J. Phys. IV France **11** (2001)
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The $Ca_{0.80}CuO_{1.93}$ phase: New way of synthesis by the sol-gel method

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Abstract. We report on the reaction kinetics for the $Ca_{0.80}CuO_{1.93}$ phase prepared by the sol-gel method using acrylamide for gelification. The phase was prepared 95% pure after a 2 hour treatment at 800°C. Comparative stability under vacuum and oxygen has been determined. The kinetics parameters for the decomposition have been established : the activation energy is E_a= 626 kJ/mol and the pseudo reaction order n = 0.5.

1. INTRODUCTION

In the course of a study on phase equilibria in the Tl-Ba-Ca-Cu-O system, we found that the $(Ca,Tl)_{1-x}CuO_z$ phase played a crucial role in the formation of the High-T_c superconducting cuprate $Tl_2Ba_2Ca_2Cu_3O_z$. This initiated further investigations on the CaO-CuO and CaO-CuO-$TlO_{1.5}$ systems. In a previous work [1,2], we discussed the formation conditions, the stability and the crystal structure of the $Ca_{0.80}CuO_{1.93}$ phase, parent compound for $(Ca,Tl)_{1-x}CuO_z$ discovered recently by Roth *et al.* [3]. We also showed (i) the difficulty to prepare this phase by classic powder metallurgy – a 100 hour treatment at 800°C in flowing oxygen with intermediate grindings is necessary to obtain a 93% pure sample - and (ii) the over-stoichiometry in oxygen which results in a mean valence for copper atoms of +2.28. However, due to slow formation and decomposition kinetics, the stability of the phase was not clearly established.

By using a sol-gel method which leads to starting powders with a submicronic grain size, we were able to reduce considerably the formation time and therefore to answer these opened questions.

2. THE PREPARATION OF THE SOL-GEL

In a first step, CuO and $CaCO_3$ were separately dissolved in concentrated nitric acid (65%) in the relevant proportion (Ca:Cu = 0.8:1). The copper cations were then complexed by ethylendiamintetraacetic acid (EDTA acid) in order to avoid a later reaction with acrylamide. After mixing the solutions, the pH was adjusted to 3 by addition of ammoniac. The second step is the formation of sol-gel at 80°C after addition of the polymerizing agents - acrylamide monomer, *i.e.* $(H_2C{=}CHCONH)_2$ and N,N'-Methylenebisacrylamide, *i.e.* $(H_2C{=}CHCONH)_2CH_2$ - and the organic initiator α,α'-Azoisobutyronitrile (AIBN), *i.e.* $C_8H_{12}N_4$.

The differential thermal analysis of the sol-gel showed that the decomposition of the organic compounds starts at 80°C and is completed at 350°C. It is accompanied by a 80% weight loss. For the regular processing of our powders, the firing temperature was fixed at 450°C which is high enough to remove all the organic compounds and too low to initiate the recrystallization of the oxides. The secondary electron picture of a fired sample is displayed in Fig. 1. Indeed, it reveals a grain size smaller than a micron, which means a high reactivity. This intermediate firing treatment avoids the appearance of a high porosity during sintering which would be detrimental to the formation of the $Ca_{0.80}CuO_{1.93}$ phase.

After the firing treatment, the organic free powder is pressed into a pellet and sintered at high temperature.

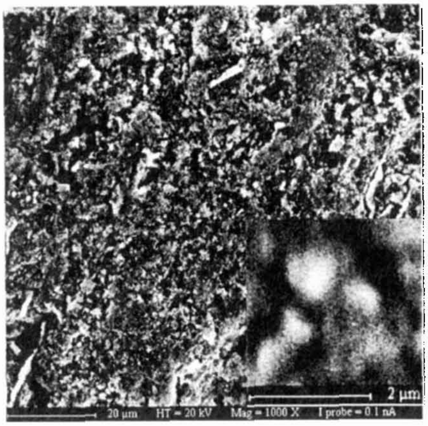

Figure 1. Secondary electron picture of the sol-gel fired at 450°C.

3. RESULTS AND DISCUSSION

3.1 FORMATION AND STABILITY OF THE $Ca_{0.80}CuO_{1.93}$ PHASE

The $Ca_{0.80}CuO_{1.93}$ phase is prepared by annealing the compacted powders at 800°C for 2 hours or at 850°C for 30 minutes in flowing oxygen. The X-ray diffraction patterns (Fig. 2) show that the samples are at least 95% pure, the main impurity phase being Ca_2CuO_3. The sintering time is therefore reduced by a factor of 50 with respect to that needed with the classic powder metallurgy.

