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Interaction between $BaZrO_3$ nano-rods and RE_2O_3 nano-dots and its effects on the flux pinning in Zr:REBCO tapes

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Outline

1. Introduction
2. Optimum Zr content for in-magnetic-field performance at low temperature
   - MOCVD for high Zr added REBCO
     - MOCVD conditions for high Zr should be different from those for low Zr
   - In field performance of Zr:GdYBCO as a function of Zr content
     - flux pinning at low temperature was enhanced with 15% Zr
   - Microstructure of Zr:GdYBCO for high Zr and low Zr
     - preventing in-plane growth of BZO was the key in growing high quality Zr:REBCO
3. Effects of rear earth composition in Zr:GdYBCO
   - RE composition effects on in-magnetic-field Ic at 77K, 40K and 30K
     – at low temperature, Ic varies more significantly with RE content than at 77K
   - RE composition effects on microstructure of Zr:GdYBCO
     - In the case of high RE content , thick RE_2O3 layers and big RE_2O_3 particles block the vertical growth of BZO nanorods and enhance in-plane growth of second phases
     - in the case of low RE content, area extended second phase, segments of BaCuO2, BZO, will form in the film and degrade the crystal quality of the HTS matrix
     - With optimum RE content, long BZO nanorods can grow through the entire thickness of the film
     - The combination of long $BaZrO_3$ nanorods and extended RE_2O_3 nano-sheets led to substantial enhancement in the in-magnetic-field performance at low temperature.
4. Effects of Cu composition in Zr:GdYBCO
   - CuO particles block vertical growth of BZO nanorods, degrade crystal quality of REBCO matrix and RE_2O_3 layers.
5. Conclusions

I. Introduction

Introducing high density of defects to act as pinning centers for the magnetic flux is the way towards a substantial improvement of Ic(B) of REBCO coated conductors

RE_2O_3 and $BaZrO_3$

- studied the most
- main nanoscale defects present in commercial 2G HTS wires

The key point is that not only they can form the size and shape required for pinning, but also they can be incorporated into REBCO in large quantity.

To optimize the pinning, it is crucial to improve the understanding of the interaction between the intrinsic and extrinsic pinning centers

Introduction – application requirement

Key factors in optimizing pinning include

- Zr content
- Composition (RE:Ba:Cu ratio)
- Rare earth substitution

Our previous study of these key factors (Y. Chen et al., IEEE Trans. Appl. Supercond., 2011) was limited to the properties at temperature of 77K and magnetic field of 1T.

Several HTS applications, including generators and motors, are targeted to be used at lower temperatures, 30 - 40K. Therefore, studying the mechanism and optimizing the microstructure of the material for lower temperature use is important.

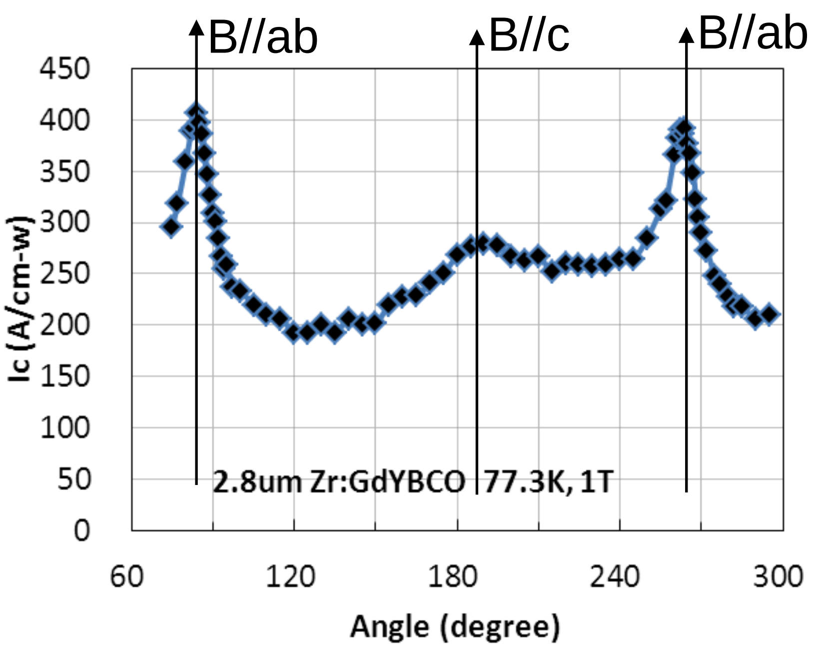
The present work is focused on the properties at 30K – 40K and 3T. We will show the significant composition effects at low temperatures.

Introduction - defects in 2 directions

Typical angular dependence curves of Ic for Zr:REBCO show peaks at *B*||*ab* and *B*||*c*

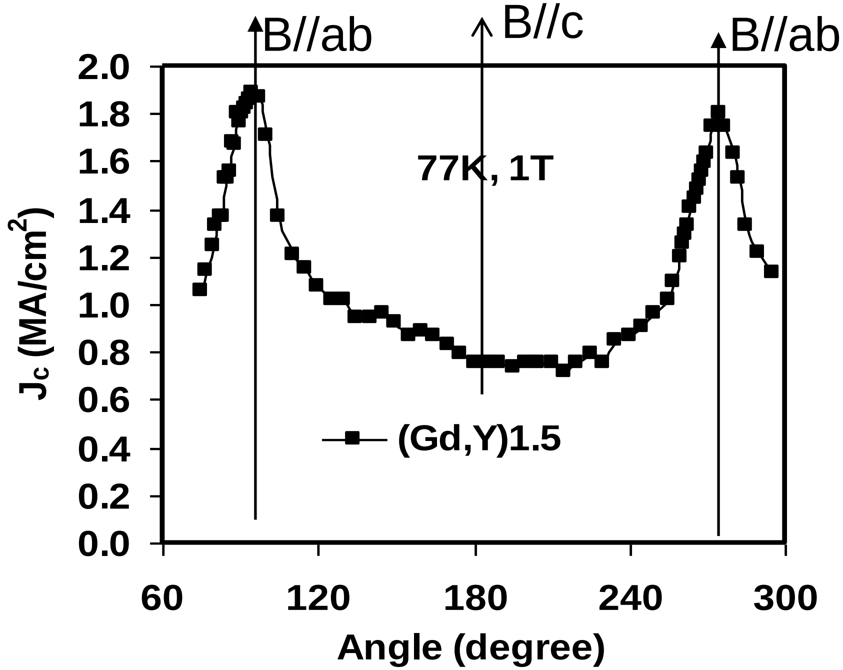
B||*c-peak* – attributed to BZO nanorods along the c-direction

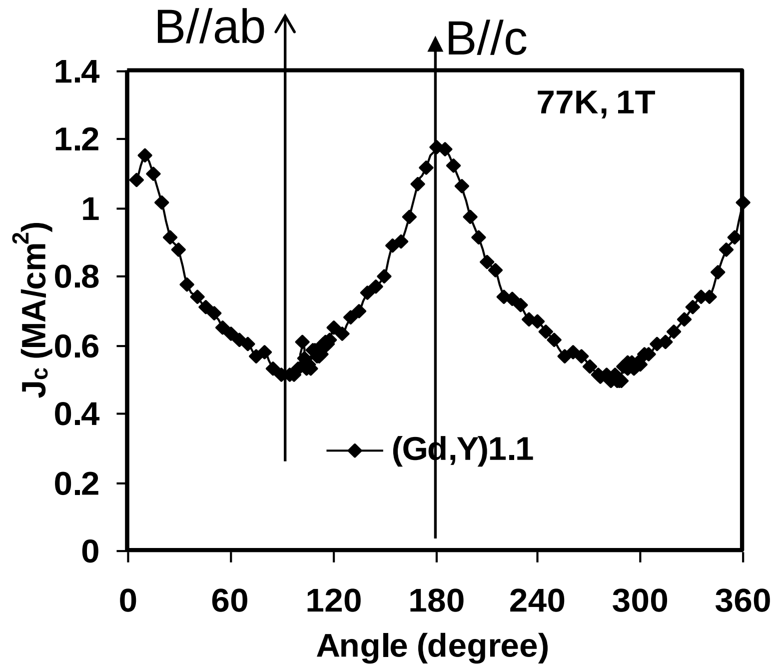
B||*ab-peak* – previously attributed to intrinsic pinning from the modulated Cu-O planes; we proposed that it could be also attributed to RE_2O_3. In fact, we could modify the intensity of the *B*||*ab-peak* by adjusting the RE composition. At certain low RE contents and deposition conditions, the ab-peak can be leveled off completely, indicating that **the *ab*-peak should be attributed to RE_2O_3 layers.**



Introduction - interactions

- Modifying the RE content in Zr:GdYBCO could not only alternate the ab-peak, but also alternate the c-peak. This indicates that the shape, size and distribution of BZO could be influenced by RE_2O_3, which prevents the vertical growth of BZO nanorods.
- High density of BZO columns influences crystal quality of the RE_2O_3 layers.





