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The effects of Ag, Mg, and Pr doping on the superconductivity and structure of BSCCO

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Abstract

The influence of Ag, Mg, and Pr additions and co-additions on microstructure and phase formation of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+d}$ (Bi2212) system is investigated. Polycrystalline Bi2212 samples were synthesized in air by solid state reaction method. Phase analysis, micro structural observations and magnetic properties were carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM) and A.C. susceptibility measurements respectively. XRD results reveal two main phases (Bi-2201 and Bi2212). SEM photographs show that the substitution by Ag, Mg or Pr affects the mechanism of the grains growth. The undoped sample has a critical temperature T_c of 65 K while in the Mg and Ag containing compounds the T_c is 77 K and 75 K respectively. The Pr containing compound exhibits no superconductivity. A valence of the Pr ion higher than 3^+ in the lattice supports the hole-filling mechanism of the suppression of superconductivity.

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1. Introduction

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+d}$ (Bi2212) is one of the most promising superconducting materials for wires and magnets due to its chemical stability and flexibility in the manufacturing process. Its applications in high fields and high temperature are limited by weak flux pinning properties and resulting reduced critical current density J_c . High anisotropy, large penetration depth and short coherence length may explain the weak flux pinning properties. In the highly two-dimensional structure of Bi2212, superconducting CuO_2 layers alternate with weakly conducting thick blocking layers. The coupling between the CuO_2 layers is controlled by these blocking layers [1]. Various groups report an improvement of flux pinning in Bi2212 single crystals heavily doped by Pb in Bi sites. Pb doping increases

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the *c*-axis conductivity by more than one order of magnitude. Partial substitution of Bi by Pb reduces structural modulation and also enhances *J_c* and the irreversibility field [2]. The normal state and superconducting properties of Bi2212 doped by rare earth (RE) have been widely studied by many groups [1]. These studies were carried out in many forms of samples, such as bulk polycrystalline forms prepared by solid-state synthesis and melt texturing, thin films or single-crystalline samples. The majority of such studies concluded that RE substitution improves the structural stability of Bi2212 and induces a change and even suppression of the critical temperature *T_c* [2]. A size effect has been seen in the values of the rates of suppression of *T_c* with substitution by non-magnetic Pr⁴⁺ in the Cu(2) sites in the CuO₂ layer. Many methods have been developed to increase flux pinning in Bi-system superconductors. One of the methods is introducing artificial defects, such as dislocations, oxygen vacancy, irradiation damage zones or various second-phase particle additions into these superconductors to provide extra flux pinning centers. B. Zacho et al showed that, below 20K, flux pinning in Bi2212 and YBa₂Cu₃O_{7-y} crystals is enhanced by introduction of nanometer sized MgO particles [3-5].

The aim of this work is to describe the effect of different additions and co-additions on structural and magnetic properties of Bi_{1.8}Pb_{0.4}Sr_{2.0}Ca_{1.1}Cu_{2.1}M_xO_y (M = Ag, Mg, Pr, Ag+Mg, Ag+Pr).

2. Experiment

Doped (Bi_{1.8}Pb_{0.4}Sr_{2.0}Ca_{1.1}Cu_{2.1}M_xO_y where M=Ag, Mg, Pr) and co-doped (Bi_{1.8}Pb_{0.4}Sr_{2.0}Ca_{1.1}Cu_{2.1}M_xO_y+0.05AgNO₃ where M = Mg, Pr) samples were prepared by a solid state reaction method using high grade purity powders of Bi₂O₃, PbO, SrCO₃, CaCO₃, CuO, MgO, AgNO₃ and Pr₆O₁₁. The rate *x* of the added element is 0.05 for Mg and Ag and 0.22 for Pr in both the doped and the co-doped samples. The powders were mixed, ground and calcined at 820C° during 20 h in alumina crucibles. The calcined mixtures were then reground, pressed into pellets and sintered at 840C° during 60 h in order to obtain the Bi_{1.8}Pb_{0.4}Sr_{2.0}Ca_{1.1}Cu_{2.1}O_{8+d} (Bi(Pb)2212) precursor. The obtained sintered pellets were ground to form a fine powder. Micrometer MgO, AgNO₃ and Pr₆O₁₁ particles were added, mixed and ground with the Bi(Pb)2212 precursor. Pellets having 13 mm in diameter and 1 mm in thickness were formed under an uniaxial pressure of 5ton/cm³. The crystal structure of the obtained samples was characterized at room temperature by X-ray powder diffraction (XRD). The calculation of *a* and *c* lattice parameters was achieved using Dicvol 06 software. The susceptibility of the samples was measured on a homemade AC magnetometer using a closed cycle helium cryostat.

