Formation and microstructure of (Bi,Pb)-2223 phase in the diffusion process

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Abstract

Bi-2223 oxide superconductors have been synthesized by the diffusion reaction between a high melting point Sr-Ca-Cu oxide substrate and a low melting point (Bi,Pb)-Cu oxide coating layer. The substrate with Sr:Ca:Cu atom ratio of 1.9:2.1:2.5 was pressed into cylindrical rods with 4 mm diameter or rectangular bars with 3 mm × 3 mm × 15 mm sizes, and then sintered. The coating layer with Bi:Pb:Cu ratio of 1.8:0.4:1 was coated around the substrate rods and bars. The heat treatment was performed to produce the (Bi,Pb)-2223 diffusion layer at 840℃ for different time. The Bi-2223 phase in the diffusion process is transformed from the Bi-2212 phase through the Bi-2201 phase. The Ag_2O added to the coating layer does not enhance the (Bi,Pb)-2223 diffusion reaction. The cylindrical sample is favorable for formation of (Bi,Pb)-2223 diffusion layer as compared with the rectangular sample. The optimum heat treatment to produce the (Bi,Pb)-2223 diffusion layer is 840℃ for 144 h.

(150 words)

PACS codes: 74.72.Hs

Keywords: Bi-2223, superconductors, diffusion, heat treatment

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1. Introduction

Among all the high-temperature superconductors discovered to date, Bi-2223 phase is the most promising material for tapes and wires for large-scale and high-current applications. Although several procedures have been previously proposed in order to increase the proportion of Bi-2223 phase in bismuth system [1-5], and especially it has been found that the addition of lead oxide (PbO) is successful in producing a high proportion of Bi-2223 phase [5], the synthesis of single-phase Bi-2223 superconductor is still difficult due to a poor understanding of its complex phase diagram, as well as melting and solidification behavior. The diffusion process facilitates the synthesis of the high-T_c oxide phase in much shorter heat treatment time than the conventional sintering process [6]. The diffusion reaction usually proceeds in a couple composed of a high melting point component and a low melting-point component. In the YBCO system, a Y-based oxide Y_2BaCuO_5 and a barium cuprate with a composition of $Ba_3Cu_5O_8$ were used as a high melting point component and a low melting-point component, respectively [7]. After heat treating the diffusion couple, a thick uniform layer of $YBa_2Cu_3O_{7-x}$ with a T_c of 91.5 K and J_c (77 K) of 1900 A cm^{-2} was successfully formed. In the Bi-Sr-Ca-Cu-O system, the Bi-2212 superconducting layer with homogeneous structure and high density was synthesized by diffusion reaction between a high melting point Sr-Ca-Cu oxide substrate and a low melting point Bi-Cu oxide coating layer [8]. However, there are no detailed studies reported on the synthesis of the Bi-2223 superconductors by a diffusion reaction. In the present study, the formation and microstructure of (Bi,Pb)-2223 phase in the diffusion process have been studied.

2. Experimental procedure

Bi-2223 oxide superconductors were synthesized by the diffusion reaction between a high melting point Sr-Ca-Cu oxide substrate and a low melting point (Bi,Pb)-Cu oxide coating layer. The powder with Sr:Ca:Cu atom ratio of 1.9:2.1:2.5 was calcined at 850℃ for 12 h, and then pressed into cylindrical rods with 4 mm diameter or rectangular bars with 3 mm×3 mm×15 mm sizes. These rods and bars were heat-treated at 850℃ for 24 h for sintering before the diffusion couple preparation. Meanwhile, the coating layer is composed of (Bi,Pb)-Cu oxide with Bi:Pb:Cu atom ratio of 1.8:0.4:1. These low melting point oxide powders with the 30wt% Ag_2O addition and without Ag_2O addition were coated around the sintered substrate rods and bars. The thickness of the coated oxide layer was about 150 μm. A two-step heat treatment was applied for the present diffusion reaction. The first heat treatment was made at 700℃ for 10 h, which produced a tight bonding between the superficial low melting point component and the high melting point substrate. The final diffusion heat treatment was made at 840℃ for 1-240 h. All heat treatments were performed in air and followed by furnace-cooling to room temperature.