Introduction – purpose

Through studying the interaction between the main contributors for the pinning in 2 directions, RE_2O_3 and $BaZrO_3$, to answer

- What is the optimum Zr concentration for effective pinning in Zr:GdYBCO for applications at 30K – 40K

- How the RE composition influence the formation of BZO nanorods

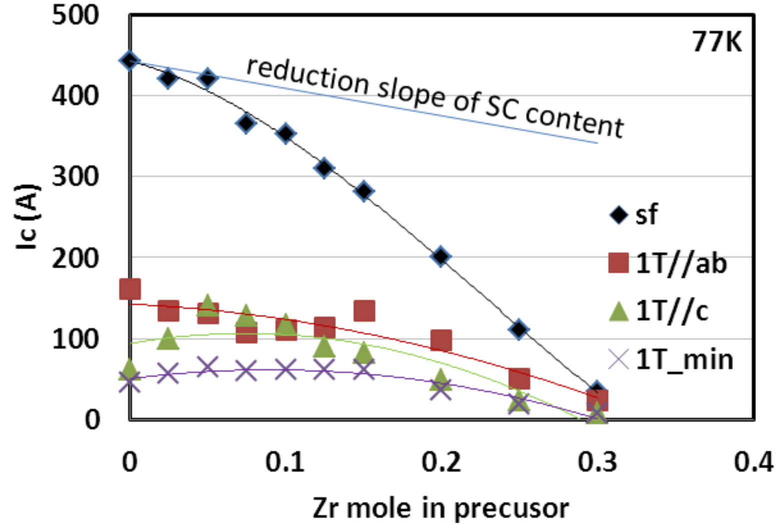
- What is the optimum RE:Ba:Cu composition ratio for the best Ic(B) at low temperatures, 30K – 40K

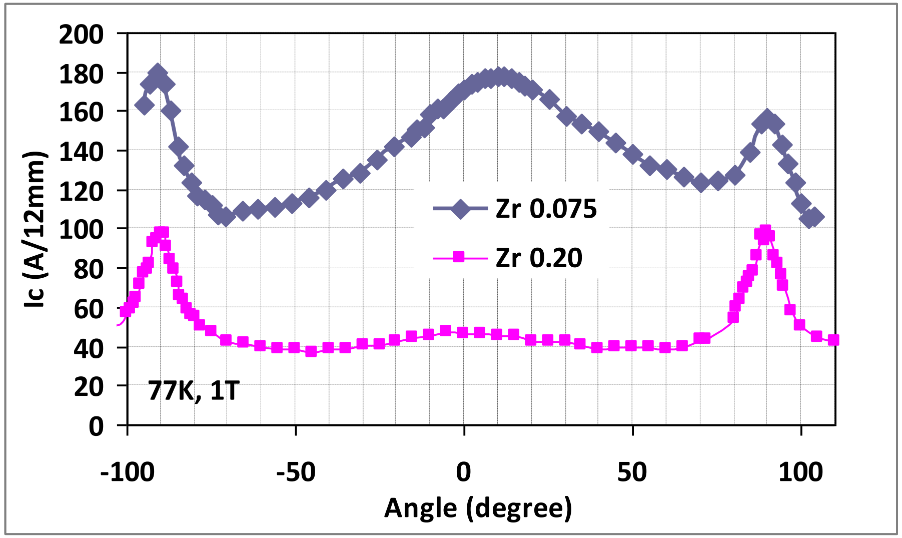
It will be shown that t**he composition effects on in-magnetic-field I_c at low temperature is significantly different from those at 77K**.

II. Zr content for low temperature applications

- For applications at 77K and 1T, the optimum mole content of Zr in the MOCVD precursor for Zr:REBCO films was 0.075
- For applications at lower temperatures and high magnetic fields, the Zr content should be higher
- However, there arose difficulties in growing high quality GdYBCO films with high Zr additions: for the high Zr films, the *c*-peak disappeared

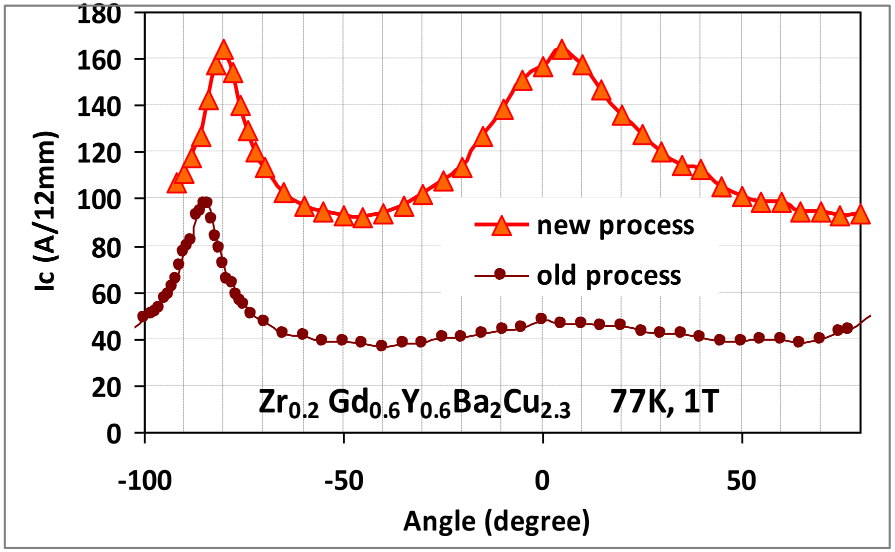
Ic as a function of Zr content, using old MOCVD conditions

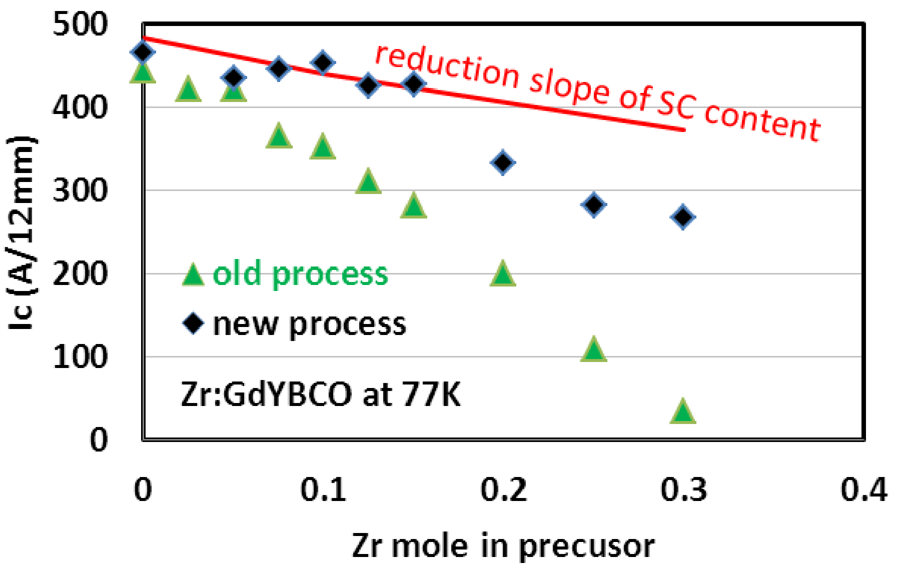




MOCVD for REBCO with high Zr additions

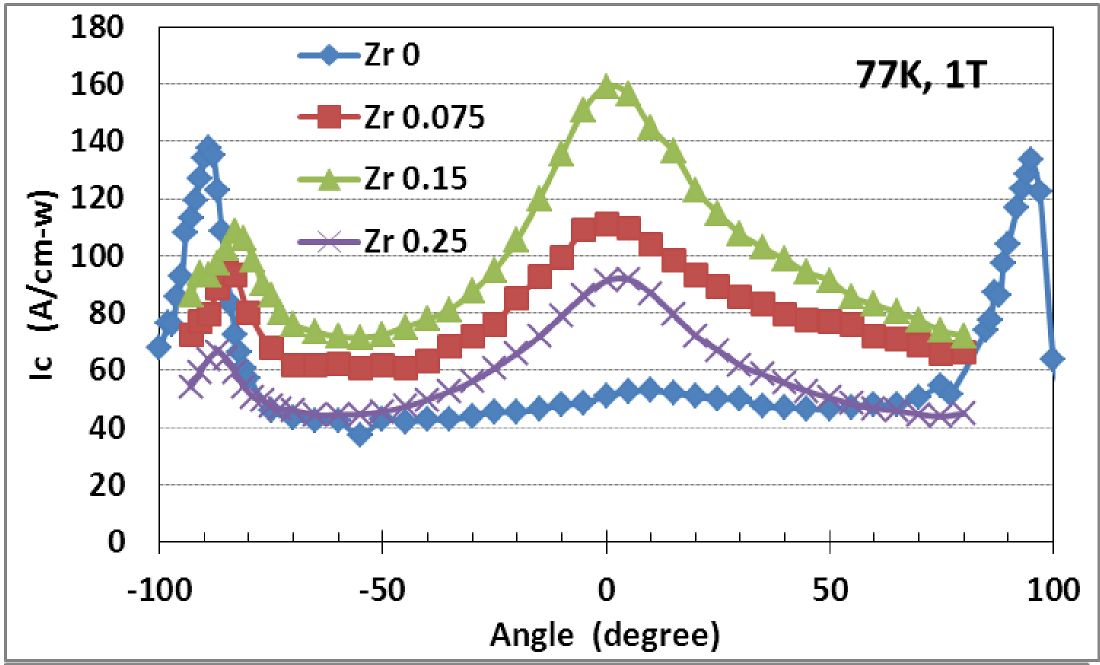
- Recently we modified MOCVD conditions for high Zr added GdYBCO films and significantly improved their performance
- The strong *c*-pinning indicated that long vertical nanorods formed
- Up to 15%-Zr, Ic(77K,0T) is high, indicating that the REBCO crystal quality was not degraded by the high Zr content
- In fact, **4µm thick 15%-Zr added GdYBCO achieved I_c(77K,0T) =1035A/cm-w**

