Role of dopants in Bi-Sr-Ca-Cu-O system

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Abstract. The role of Al and Ag dopants in the nominal composition, 4336 of Bi-Sr-Ca-Cu oxide has been studied, using a new chemical phase analysis method known as differential dissolution besides XRD and resistivity and magnetic susceptibility measurements. Our investigation reveals that (a) it is relatively easy to realize high- T_c phase (2223) in both Al- and Ag-doped samples with the same nominal composition and heat treatment history (b) both samples consist of superconducting phases with more or less the same basic composition and equal amounts, (c) 2112 phase may be a superconductor and (d) superconducting properties with Al and Ag dopants are different.

Keywords. High-temperature superconductivity; Bi-Sr-Ca-Cu-O; dopants, differential dissolution phase analysis, polytypoid structures; long-range ordering.

1. Introduction

It is well known that there are two high temperature superconducting phases in the family of Bi-Sr-Ca-Cu-O (Maeda *et al* 1988). They are three-layered structures with a chemical composition, $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ and a superconducting transition temperature, T_c of 110–115 K (high- T_c phase) as well as a double perovskite-layered phase, $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ with T_c of 75–85 K (low- T_c phase). The latter is formed relatively easily. Recently it was shown that the high- T_c phase precipitates at the interface between the eutectic products—low- T_c phase and Ca_2CuO_3 phase—and is controlled by calcium and copper diffusion (Shi *et al* 1989). Therefore many attempts were made to realize high- T_c single phase with a careful sintering schedule of proper composition in the narrow temperature range and/or with dopants (Jin *et al* 1988; Green *et al* 1989; Kanai *et al* 1989; Reddi *et al* 1989a,b). But there is little information on such dopants whether they merely act as catalysts in the nucleation and growth process and/or whether they participate in the crystal lattice of high- T_c phase. Only a part of the information could be obtained using diffraction techniques.

In the present study, we have followed a new technique, namely differential dissolution (DD) phase analysis, based on the theoretical background laid by one of the present authors (Malachov 1986, 1989). This method, unlike other diffraction methods, identifies the phases not by their crystal structure but by their composition. It also gives information about the phases present and the degree of dispersion of solute in the material. The advantages of this method have been described elsewhere (Vasilyeva *et al* 1990). The electrical resistivity and susceptibility were measured along with X-ray analysis to monitor the relationship between superconducting transition temperature and the phases present in the sample. In this paper, the role of dopants, Ag and Al on the nominal composition of $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_6\text{O}_x$ under identical conditions of synthesis is reported.

2. Experimental

Specimens with nominal compositions of $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_6\text{O}_x$ (hereafter called Bi), $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_6\text{Al}_{0.2}\text{O}_x$ (Bi-Al) and $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_6\text{Ag}_{0.2}\text{O}_x$ (Bi-Ag) were prepared from powders of Bi_2O_3 , CuO , Al_2O_3 , SrCO_3 , CaCO_3 and metallic silver of not less than 99% purity. They were calcined at 782°C for 24 h followed by grinding and calcination first at the same temperature for 14.5 h and then at 800°C for 145 h in air. Tablets made from such calcined powders were sintered in air at 848°C for 119 h.

Nitric acid was used as a solvent in the DD method. Total dissolution of the specimen was achieved in about 30 min, by which time up to 50 samples of the solution with 1–2 ml volume were taken and all the elements except oxygen determined. Bi, Ca, Cu, Al and Ag were determined by the method of atomic absorption while Sr was found by flame emission or by atomic emission analysis of the solutions, using the method of inductive plasma. X-ray phase analysis was done on diffractometer (DRON-3M, USSR make) with filtered CuK_α radiation.

Electrical resistance was measured with In-Ga paste contacts in the standard four-point configuration and the temperature dependence of dynamic susceptibility $\chi' - i\chi''$ measured using the mutual inductance method (Maxwell 1965).

3. Results and discussion

A series of parametric dependences for each sample were set out from the data generated in DD method. The total number of parametrical dependences was determined by the number of pair combinations of all the elements except oxygen. The data on parametrical dependences were obtained from the number of moles of each elements in the pair transforming into the solution from the specimen at every moment of time. Thus the number of parametric dependences (c) is determined by the following formula, $c = m/2(m - 2)$ where m is the number of elements (except oxygen) making the sample. There were 6 dependences for undoped (figure 1) and 10 for Ag or Al-doped samples (figure 2) in our work. From these parametric dependences, their inter-relationship and kinetic data and qualitative and quantitative information on phase composition were obtained. As shown in figure 2, the specimens, Bi-Al and Bi-Ag have nonlinear segments, indicating combined dissolution along with neighbouring phases during the corresponding period. The phase uniformly distributed in the sample and dissolved at the end (last phase) has approximate composition, $\text{Bi}:\text{Sr}:\text{Ca}:\text{Cu} = 1.5\text{--}2.0:0.5\text{--}0.8:0.7\text{--}0.9:2$. This phase probably acquires an intergrowth structure, which is characteristic for this class of material (Tallon *et al* 1988). The composition of the main phase was determined sufficiently accurately from the largest segment of parametrical dependence and was found to have $\text{Bi}:\text{Sr}:\text{Ca}:\text{Cu}:\text{Ag}(\text{Al}) = 1:1:1:1.5:0.08(0.05)$. It represents the phase $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (2223). Therefore the presence of Al(0.05) and Ag(0.08) in 2223 phase was confirmed. A part of Ag remained as a separate phase, may be in the form of metallic silver. Besides Ag, copper and calcium oxides in highly dispersed state were found in the Bi-Ag sample. These may be the products of secondary processes like substitution, decay and degradation, and that they are not segregated but dispersed uniformly throughout the sample.

