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Influence of ZnO doping on superconductivity and crystal structure of (Bi, Pb)-2223 superconductor

Tomoyuki Kozuka [a,*], Hirotaka Ogawa [a], Akinori Kan [a], Akio Suzumura [b]

[a] *Faculty of Science and Engineering, Meijo University, 1-501 Shiogamaguchi, Tempaku-ku, Nagoya 468-8502, Japan*

[b] *Department of Mechanical and Aerospace Engineering, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552, Japan*

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Abstract

The crystal structures of the high-T_c (2223) phase with ZnO were refined using Rietveld analysis in order to clarify the possibility of Zn substitution for Cu sites. In addition, the effects of ZnO doping on the Bi-2223 phase were investigated by means of evaluations of the superconducting properties. From the results of the Rietveld analysis, it is suggested that the variations in the lattice parameter are mainly due to those in the atomic distances of the CuO_5 pyramid induced by Zn substitution for Cu(2) site in the Bi-2223 phase, indicating the lattice parameters, *b* and *c*, of the ZnO-doped Bi-2223 phase by increasing ZnO content are decreased, whereas the lattice parameter *a* is increased. The solid-solubility of Zn in the Bi-2223 phase is estimated $\sim$2 wt.% from the variations in the lattice parameters. From the experimental results of the ZnO-doped Bi-2223 phase, it was clarified that the melting temperature of the Bi-2223 phase is lowered and critical temperature (T_c) is not affected.

Keywords: Oxide superconductors; Powders: solid state reaction; Superconductivity; X-ray methods; ZnO

1. Introduction

Ag and/or Ag_2O additions to the Bi-system superconducting ceramics are known to improve mechanical properties and critical current density (J_c), and known to be favorable for the phase evolution in the Bi-2223 phase.[1–3] Therefore, Ag is widely used as a sheath material for processing Bi-2212 and Bi-2223 tapes and/or wires. However, a study of other element additions to the Bi-system superconducting ceramics, which have the same functions as Ag and/or Ag_2O additions, may prove useful in making a progressive use of the Bi-2212 and Bi-2223 phases.

On the other hand, there are a few reports concerning Zn substitution for Cu in the crystal structures of the Bi-system superconducting ceramics.[4–6] Akoshima et al.[4] reported an anomalous suppression of superconductivity and transport properties which exhibit less metallic behavior than usual in the Zn-substituted $Bi_2Sr_2(Ca_{1-x}Y_x)(Cu_{1-y}Zn_y)_2O_{8+\delta}$. Anisotropic transport properties due to Zn substitution for Cu of the Bi-2212 phase were reported by Jeon et al.[5] In the case of Zn substitution for Cu of the Bi-2223 phase,[6] however, there are no reports regarding the solid-solubility of Zn in the Bi-2223 phase and the details on ZnO doping.

This paper provides some details of the crystal structures of the ZnO-doped Bi-2223 phase which are refined to elucidate whether Zn substitution for Cu sites in the crystal structure takes place or not, using the Rietveld method.[7] Moreover, the effects of ZnO additions on superconductivity in the Bi-2223 phase are investigated.

2. Experimental

The high-T_c (2223) phase of a nominal composition $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_{10+x}$ was prepared by the conventional solid-state reaction method, using the powders of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO of 99.9% purity as the starting materials.[8] The powders weighed by stoichiometry were mixed in acetone, pressed into pellets, i.e. 12 mm in diameter and 2 mm thick under a pressure of 100 MPa, and sintered at 850°C for 120 h after calcining at 800°C for 30 h in air. They were then

* Corresponding author. Tel.: +81-52-832-1151; fax: +81-52-832-1253.

E-mail address: c3003012@meijo-u.ac.jp (T. Kozuka).

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reground, ZnO powder of 99.9% purity ranging from 0 to 50 wt.% was added, and mixed in ethanol. Subsequently, these ZnO-doped samples were pressed into pellets and heated at sintering temperatures that were determined by differential thermal analysis (DTA) for 30 h.

DTA curves were taken upon heating at a rate of 5°C/min to determine the partial melting temperatures for the ZnO-doped and undoped samples. The phases of the synthesized materials were identified by X-ray diffraction (XRD), using CuK_α filtered through Ni foil. The lattice parameters and crystal structures of the Bi-2223 phase with ZnO were refined using the Rietveld analysis program, RIETAN.[9] The transport current and electrical resistivity were measured by a standard four-probe method for bar-shaped specimens (~10×0.7×0.4 mm^3) cut from the sintered pellets, and the measurements of critical current density (J_c) were carried out at 77 K and 0 T with 1 μ V/cm criterion.