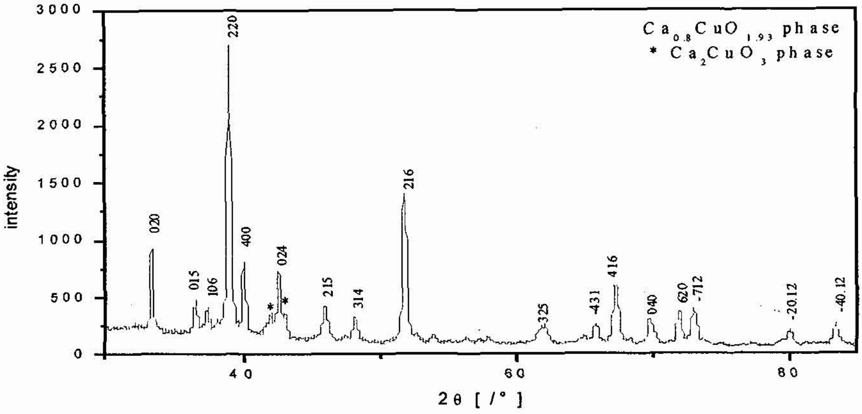

Figure 2. X-ray diffraction pattern of a $Ca_{0.80}CuO_{1.93}$ sample sintered for 2 hours at 800°C in flowing oxygen.

The differential thermal analysis and thermogravimetry analysis (DTA/TG), carried out in flowing oxygen, shows an endothermic decomposition at 920°C with a weight loss associated to oxygen departure (Fig. 3). This result confirms that the $Ca_{0.80}CuO_{1.93}$ phase does not belong to the CaO-CuO section of the Ca-Cu-O equilibrium diagram and the decomposition occurs with a significant delay as observed during our preview study [1,2]. However, high temperature X-ray diffraction experiments show that the phase is actually stable up to 870°C and decomposes into Ca_2CuO_3 and CuO above this temperature (Fig. 4). Under vacuum, the decomposition temperature is lowered to 720°C. The high reactivity and homogeneity of the powders obtained by the so-gel method lead us to prepare the two phases of the CaO-CuO system,

Ca_2CuO_3 and $CaCu_2O_3$. Besides the expected time reduction for the sintering treatment, no noticeable modification of the invariant lines in the equilibrium diagram (Fig. 5) has been observed.

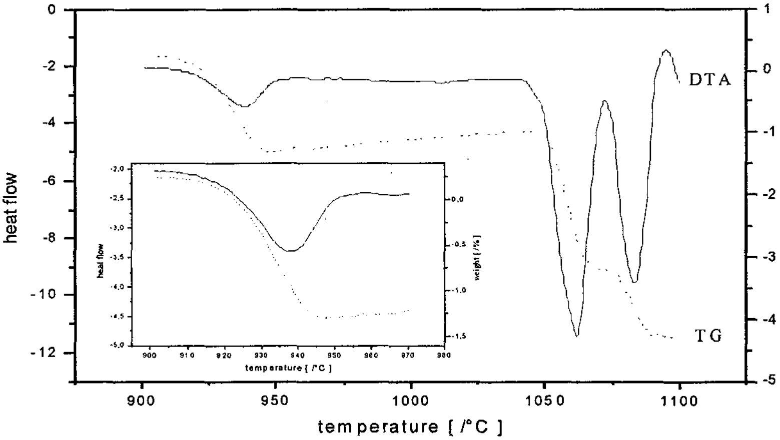

Figure 3. DTA/TG under oxygen flow of the $Ca_{0.80}CuO_{1.93}$ phase.

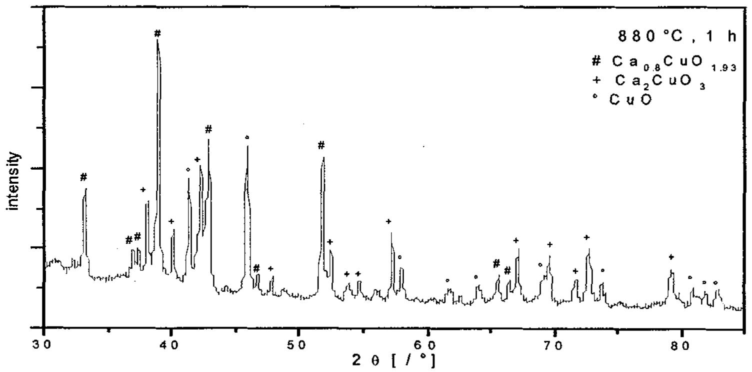

Figure 4. High-temperature X-ray diffraction pattern of a $Ca_{0.80}CuO_{1.93}$ sample after 1 hour at 880°C in flowing oxygen.

