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Orthorhombic to tetragonal phase transition and superconductivity in $Ba_2Cu_3O_4Cl_2$

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The orthorhombic to tetragonal phase transition in $Ba_2Cu_3O_4Cl_2$ has been investigated. This transition was observed by X-ray powder diffractometry carried out in samples heat treated between 700 and 750 °C. Results of X-ray diffractograms simulation confirm the phase transition. *dc*-Magnetization measurements performed in SQUID showed the existence of a signal due to diamagnetism. The results suggest the existence of localized superconductivity and explain the different magnetic properties reported in the literature for the $Ba_2Cu_3O_4Cl_2$ compound.

Key words: *oxychloride; structural transition; diamagnetism*

1. Introduction

Copper oxyhalide compounds have received much attention in recent years because of their similar structures to high critical temperature (high-T_C) superconducting oxides. The discovery of superconductivity in $Sr_2CuO_2F_{2+\delta}$ [1] stimulated further effort in the area and many new copper oxyhalide systems have been fabricated [2]. Among them, $Ba_2Cu_3O_4Cl_2$ (Ba2342) is one of the most interesting materials. Ba2342 seems to be an insulator with a tetragonal structure (space group: *I*4/*mmm*) and lattice constants a = 5.517 Å and c = 13.808 Å. This compound crystallizes in a layered structure composed of Cu_3O_4, Ba and Cl layers [3]. The Cu_3O_4 layers contain two types of Cu sites: Cu_I and Cu_{II} sites. The Cu_I have an octahedral coordination with four square-planar oxygen ions in the basal plane, two chlorine ions at the apices, whereas the Cu_{II} ions are surrounded only by four square planar oxygen ions. On the other hand, it is known that the Cu_I spin is antiferromagnetically ordered and Cu_{II} is paramagnetically ordered at room temperature [4, 5]. The competition between these magnetic effects is considered to result in the multi-steps magnetic transitions in this compound. Furthermore, two magnetic transitions were observed in Ba2342; one at

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$T \sim 330$ K (denoted by T_H) and another at $T \sim 30$ K (T_L) [6, 7]. Between T_H and T_L, the compound displays weak ferromagnetism. Noro et al. [8] studied the effect of the substitution of Cu for Ni and reported the disappearance of a weak ferromagnetic moment which decreased drastically by introducing a small amount of Ni as a dopant.

In contrast to the exposed above, diamagnetism and metal-like behaviour have been observed for the Ba2342 compound at low temperatures which suggest the existence of superconductivity in this compound as reported previously by some authors [9, 10]. In addition, some other copper oxyhalide compounds are superconductors. Another important aspect is that most of the high-T_c superconductors have crystalline structure containing Cu–O layers with CuO stoichiometry. In particular, $YBa_2Cu_3O_{7-\delta}$ shows a phase transition from tetragonal to orthorhombic structure, which occurs near 700 °C in an oxygen atmosphere [11]. The critical transition temperature depends on the oxygen partial pressure and occurs when the stoichiometry is near $YBa_2Cu_3O_{6.5}$. The highest superconducting transition temperature ($T_C \sim 90$ K) is only observed for the orthorhombic structure [11]. In addition, some other copper oxyhalide compounds are superconductors [1, 12, 13]. Also, high-pressure synthesis (at GPa) has been responsible for inducing superconductivity in $(Ca, K)_2CuO_2Cl_2$ ($T_C = 24$ K) [14] and $(Ca, Na)_2CaCu_2O_4Cl_2$ ($T_C = 49$ K) [15].

In this paper, results of X-ray powder diffractometry are reported which suggest the existence of an orthorhombic to tetragonal transition in the $Ba_2Cu_3O_4Cl_2$ compound. Magnetic measurements show a diamagnetic signal, and are in agreement with previous results: this suggests the existence of localized superconductivity in this compound [9, 10].