The formation of the (Bi,Pb)-2223 phase was analyzed both X-ray diffraction analysis and AC susceptibility measurement. Scanning electron microscopy (SEM) with energy-dispersive spectroscopy (EDS) was used to analyze the microstructure on the cross section of the prepared sample.

3. Results and discussion

Fig. 1 shows the temperature dependence of the susceptibility for Ag_2O-free cylindrical samples reacted at 840℃ for different time. It can be seen that the susceptibility changes at about 25 K due to the Bi-2201 phase in the sample reacted 840℃ for 1 h in one step. On the other hand, for the samples reacted at 840℃ for 24 h, 72 h, 144 h and 240 h, the changes in susceptibility occur in two steps. One change at 108 K due to the diamagnetic of the Bi-2223 phase and another change at 75 K due to the diamagnetic of the Bi-2212 phase, are observed. However, with the increase of reaction time (τ), the diamagnetic height of the Bi-2223 phase increases (24 h≦ τ ≦144 h), and then decreases (τ ≧144 h). The highest diamagnetism of the Bi-2223 phase exists in the sample reacted at 840℃ for 144 h.

Fig. 2 shows the temperature dependence of the susceptibility for four kinds of samples reacted at 840℃ for 144 h. It can be seen that the diamagnetic height of the Bi-2223 phase are very sensitive to the Ag_2O addition and the shape of samples. The highest diamagnetism of the Bi-2223 phase exists in the Ag_2O-free cylindrical rod. The result suggests that the Ag_2O added to the coating layer does not enhance the (Bi,Pb)-2223 diffusion reaction. The cylindrical sample is favorable for formation of (Bi,Pb)-2223 diffusion layer as compared with the rectangular sample.

Fig. 3 shows X-ray diffraction patterns taken on the surfaces of the Ag_2O-free cylindrical samples reacted at 840℃ for 1 h, 24 h and 144 h. All samples indicate an extremely strong (200) peak. The Bi-2201 phase as major phase exists on the surface of the sample reacted at 840℃ for 1 h. Whereas on the surface of the sample reacted at 840℃ for 24 h, the main crystalline phase is the Bi-2212 phase. The Bi-2223 phase and Bi-2212 phase coexist on the surface of the sample reacted at 840℃ for 144 h. This results may indicate that the Bi-2223 phase in the diffusion process is transformed from the Bi-2212 phase through the Bi-2201 phase.

The results of the XRD diffraction measurement on the surfaces of four kinds of samples reacted at 840℃ for 144 h are shown in Fig. 4. It can be seen that the Bi-2223 phase and the Bi-2212 phase are the main constituents of all samples. However, the line intensities of the Bi-2223 phase are very sensitive to the Ag_2O addition. A peak in the line intensities of the Bi-2223 phase appears in the Ag_2O-free cylindrical rod. This result is in agreement with that shown by AC susceptibility measurement.

Fig. 5 shows X-ray diffraction patterns taken at different distance from the surface of the Ag_2O-free cylindrical sample reacted at 840℃ for 144 h. From Fig. 5, it is found that line intensities of the Bi-2223 phase are different for the different distance. A peak in the line intensities of the Bi-2223 phase appears in the diffusion layer near the interface of the substrate (Fig. 5b).

Fig. 6 shows a SEM micrograph, and the corresponding EDS compositional maps of Bi, Sr and Ca taken on the cross section of the Ag_2O-free cylindrical rod reacted at 840℃ for 144 h. An uniform diffusion layer, about 150 μm in thickness, is formed on the high melting point substrate. The diffusion layer is composed of plate-like 2212 and 2223 grains in the diffusion direction, i.e., in the radial direction of the cylindrical rod. The Bi diffuses inwards from the superficial low melting point component to the substrate, while the Sr and Ca diffuse outwards from the substrate to the low melting point component. These results are in agreement with those reported in reference [8].

4. Conclusion

Bi-2223 oxide superconductors have been synthesized by the diffusion reaction between a high melting point Sr-Ca-Cu oxide substrate and a low melting point (Bi,Pb)-Cu oxide coating layer. The substrate with Sr:Ca:Cu atom ratio of 1.9:2.1:2.5 was pressed into cylindrical rods with 4 mm diameter or rectangular bars with 3 mm×3 mm×15 mm sizes, and then sintered. The coating layer with Bi:Pb:Cu ratio of 1.8:0.4:1 was coated around the substrate rods and bars. The heat treatment was performed to produce the (Bi,Pb)-2223 diffusion layer at 840℃ for different time. The Bi-2223 phase in the diffusion process is transformed from the Bi-2212 phase through the Bi-2201 phase. The Ag_2O added to the coating layer does not enhance the

(Bi,Pb)-2223 diffusion reaction. The cylindrical sample is favorable for formation of (Bi,Pb)-2223 diffusion layer as compared with the rectangular sample. The optimum heat treatment to produce the (Bi,Pb)-2223 diffusion layer is 840℃ for 144 h.