3. Results and discussion

The XRD patterns of the obtained samples are shown in figure 1. The detected phases are the main phase Bi2212 accompanied by parasitic phases Bi2201 and Ca₂PbO₄. These patterns show that the addition of Ag and Mg+Ag (co doping) reduces the volume fractions of Bi2201 and Ca₂PbO₄ parasitic phases. Bi2201 is frequently observed as a major impurity phase in Bi2212 samples. The hypothesis that, as it was shown by E. Guilmeau et al [6] for Bi2223 samples, the added Mg and Ag particles do not react with Bi2212 grains is not verified when a Bi(Pb)2212 precursor phase is used. We note also that, in Mg and Ag co-doped sample, the peaks are sharper with an increased intensity. The co-doping with Mg and Ag gives a higher crystalline grade.

Doping the Bi(Pb)2212 phase with Mg, Pr or Pr+Ag gives more dramatic results as revealed by the XRD patterns shown in figure 1. The changing or the disappearance of the peaks of the Bi(Pb)2212 precursor phase shows that

there is a reaction between that phase and the added elements. The addition of MgO transforms the Bi(Pb)2212 phase in a minor phase. With the addition of Pr₆O₁₁ alone or together with AgNO₃ the Bi(Pb)2212 phase disappears giving way to another structure with some peaks of Bi2212. Some small extra peaks may be indexed to Ca₂PbO₄ and CuO phases.

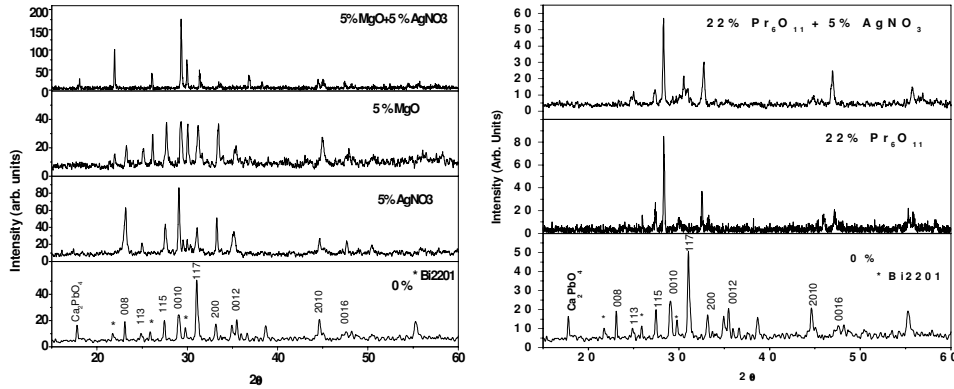


Fig.1. XRD patterns of Bi(Pb)2212 samples doped and co-doped by Mg and Ag (left) and by Pr and Ag (right).

There is a reaction between that phase and the added elements. The addition of MgO transforms the Bi(Pb)2212 phase in a minor phase. With the addition of Pr_6O_{11} alone or together with AgNO_3 the Bi(Pb)2212 phase disappears giving way to another structure with some peaks of Bi2212. Some small extra peaks may be indexed to Ca_2PbO_4 and CuO phases.

The XRD patterns have been indexed to a tetragonal unit cell. The variations of the lattice parameters versus the doping element are shown in figure 2. The effect of the added element on the structure of the samples is evident from this figure. As shown by the XRD patterns, there is not a great change in structure when Ag or Ag+Mg is added. The change in structure is important when Mg, Pr or Ag+Pr is added. The c axis cell parameter has an important decrease when these elements are added. Its value (about 21.48 Å) is near the value of the Bi2201 phase c axis cell parameter but with a axis cell parameter very different. The lowering of the c axis cell parameter (15.37 Å and 14.24 Å) is more important when Pr or Pr+Ag is added. These important reductions of the c axis cell parameter

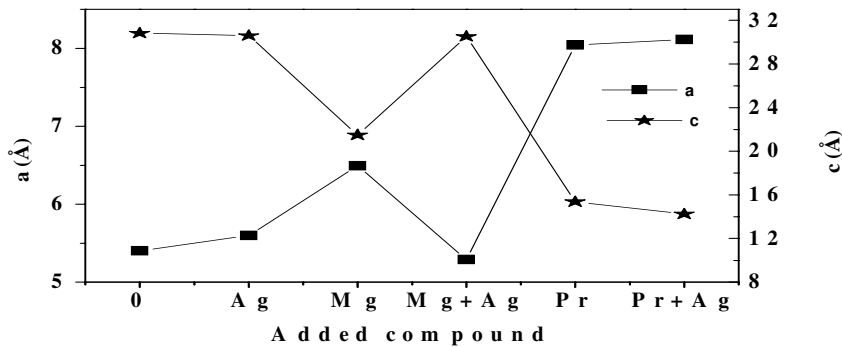


Fig.2 Variation of *a* and *c* cell parameters versus the different elements added to Bi(Pb)2212 (the lines are put for guide eyes). The concentration is 5% for Ag and Mg and 22% for Pr.