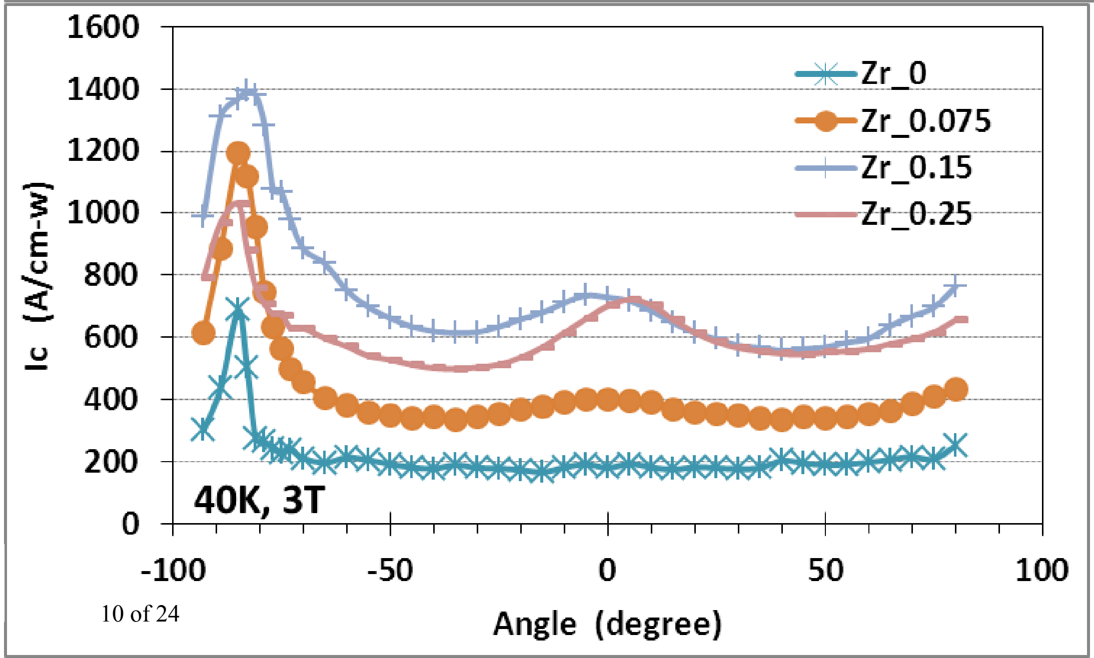




Angular dependence of Ic for Zr:GdYBCO

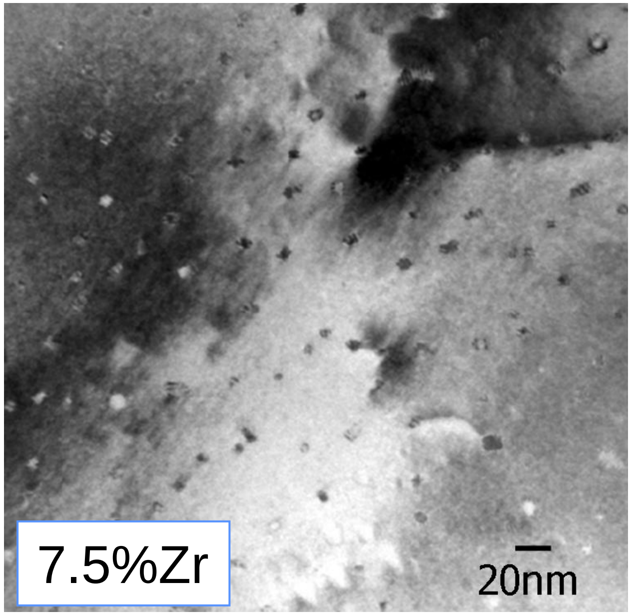
- In varying Zr content, (Gd,Y) content was fixed at 1.2
- At lower temperature, higher Zr showed better performance
- Process for 15%-Zr added GdYBCO has been reproducible
- Process for Zr>20% is being further studied, because the zero-field Ic is lower
- Addressed below is the analysis on further improvements needed.

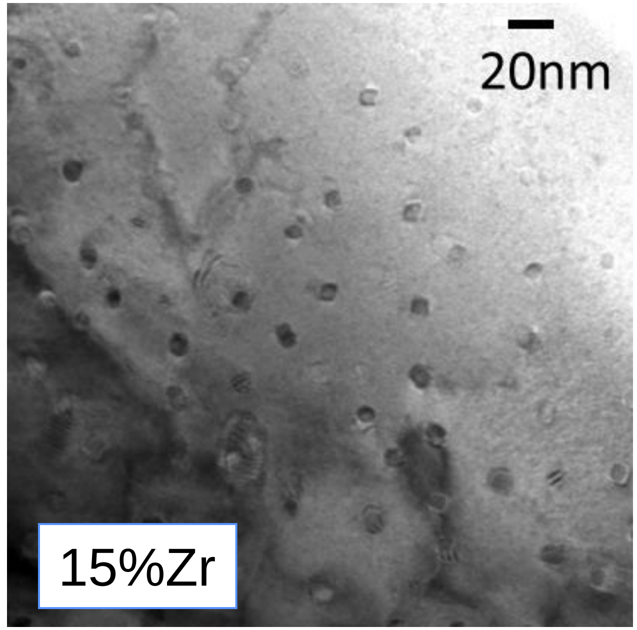


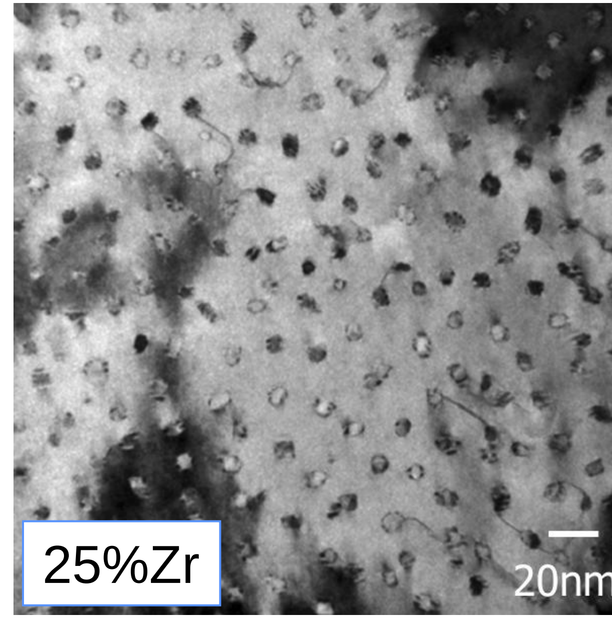


Film thickness ~ 0.9μm

Microstructure of Zr:GdYBCO – TEM planview







Distance between BZO rods:
20~50 nm

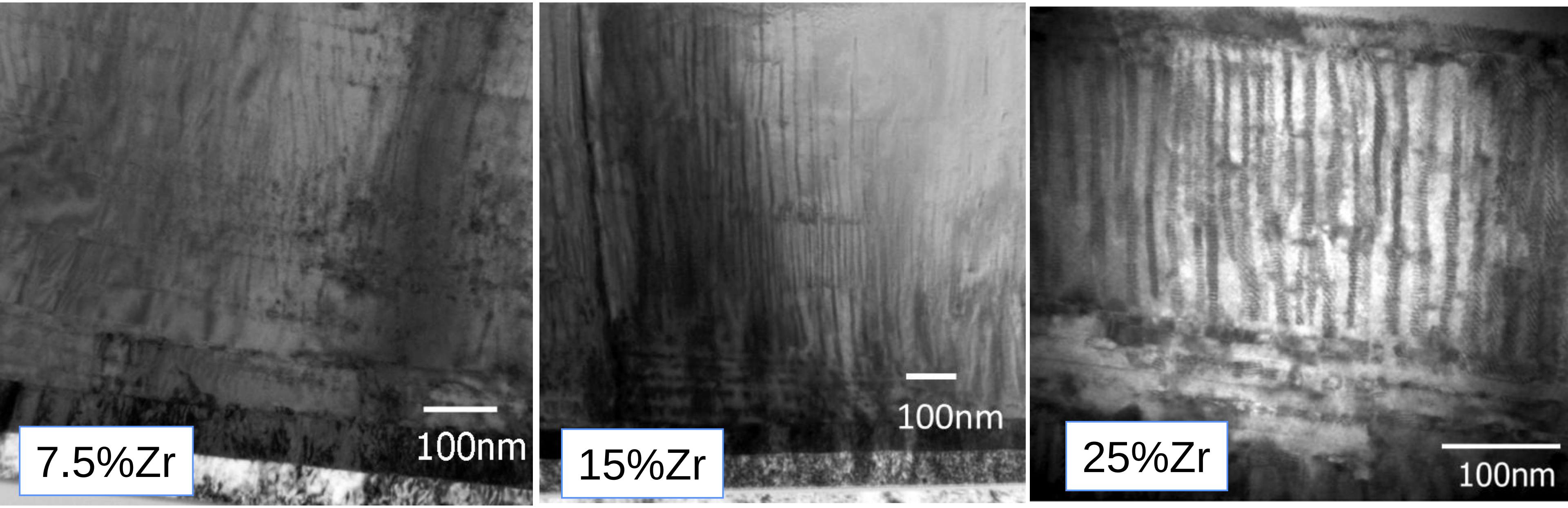
Distance between BZO rods:
~26nm

Distance between BZO rods:
~16nm

Low Zr: Distance between BZO rods varies in a large range.
There is room for more rods.
High Zr: Very dense rods.