References

[1] S.Koyama, U.Endo and T.Kawai, Japan.J.Appl.Phys. 27（1988）L1861.

[2] S.E.Dorris, B.C.Prorok, M.T.Lanagan, N.B.Browning, M.R.Hagen, J.A.Parrell, Y.Feng, A.Umezawa and D.C. Larbalestier, Physica C 223（1994）163.

[3] D.Pandey, A.K.Singh, P.K.Srivastava, A.P.Singh, S.S.R.Inbanathan and G.Singh, Physica C 241（1995）279.

[4] J.C.Toledano, D.Morin,J.Schneck, H.Faqir, O.Monnereau, G.Vacquier, P.Strobel and V.Barnole, Physica C 253（1995）53.

[5] M.Takano, J.Takada, K.Oda, H.Kitaguchi, Y.Miura, Y.Ikeda, Y.Tomii and H.Mazaki, Japan.J.Appl.Phys. 27（1988）L1041.

[6] Y.Yamada, F.Yamashita, K.Wada and K.Tachikawa, J.Japan Inst. Matals, 61-9 (1997) 836.

[7] K.Tachikawa, N.Sadakata, M.Sugimoto and O.Kohno, Japan.J.Appl.Phys. 27（1988）L1501.

[8] K.Tachikawa, T.Watanabe and T.Inoue, Supercond. Sci. Technol. 3 (1990) 180.

Figure captions

Fig.1. Temperature dependence of the susceptibility for Ag_2O-free cylindrical samples reacted at 840℃ for different time.

Fig. 2. Temperature dependence of the susceptibility for four kinds of samples reacted at 840℃ for 144 h. A: Ag_2O added rectangular bar, B:Ag_2O added cylindrical rod, C: Ag_2O-free rectangular bar, D:Ag_2O-free cylindrical rod.

Fig.3. XRD patterns taken on the surfaces of the Ag_2O-free cylindrical samples reacted at 840℃ for 1 h, 24 h and 144 h.

Fig. 4. XRD patterns taken on the surfaces of four kinds of samples reacted at 840℃ for 144 h. (a) Ag_2O added rectangular bar, (b) Ag_2O added cylindrical rod, (c) Ag_2O-free rectangular bar, (c) Ag_2O-free cylindrical rod.

Fig. 5. X-ray diffraction patterns taken at different distance from the surface of the Ag_2O-free cylindrical samples reacted at 840℃ for 144 h.

Fig. 6. SEM micrograph (a) and mapping analysis of Bi (b), Sr (c) and Ca (d) taken on the cross section of the Ag_2O-free cylindrical rod reacted at 840℃ for 144 h.