3. Results and discussion

Fig. 1 shows DTA curves of the high-T_c (2223) phase with ZnO as a function of temperature. The partial melting temperature of the ZnO-doped samples were observed at the endothermic reaction peak with an onset temperature, at which temperatures are ~20°C lower than the undoped sample regardless of ZnO content. Therefore, it was observed that the Bi-2223 phase melts at a lower temperature with ZnO doping, as well as Ag and/or Ag_2O doping.[10]

The refined XRD patterns of the samples with and without 50 wt.% ZnO sintered at 840°C for 30 h are shown in Fig. 2. The X-ray peaks obtained from the undoped sample appeared to be mainly the Bi-2223 phase, containing 2.15 wt.% Bi-2212 phase estimated by using a quantitative phase analysis.[11] Then, ZnO peaks increased by increasing ZnO content in the Bi-2223 phase and no peaks resulting from compounds containing Zn were detected, except for ZnO.

The lattice parameters obtained from the Rietveld analysis of the ZnO-doped samples are shown in Fig. 3, from which it can be seen that the lattice parameter *a*

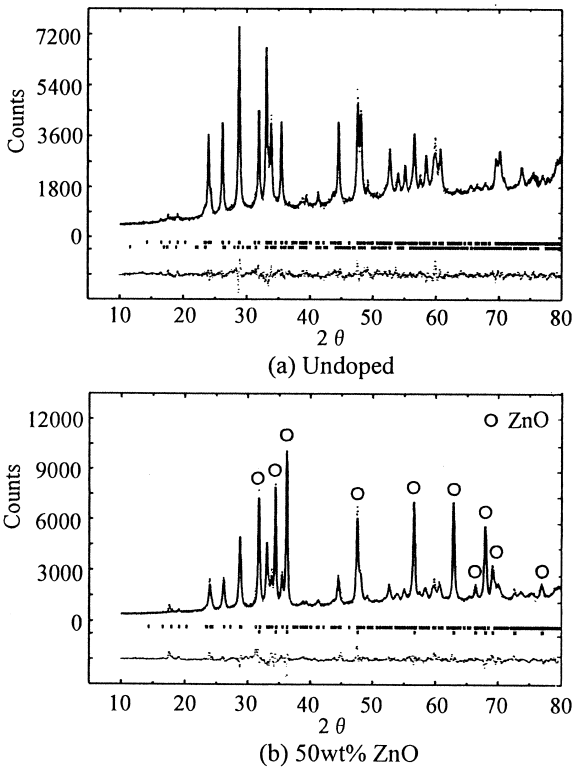

Fig. 2. Refined XRD patterns of (a) undoped sample and (b) 50 wt.% ZnO-doped sample.

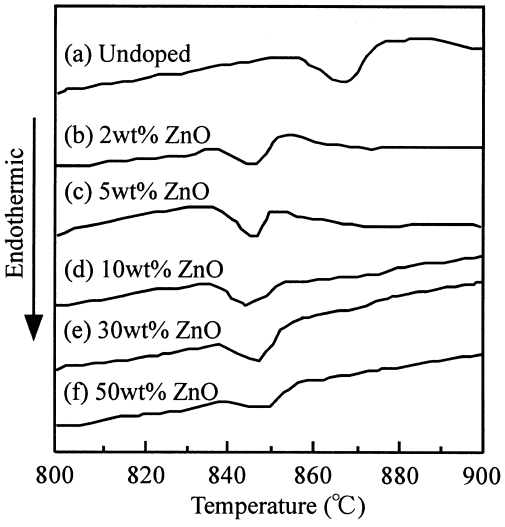

Fig. 1. DTA curves of ZnO-doped samples as a function of temperature.

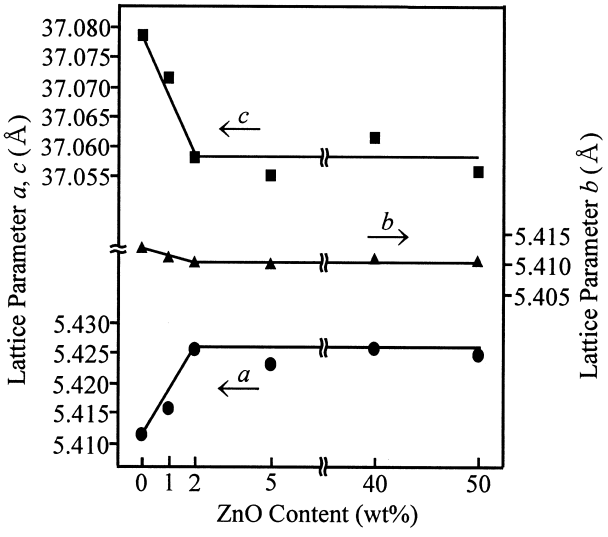

Fig. 3. Lattice parameter versus ZnO dopant content for the Bi-2223 phase.

has increased, whereas the lattice parameters b and c are decreased as ZnO content increased. Therefore, from the variations in the lattice parameters, the solid-solubility of Zn in the Bi-2223 phase is considered to be equal to ~ 2 wt.%. Thus, the solid-solubility of Zn indicates that these variations in the lattice parameters are closely related to the ionic radius of Zn ions and to the substitution site of Zn in the crystal structure of the Bi-2223 phase.

