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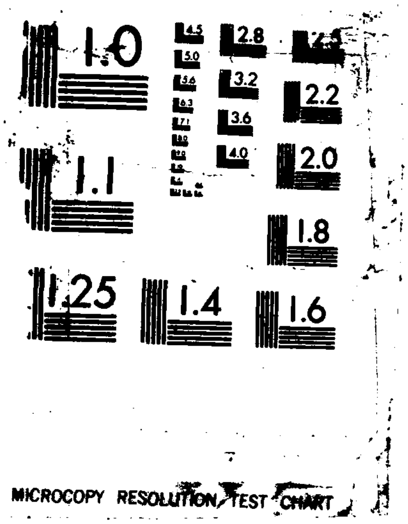
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# Preparation and Characterization of $Ba_2YCu_3O_{7.01(2)}$

by

S. Davison, K. Smith, R. Kershaw, K. Dwight and A. Wold

Prepared for Publication in

MATERIALS RESEARCH BULLETIN

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**Samples of $Ba_2YCu_3O_7$ were prepared both by ceramic techniques using $BaCO_3$, $Y_2O_3$, and CuO as well as by the decomposition of the corresponding nitrates. The preparations by each method are discussed and compared. In addition, the chemical instability of the pure phase $Ba_2YCu_3O_7$ in moist air is discussed.**

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# PREPARATION AND CHARACTERIZATION OF $Ba_2YCu_3O_{7.01(2)}$

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## ABSTRACT

Samples of $Ba_2YCu_3O_7$ were prepared both by ceramic techniques using $BaCO_3$, $Y_2O_3$, and CuO as well as by the decomposition of the corresponding nitrates. The preparations by each method are discussed and compared. In addition, the chemical instability of the pure phase $Ba_2YCu_3O_7$ in moist air is discussed.

MATERIALS INDEX: Stoichiometry, superconducting transition, stability

## Introduction

Several investigators have reported that the phase responsible for the 93 K superconductor is $Ba_2YCu_3O_7$ (1-3). This compound crystallizes as a defect perovskite. The space group is Pmmm with a = 3.8198, b = 3.8849 and c = 11.6762. Barium and yttrium are ordered on the A-site to give a tripled cell along the c direction. The oxygens occupy 7/9 of the perovskite anion sites and are ordered such that 1/3 of the Cu is four-fold coordinated and 2/3 is five-fold coordinated (2).

Very little detailed information has appeared in the literature concerning the optimum conditions for the synthesis of $Ba_2YCu_3O_7$. Conditions necessary for obtaining the pure phase, utilizing the decomposition of the corresponding nitrates, are discussed and compared to the conventional ceramic techniques using $BaCO_3$, $Y_2O_3$, and CuO. The chemical instability of the pure phase towards moist air will also be discussed.

## Experimental

$Ba_2YCu_3O_7$ was prepared by two different procedures. The preparation of $Ba_2YCu_3O_7$ from $BaCO_3$ (Fisher certified ACS lot 745985, preheated to 400°C for 3 hours), $Y_2O_3$ (Aesar 99.99% lot R-3529, preheated to 800°C for 12 hours) and analyzed CuO (J.T. Baker lot 32027) involved the usual ceramic techniques. The mixture of the carbonate and oxides was heated at 900°C for 24 hours.

For the preparation involving the nitrates, stoichiometric quantities of $Y_2O_3$, $BaCO_3$, and copper metal (Aesar 99.999% lot 060586) were placed in porcelain crucibles and dissolved by slowly adding concentrated nitric acid (20 ml/g Cu). The excess $HNO_3$ was removed by gentle boiling and the samples were heated to 130°C for 6 hours. The sample was then heated to 400°C for 3 hours and ground. The sample was transferred to a stabilized zirconia crucible and heated to 800°C for 12 hours. Pellets were cold-pressed at 6 kbar and heated to 950°C for 12 hours. The pellets were then heated to 425°C for 6 hours and the temperature decreased at 50°C/hr to room temperature.

Powder samples used for TGA studies were prepared by partial decomposition of the nitrate mixture at 400°C followed by a second heating at 900°C for 24 hours.

## Characterization

X-ray powder diffraction patterns of the samples were obtained using a Philips diffractometer and monochromated high intensity CuK$\alpha_1$ radiation ($\lambda$ = 1.5405 Å). The diffraction patterns were taken in the range $12° < 2\theta < 72°$ with a scan rate of 1° 2θ/min and a chart speed of 30 in/hr.