Fig.1

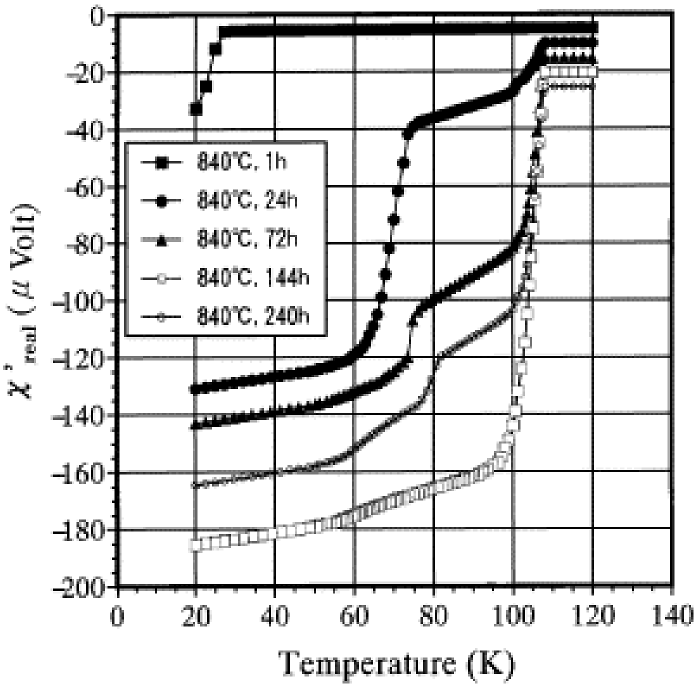

0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
$\chi'_{\rm real}$ (μ Volt)
0
20
40
60
80
100
120
140
Temperature (K)
840℃, 1h
840℃, 24h
840℃, 72h
840℃, 144h
840℃, 240h

Fig.2

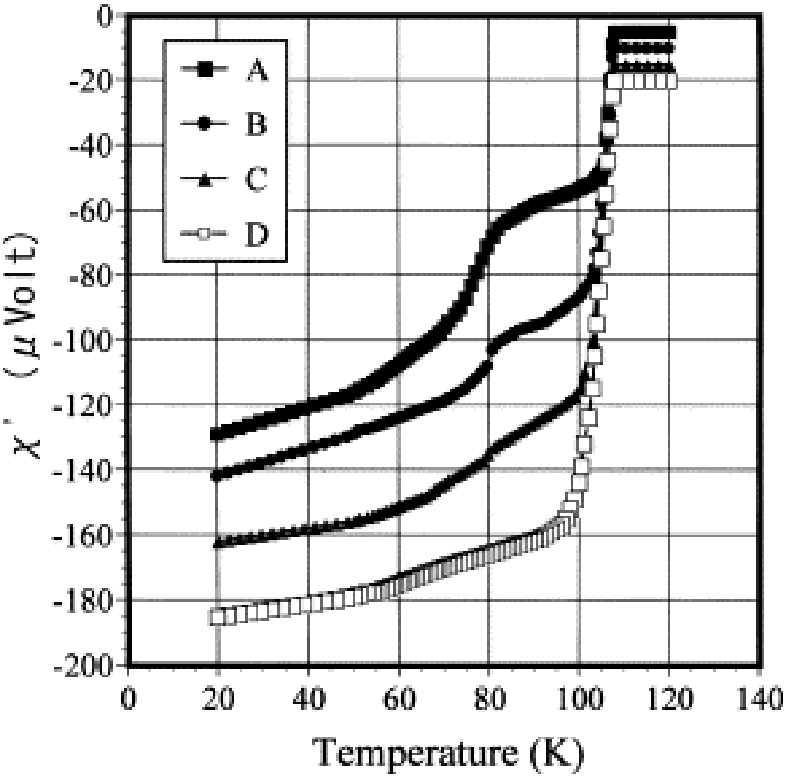

A
B
C
D
χ'（μVolt）
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
0
20
40
60
80
100
120
140
Temperature (K)