Though the average distance between BZO rods decreases with increasing Zr content, the size of the BZO rod does NOT depend on the Zr content. The diameter of BZO rods ranges from 3nn to 7nm, depending on the deposition temperature.

Microstructure of Zr:GdYBCO – TEM cross section



For 7.5%Zr and 15%Zr, the microstructure is characterized by vertical BZO nanorods and horizontal RE_2O_3 nano-sheets embedded in GdYBCO matrix with good crystal quality.

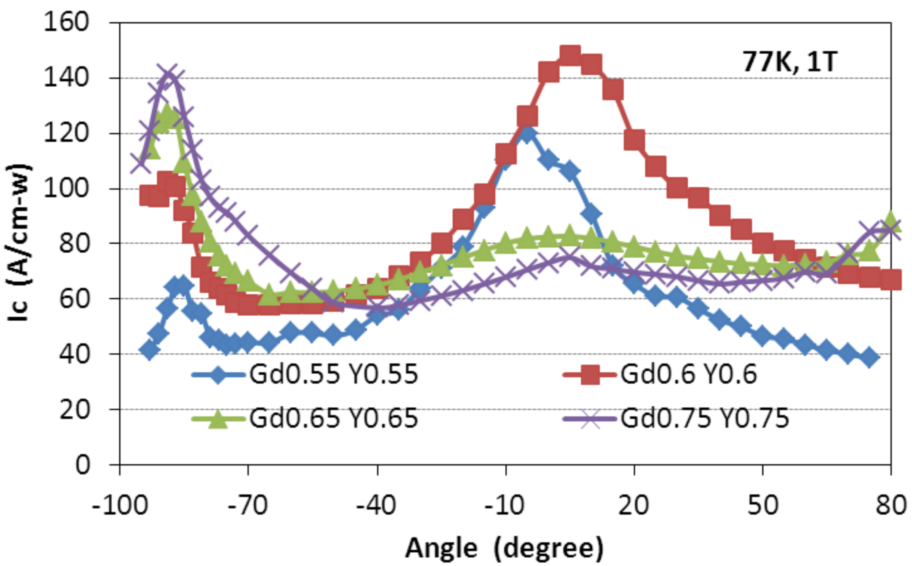
For 25% Zr, the crystal is not uniform, Some parts are of the same structure as that for 15%Zr ; some parts are of high density of in-plane-grown BZO and other second phases.

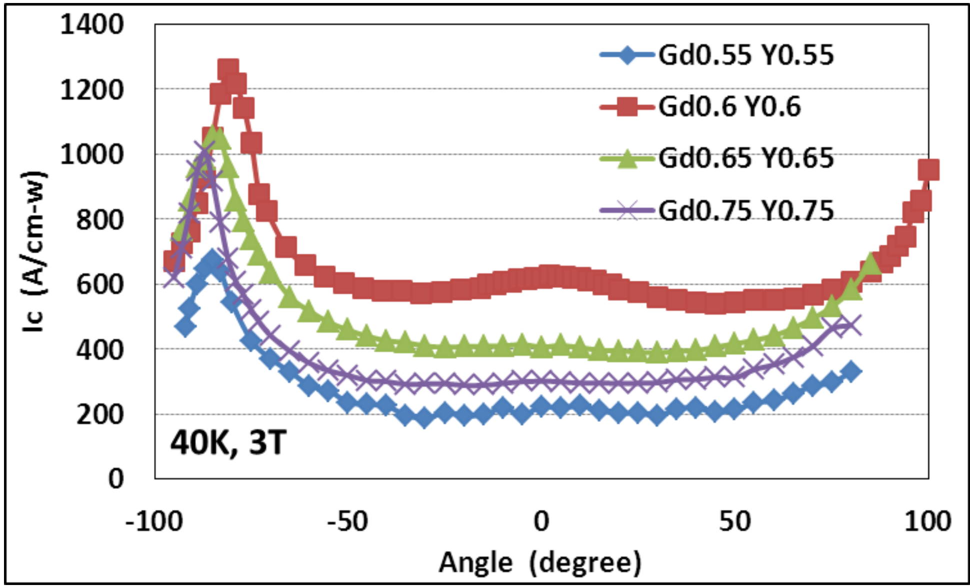
The structural variation along the vertical direction was caused by the non-uniform MOCVD condition in the reactor. Improvement in uniformity over the whole deposition area is needed to prevent the in-plane growth of BZO and other second phases.

III. Effects of Rare Earth Composition

The RE composition effects were studied for 15%-Zr added GdYBCO

- At 77K and 1T,
  - Ic_min (minimum Ic for all field angle) varies slightly for (Gd+Y) range 1.2 -1.5
  - *ab*-peak enhanced and *c*-peak suppressed with increasing (Gd,Y)
- At 40K and 3T,
  - $(Gd,Y)_{1.2}$ exhibits strongest flux pinning

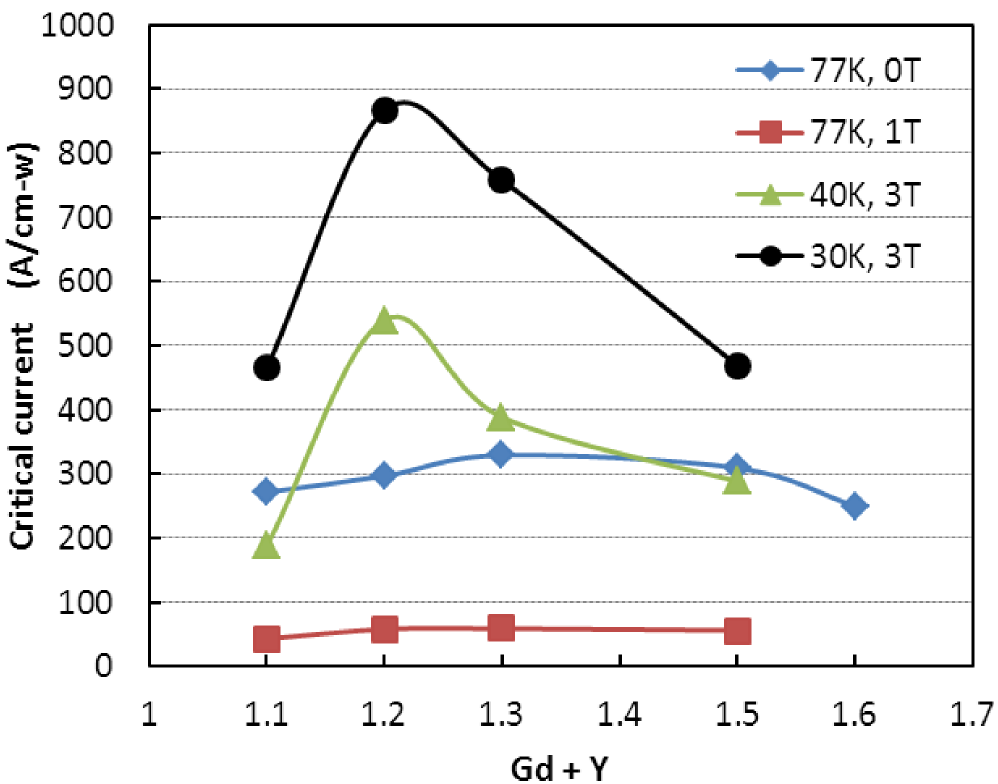




The RE composition effects on I_c for 15%-Zr added GdYBCO

- At 77K and 1T, Ic_min varies slightly for (Gd+Y) range 1.2 -1.5;
- At 40K and 3T, $(Gd,Y)_{1.2}$ exhibits strongest flux pinning.

