JOURNAL OF MATERIALS SCIENCE 28 (1993) 5262–5264

Formation of high-T_c $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{0.9}Ti_{0.1})_3O_x$

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Influences of sintering conditions on T_c are studied for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{0.9}Ti_{0.1})_3O_x$. High T_c values are obtained at 1123±5 K sintering temperature and over 50 h sintering time. In order to explain the T_c changes, morphological discussion is attempted.

1. Introduction

High T_c has been reported above 100 K for Bi–Pb–Sr–Ca–Cu–O [1–3]. It is important to know the effects of solutes on T_c. Although a large amount of Ti is added, high T_c (above 100 K) samples are found below 0.1 of z for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{1-z}Ti_z)_3O_x$ [4]. Thus, we undertook to obtain formation of high-T_c $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{0.9}Ti_{0.1})_3O_x$ and to study the sintering conditions of this compound.

2. Experimental procedure

Samples with nominal composition were prepared from high-purity powders of CuO (99.9 wt %), TiO_2 (99.9 wt %), Bi_2O_3 (99.99 wt %), PbO (99.9 wt %), $SrCO_3$ (99.9 wt %) and $CaCO_3$ (99.9 wt %). The powders were mixed and sintered in air at 1023 K for 6 h and then air-cooled. After crushing, the sintered powders were re-sintered in air at 1073 K for 18 h and then air-cooled. After crushing, a pelletized tablet 1 mm thick and 13 mm diameter was sintered in air at 1123 K for 100 h and then furnace-cooled.

The electrical resistivity [2, 3] was measured in a cryostat at equilibrium temperatures. The electrical resistivity was measured using a standard four-probe technique and a Keithley 181 nanovoltmeter. The temperature was measured by an Au, Fe-Chromel thermocouple attached to the specimen [2, 3]. Fig. 1 shows the temperature dependence of electrical resistivity of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{0.9}Ti_{0.1})_3O_x$. Offset T_c^{off} and onset T_c^{on} of the transition are defined as the temperatures corresponding to the achievement of zero resistivity (below 10^{-9} Ωm at 1 mA mm^{-2} current density) and to the deviation of the electrical resistivity. The deviation point is taken at $d(R/R_{300\,K})/dT = 0.004$, where $d(R/R_{300\,K})/dT$ and $R_{300\,K}$ are slope of the reduced electrical resistivity ($R/R_{300\,K}$) against temperature graph and the resistivity at 300 K, respectively. T_c^{off} and T_c^{on} of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{0.9}Ti_{0.1})_3O_x$ are 103.7 and 133.4 K, respectively.

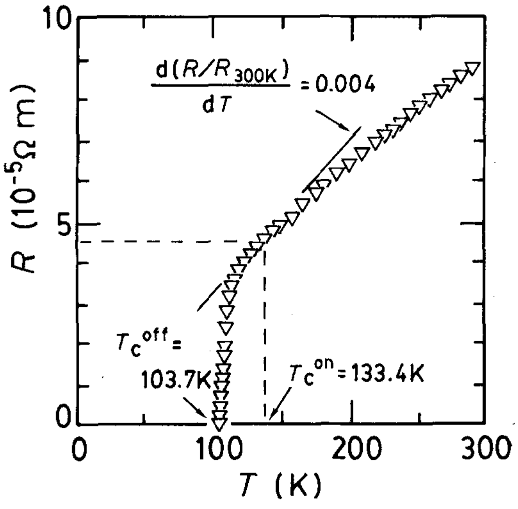

Figure 1 Temperature dependence of the electrical resistivity of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{0.9}Ti_{0.1})_3O_x$.