2. Experimental

Polycrystalline samples of $Ba_2Cu_3O_4Cl_2$ were prepared by the solid state diffusion method using $BaCO_3$, CuO and $BaCl_2{\cdot}2H_2O$ powders of high purity. The powders were mixed, ground, calcined at 700 °C for 24 h, pressed into pellets, sintered at 750 °C for 48 h followed by cooling to room temperature. In addition, the samples were heat treated at 700 °C. The samples were characterized by X-ray powder diffractometry (Rich. Seifert-ISO Debyeflex 1001) which was carefully indexed using the reference [16]. The X-ray diffraction intensity data of 2θ were collected from 10 to 50°. A step-scan mode was adopted with a scanning step of 0.02° (in 2θ) and duration of 2 s. The samples were also characterized by scanning electron microscopy (Jeol -JXA840) with energy dispersive spectrometry (EDS) in order to study the granular structures and grain compositions of the samples.

Using the Powder Cell software [16] to calculate lattice parameters and to simulate X-ray powder diffractograms (XRD), we were able to study the experimental X-ray diffractograms and the influence of the heat treatment on the crystalline structure of the $Ba_2Cu_3O_4Cl_2$ compound.

Magnetization measurements were performed using a quantum design superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

Figure 1 shows the XRD for the $Ba_2Cu_3O_4Cl_2$ sample heat treated at 750 °C (a) and 700 °C (b). Both diffractograms display single phases, but a careful analysis of them shows the existence of distinct peaks for the sample heat treated at 750 °C, see for example 103 reflections in the insets. This result is an evidence for a phase transition from orthorhombic to tetragonal structure in the $Ba_2Cu_3O_4Cl_2$ compound. In order to confirm this phase transition we performed simulation for the tetragonal and orthorhombic X-ray diffractograms. We adopted the crystallographic parameters shown in tables 1 and 2 using the following space groups: *I*4/*mmm* and *Immm* for the tetragonal and orthorhombic, respectively. The orthorhombic symmetry (*Immm*) was chosen because it is a subgroup of *I*4/*mmm* and the atomic positions were based on the International Tables for Crystallography [16]. The lattice parameters were tested until the best agreement between experimental and simulated X-ray powder diffractograms was obtained.