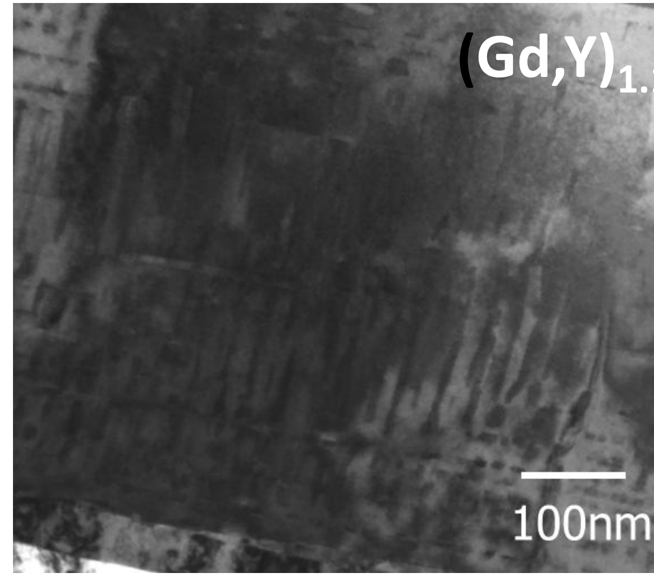
Ic at low temperature is more sensitive to RE composition than at 77K.

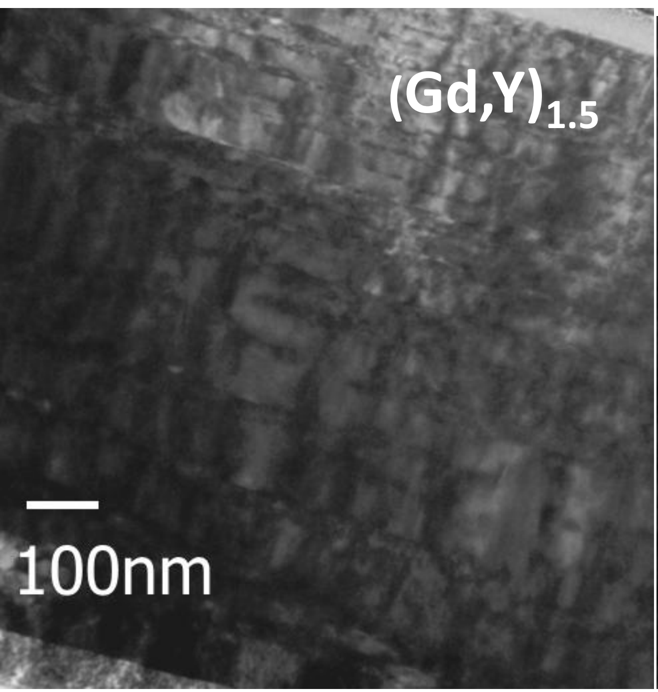


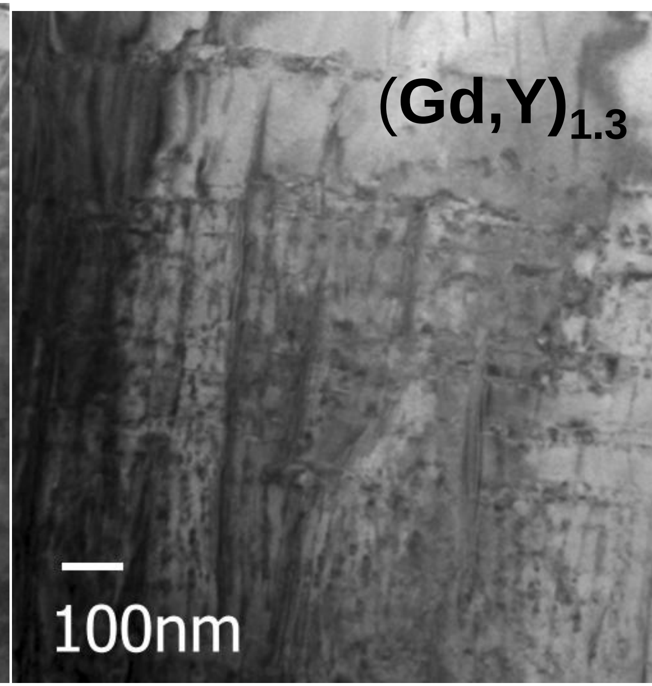
The critical currents in the figure are the minimum values of Ic for any field angle.

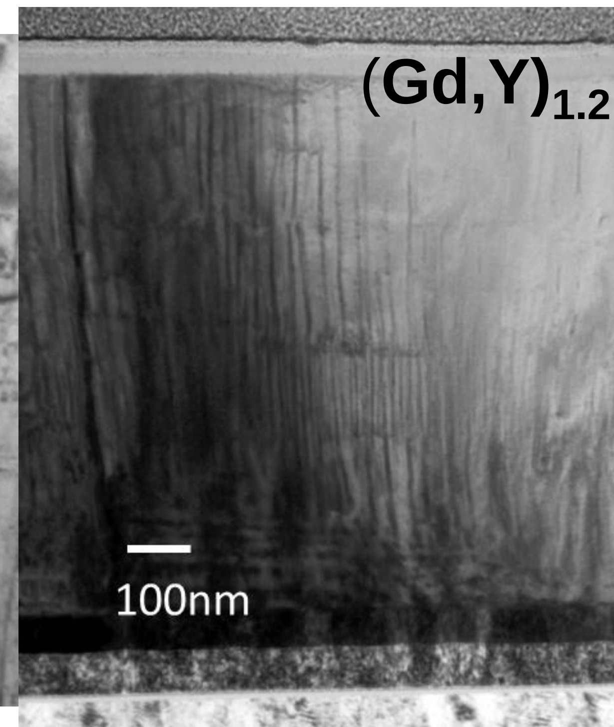
Effects of RE composition on microstructure