The phase (*Cccm* No.66) has an orthorhombic crystal structure with a $Cu(1)O_4$ plane and two $Cu(2)O_5$ pyramids placed between two $(Bi,Pb)_2O_2$ planes. In order to clarify the Zn substitution site in the crystal structure, the possibility of Zn substitution was discussed by using the Hume-Rothery rule and ionic radius reported by Shannon. As a result, the possibility of Zn^{2+} ions being substituted for Cu^{2+} ions of Cu(1) or Cu(2) site was suggested in this study. However, it was not made clear which particular site of Cu^{2+} ions is replaced by Zn^{2+} ions. Then, in order to determine the Zn substitution site, the calculations of the bond valence sum were carried out by using the bond strength parameter obtained by Brown et al.[12] The bond strength s is given by the following equation:

$$s = (R_o/R)^N \quad (1)$$

where R and R_o are the cation-oxygen bond and average bond lengths respectively, and R_o and N are empirical constants. The ionic valences are easily assessed because they equal to the sum of each bond strength between cation and oxygen. The bond strength parameters and cation-oxygen atomic distances obtained by using the Rietveld method were substituted into Eq. (1), and the ionic valence estimated of Cu(2) site was 2.52. This value indicates that Cu ions in Cu(2) sites are divalent and/or trivalent. Furthermore, by calculating the valences of Cu(1) and Cu(2) sites of the $Bi_2Sr_2Ca_2Cu_3O_{10}$, it was confirmed that the valence of Cu(1) site equals to $+1$ and the valences of Cu(2) sites do to $+2$ and $+3$ because the total valence of the three Cu sites has to be $+6$, and the Cu(1) site is single in the Bi-2223 phase, whereas the Cu(2) site is double. This suggests that Zn^{2+} ions are substituted for Cu^{2+} ions in Cu(2) sites.

Table 1 shows the results of the atomic distances and bond angles in the MO_5 (M = Cu(2) and/or Zn) pyramid refined by the Rietveld analysis, and Fig. 4 shows the MO_5 pyramidal structure. The atomic distance of M-O(4) which is nearly parallel to the c-axis and those of O(3)-O(2′) and O(2)-O(3′) in the direction of the b-axis are decreased respectively, whereas those of O(3)-O(2) and O(2′)-O(3′) in the direction of the a-axis are increased by Zn substitution for Cu(2). In this manner, the variations in the atomic distances and bond angles for the MO_5 pyramid are nearly similar to those on the lattice parameters. Therefore, the variations in the lattice parameters as described above are considered to be mainly due to those in the atomic distances of MO_5 pyramid induced by Zn substitution for Cu(2) site.

The J_c values of the ZnO-doped samples are plotted against the quantitative change in its additions in Fig. 5. The J_c values of the samples with additions of 0–2 wt.% ZnO are almost constant in this composition range, and they are then decreased by increasing ZnO content. The decreases of J_c values by increasing ZnO content may be considered to be mainly due to increasing ZnO particles in the Bi-2223 phase. The temperature dependence of resistivity for the samples with and without 50 wt.%

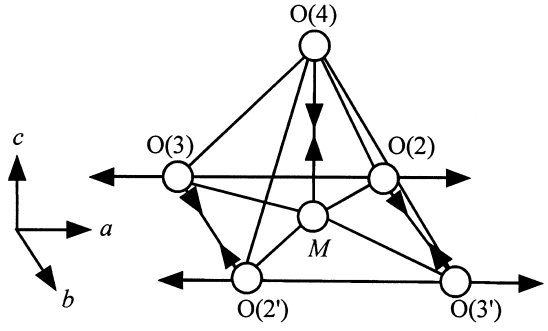

Fig. 4. MO_5 (M = Cu(2) and/or Zn) pyramidal structure.

