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Diamagnetism and Structural Transition in the $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ Compound

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This work presents a study of structural and magnetic properties of the $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ (Ba2342) compound. Doped samples with K or Sr in the Ba site and Zn or Mg in the Cu site of the Ba2342 were prepared using a solid state diffusion method. They were characterized by X-ray powder diffractometry, scanning electron microscopy and *dc*-magnetization. Samples with Ba2342 composition presented tetragonal structure of the $I4/mmm$ space group when heat-treated at 750°C . A structural transition was observed when the samples were doped with Zn or Mg or heat-treated at 700°C . *dc*-Magnetization measurements performed in SQUID showed the existence of diamagnetic signal. A difference of the magnetic moments measured at zero field cooled (ZFC) and field-cooled (FC) procedures was observed suggesting the existence of localized superconductivity in this oxy-chloride system.

I Introduction

In the last years great attention has been given to the study of the magnetic properties in the $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ (Ba2342) compound, specially due to the presence of copper-oxygen planes with Cu_3O_4 stoichiometry and distance between Cu-O atoms similar to the high-critical temperature ceramic superconductors (1.95 \AA) [1-5]. The Ba2342 compound is reported to have tetragonal structure of the $I4/mmm$ space group and two kind of Cu atoms in the crystalline structure. Due to this structure several authors have reported different magnetic effects [2-7]. To obtain information about the influence of the La in the Ba site, recently, Jinhua Ye *et al.* [8] presented results showing a diamagnetic transition close to 20K and a metal like behavior to the electrical resistance in the normal state. They argued that this behavior was caused by the substitution with La^{3+} .

Thus, in order to obtain more information about magnetic and structural properties of Ba2342, we have doped this compound with K or Sr in the Ba site and Zn or Mg in the Cu site and performed measurements of X-ray powder diffractometry, scanning electron microscopy, *dc*-magnetization and electrical resistance.

II Experimental procedure

Samples with $\text{Ba}_{2-x}\text{K}_x\text{Cu}_3\text{O}_4\text{Cl}_2$ ($0 \leq x \leq 0.1$), $\text{Ba}_{1.8}\text{Sr}_{0.2}\text{Cu}_3\text{O}_4\text{Cl}_2$, $\text{Ba}_2\text{Cu}_2\text{ZnO}_4\text{Cl}_2$ and $\text{Ba}_2\text{Cu}_2\text{MgO}_4\text{Cl}_2$ nominal composition were prepared

by solid state diffusion method using SrCO_3 , BaCO_3 , $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, CuO , K_2O , ZnO and MgO powder of high purity. These powders were grounded in the appropriated amounts and calcined at 650 - 700°C . After this procedure, the calcined powders were compacted into pellets at 500 MPa and sintered between 700 and 750°C depending on starting composition. All prepared samples were characterized by X-ray powder diffractometry, electrical resistance and *dc*-magnetization measurements performed in a SQUID (Quantum Design) in the zero field cooled (ZFC) and field cooled (FC) procedures. Some samples were also characterized by scanning electron microscopy accomplished with energy dispersive spectroscopy (EDS).

III Results and discussion

Fig. 1 presents X-ray diffractograms for the $\text{Ba}_{2-x}\text{K}_x\text{Cu}_3\text{O}_4\text{Cl}_2$ system. The (hkl) presented in the top of the Fig. 1 is in agreement to the Kipka and Buschbaum reference's [1]. We can see that the samples are single phase in the x range of K doping. At the same heat treatment, we also observe that an increase of K composition to $x = 0.15$ produces impurity phases in this system. Using these x-rays diffractograms we can calculate the lattice parameters. Fig. 2 shows a slow increasing of the *a* and *b* parameters, therefore, *c* axis decreases as a function of the K content, suggesting an approximation of the Cu-O planes. Sample with $\text{Ba}_{1.8}\text{Sr}_{0.2}\text{Cu}_3\text{O}_4\text{Cl}_2$ heat treated at 700°C for 48 hours

presents a similar x-ray powder diffractogram such as non-doped sample. When, samples were doped with Zn or Mg and heat treated at 730°C , one can see an enlargement of some peaks. Fig. 3 shows results to the doping with ZnO for a sample with $\text{Ba}_2\text{Cu}_2\text{ZnO}_4\text{Cl}_2$ nominal composition. We observe that there is in this sample minor ZnO impurities (see \square symbol). Therefore, we can relate the others peaks with the Ba2342 structure. Results of scanning electron microscopy and EDS provide that the Zn is effectively incorporated into the grains. Essentially, the same results were obtained to the Mg doping.