15%-Zr added GdYBCO with
Gd+Y = 1.1, 1.2, 1.3 and 1.5
General cross section view



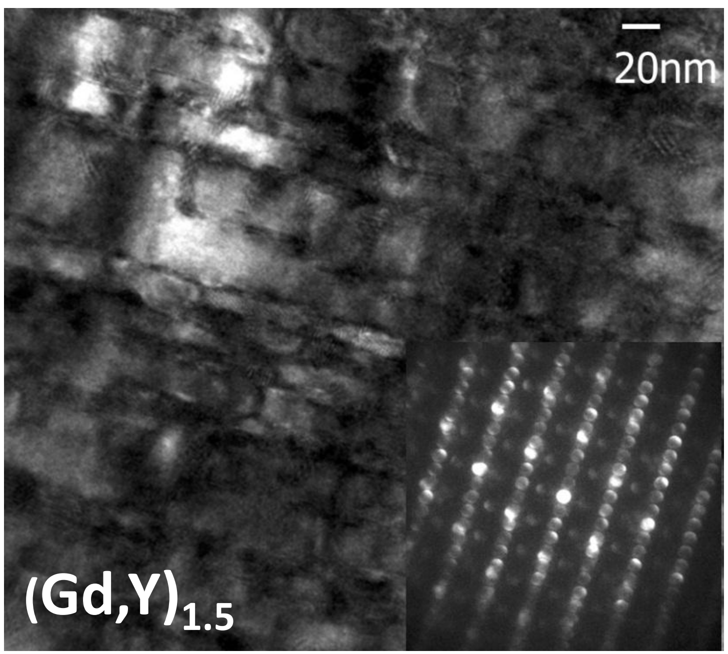


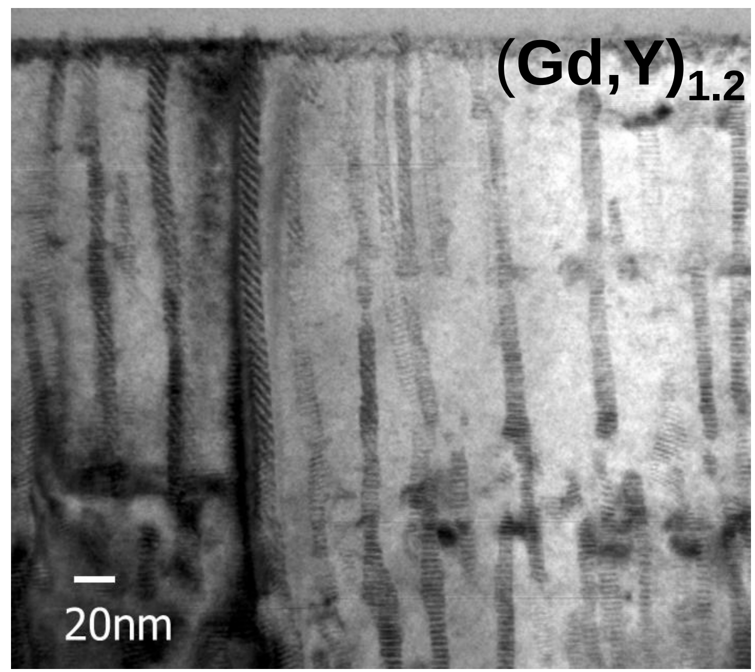




Effects of RE composition on microstructure

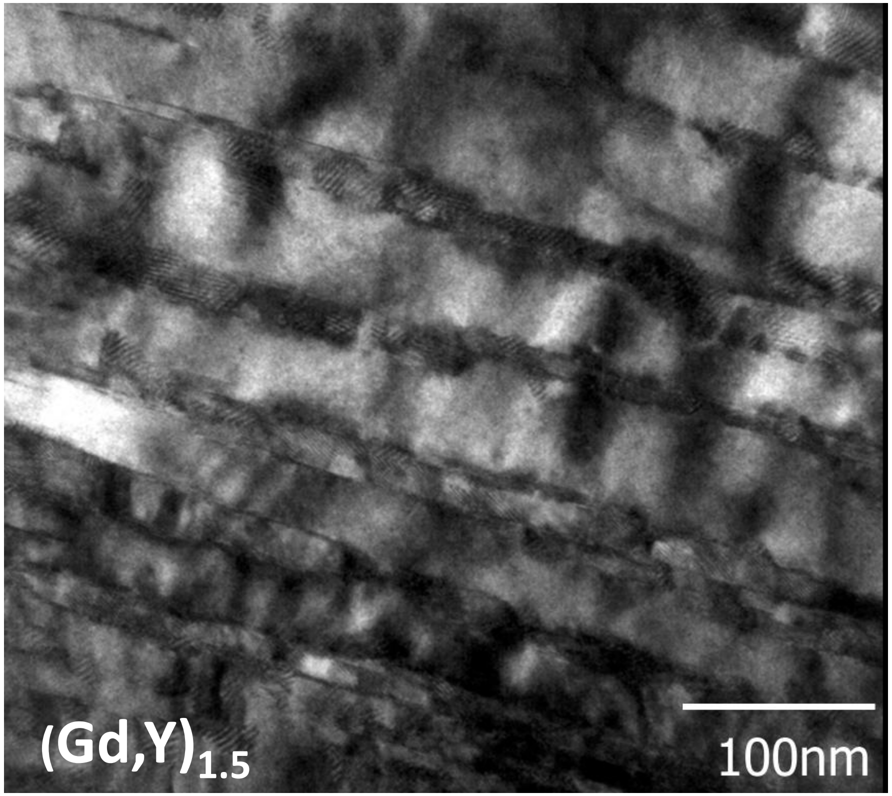
- **15%-Zr added (Gd, Y)$_{1.5}$BCO**
  - The structure is dominated by horizontal layers of RE_2O_3
  - Layer thickness >5 nm
- **15%-Zr added (Gd, Y)$_{1.2}$BCO**
  - The structure is of vertical rods, size 3 – 7 nm, and some thin horizontal layers

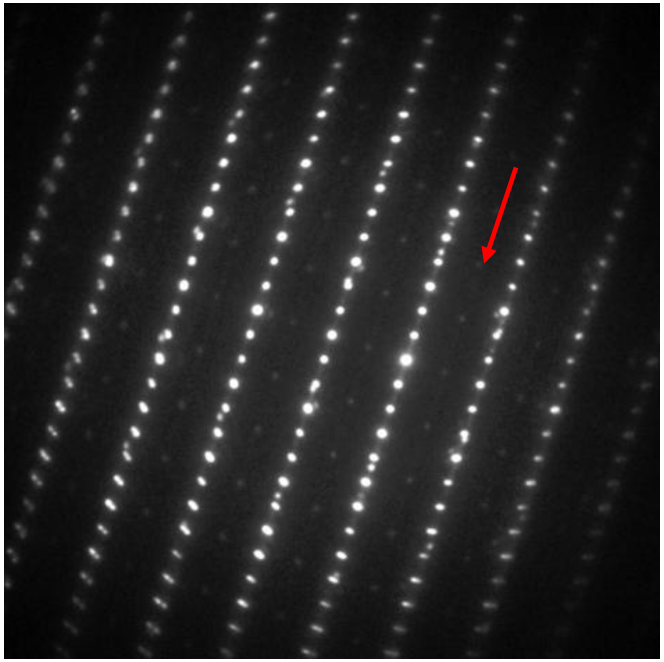




Interaction between RE_2O_3 and BZO

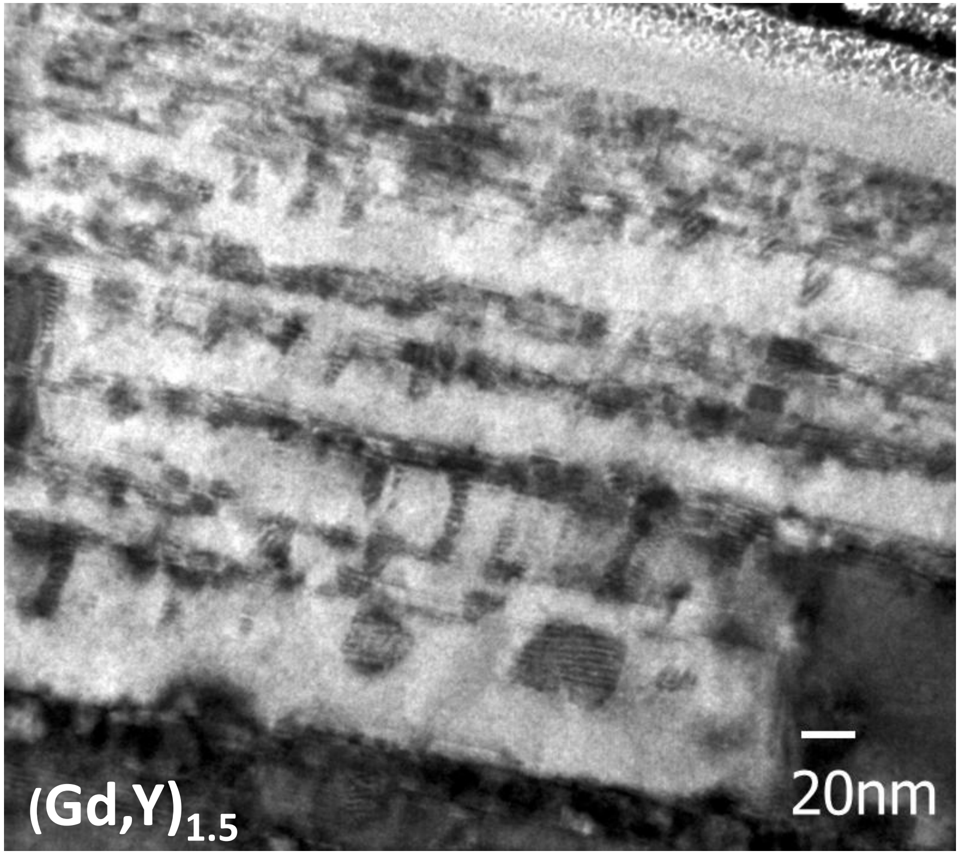
- **15%-Zr added $(Gd, Y)_{1.5}$BCO**
  - The horizontal layers are mainly RE_2O_3
  - The thick layers can prevent the growth of vertical nanorods





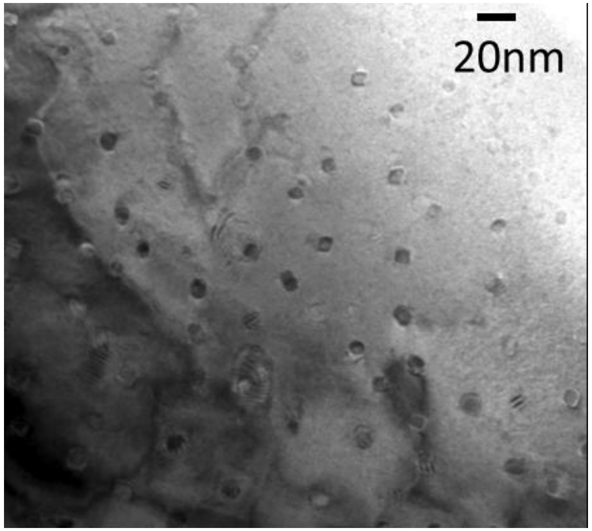
Interaction between RE_2O_3 and BZO

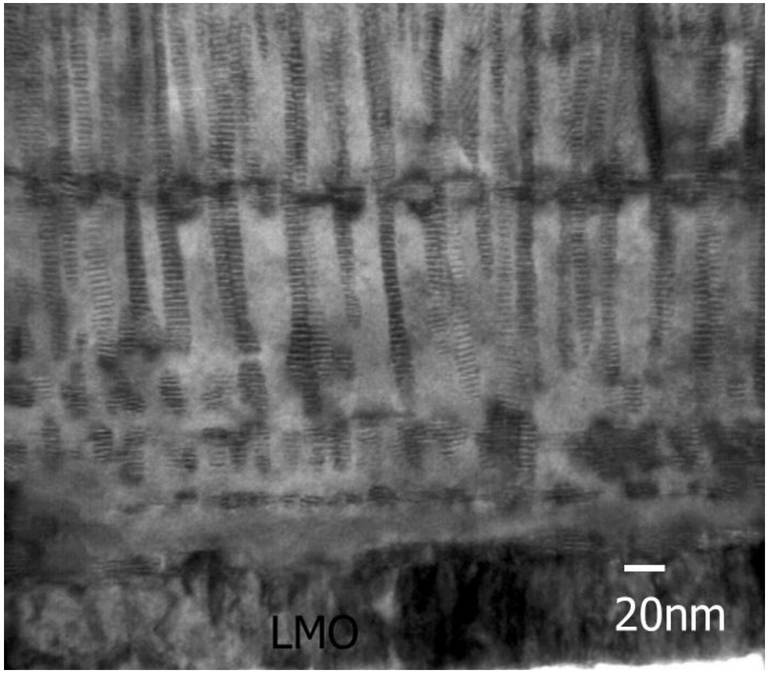
- **15%-Zr added $(Gd, Y)_{1.5}$BCO**
  - BZO exist only in the form of short segments
  - The layers stopped the continuous growth of the BZO rods, resulting in strong *ab*-pining and weak *c*-pinning

