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Synthesis, thermodynamics and electrical properties of non-stoichiometric $Ba_2CuO_{3+\delta}$

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Abstract

The oxide $Ba_2CuO_{3+\delta}$ was synthesized and a maximum oxygen content of 3.5 was found corresponding to an orthorhombic structure. The departure from stoichiometry was measured at various temperatures and the experimental results were interpreted in terms of two domains of oxygen vacancies. The electrical conductivity was measured in the same conditions and two behaviours were found, in good agreement with the departure from stoichiometry. © 1997 Elsevier Science S.A.

Keywords: $Ba_2CuO_{3+\delta}$; Non-stoichiometry; Electrical resistance; Activated conductivity

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1. Introduction

Since the discovery of high-T_c superconductors, compounds of barium cuprates have become important as the precursors to many series of superconducting families. In particular, Ba_2CuO_3 is a precursor for the synthesis of $HgBa_2CuO_4$. Very few studies [1–3] concern this oxide, but it seems to be non-stoichiometric and presents an orthorhombic–tetragonal transition. The orthorhombic structure was obtained by annealing the specimens at 1103 K for 50 h followed by slow furnace cooling. On the other hand, by quenching the samples from 1103 K, a tetragonal structure was observed. Above 1193 K a peritectic reaction liquid + BaO = Ba_2CuO_3 occurs.

The aim of this study is to measure the thermodynamic properties and the electrical resistance vs. the temperature and the oxygen content.

2. Experimental procedures

Appropriate amounts of BaO_2 (Aldrich 99%) or $BaCO_3$ (Cerac 99.999%) and CuO (Fluka 99.99%) powders were mixed in an agate mortar. The mixtures were calcined at 1173 K for 12 h in flowing oxygen. The calcined powders were pulverized, pressed into pellets and again sintered at 1173 K for 12 h. The samples were then slowly cooled to room temperature by furnace cooling. The samples were identified by the X-ray diffraction method using the Cu K_α radiation.

For the determination of the maximum oxygen content, an appropriate amount of $BaCO_3$ and CuO was carefully and finely mixed and pressed into a pellet to promote the solid state diffusion. This pellet put into an alumina crucible within a Setaram B60 thermobalance was heated at 1173 K for 3 days until the weight was constant according to the reaction:

$$2BaCO_3 + CuO + \delta/2O_2 \rightarrow 2CO_2 + Ba_2CuO_{3+\delta}.$$

Then the sample was slowly cooled in steps of 50°C. We assumed that the equilibrium was reached when the weight remained constant during a reasonable time related to the reaction kinetics (24–72 h). The equilibrium durations varied from 15 h at high temperature to 72 h at 573 K. We observed an increase of the weight down to 623 K. Starting from the maximum oxygen content, we performed thermogravimet-

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ric measurements under pure oxygen pressure to find departure from stoichiometry. The temperature was raised from 623 K to 1123 K.

For measurements of the electrical properties, a sample was prepared from fine powder pressed in the shape of a parallelepiped bar and sintered in pure oxygen at 1173 K. The length of the sample was 20 mm and the section 5 × 5 mm. The resistance R was measured by the four-wires DC method with a Keithley 191 multimeter. These measurements were carried out in the same conditions of temperature and oxygen pressure than in the thermogravimetric experiments.

3. Results

3.1. X-ray diffraction analysis

The X-ray diffraction pattern is shown in Fig. 1 and corresponds to an orthorhombic structure in good agreement with the results of Abbattista et al. [1] and Zhang et al. [2].

3.2. Thermodynamic properties

The maximum oxygen content was found to be 3.503 ± 0.005 that implies a valence state 3+ for Cu and the departure from stoichiometry was calculated from $\delta = 0.5$. The values are plotted in Fig. 2 and correspond to two domains. A low temperature domain (I) with small departure from stoichiometry and a high temperature domain (II) with large departure within a narrow temperature range.

3.3. Electrical properties

The experimental values of log R are plotted in Fig. 3. The results correspond also to two domains (I) and (II), in good agreement with the thermodynamic properties.

