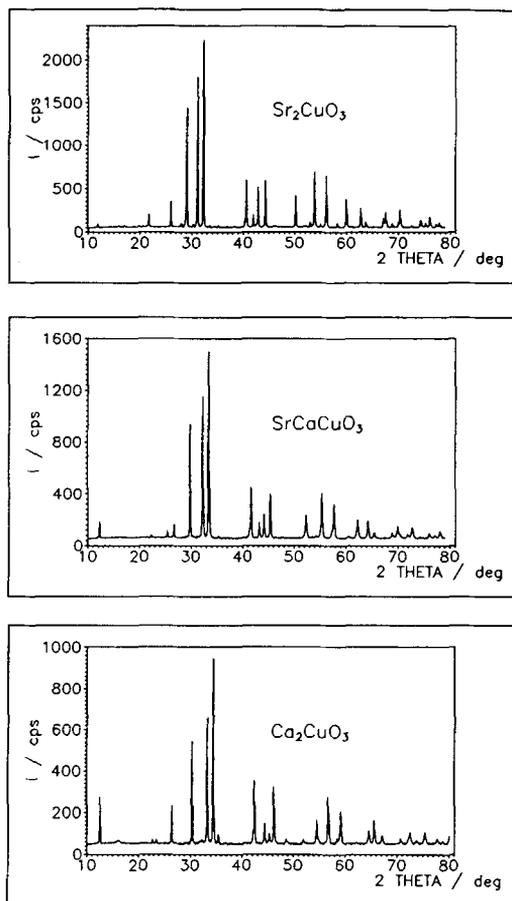
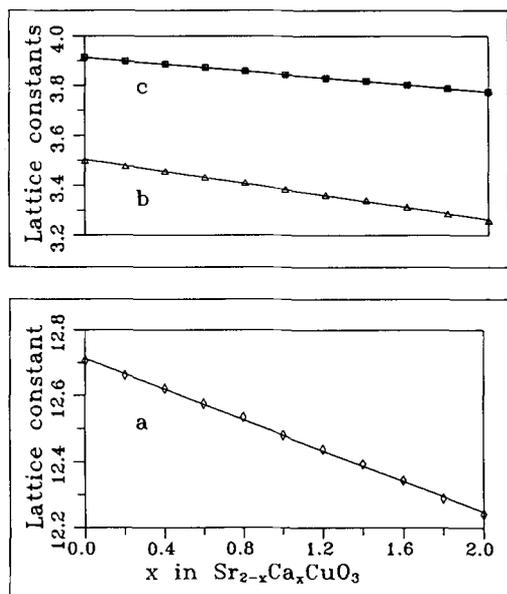


FIG. 1. XRD pattern of Ca_2CuO_3 , Sr_2CuO_3 , and SrCaCuO_3 .

ful at prolonged heating starting from the components (Sr_2CuO_3 and Ca_2CuO_3). Figure 1 shows the X-ray pattern of the three major compounds in this system.

The results of the Rietveld refinement (Fig. 2) show the lattice constants to follow exactly linear trends with composition in the whole composition range. The substitution of Sr by Ca leads to decreasing lattice constants, especially of the a parameter.

At a substitution rate higher than $x = 0.3$, a change in bonding constitution is observed. This follows from possible separate

FIG. 2. Lattice constants of $\text{Sr}_{2-x}\text{Ca}_x\text{CuO}_3$.

fitting of Ca- and Sr-atom positions. Both atoms are moved within the cell against each other, and the oxygen coordination polyeder do not lie in the same plane anymore. The bond lengths of the metal atoms become smaller.

Because of the exact linear change of lattice constants within the whole composition range, it can be stated that the compounds form substitution mixed crystals. The parameters of the lattice constants' changes were estimated by linear regression for $\text{Sr}_{2-x}\text{Ca}_x\text{CuO}_3$ as follows:

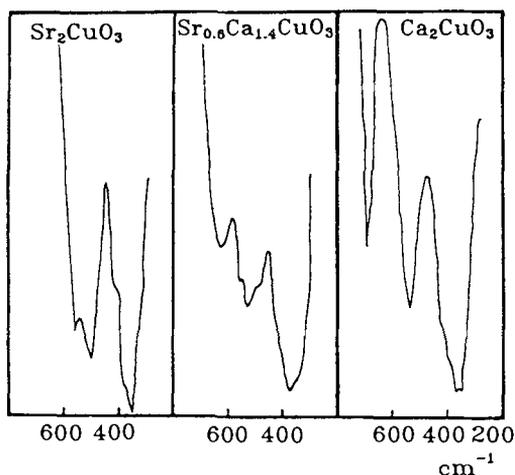
$$a = -0.232x + 12.712$$

$$b = -0.120x + 3.503$$

$$c = -0.069x + 3.914.$$

From these equations, we can deduce that the determined cell dimensions for SrCaCuO_3 given by ROTH *et al.* (7, 8) ($a = 12.319$, $b = 3.306$, $c = 3.807$) would correspond to a composition of $\text{Sr}_{0.4}\text{Ca}_{1.6}\text{CuO}_3$.

Only slight changes in dependence of the

FIG. 3. IR spectra of $\text{Sr}_{2-x}\text{Ca}_x\text{CuO}_3$.

Sr substitution are observed in the case of the IR spectra. They are similar to that of the components and look like a superposition of the individual spectra. There are only small shifts to higher or lower wave numbers. Figure 3 shows some spectra.