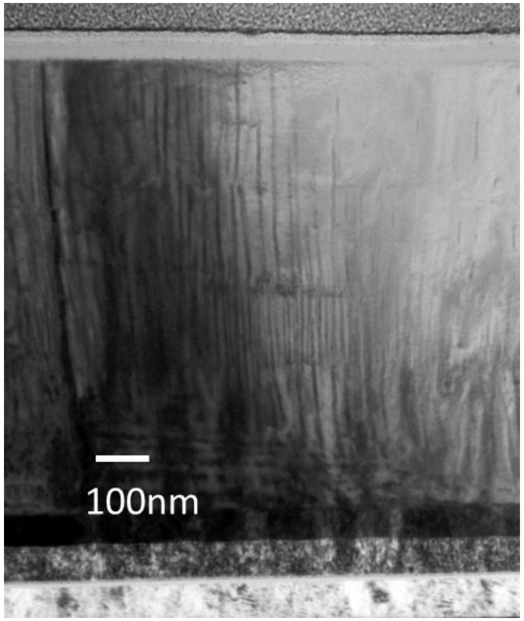


Interaction between RE_2O_3 and BZO

- **15%-Zr added $(Gd, Y)_{1.2}$BCO**
  - BZO nanorods grown vertically through the film
  - Size 3 – 8 nm, spacing 26nm
  - There are very few in-plane grown layers
  - The column growth limited the formation of RE_2O_3 layers
  - Suppressed the *ab*-pinning, enhanced *c*-pinning

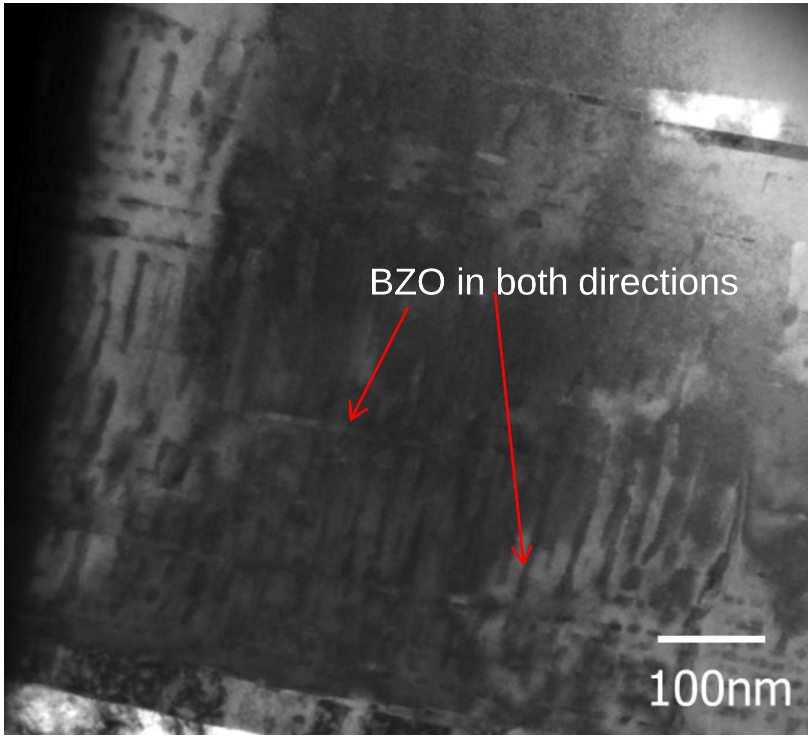


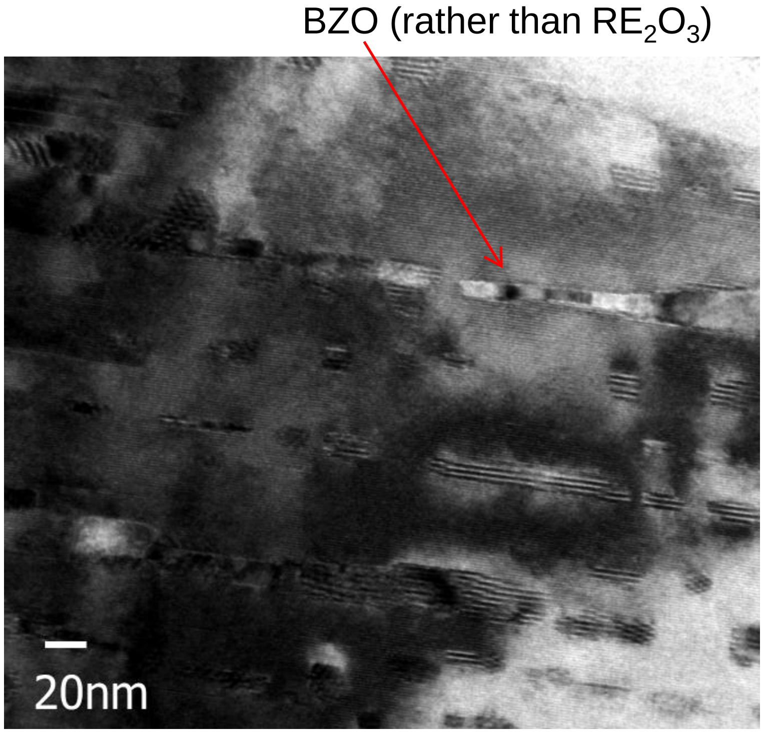




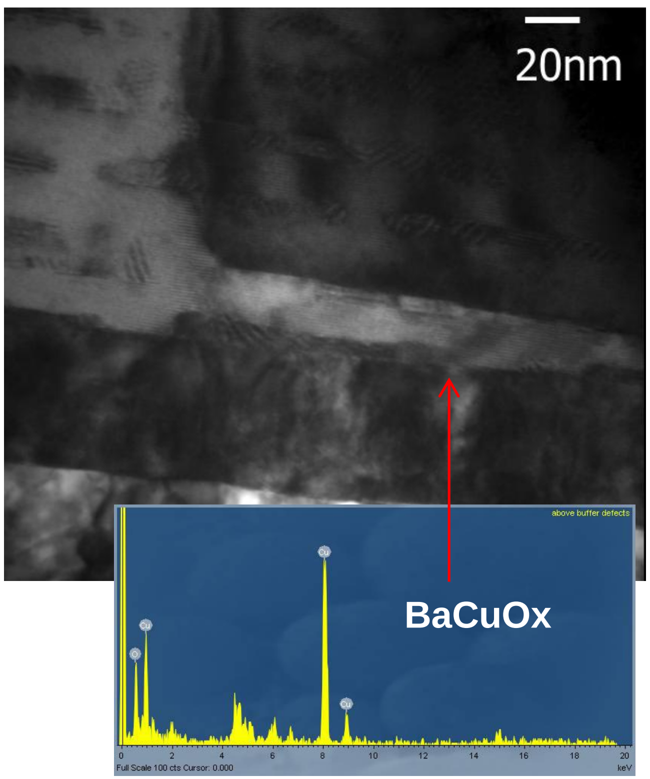
Interaction between RE_2O_3 and BZO

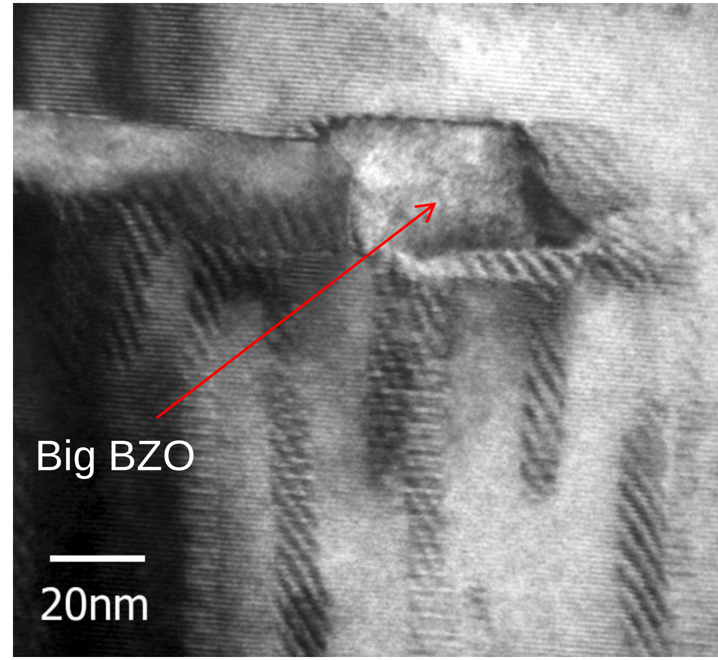
- **15%-Zr added $(Gd, Y)_{1.1}$BCO**
  - For $(Gd,Y)_{1.1}$, the structure of films with high Zr content could be different from that of films with low Zr content, as the large quantity of Zr compounds have the possibility of in-plane growth
  - Some of the in-plane segments are Zr compounds

