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THERMAL ANALYSIS IN THE M-Ba-Cu-O SYSTEMS (M = Y, La, Pr) IN RELATION TO HIGH T_c SUPERCONDUCTORS.

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ABSTRACT

Metallographic, X-ray diffraction and differential thermal analyses were employed to scan suitable limited sections of M-Ba-Cu-O systems (M = Y, La, Pr) in order to determine the thermal stability of the occurring phases.

Particularly in the above systems the thermal stability and structural data of the bounding oxide Y_2O_3 - BaO, La_2O_3 - BaO and PrO_x - CuO systems are reviewed.

Significant results were obtained in determining the crystal structure of BaY_2O_4 phase ($CaFe_2O_4$ - type) and in the identification of a new phase in the BaO -La_2O_3 system.

INTRODUCTION

A large amount of data have been produced in the last few months starting from the discovery of the superconductivity above 30 K as initially reported by Bednorz and Müller[1] in a multiphase system having a nominal composition $La_{(5-x)}Ba_xCu_{5(3-y)}$. The superconducting phase was subsequently identified as $(La_{1-x}Ba_x)_2CuO_4$ with the K_2NiF_4 - type structure[2]. Successively a report of superconducting transitions near 95 K emerged [3,4]. In these initial papers, there was some confusion about the actual phase that was responsible for the superconductivity. Careful structural determinations and phase diagram studies resulted in the identification of the super-

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conducting phase as $Ba_2YCu_3O_{7-x}$[5]. Systematic work should be done in determining the thermal stability of the equilibrium phases occurring in the "ternary" diagrams of the ceramic oxides and using structural methods in determining their real composition. The present work is included in a program for synthesising and characterising superconducting ceramics.
We describe that our procedure of obtaining ceramic oxides started from the decomposition of BaO_2 instead of $BaCO_3$.

EXPERIMENTAL

A large number of samples of various compositions were prepared by a standard method used in our Laboratory [6] starting with Y_2O_3, La_2O_3 (3N pure) and Pr_6O_{11}(2N pure) thoroughly mixed with BaO_2 and CuO powders. The samples were sintered at 950°C in air for 12 hours, then furnace cooled.

X-ray powder diffraction patterns were obtained using a PW 1729 PHILIPS diffractometer. X-ray examination was carried out both on presintered materials and on DTA samples, after several cycles at different temperature rates.

Single crystals obtained from the melted and partially melted samples were analysed using both the standard X-ray techniques and an automatic ENRAF-NONIUS CAD-4 diffractometer.

DTA measurements were performed on the samples enclosed in Al_2O_3 crucibles using a NETZSCH instrument till a maximum temperature of 1500°C in an O_2 atmosphere(P = 1 atm).

Microscopic observation was carried out using a Leitz metallographic microscope in order to check the homogeneity of the samples.

RESULTS AND DISCUSSION

In figures 1, 2 and 3 the "binary" phase diagrams BaO - $YO_{1.5}$, BaO - $LaO_{1.5}$ and CuO - PrO_x are reported, showing part of the results obtained in this work from DTA, micrographic and X-ray investigations.

With filled triangles we have denoted thermal effects due to decomposition of high or low temperature phases. Open triangles correspond to chemical reactions detected by exothermic effects during the heating and endothermic effects during the cooling. The open squares are thermal effects due to the residual presence of the BaO_2 starting material.

In particular, we can examine separately the results obtained in the bounding oxide systems.

$BaO - YO_{1.5}$ system

The presintered powder materials present at the X-ray examination the pattern of BaY_2O_4, orthorhombic $CaFe_2O_4$ type with a = 10.394(3) Å, b = 3.450(1) Å, c = 12.113(4) Å. In the samples formed by solid state reaction at low temperature (up to 1000°C) the BaY_20_4 phase is always present, but it peritectically decomposes at about 1030 ± 10°C. Decomposed samples show the presence of the $Ba_3Y_4O_9$ till to room temperature, suggesting that this phase will be found metastable at low temperature. A pronounced hysteresis can be found also in the decomposition and peritetctic formation temperature of BaY_2O_4. The "$Ba_2Y_2O_5$" and "$Ba_4Y_2O_5$" phases reported by Roth et al. [7] were not detected, because they are in effect oxycarbonates ($Ba_2Y_2O_5.2CO_2$ and $Ba_4Y_2O_7.CO_2$) [8] and observable only when the preparation reaction involving $BaCO_3$ is followed.

$BaO - LaO_{1.5}$ system

The existence of $BaLa_2O_4$ was confirmed. Samples of $BaLa_2O_4$ were DTA analysed up to 1450°C: thermal effects were detected at 1010°, 1200° and 1380°C: the peritectic temperature of formation for $BaLa_2O_4$ is 1010 ± 10°C.

The presintered powder materials present at X-ray examination the pattern of $BaLa_2O_4$, while the pattern of partially melted samples appears to have more reflections.