3. Results and discussion

3.1. Sintering temperature

Fig. 2 shows changes in T_c at 1 mA mm^{-2} against the sintering temperature of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{0.9}$

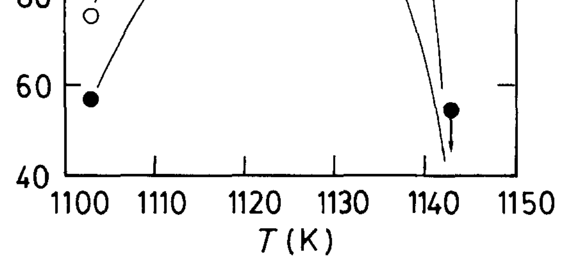

Figure 2 Changes in T_c at 1 mA mm^{-2} against sintering temperature of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{0.9}Ti_{0.1})_3O_x$: (○) T_c^{on}, (●) T_c^{off}. Samples were sintered for 100 h.

0022-2461

$Ti_{0.1})_3O_x$. The samples are sintered for 100 h. The high T_c values are obtained at 1123 ± 5 K sintering temperature.

Fig. 3 shows X-ray diffraction peaks for the (0 0 2) plane against the sintering temperature of the compound. Here, solid and dotted lines are for powder and bulk samples, respectively. The powder method is useful to evaluate the structure and composition because the peaks are not affected by the preferred orientation. On the other hand, the bulk method is useful to evaluate the residual stress and lattice defects. The (0 0 2) peaks of the low-T_c phase appear at 5.9° and show that a double CuO layer is present [5]. On the other hand, the high-T_c phase has a triple CuO layer, whose peak is found at 4.8° [6]. Fig. 4 shows changes in the lattice constant c of the (0 0 2) plane

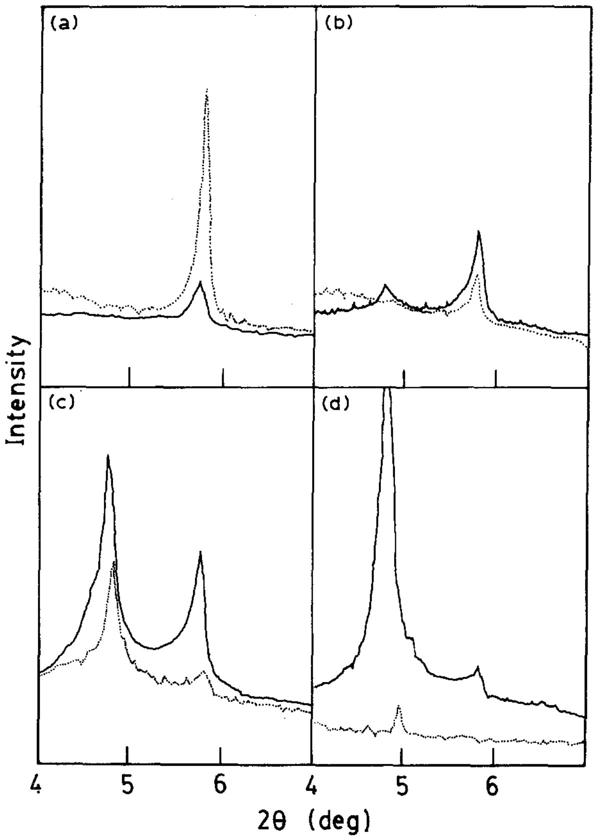

Figure 3 X-ray diffraction peaks of (0 0 2) plane against sintering temperature of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{0.9}Ti_{0.1})_3O_x$ for (——) powder and (···) bulk samples. (a) $T = 1103$ K, $T_c^{off} = 57.8$ K; (b) $T = 1120$ K, $T_c^{off} = 99.8$ K; (c) $T = 1123$ K, $T_c^{off} = 103.7$ K; (d) $T = 1133$ K, $T_c^{off} = 98.9$ K.