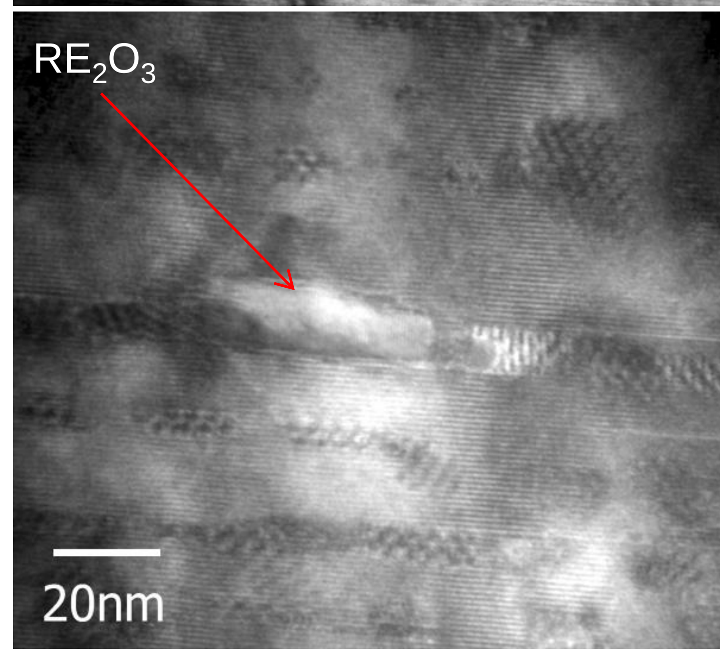




- **15%-Zr added $(Gd, Y)_{1.1}BCO$**
  - In films with low RE content, many big segments of second phases were found. These area extended defects with large lattice mismatch, degraded the crystal quality of the HTS matrix, and resulted in poor performance

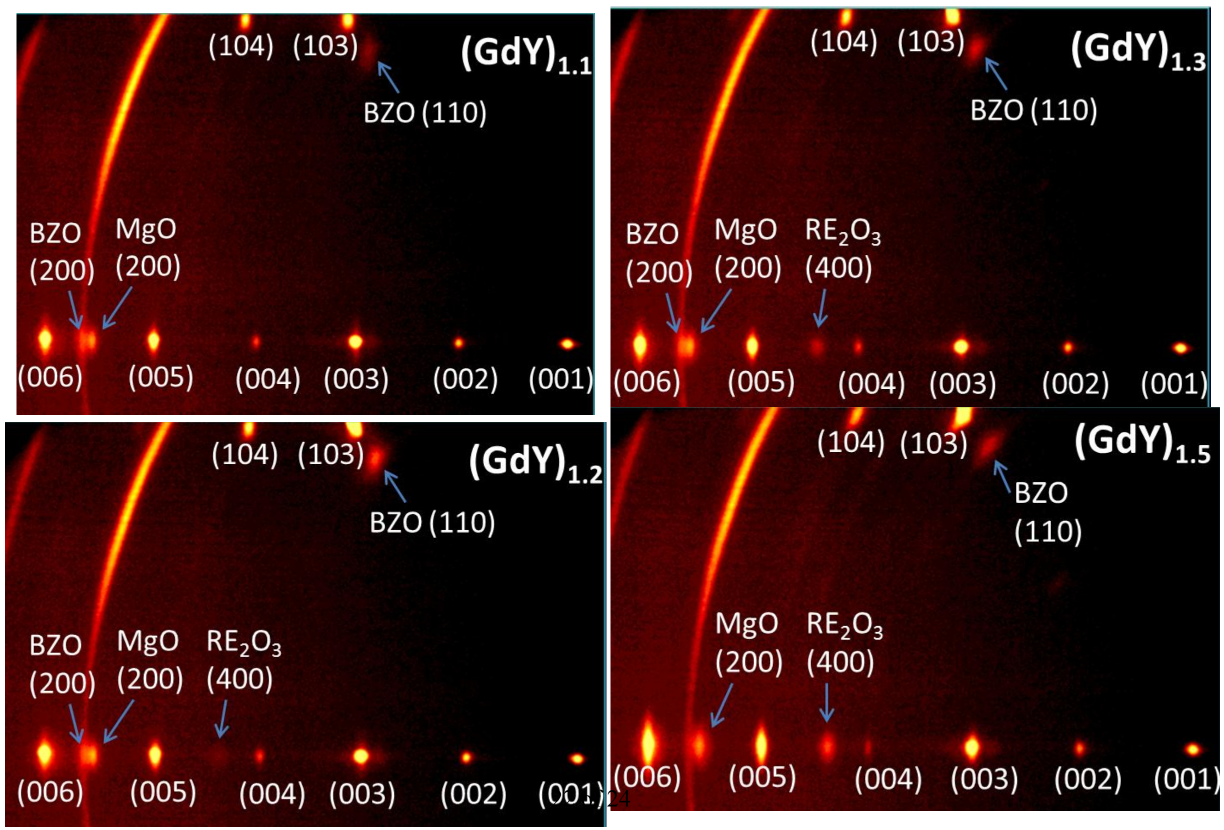






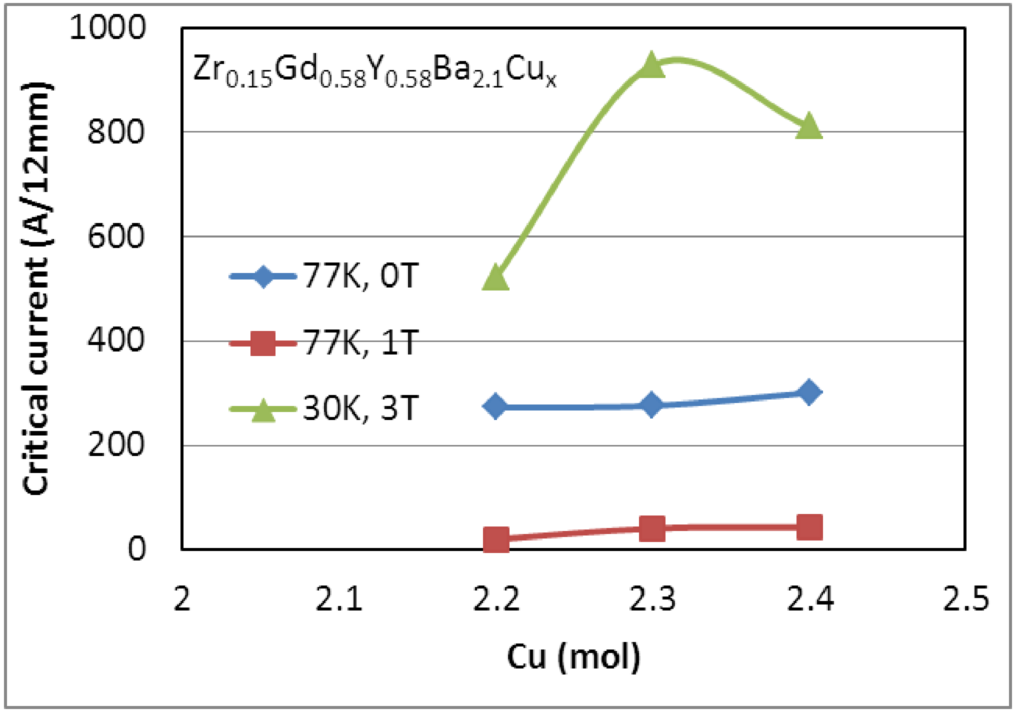
XRD study of interaction between RE_2O_3 and BZO

- For $(Gd,Y)_{1.1}$, the diffraction by RE_2O_3 was not seen. Ic was low
- For $(Gd,Y)_{1.5}$, the diffraction by RE_2O_3 was strong, while the diffraction by BZO was broad. High RE caused misalignment of BZO.
- For $(Gd,Y)_{1.2}$, week diffraction by RE_2O_3 was seen; strong and focused diffraction spot by BZO was also seen. This is the optimum structure.



IV. Effects of Cu Composition

Critical current (minimum for all field angle) as a function of Cu content in precursor of $Zr_{0.15}Gd_{0.58}Y_{0.58}Ba_{2.1}Cu_x$



Ic is more sensitive to Cu composition at low temperature than at 77K

V. Conclusions

1. Up to 15% Zr was added into GdYBCO films without degrading the quality of the HTS matrix
2. Flux pinning in the HTS tapes at low temperature was remarkably enhanced using 15%-25% Zr addition
3. In films with high Zr content, the large quantity of Zr compound can form vertically grown nanorods or horizontally grown plates, depending on the RE:Ba:Cu composition in precursor and the deposition conditions
4. Critical current I_c(B) at low temperature is more sensitive to RE:Ba:Cu composition than that at 77K
5. High RE content increase the in-plane grown defects, such as RE_2O_3 , BZO, and blocks the growth of long vertical rods. As a result, it dramatically reduces the pinning force at low temperatures
6. In the films with low RE content and high Zr content, area extended second phase, segments of $BaCuO_2$ and BZO, will form in the film and degrade the crystal quality of the HTS matrix
7. With RE=1.2, **long** BZO nanorods can be vertically grown in the film and strongly enhance the flux pinning at low temperature.
8. At low temperature, the long rods are of stronger pinning force than the short rods