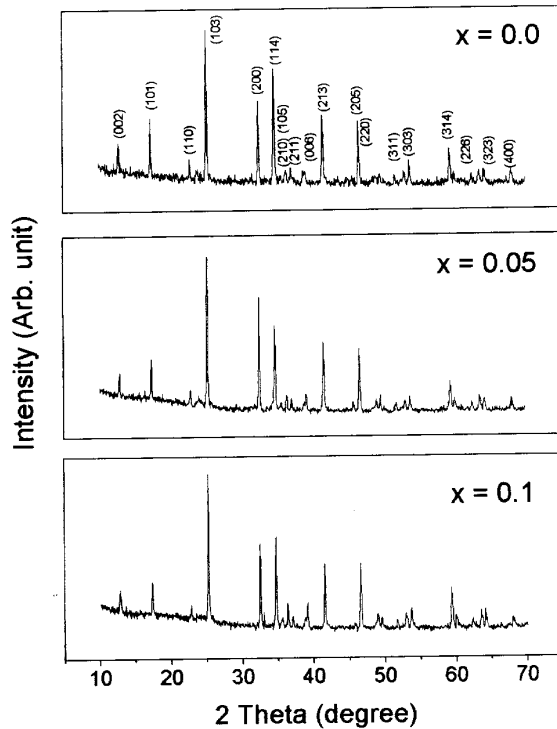


Figure 1. X-ray diffractograms for the $\text{Ba}_{2-x}\text{K}_x\text{Cu}_3\text{O}_4\text{Cl}_2$ system.

On the other hand, in order to verify if there is the same split of peaks to non-doped samples, we have performed heat treatments at 700°C . Fig. 4 presents a resume to the (103) and (114) peaks for several compositions heat treated at different temperatures. We can observe the presence of enlarged peaks for the samples heat treated at lowest temperatures. In Zn-doped sample treated at 730°C (Fig. 4 c), we can unambiguously observe two peaks for each (hkl). These results suggest that there is a phase transition in this oxy-chloride system. Preliminary results of powder diffraction simulation, suggest that this behavior is related to a tetragonal to orthorhombic phase transition with decreasing temperature, which is similar to the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ transition [9].

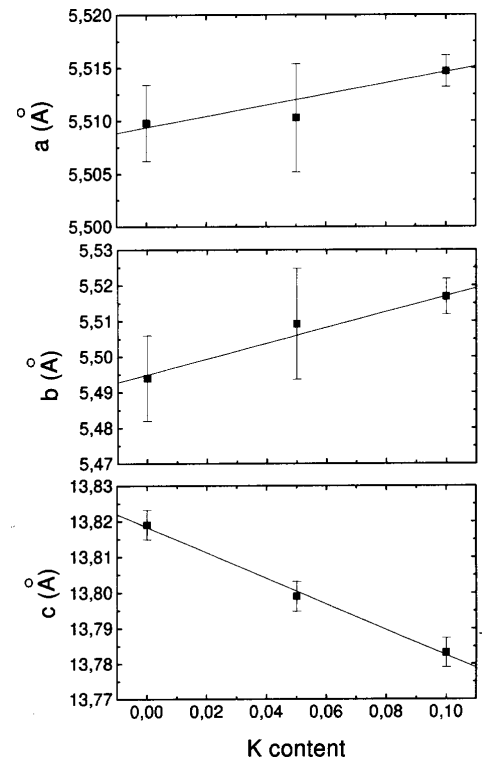


Figure 2. Lattices parameters for the $\text{Ba}_{2-x}\text{K}_x\text{Cu}_3\text{O}_4\text{Cl}_2$ system.

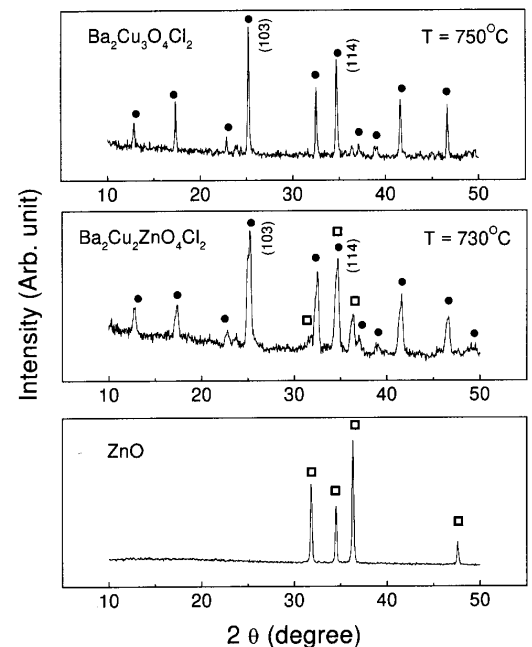


Figure 3. X-ray powder diffractograms for $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ (top) and $\text{Ba}_2\text{Cu}_2\text{ZnO}_4\text{Cl}_2$ (middle) samples. In bottom is presented the diffractogram of the ZnO phase.