Temperature programmed reduction of prepared samples was carried out using a Cahn System 113 thermal balance. A flowing atmosphere of 85%Ar/15%$H_2$ (60 ml/min) was predried by passing it through a $P_2O_5$ column and was then passed through a hot Cu column to remove oxygen. The temperature was increased at 50°C/hr up to 1000°C until no further decrease in weight was observed.

The van der Pauw method was used to measure the electrical resistivity. Contacts were made by ultrasonically soldering indium directly onto the sintered discs of $Ba_2YCu_3O_7$, and their ohmic behavior was established by measuring their current-voltage characteristics. The sample and thermocouple were in close proximity and located inside a small cavity of a massive copper body. This assembly was first cooled to 77 K and then allowed to slowly warm to room temperature.

Magnetic susceptibility measurements were carried out using a Faraday balance (4) from 77 to 300 K with a field strength of 10.4 kOe. Honda-Owens measurements were carried out at both 77 and 300 K.

## Results and Discussion

$Ba_2YCu_3O_7$ was prepared both by the reaction of $BaCO_3$, $Y_2O_3$, and CuO according to published procedures and by the decomposition of the corresponding mixed metal nitrates. The changes in weight are plotted as functions of temperature for both reaction mixtures in Fig. 1. Copper nitrate and yttrium nitrate are completely converted to oxides by 400°C, so that the TGA results shown in Fig. 1 represent the ease of decomposition of barium nitrate compared to barium carbonate. It can readily be seen that barium nitrate is decomposed by 650°C whereas the carbonate does not decompose substantially until 900°C. It should therefore be possible to prepare $Ba_2YCu_3O_7$ more readily via the decomposition of the mixed metal nitrates. From Fig. 2 it is seen that the phase $Ba_2YCu_3O_7$ is not completely formed even after a 24 hour heat treatment of barium carbonate, yttrium oxide and copper (II) oxide at 900°C. However, from Fig. 3 the product is readily formed from the nitrates after being heated at

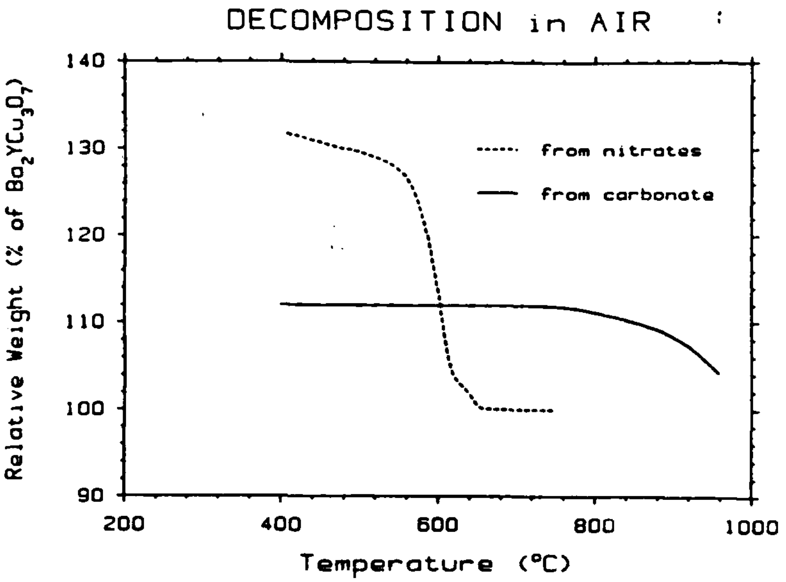

Fig. 1. Decomposition in air of a mixture of $BaCO_3$, $Y_2O_3$ and CuO compared with that of a mixture of the nitrates.

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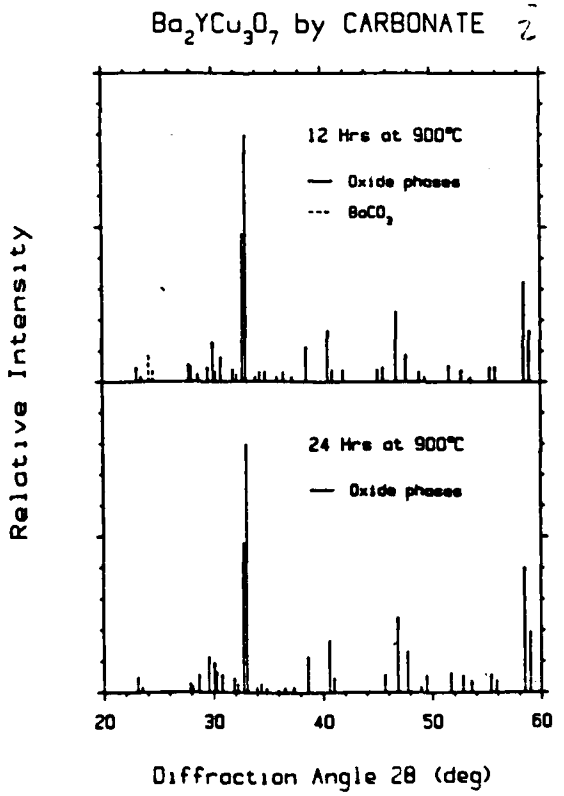