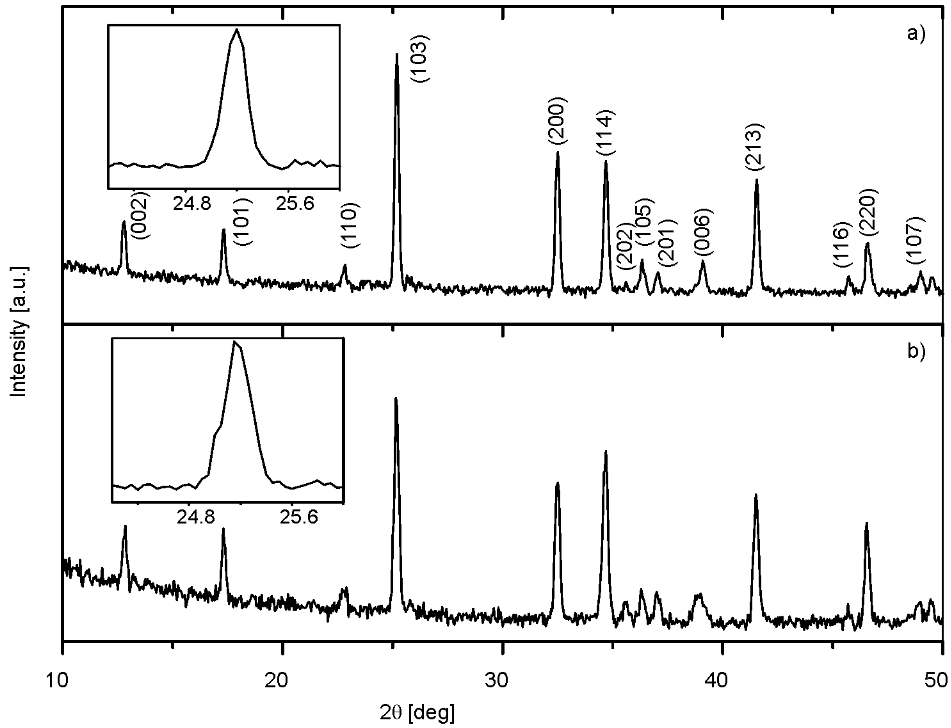

Fig. 1. Experimental diffractograms for the sample $Ba_2Cu_3O_4Cl_2$ heat treated at 750 °C (a) and 700 °C (b). Insets show 103 reflections

Table 1. Atomic positions for $Ba_2Cu_3O_4Cl_2$ with tetragonal (*I*4/*mmm*) and orthorhombic (*Immm*) symmetries [16]

Atom	*I*4/*mmm*	*I*/*mmm*	*x*	*y*	*z*
Ba	4e	4i	0.000	0.000	0.365
Cu1	4c	2d	0.000	0.500	0.000
Cu2	2a	2a	0.000	0.000	0.000
O	4d	4j	0.000	0.500	0.250
Cl	8h	4e	0.250	0.000	0.000

Table 2. Lattice parameters for $Ba_2Cu_3O_4Cl_2$ sample

Heat treatment temperature [°C]	Lattice parameters [Å]			Structure
	a	*b*	*c*	
750	5.5129	5.5129	13.8216	tetragonal
700	5.4902	5.5249	13.7925	orthorhombic

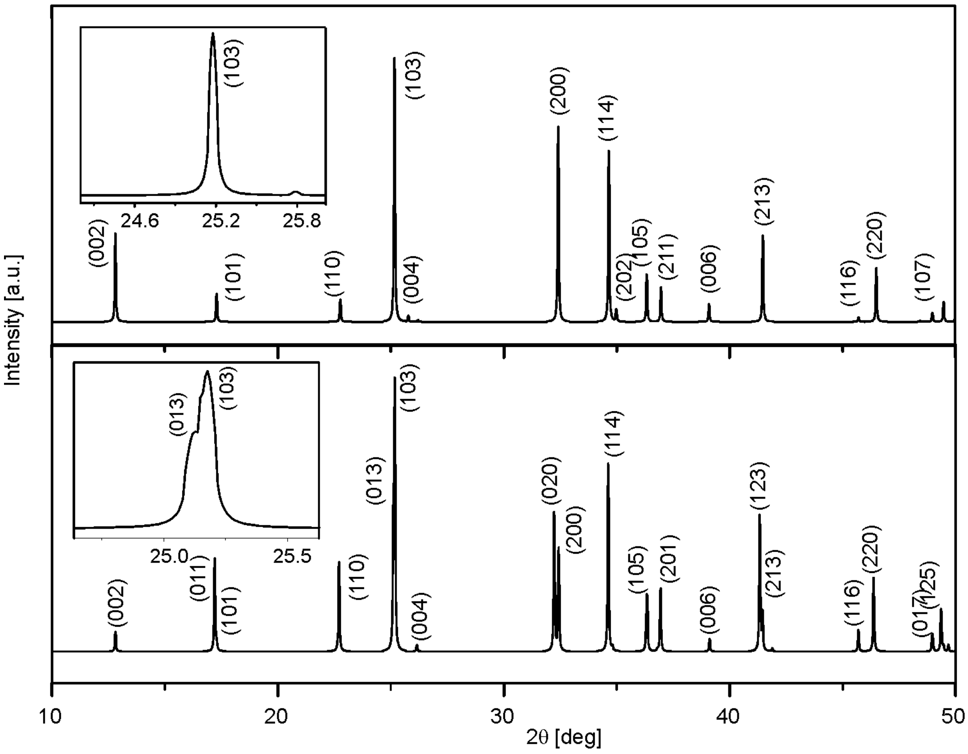

Fig. 2. Simulated X-ray powder diffractograms for the $Ba_2Cu_3O_4Cl_2$ with tetragonal (a) and orthorhombic (b) symmetries. Insets highlight the 103 simulated reflections