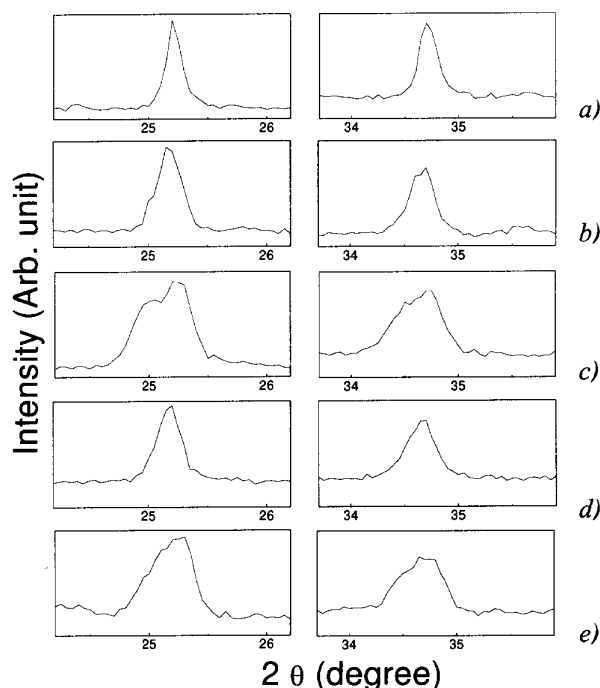


Figure 4. Zooming of the (103) and (114) peaks for the following nominal compositions and heat treatments: a) $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ at 750°C , b) $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ at 700°C , c) $\text{Ba}_2\text{Cu}_2\text{ZnO}_4\text{Cl}_2$ at 730°C , d) $\text{Ba}_2\text{Cu}_2\text{ZnO}_4\text{Cl}_2$ at 750°C and e) $\text{Ba}_2\text{Cu}_2\text{MgO}_4\text{Cl}_2$ at 730°C .

Finally, in order to verify the magnetic behavior of this system, we have performed several *dc*-magnetization measurements in SQUID. In Fig. 5 is presented some ZFC and FC magnetization curves as a function of temperature measured at 20 Oe. Depending on the sample composition, we can observe a diamagnetic signal accomplished with two transitions close to 30 K and 100 K. The most important fact of these magnetization measurements is related to the existence of difference between ZFC and FC curves. This can indicate the presence of superconductivity in this system. To verify this possibility, transport properties were performed using standard four-probe method, which demonstrated that all samples are insulators below room temperature. These results suggest that if there is superconductivity in the samples it must be localized in the crystalline structure [10].

IV Conclusion

This work presents the doping effects of K, Sr, Zn and Mg atoms on the Ba2342 compound. The doping studies provide a split of the peaks, which was interpreted as an experimental evidence of a phase transition in this oxy-chloride system. *dc*-Magnetization measured as a function of temperature presented diamagnetic signals in the some samples. A difference of

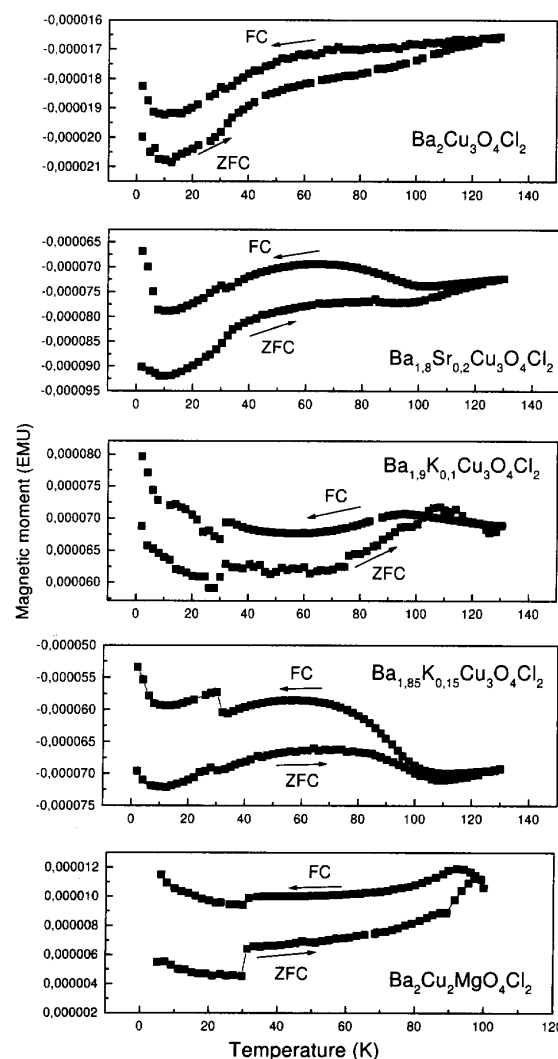


Figure 5. Magnetic moment as a function of temperature measured at 20 Oe for several starting nominal compositions. The difference of ZFC and FC magnetization suggests the existence of superconductivity in the Ba2342 system.

ZFC and FC procedures were interpreted as a evidence of localized superconductivity in the Ba2342 compound.

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