4. Discussion

4.1. Thermodynamic properties

The departure from stoichiometry can be interpreted in term of point defects. Starting from $\delta = 0.5$, when the temperature increases, the release of oxygen is related to the formation of oxygen vacancies according to the reaction, using the Kröger notation:

$$O_O^X \rightarrow V_O^{\bullet\bullet} + 1/2O_2 + 2e'$$

O_O^X is an oxygen on a normal site of the oxygen

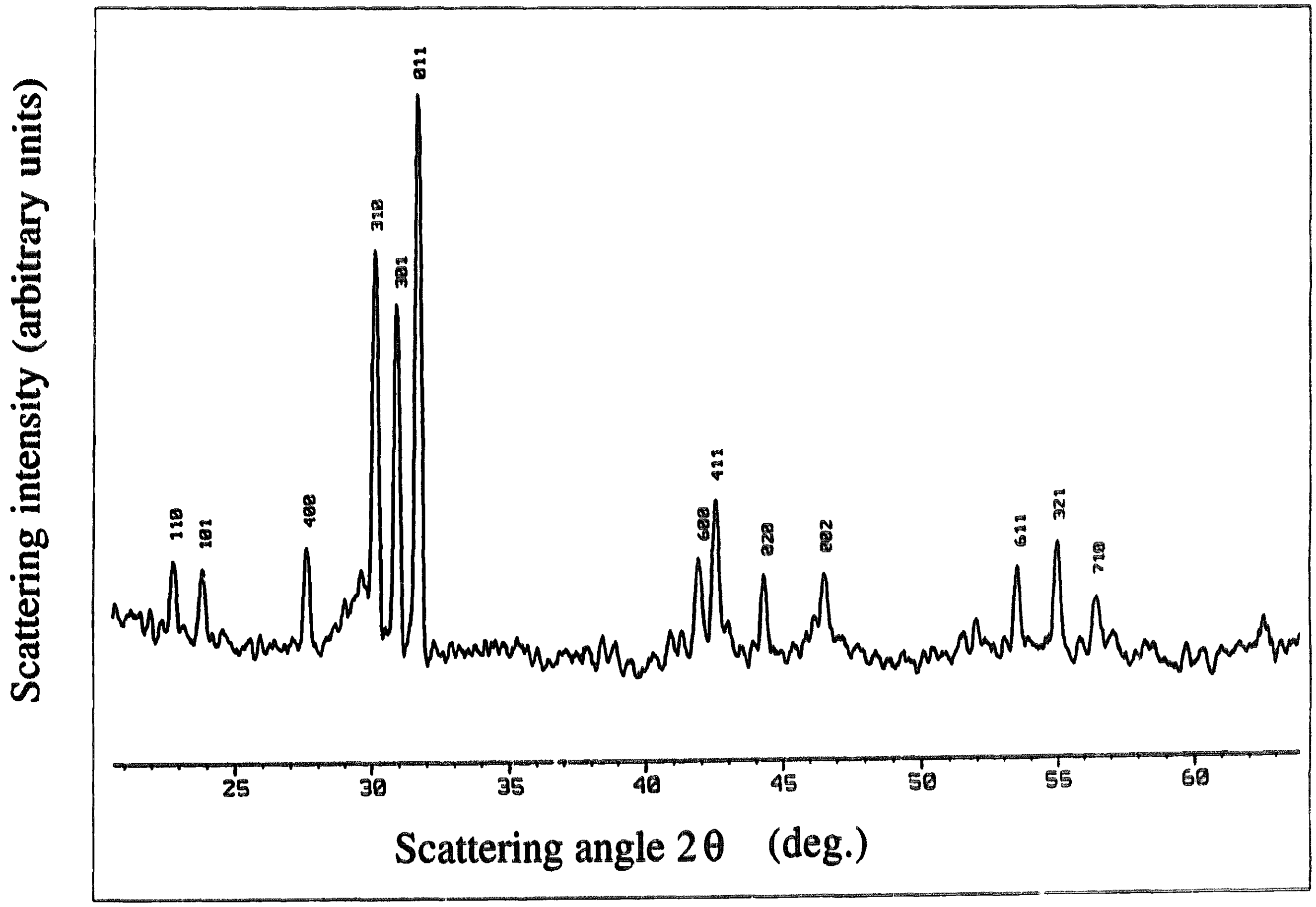

Fig. 1. X-ray powder pattern using Cu K_α – radiation for the orthorhombic Ba_2CuO_3 sample.

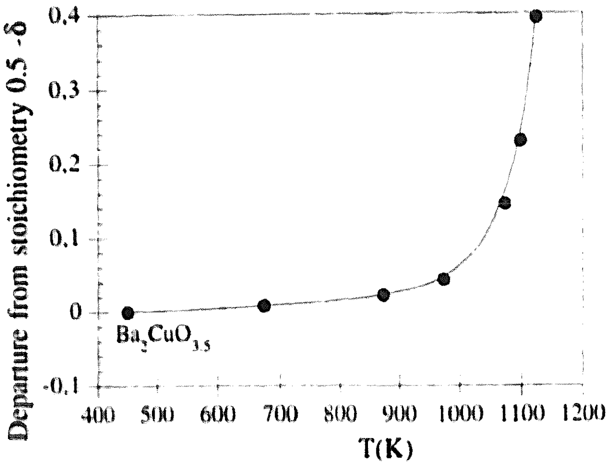

Fig. 2. Departure from stoichiometry $0.5-\delta$ vs. temperature (K).

