Microsc. Microanal. 8 (Suppl. 2), 2002
DOI 10.1017.S1431927602103382



# On the Half Unit Cell Intergrowth of $Bi_2Sr_2Ca_3Cu_4O_x$ with Other Superconducting Phases in Two-step Annealed LFZ Fibers

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Laser floating zone melting (LFZ) is a non-equilibrium texturing technique. The c-axis of Bi-based superconducting phases ($Bi_2Sr_2Ca_{n-1}Cu_nO_x$, n=1, 2, 3) in fibres produced by this technique is predominantly perpendicular to the fibre growth direction [1]. The fibres without Pb and Ag additions are most suitable for the phase evolution research. It was found in our recent work that the fibres with nominal composition of $BiSr_2Ca_3Cu_5O_z$ after annealing at 870°C for 10 min. and then at 830°C for 72 h, had the superconductivity much improved. The onset Tc is about 105K. Below a second transition temperature of about 95K, the diamagnetic signal dropped steeply [2]. In this paper, the two-step annealed Bi-1235 LFZ fibres are investigated by transmission electron microscope (HITACHI-9000NA) and X-ray energy dispersive spectrometry (RONTEC). The samples were prepared by conventional ion milling under liquid nitrogen cooling. HREM images of the superconducting grains reveal important features of the microstructures. Half unit cell intergrowth of 2234 phase with 2223 phase, or 2212 phase is observed. The results provide not only explanations to the properties but also to the mechanism of the phase evolution.

a) Half unit cell intergrowth of 2234 phase with 2223 phase, or 2212 phase is observed in the grains, as shown in FIG. 1a. Most of the 2234 half unit cell layers combine with 2212 half unit cell layers. They normally extend more than 100nm along the fibre growth direction. It should be noted that, besides the difference in the lattice spaces, the details in the half unit cell of 2234 phase are different from those in 2223 phase or 2212 phase. Transformation of the intergrowth of 2234/2212 into area of regular 2223 phase is also observed.

b) FIG. 1b is the corresponding selected area electron diffraction (SAED) pattern. It evidences the coexistence of several kinds of c spacing. The strongest diffraction spots have the c spacing of 3.4nm, suggesting the dominance of the intergrowth of 2212/2223 phases in the observed area. EDS results also support the dominance of this intergrowth of phases.

c) The HREM images show more details of the superconducting grains. Besides well-developed stripes of 2212 phase and 2223 phase, relatively stable phase domains that contain the intergrowth of 2212/2223 are revealed to exist in the grains. The frequently found half unit cell intergrowth of 2212/2223 phases very often occupies over half of the observed area. The crystalline lattices in this intergrowth layers seems much better resolved than that in the 2234 half unit cell layer or in the intercalation layer of $Ca/CuO_2$. FIG. 1c is one of the HREM images, representative of the 2212/2223 intergrowths. In the intercalation area, as indicated by the black bars, the fringe interval changes from 1.86nm to 2.18 nm =1.86nm+0.32nm, showing the occurrence of the phase evolution from 2223 to 2234 due to the intercalation of $Ca/CuO_2$ layer. In other regions, the change of interval 1.54nm to1.86nm = 1.54nm +0.32nm can also be measured out. In average, the inserting length is more than 50nm along the fibre growth direction.