Fig.3

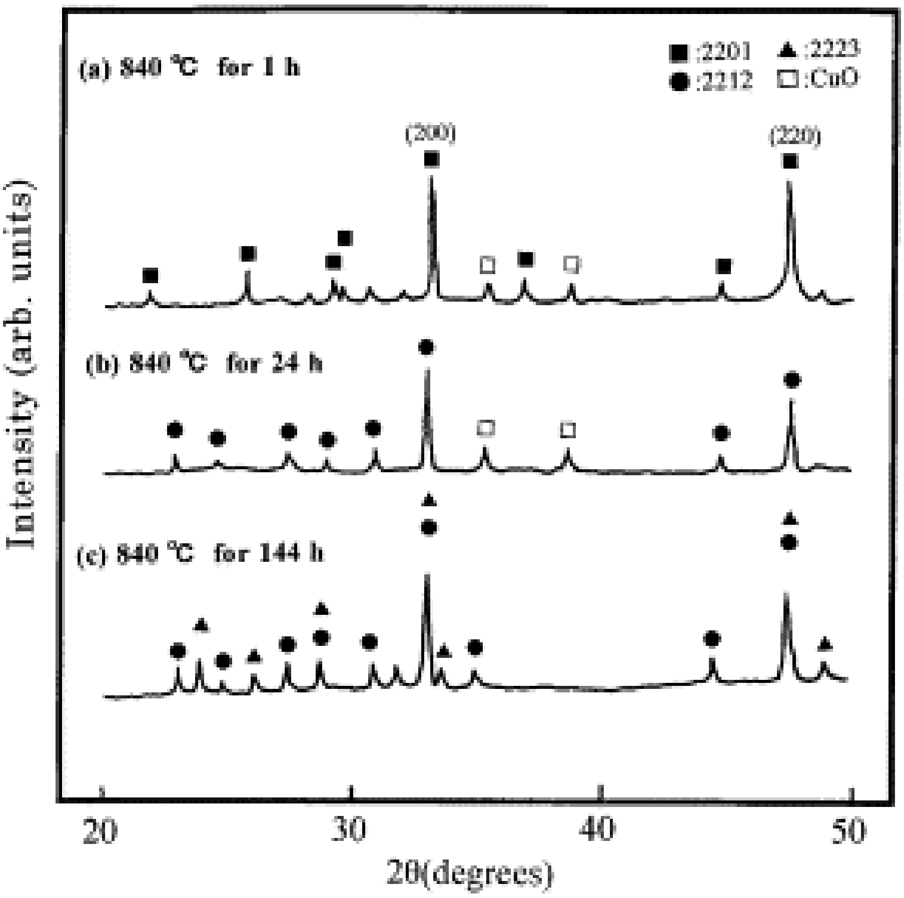

(a) 840 ℃ for 1 h
■:2201
▲:2223
●:2212
□:CuO
(200)
(220)
(b) 840 ℃ for 24 h
(c) 840 ℃ for 144 h
Intensity (arb. units)
20
30
40
50
2θ(degrees)