The remaining matrices, also called equilibrium matrices (figure 3), give full information of phase compositions of the sample where the data of total mole amount of

Figure 1. Parametric dependences of the elements in the undoped sample.

Figure 2. Parametric dependences of the elements in Ag-doped (O) and Al-doped (●) samples.

Figure 3. Balance matrices of (a) undoped, (b) Al-doped and (c) Ag-doped samples.

each component except oxygen, obtained in the DD method is represented by the rows with the columns showing the elements present in the specimen.

As pointed out earlier (Vasilyeva *et al* 1990) X-ray analysis reveals that the main high- T_c phase is affected only in the presence of Ag or Al. XRD patterns show the differences between Ag- and Al-doped samples. These differences are associated with classical polytypoid phase, 2223. The alloying with Ag or Al leads to subsequent demarcation of polytypoid order. Addition of Al causes local deformation of phase lattice 2223. It is possible that the polytypoid phase of 2112 may also occur with these dopants.

Presence of these dopants in phases and oxides of copper and calcium and their spatial distribution affects the superconducting properties. According to $R(T)$ and the

Table 1. Superconducting transition temperature and transition width (ΔT_c) of high- $T_c(T_{c1})$ and low- $T_c(T_{c2})$ phases obtained from resistivity and susceptibility measurements.

Specimen	$R(T)$ measurement				$\chi'(T)$ Measurement	
	T_{c1}	T_{c2}	ΔT_{c1}	ΔT_{c2}	T_{c1}	T_{c2}
Bi					95	78
Bi-Al	107	70	5	10	104	87
Bi-Ag	110	80	3	3	107.5	79

real part $\chi'(T)$ measurements, there are two superconductive transitions indicating the presence of two superconducting phases in the Bi-Al and Bi-Ag specimens with predominant high T_c -phase T_{c1} . It may be stated that another phase with approximate composition of 2112, detected by us is superconducting at the lower temperature, T_{c2} . Other parameters like width of the transition of high (ΔT_{c1}) and low (ΔT_{c2}) superconducting phases are shown in table 1.

It is clear from the table that the superconducting properties of these samples are markedly different from each other depending on the nature of the dopant. Though, in general, high-transition temperatures are observed in both the doped samples, the transition width is greater in the Al-doped sample due to the effect of greater local distortion caused by the presence of aluminium.

It may be noted that the $R(T)$ data on Bi-Ag indicate higher content of high- T_c phase, 2223 which does not agree with that of $\chi'(T)$ and the DD method. Further two interesting peculiarities are observed in the Ag-doped sample. $T_c(R=0)$ changes with increase in the sample current density when it is 0.3 A/cm² or more. It is considerably less than the critical current in the ceramic samples indicating the weak links of intergranular boundaries in the Bi-Ag sample. The second peculiarity is related to the growth of dome (cupola) on the $R(T)$ curve at 85 K with increase in current density. This shows the presence of phase shunt with $T_c \simeq 85$ K and high temperature phase which is supplied with increased current density. This observation agrees with our earlier remark on the blocking of dispersion segments of low- T_c phase with high- T_c phase, 2223. In other words, there are intergrowth structures in the sample. It may be pointed out that the superconducting properties of Bi-Ag sample are similar to lead-doped sample (Kravchenko *et al* 1990).

4. Conclusion

The study of superconducting properties of doped samples with their phase composition reveals the effect of alloying that leads to the formation of different polytypoids with high- T_c phase 2223, a varied degree of local lattice distortion of the superconducting phases and a sharp spatial distribution of impurity phases in the specimens. The degree of long-range ordering that distinguishes one polytypoid from the other also determines the superconducting properties. Such a correlation found by us using the DD method clearly focusses the importance of long-range ordering in the Bi-based systems. Our work also points the need for other alloying elements that would stabilize the orderly arranged multilayer structure in Bi-based high- T_c phase.

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References

- Green S M, Mei Y, Manzi, Luo H L, Ramesh R and Thomas G 1989 *J. Appl. Phys.* **66** 728
Jin S, Sherwood R C, Tiefel T H, Kammlott, Fastnacht R A, Davis M E and Zahurak 1988 *Appl. Phys. Lett.* **52** 1628
Kanai T, Kamo T and Matsudo S 1989 *Jpn J. Appl. Phys.* **28** L551
Kravchenko V S et al 1990 *Izv. Sib. Br. Acad. Sci. Series* (accepted)
Maeda H, Tanaka Y, Fuzitomi M and Asano T 1988 *Jpn J. Appl. Phys.* **27** L209
Malachov V V 1986 *Dokl. Acad. Sci. USSR* **290** 1152
Malachov V V 1989 *J. Anal. Chem.* **19** 1177
Maxwell E 1965 *Rev. Sci. Instrum.* **36** 533
Reddi B V, Bezverkhy P P, Bogoljubov N A, Martynets V G and Matizen E V 1989a Preprint
Reddi B V, Romanenko A I, Mirunov Yu I, Kozeeva L P, Shaburova V P and Fedorov 1989b Preprint
Shi D, Tang M, Vandervort K and Claus H 1989 *Phys. Rev.* **B39** 9091
Tallon J L, Buckley R G, Gilberd, Presland M R, Brown I W M, Bowden M E, Christian L A and Goguel R 1988 *Nature (London)* **333** 153
Vasilyeva I G, Reddi B V, Boldireva N N, Kuropjatnik I N, Romanenko A I and Malachov V V 1990 *Superconductivity: Physics, Chemistry and Engineering* (Moscow) (accepted)