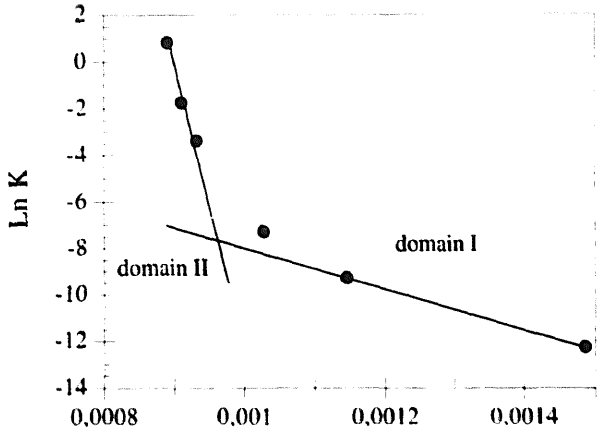

Fig. 4. Ln K vs. $1/T$.

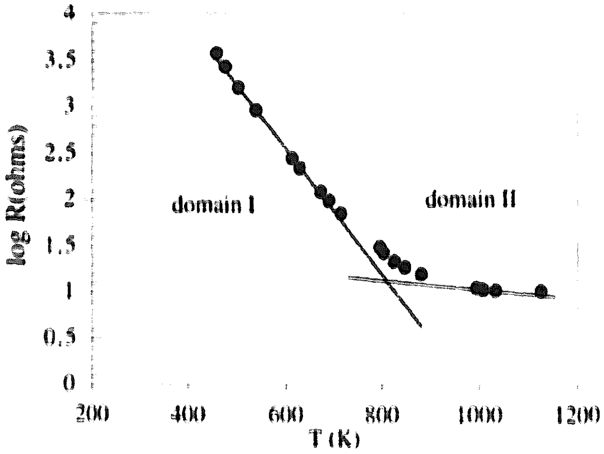

Fig. 3. Log R vs. temperature (K).

lattice, $V_O^{\bullet\bullet}$ is a doubly ionized oxygen vacancy and e′ is an electron released by the disappearance of an oxygen ion.

We can express the mass action law constant, substituting activities by concentrations:

$$K=\frac{[V_O^{\bullet\bullet}].[e']^2}{[O_O^X]}p_{O_2}^{1/2}$$

Expressing the concentrations in term of site fractions:

$$[O_O^X]=0.5-\delta \text{ and } [e']=2\delta$$

then

$$K=\frac{4\delta^3}{0.5-\delta}\cdot p_{O_2}^{1/2}\quad \text{with}(p_{O_2}=1\ \text{atm})$$

The values of ln K vs. $1/T$ are plotted in Fig. 4. The curve can be divided into two domains. The transition between the two domains occurs at approx. 770 K. In the domain (I), the departure from $Ba_2CuO_{3.5}$ stoichiometry is related to the release of oxygen from two sites of the orthorhombic structure. In the domain (II), the departure from stoichiometry is assumed to be related only to the occupancy of a single site of the tetragonal structure proposed by Zhang and Osamura [2]. From the van't Hoff relation, we calculate the formation enthalpy ΔH°_{VO} of these vacancies:

$$\Delta H^{\circ}_{VO}=-R\frac{d(\ln K)}{d(1/T)}$$

We obtain:

Domain (I): 0.9 eV (cf. $HgBa_2CuO_{4+\delta}$ 0.8 eV [4]).
Domain (II): 8.5 eV.

4.2. *Electrical resistance R*

In the domain (I) (Fig. 3), the decrease of the resistance is related to an activated process which may corresponds to a hopping process between the two oxidation states (polarons) whereas the high temperature domain (II) corresponds to a constant resistance. The activation energy for the polaron hopping was calculated from the slope of the experimental curve and corresponds to 0.3 eV.

5. Conclusion

The oxide $Ba_2CuO_{3+\delta}$ has an homogeneity range $0<\delta<0.5$ and may be considered as an oxygen deficient compound $Ba_2CuO_{3.5-x}$. The departure from stoichiometry is interpreted in term of oxygen vacancies, the formation enthalpy of which being as weak as in YBaCuO, 0.8 eV [5]. For a small departure from stoichiometry, the electrical conductivity may be explained by a hopping process whereas for a large departure, a constant resistance appears.

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