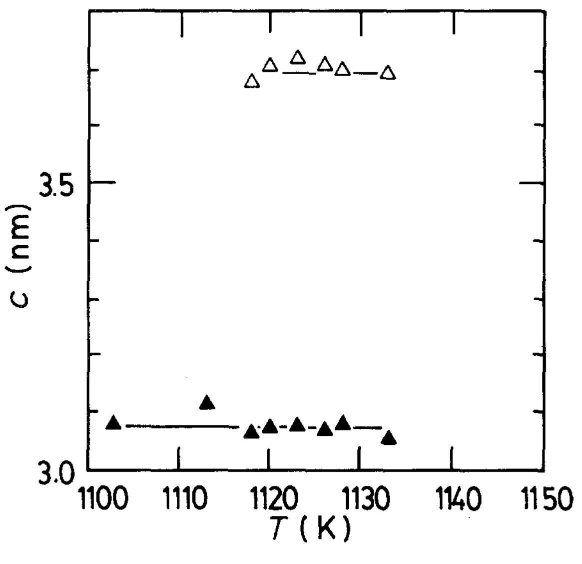

Figure 4 Changes in lattice constant of (0 0 2) plane against sintering temperature: (▲) low-T_c phase, (△) high-T_c phase.

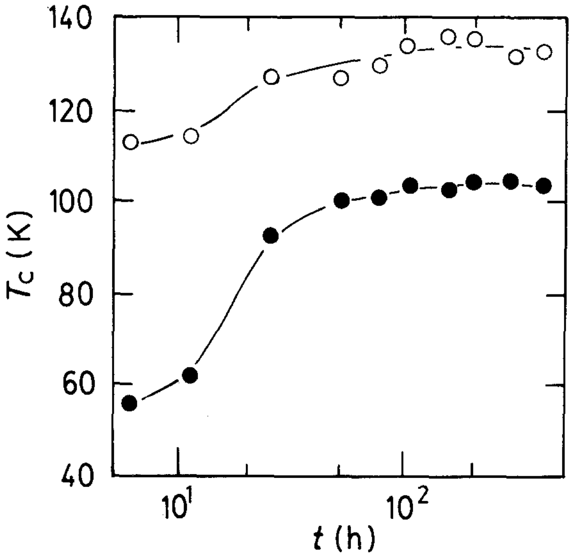

Figure 5 Changes in T_c at 1 mA mm^{-2} against sintering time of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{0.9}Ti_{0.1})_3O_x$. Samples were sintered at the temperature (1123 K) of the most favourable conditions. (○) T_c^{on}, (●) T_c^{off}.

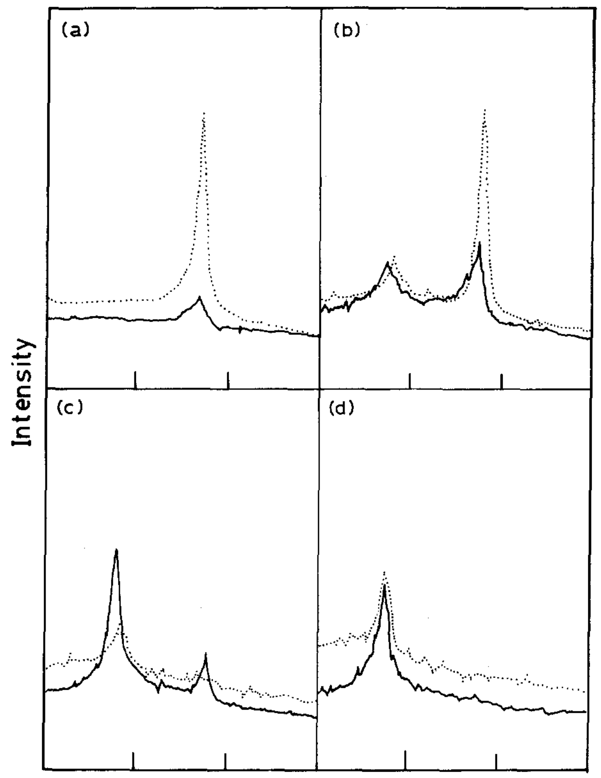

Figure 6 X-ray diffraction peaks of (0 0 2) plane against sintering time of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{0.9}Ti_{0.1})_3O_x$ for (——) powder and (···) bulk samples. (a) $t = 6$ h, $T_c^{off} = 56.1$ K; (b) $t = 50$ h, $T_c^{off} = 99.7$ K; (c) $t = 300$ h, $T_c^{off} = 104.6$ K; (d) $t = 400$ h, $T_c^{off} = 103.9$ K.

against the sintering temperature. The sample sintered at 1103 K does not show a high-T_c phase. Although the lattice constants are approximately equal, the samples for which T_c become high, show a high-T_c phase. The higher the sintering temperature, the larger the amount of the high-T_c phase becomes, resulting in a higher T_c (see Fig. 2).