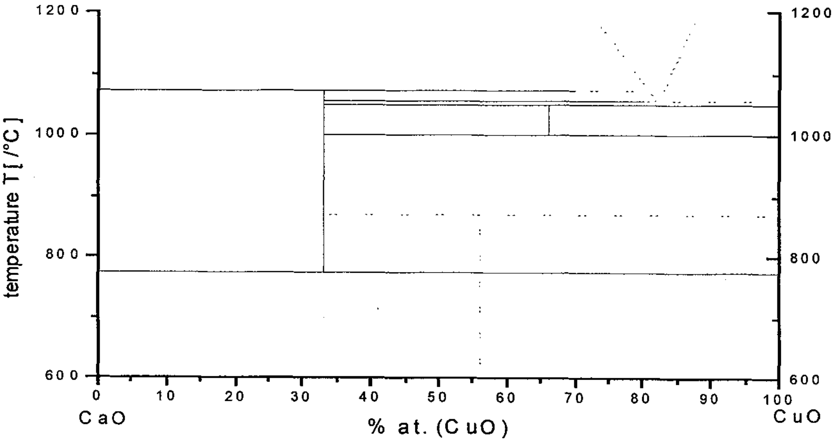

Figure 5. CaO-CuO phase diagram. The invariant relative to the decomposition of the $Ca_{0.80}CuO_{1.93}$ phase and the high temperature CuO rich region are drawn in dashed lines because they do not belong to the CaO-CuO equilibrium diagram.

3.2 DECOMPOSITION KINETCS OF THE $Ca_{0.80}CuO_{1.93}$ PHASE

The decomposition kinetics of $Ca_{0.80}CuO_{1.93}$ have been studied from a non isothermal analysis of the weight losses under vacuum, with a heating rate of $\beta = 5$ K/min. We used the same method as Phadnis and Deshpande [4] for the study of the decomposition of $CdCO_3$. This analysis consists in expressing the reaction rate $d\alpha/dt$ as a product of two functions: $f(\alpha) = (1-\alpha)^n$ which depends only on the proportion α of transformed phase and characterizes the decomposition mechanism, and the Arrhenius term $k(T)=k_0.\exp(-E_a/RT)$. Based on this model, the activation energy E_a is expressed as a function of the parameters T_{max}, α_{max} et $(d\alpha/dT)_{max}$ taken at the maximum transformation which allows us to establish the quasi-order n of the reaction.

Under vacuum, the $Ca_{0.8}CuO_{1.93}$ phase starts to decompose at 995 K. For $\beta = 5$ K/min, the decomposition is total at 1080 K. We found $n = 1/2$ which suggests a decomposition mechanism limited by a 2D diffusion process [5]. Such a process is compatible with structural data. Indeed both structures contain linear chains of edge-shared CuO_4 squares directed along a unique axis [2,6]. The transformation from $Ca_{0.80}CuO_{1.93}$ to Ca_2CuO_3 could occur by a diffusion of copper and oxygen atoms within the chain planes out of the structure of $Ca_{0.80}CuO_{1.93}$. The activation energy E_a deduced from the variation of $\ln[(d\alpha/dT)/(1-\alpha)^{1/2}]$ as a function of $1/T$ (insert Fig.6) in the linear range (1020 K < T < 1060 K) is 626 kJ/mol.

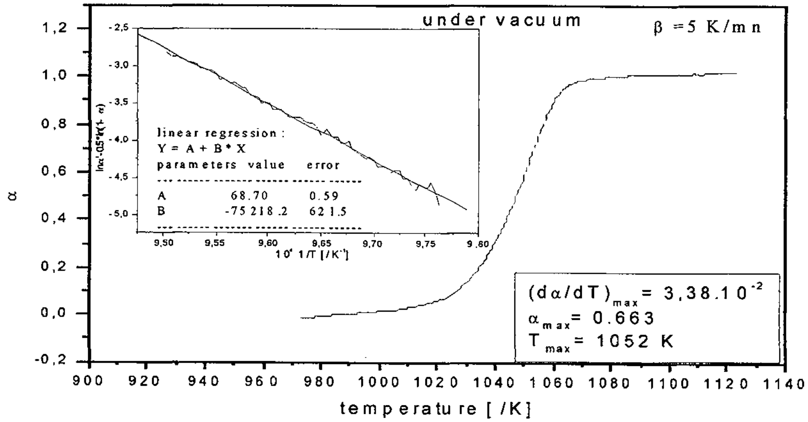

Figure 6. Variation of α as a function of $1/T$. Insert: $\ln(d\alpha/dt)-1/2\times\ln(1-\alpha)$ as a function of $1/T$.

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