The micrographic examination carried out on partially melted samples showed three phases in equilibrium, revealing that the oxygen activity here plays a very important role and that equilibrium cannot be considered only between BaO and $LaO_{1.5}$. Two of these phases were analysed by single crystal methods and the determination of the exact composition is in progress. The third phase gave twinned crystals and we are trying to determine at least the crystal symmetry.

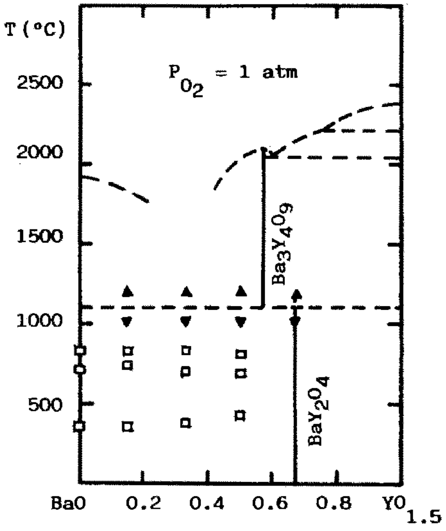

Fig. 1. The $BaO-YO_{1.5}$ system

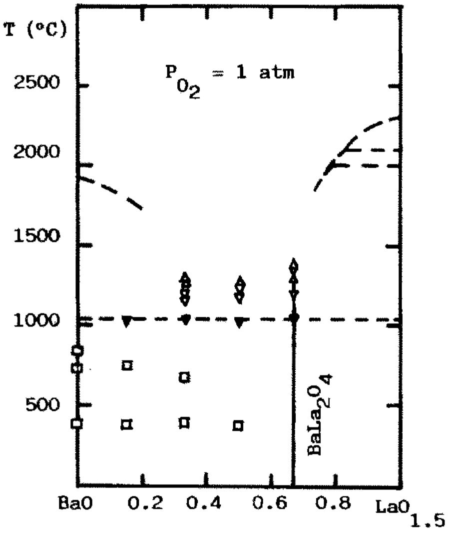

Fig. 2. The $BaO-LaO_{1.5}$ system

CuO - PrO_x system

The presence of at least one phase in the low temperature region , probably $Pr_2Cu_2O_5$, was confirmed. This oxide decomposes peritectically at 1010 ± 10°C. It seems that CuO region does not contain other phases, as X-ray patterns of the sintered samples show only the reflections of CuO and $Pr_2Cu_2O_5$ phases. The study of PrO_x region is in progress and appears more complex.

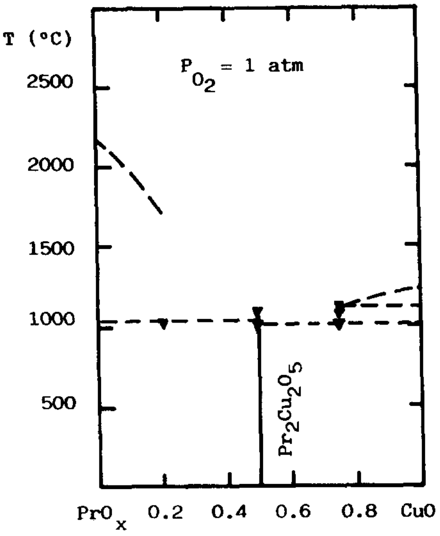

Fig. 3. The sketched $CuO-PrO_x$ system

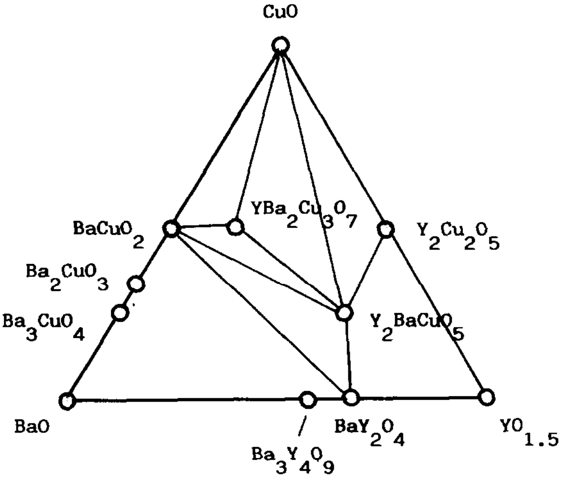

Fig. 4. The $BaO-YO_{1.5}-CuO$ 980°C isotherm

$BaO - YO_{1.5} - CuO$ system

The isotherm section (980°C) of the BaO - $YO_{1.5}$ system is reported in Fig. 4. The $YBa_3Cu_2O_{6.5}$ phase reported byin the literature [7] was not detected. The well known, yet cited, CO_2 stabilized phases were omitted. Also we omitted a number of phases, already reported in the literature [7,8,9] that could not be confirmed crystallographically.

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