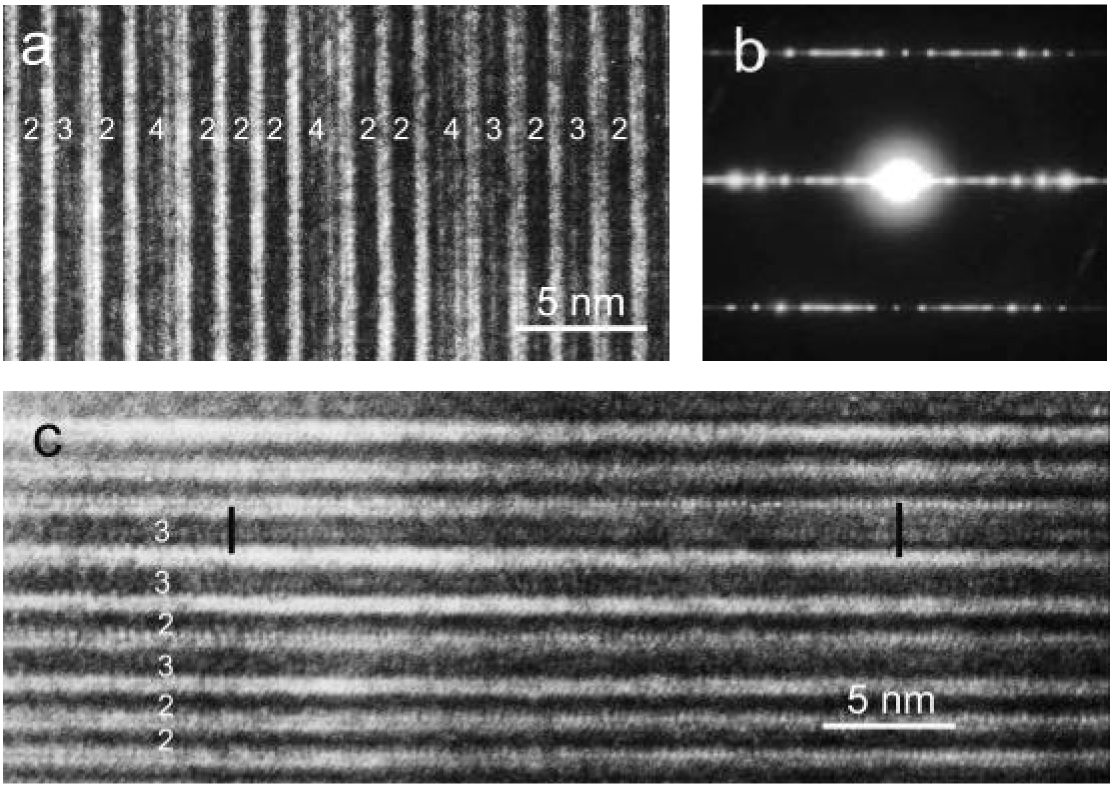


FIG. 1a. HREM images evidenced the half unit cell intergrowth of 2234/2223 and 2234/2212.
FIG. 1b. SAED pattern taken from the same grain as FIG. 1a and FIG. 1c.
FIG. 1c. HREM images evidenced the half unit cell intergrowth of 2212/2223 and the intercalation of $Ca/CuO_2$ layer, the black bars display the difference in the fringe spacing.

In this report on the observation of Bi-2234 phase from the LFZ fibres, the HREM images evidenced details in the half unit cell of 2234 phase that are clearly distinguished from the 2223 phase or 2212 phase. The superconducting grains are mainly composed of 2212/2223 intergrowth. The intercalation of $Ca/CuO_2$ layers can be observed in some intergrowth areas. It should be noted that, the time for pre-nucleation of 2223 phase is very short while the temperature for the crystal growth is rather low. However, the improvement of the superconductivity is obvious [2]. T. Kawai et al. reported the preparation of $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ film with n up to 8 using molecular-beam epitaxy technique [3]. They argued the importance of growing the $Ca(Sr)CuO_2$ parent material during the preparation process. Observations here suggest that during our heat treatment process, some local chemical and energy environment facilitated the intercalation of $Ca/CuO_2$ perovskite layer into 2212 or 2223 lattices to transform them into 2223 or 2234 phases, respectively.

References

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[4] Li Yang gratefully acknowledges the support from Research Contract POCTI/35462/CTM/2000 and POCTI/35492/CTM/1999.

https://doi.org/10.1017/S1431927602103382 Published online by Cambridge University Press