Table 1
Atomic distances and bond angles of MO_5 (M = Cu(2) and/or Zn) pyramid

	Undoped	2 wt.% ZnO	5 wt.% ZnO	40 wt.% ZnO	50 wt.% ZnO
Distance (Å)					
M-O(4)	1.179(1)	1.158(2)	1.151(6)	1.162(5)	1.159(9)
O(3)-O(2′)	2.705(8)	2.704(3)	2.699(8)	2.703(1)	2.698(2)
O(2)-O(3′)	2.705(8)	2.703(4)	2.701(0)	2.700(7)	2.702(3)
O(3)-O(2)	2.706(4)	2.722(5)	2.723(1)	2.723(6)	2.724(5)
O(2′)-(O3′)	2.706(4)	2.723(6)	2.725(2)	2.722(5)	2.725(6)
Angle (deg.)					
∠O(3)MO(2′)	87.87(3)	86.40(8)	86.62(1)	86.24(2)	86.55(3)
∠O(2)MO(3′)	87.83(3)	86.45(2)	86.51(9)	86.79(8)	86.50(9)
∠O(2)MO(3)	87.85(8)	88.65(3)	88.74(5)	88.78(1)	88.65(3)
∠O(3′)MO(2′)	87.81(7)	88.69(8)	88.59(6)	88.82(8)	88.60(8)

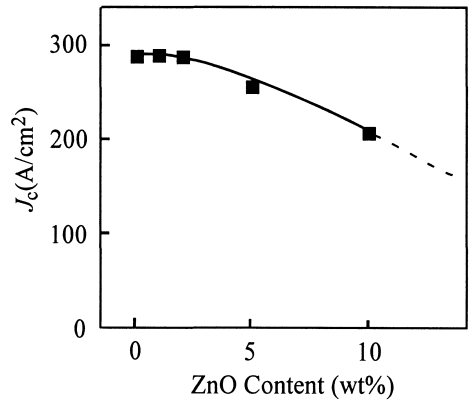

Fig. 5. Relationship between critical current density and ZnO dopant content.

ZnO is shown in Fig. 6. It is considered that ZnO additions to the Bi-2223 phase do not have a detrimental effect on the T_c value and even the 50 wt.% ZnO-doped sample shows the superconductivity.

Chiu et al.[10] reported that the addition of Ag_2O to Bi-2223 phase lowers the peritectic temperature thereby promoting extra liquid formation and affecting the stability of the Bi-2223 phase. Furthermore, they reported that Ag_2O additions had no significant effect on T_c of the Bi-2223 phase, depending on the sintering conditions. Grivel et al.[13] indicated that the substitution of Ag in the Bi-2223 phase is not admitted because the lattice parameters of the Bi-2223 phase with Ag do not vary with Ag content. Based on the results shown above, it is suggested that ZnO additions to the Bi-2223 phase indicated the same behavior as Ag and/or Ag_2O additions lower the melting temperature and are immune against T_c. However, these dopants differ from the solid-solubility in the Bi-2223 phase, in which ZnO forms a solid solution with the Bi-2223 phase up to 2 wt.% in this study, whereas Ag does not form a solid solution with the Bi-2223 phase.

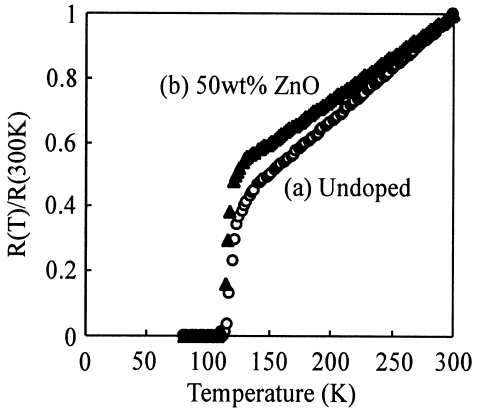

Fig. 6. Temperature dependence of normalized resistivity for (a) undoped sample and (b) 50 wt.% ZnO-doped sample.

4. Conclusions

The $Bi_2Pb_{0.5}Sr_2Ca_{2.5}Cu_{3.5}O_{10+x}$ compound was prepared and doped with ZnO by the solid-state reaction method. We discussed the influence of ZnO doping on the crystal structure in the Bi-2223 phase, and what kind of site is replaced by Zn^{2+} ions. From the calculation of the bond valence sum, it is suggested that Zn^{2+} ions are substituted for Cu^{2+} ions in Cu(2) sites, and the crystal structures of the Bi-2223 phase with ZnO were refined. It is recognized that the solid-solubility of Zn in the Bi-2223 phase is ~2 wt.% based on the variations in the lattice parameters. In addition, these variations are considered to be mainly caused by the variations in the atomic distances and bond angles of $Cu(2)O_5$ pyramidal structure in the Bi-2223 phase because these variations are nearly similar to those on the lattice parameters. From the experimental results of the Bi-2223 phase with ZnO, it is also recognized that there are significant similarities between ZnO additions and Ag and/or Ag_2O additions to the Bi-2223 phase, resulted in the lowering of the melting temperature and no detrimental effect on T_c.

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