Fig. 2. X-ray diffraction patterns of a mixture of $BaCO_3$, $Y_2O_3$ and CuO heated at 900°C showing the presence of unreacted $BaCO_3$ after 12 hrs and a multiphase product after 24 hrs.

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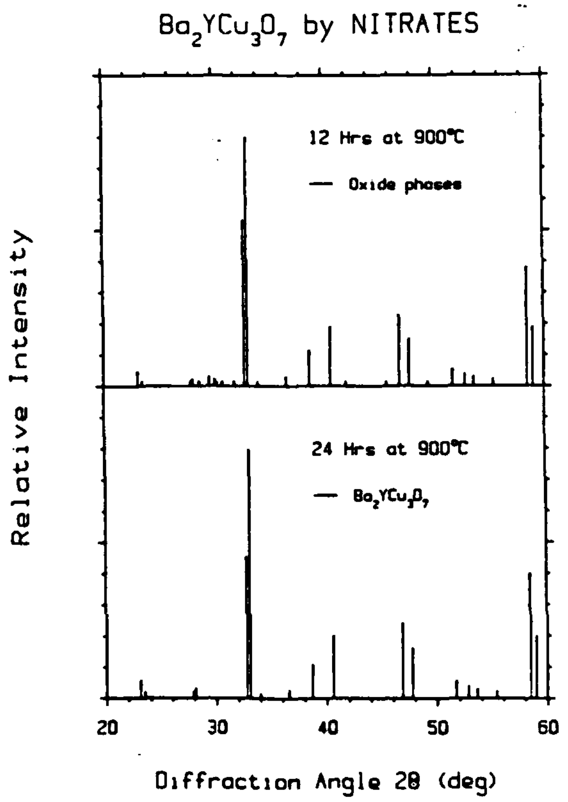

Fig. 3. X-ray diffraction patterns of a mixture of the nitrates heated at 900°C for 12 and 24 hrs showing the final product to be single-phase $Ba_2YCu_3O_7$.

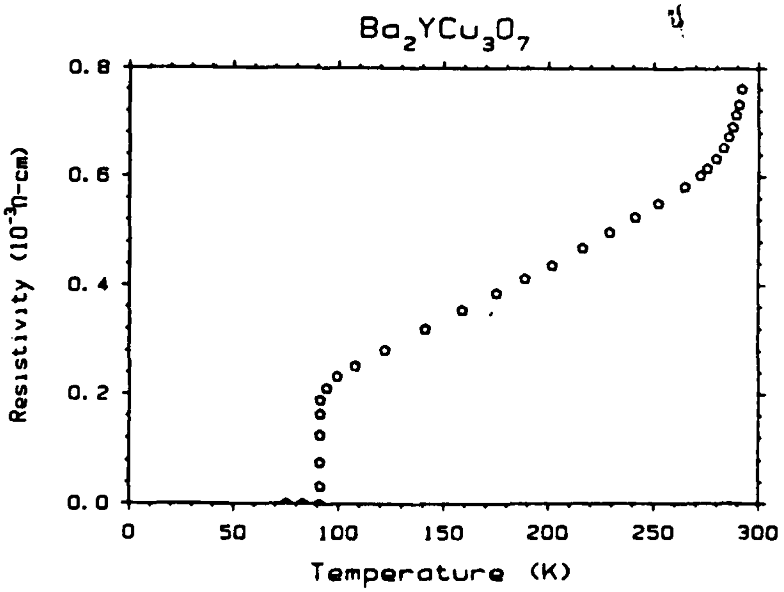

Fig. 4. Resistivity of $Ba_2YCu_3O_7$ as a function of temperature.