cannot be the result of an electrostatic effect between the Bi-O layers [7] induced by a charge balancing of the added element. It is not also a size effect of the added element. Mg and Pr have been added successfully at higher concentrations but without the use of a precursor phase [7] or in the free lead Bi2212 phase [8,9]. Using a precursor Bi(Pb)2212 phase and unsuitable temperatures and heat treatment cycles may lead to a reaction between the precursor and the added oxide as it is evident from our results. As it has been showed by C.A.M. dos Santos et al

[9], the Mg and Pr added samples need more time of heat treatment and a better choice of temperature to obtain a pure Bi(Pb)2212 phase.

The figure 3 shows the dependence in temperature of the AC magnetic susceptibility of the samples. This dependence is showed for a temperature varying between 40 and 80 K for the undoped and Ag and Mg doped samples and between 5 and 80 K for the Pr and Pr+Ag doped samples. The superconductivity is confirmed in the Ag and Mg added samples. These two samples show that the addition of Ag or Mg improves the superconducting properties enhancing the T_c (from about 60 K for the undoped sample to 77 K and 75 K for the Ag and Mg doped samples respectively) and also the apparent superconducting volume fraction. The susceptibility of the Mg doped sample shows also that the Bi(Pb)2212 phase is present but with reduced apparent superconducting volume fraction. This confirms the needing of more time of heat treatment for this sample.

For the Pr and Pr+Ag doped, the AC susceptibility measurements confirm the results obtained by the XRD analysis. The samples are not superconductive but show an antiferromagnetic behaviour with a Neel temperature T_N growing (from 27.65 K to about 55.65 K) when Ag is added.

These results show that the supply of extra oxygen to the growing phase through the decomposition of AgNO_3 has not the same effect when AgNO_3 is used alone or together with MgO or Pr_6O_{11} . In this last case, more time of heat treatment is needed because we started with a Bi(Pb)2212 precursor phase.

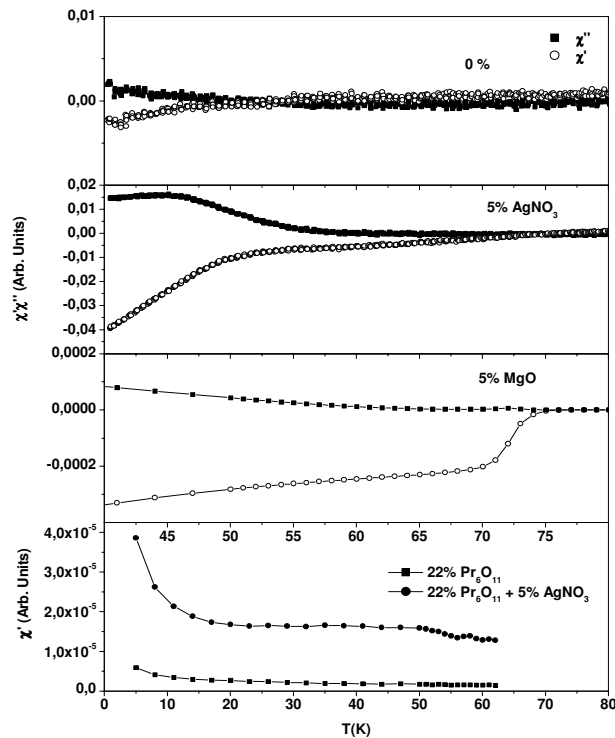


Fig.3. Real (χ') and imaginary part (χ'') of the AC susceptibility dependence in temperature of $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{1.1}\text{Cu}_{2.1}\text{M}_1\text{O}_x$ samples (M= Ag, Mg, Pr and Pr+Ag).

4. Conclusion

This work demonstrates that AgNO_3 or $\text{MgO} + \text{AgNO}_3$ particles with concentrations of 5% can be successfully embedded into the matrix of $(\text{Bi,Pb})_{2212}$ superconductors. The apparent superconducting volume fraction increases when AgNO_3 is added. Significant enhancement of T_c is observed when 5% of MgO is added but there is a reaction between the added element and the $(\text{Bi,Pb})_{2212}$ precursor phase. A reaction with the precursor phase is also observed when Pr particles (concentration of 22%) are added, alone or together with 5% of AgNO_3 , and non superconducting phases are obtained.

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