In Figure 2, we can observe that the result for the simulation of the tetragonal structure is in good agreement with the experimental X-ray powder diffractograms shown in Fig. 1. For the orthorhombic structure, we can see the appearance of double peaks (see for example the inset of this figure and also 200 reflections) which is similar to the sample heat treated at 700 °C (Fig. 1b). The similarities between experimental and simulated diffractograms suggest that this oxychloride system has a phase transition from orthorhombic (*Immm*) to tetragonal (*I*4/*mmm*) structure. We have noted that the X-ray powder diffractograms have some similarities with those of $YBa_2Cu_3O_{7-\delta}$ ceramic superconductor which also shows a phase transition as a function of oxygen content [11]. Thus, the phase transition observed in this work could explain the appearance of the diamagnetic signal and different magnetic properties reported for the $Ba_2Cu_3O_4Cl_2$ compound [9, 10].

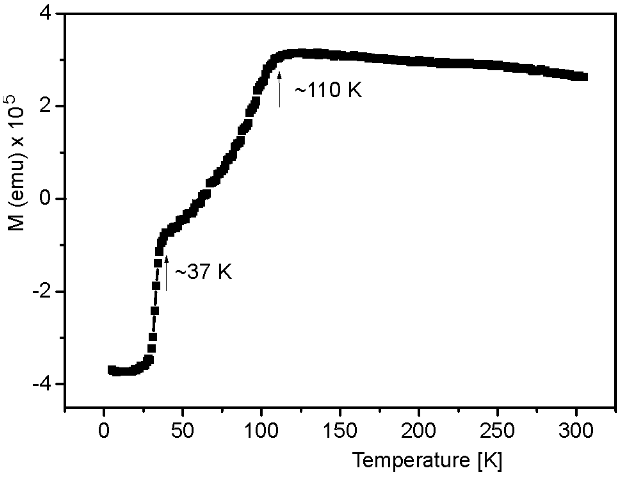

Fig. 3. Magnetic moment as a function of temperature for a $Ba_2Cu_3O_4Cl_2$ sample heat treated for 72 h at 700 °C

Figure 3 illustrates the temperature dependence of the magnetic moment for a sample of $Ba_2Cu_3O_4Cl_2$ heat treated at 700 °C (with orthorhombic symmetry). The presence of diamagnetism can be unambiguously observed, and it is in agreement with results reported previously [9, 10]. Thus, our results are another indication of the existence of superconductivity in the $Ba_2Cu_3O_4Cl_2$ compound. We suggest that the orthorhombic phase can be responsible for the diamagnetic behaviour, but the superconductor volume in this system is small and it is probably related to the coexistence between orthorhombic and tetragonal phases. We speculate that the high pressure synthesis would be able to stabilize the orthorhombic phase and promote the appearance of superconductivity in $Ba_2Cu_3O_4Cl_2$.

4. Conclusion

This work reports heat treatment effects on the $Ba_2Cu_3O_4Cl_2$ samples. We have observed the formation of double peaks in the X-ray diffractograms of $Ba_2Cu_3O_4Cl_2$

samples heat treated at lower temperatures, which were interpreted as a consequence of a structural transition in this compound. Simulations of X-ray powder diffractograms confirm this idea and suggest that the phase transition is related to a change from orthorhombic to tetragonal structure. dc-Magnetization measurements performed in SQUID showed the existence of diamagnetism in the signal. The structural transition and the diamagnetism suggest the existence of superconductivity and can explain the different magnetic behaviors reported in the literature about the $Ba_2Cu_3O_4Cl_2$ compound.

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