Fig.4

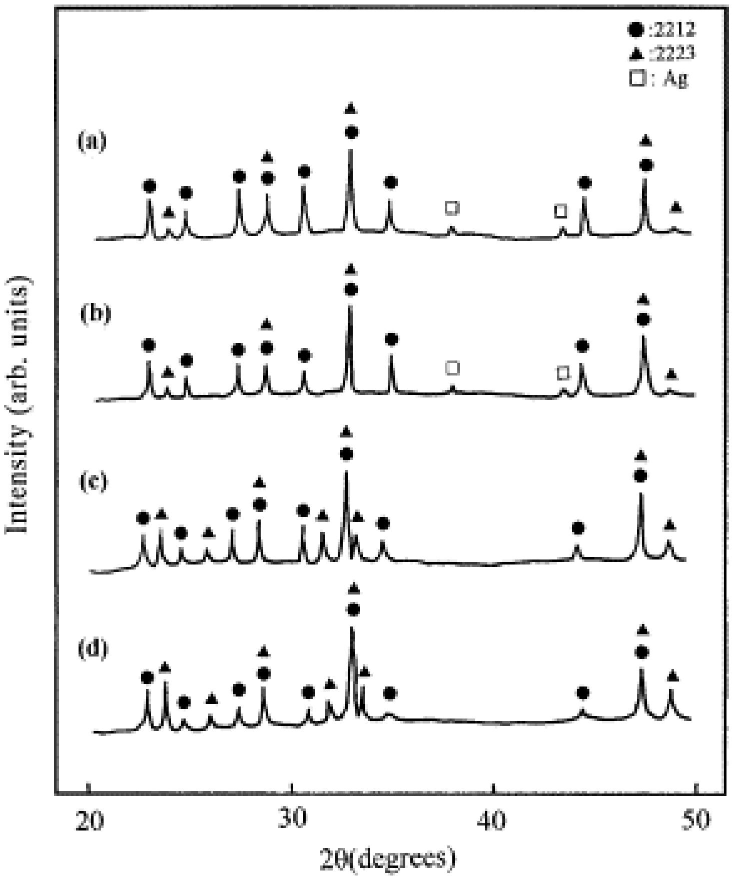


Fig.5

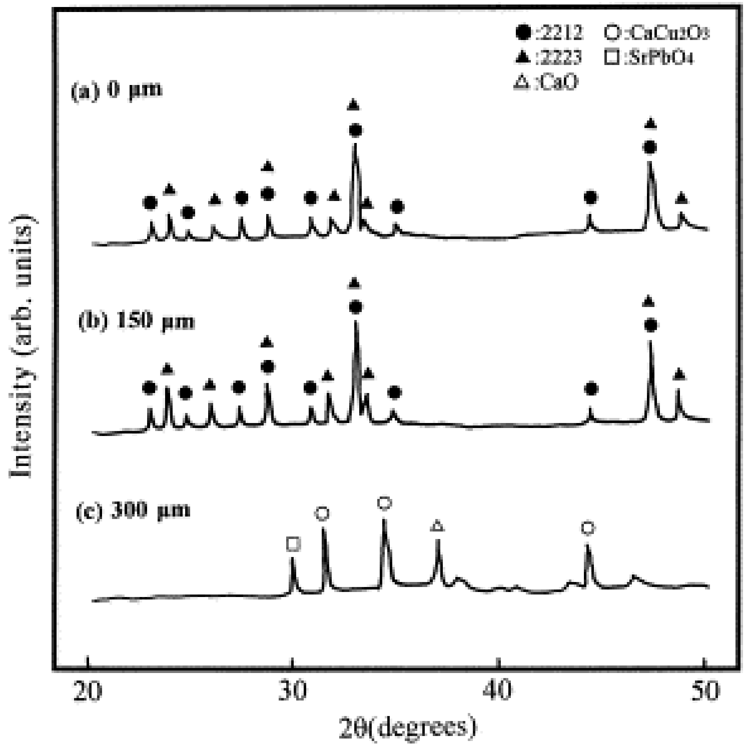
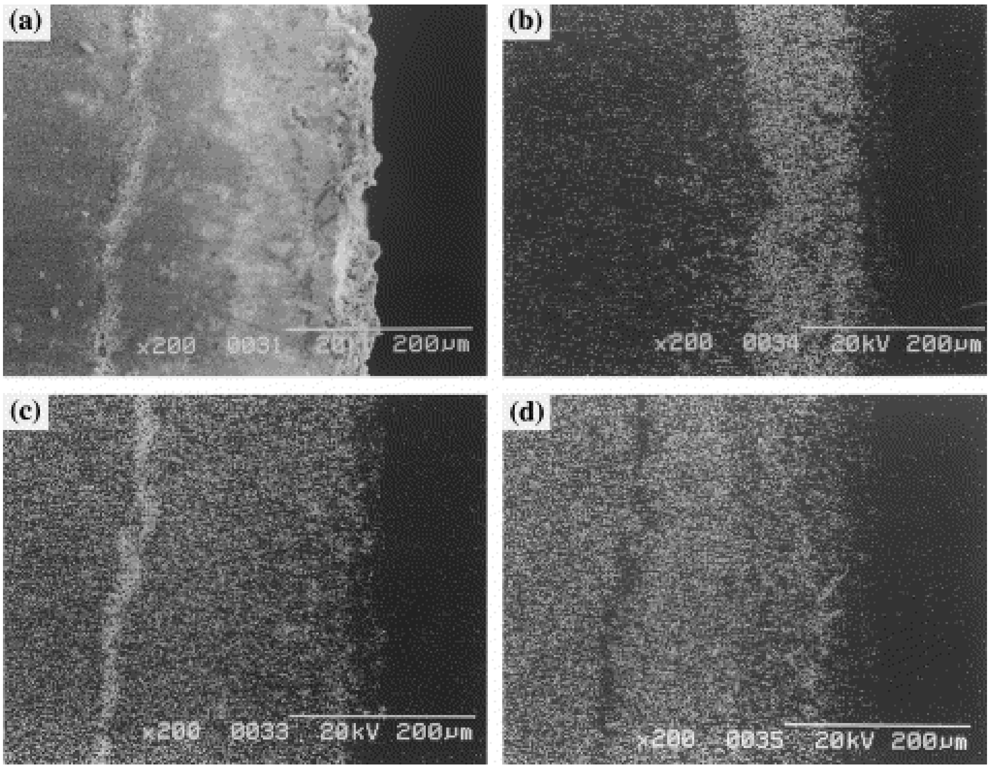

●:2212
○:CaCu2O3
▲:2223
□:SrPbO4
△:CaO
(a) 0 μm
(b) 150 μm
(c) 300 μm
Intensity (arb. units)
20
30
40
50
2θ(degrees)

Fig.6


(a)
x200 0031 200µm
(b)
x200 0034 20kV 200µm
(c)
x200 0033 20kV 200µm
(d)
x200 0035 20kV 200µm