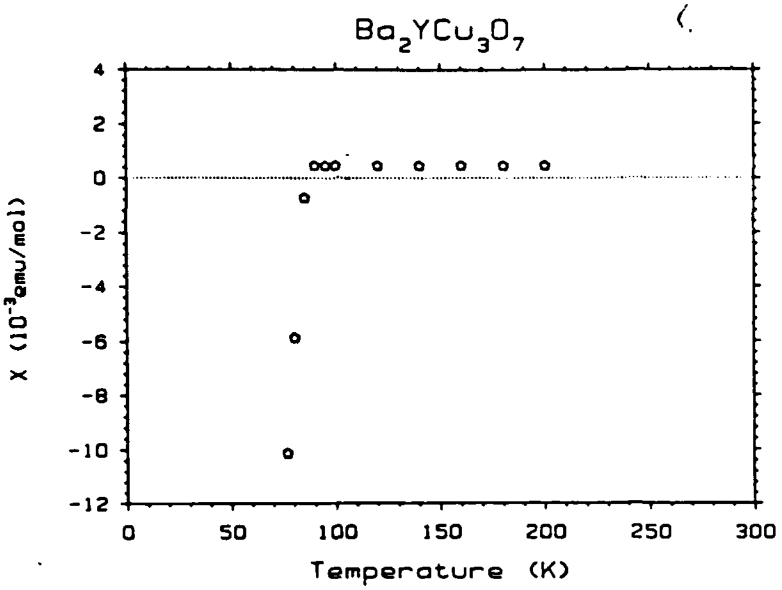

Fig. 5. Magnetic susceptibility of $Ba_2YCu_3O_7$ as a function of temperature.

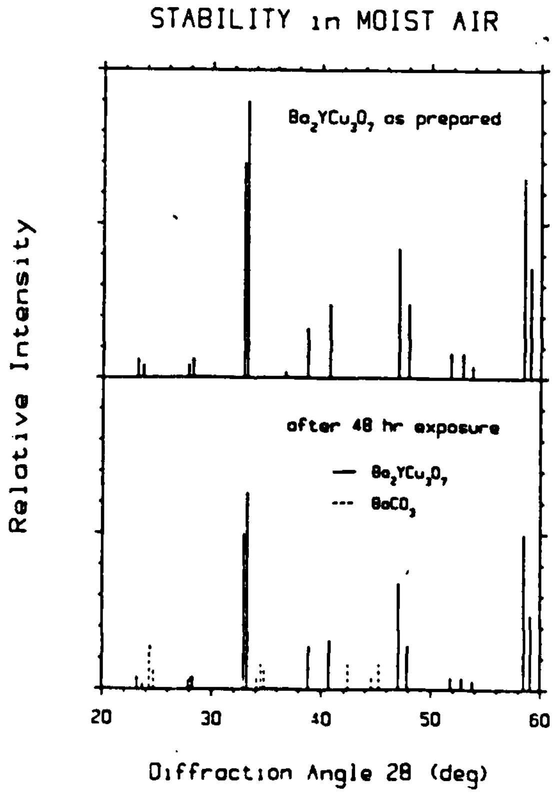

Fig. 6. X-ray diffraction patterns of $Ba_2YCu_3O_7$ as prepared for the nitrates and after 48 hrs of exposure to moist air, showing partial decomposition of the sample.

900°C for 24 hours.

An important part of the preparative procedure is annealing the phase formed at 900-950°C in a flowing oxygen atmosphere at 425°C. This step assures a product which closely approaches the stoichiometric composition of $Ba_2YCu_3O_7$. Samples which were annealed at 425°C in oxygen and allowed to cool slowly at 50°C/hr were analyzed by reduction in an 85%Ar/15%$H_2$ atmosphere. As determined from the measured weight loss, the formula may be represented as $Ba_2YCu_3O_{7.01(2)}$.

The electrical resistivity and magnetic susceptibility of these samples were measured as functions of temperature and the results are plotted in Figs. 4 and 5. As can be seen from Fig. 4, the resistivity data defines an extremely sharp transition at a temperature of 92 K. The superconducting nature of the compound below this temperature is verified by the Meissner effect evident in the susceptibility data shown in Fig. 5.

The pure samples of $Ba_2YCu_3O_7$ prepared from the nitrates were placed on a watch glass which was transferred to a desiccator containing water in place of the desiccant. After 48 hours, the sample was removed and subjected to visual and x-ray analysis. The black product contained numerous aggregated white particles. The x-ray analysis of the product is shown in Fig. 6 and indicates the formation of $BaCO_3$. These results would indicate that the product is attacked by moist air and the instability of $Ba_2YCu_3O_7$ will present problems for any practical device application.

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