3.2. Sintering time

Fig. 5 shows changes in T_c at 1 mA mm^{-2} against the sintering time of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{0.9}Ti_{0.1})_3O_x$. The samples are sintered at the temperature (1123 K) of the most favourable conditions. The longer the sintering time, the higher the T_c becomes. Samples with T_c above 100 K are obtained for over 50 h sintering time.

Fig. 6 shows X-ray diffraction peaks for the (0 0 2) plane against sintering time. Here, solid and dotted lines are for powder and bulk samples, respectively. Fig. 7 shows changes in the lattice constant c of the (0 0 2) plane against sintering time. The sample for 6 h does not show a high-T_c phase. The longer the sintering time, the larger the amount of high-T_c phase becomes, resulting in a higher T_c (see Fig. 5). Hence the sintering condition is one of the dominant factors controlling the T_c of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{0.9}Ti_{0.1})_3O_x$.

4. Conclusion

In summary, the sintering conditions to obtain high T_c are investigated for $Bi_{1.6}Pb_{0.4}Sr_2Ca_2(Cu_{0.9}Ti_{0.1})_3O_x$. High-$T_c$ samples (above 100 K) are found for long sintering times (over 50 h) at the most favourable temperature (1123 K). Based on the results of the X-ray diffraction, we conclude that the changes in the volume of the high-T_c phase agree with the changes in the sintering conditions.

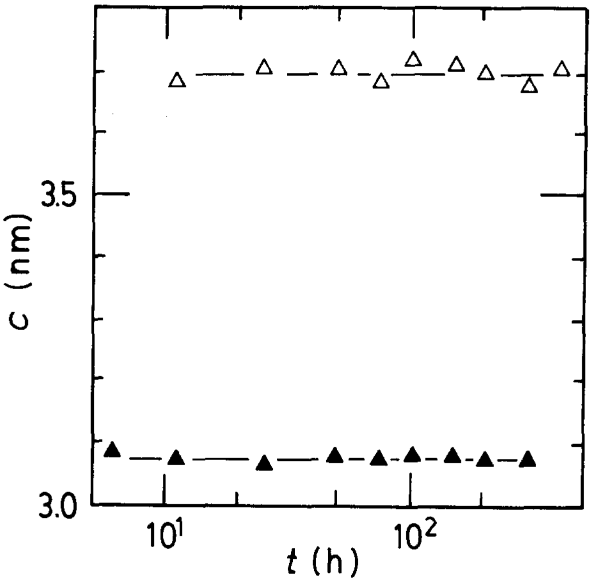

Figure 7 Changes in lattice constant of (0 0 2) plane against sintering time. (▲) Low-T_c phase, (△) high-T_c phase.

References

1. Y. NISHI, S. MORIYA and T. MANABE, *J. Appl. Phys.* **65** (1989) 2389.
2. Y. NISHI, K. OGURI, H. OHINATA, K. TANIOKA, Y. KITA and N. NINOMIYA, *Phys. Rev. B* **41** (1990) 6520.
3. Y. NISHI, Y. KITA and K. TANIOKA, *J. Mater. Sci.* **25** (1990) 5105.
4. Y. NISHI, K. NOZAKI, T. KUROTAKI, Y. KITA and K. OGURI, *J. Appl. Phys.* **71** (1992) 350.
5. M. ONODA, A. YAMAMOTO, E. TAKAYAMA-MUROMACHI and S. TAKEKAWA, *Jpn J. Appl. Phys.* **27** (1988) L833.
6. U. ENDO, S. KOYAMA and T. KAWAI, *ibid.* **27** (1988) L1476.

Received 30 March 1992
and accepted 24 February 1993