Another property which changes with Sr substitution is the specific heat. This value plays an important role for the determination and estimation of thermodynamic data. Enthalpy and entropy, measured at 298 K, for example by solution calorimetry, can be estimated for other temperatures, if c_p is known. Our measurements of c_p were performed in flowing oxygen to avoid the formation of carbonates. In Table I the measured values at 350 K are compared with

TABLE I
SPECIFIC HEAT VALUES OF $\text{Sr}_{2-x}\text{Ca}_x\text{CuO}_3$

Compound	$C_p/\text{J/gK}$ (estimated)	$C_p/\text{J/gK}$ (measured)
Sr_2CuO_3	0.46	0.46
SrCaCuO_3	0.54	0.59
Ca_2CuO_3	0.67	0.71

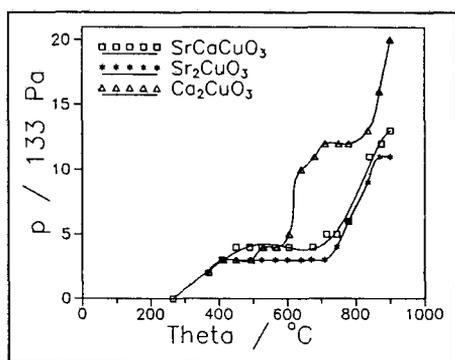


FIG. 4. Equilibrium pressure measurements of $\text{Sr}_{2-x}\text{Ca}_x\text{CuO}_3$.

estimated ones following the rule of Neumann and Kopp at 298 K.

The determination of thermodynamic data would allow one to define thermal stability as well, especially on dependence of oxygen partial pressure and temperature. For Sr_2CuO_3 even data concerning the stability in air at temperatures higher than 800°C are lacking.

XRD and thermoanalytical investigations show the compound to be stable at least up to 1200°C. Above this temperature, reaction with the crucible (Al_2O_3) took place. Another aspect of thermal stability consists in a possible oxygen homogeneity range of the compounds and their decomposition (reduction) into a Cu(I) compound. Using a special apparatus (closed system), which was developed for defined oxygen stoichiometry adjustment and measurement of copper containing superconductors (9), thermal stability of Ca_2CuO_3 , Sr_2CuO_3 , and SrCaCuO_3 was investigated. The results are shown in Fig. 4.

The curves, showing 2 or, in the case of Ca_2CuO_3 , even 3 steps can be interpreted as follows. The first step at approximately 3×133 Pa (3 Torr) can be attributed to a moisture loss of the powders, i.e., the decomposition of hydroxides. The second step

(11×133 Pa) we can discuss as equilibrium in the following form:



The results point to a small and comparable nonstoichiometry x . An estimation of the solid phase stoichiometry at 800°C leads to values of $x = 0.035$ for $\text{Ca}_2\text{CuO}_{3-x}$ and $x = 0.036$ for $\text{Sr}_2\text{CuO}_{3-x}$ at 900°C. These preliminary values, which have to be confirmed by further investigation, can be explained in terms of a very slight oxygen homogeneity range and are caused by the crystal structure which contains Me-O double chains.

Ca_2CuO_3 decomposes already at 900°C into Cu(I) compounds. The reabsorption of oxygen following Eq. (1) is reversible, and equilibrium is gained after 3–4 hr. The starting stoichiometry of the specimen was analyzed by iodometric titration after an additional thermal treatment at 400°C in dry oxygen.

The nonstoichiometry values are not significantly higher than the titration errors, not taking into account the possible influence of absorbed moisture. Therefore, we can state as an upper phase boundary the stoichiometry Me_2CuO_3 .

In order to explain the absorption of water by the compounds and to study their decomposition mechanism in moist air, several specimens were exposed to water vapor-saturated air for defined periods of time. The weight change is shown in Fig. 5.

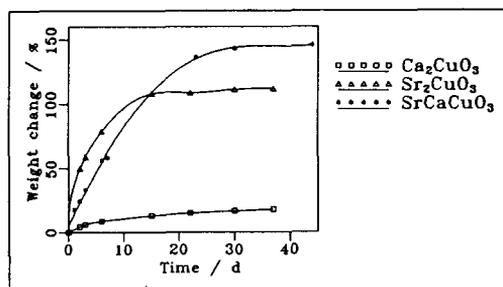
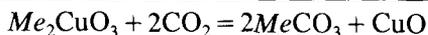
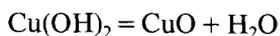
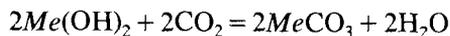
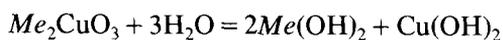


FIG. 5. Weight change in water saturated air.

XRD and IR spectroscopy show the following decomposition products: $Me(OH)_2$, $MeCO_3$, and CuO , besides unreacted Me_2CuO_3 . This leads to the following decomposition path: water attacks the crystals and forms $Me(OH)_2$ ($Me = Ca, Sr, Ba$). Probably $Cu(OH)_2$ is formed, as well, but because of its amorphous state it cannot be detected by XRD. This is confirmed by the color change of the specimen from black to light blue. As a second step, CO_2 reacts with the alkaline earth hydroxide, and the corresponding carbonates are formed. Amorphous $Cu(OH)_2$ decomposes to CuO and water.



Following the reaction by XRD, all decomposition products besides $Cu(OH)_2$ were detected.

The high reactivity against water shows the necessity of avoiding moisture, espe-

cially at elevated temperatures, and of storing the compounds in dry air.

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