HIGH-TEMPERATURE X-RAY DIFFRACTION STUDY OF PHASE EVOLUTION IN Ba₂YCu₃O₆+ₓ FILMS USING THE “BaF₂ CONVERSION PROCESS”

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ABSTRACT

In-situ high-temperature x-ray diffraction (HTXRD) was used to study the phase formation and reaction kinetics of the Ba₂YCu₃O₆+ₓ (Y-213) phase using the ex-situ “BaF₂ conversion process”. Three sets of films on single crystal SrTiO₃ substrates were prepared using the e-beam co-evaporation technique of BaF₂, Y and Cu targets. HTXRD studies were conducted on precursor films with thicknesses of 0.3 µm and 1.0 µm. The 0.3 µm films showed mainly (00l) texture whereas the 1.0 µm films showed a significant volume fraction of (h00) texture as well. A semi-quantitative estimate of the texture fraction was obtained using the software TexturePlus. The growth of Y-213 and the consumption of BaF₂ were found to be approximately linear in time.

INTRODUCTION

Today, the coated conductor technology holds tremendous promise for the superconductor industry. The key feature of the coated-conductor process is the deposition onto polycrystalline substrates (usually Ni or Ni-alloy) of superconductor films that are biaxially textured. Currently the principal techniques for preparing biaxially textured templates are: rolling-assisted bi-axially textured substrate (RABiTS) deposition [1], ion-beam assisted deposition (IBAD) [2], and inclined substrate deposition (ISD) [3].

The primary issue in the development of coated conductors for practical use is the application of this technology to the production of long-length tapes. The “BaF₂” ex-situ process is currently one of the most promising methods for producing long-length tapes [4-7]. This 2-step process involves a low-temperature deposition of precursor layers using either high-rate e-beam deposition of Y, BaF₂ and Cu onto a substrate, or open-air solution techniques, both of which are followed by a post-annealing at high-temperature in the presence of water vapor under reduced atmosphere. The process occurs between 700°C and 800°C. The overall reaction for the process can be written as: 2BaF₂ + ½Y₂O₃ + 3CuO + 2H₂O → Ba₂YCu₃O₆.₅ + 4HF. In order to control and optimize the BaF₂ process, it is important to understand the detailed mechanism of the Y-213 phase formation. In the present work we report preliminary results of the high-temperature x-ray diffraction (HTXRD) studies aimed to understand the chemistry, mechanism, and kinetics involved in converting the BaF₂-Y-Cu precursor films to Y-123 in the presence of H₂O vapor.

EXPERIMENTAL¹

Film deposition
The “BaF₂” precursor films were prepared by electron beam evaporation of Cu and Y metal and BaF₂ as described in [4]. The substrates were not intentionally heated during the deposition. Three sets of films, one with thickness of 0.3 µm and two with 1 µm, respectively, were...
This document was presented at the Denver X-ray Conference (DXC) on Applications of X-ray Analysis.

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deposited on the model (100) SrTiO$_3$ substrate. These SrTiO$_3$ substrates were annealed at 1000 °C in 1 atm of O$_2$ prior to the precursor deposition. The typical size of the films for the x-ray experiments is about 4 mm x 3 mm.

**High Temperature X-ray Diffraction (HTXRD)**
A high-temperature Siemens 5000 X-ray diffractometer which was equipped with either a scintillation counter or a position sensitive detector (PSD, installed at a later stage), and a high-temperature furnace, was modified for the present study by adding a gas flow apparatus. This apparatus includes a series of bubblers containing NaCl-saturated water at room temperature and an oxygen analyzer. Helium gas containing ~ 100 ppm to 200 ppm O$_2$ by volume was flowed through the bubblers and passed directly over the sample in the enclosed furnace chamber. Because of the θ-θ geometry, the specimen remained fixed in a horizontal position during the experiments. Cu K$_α$ radiation was used for the studies. For a scintillation counter, the X-ray patterns with acceptable signal-to-noise ratio were recorded in the 14°-26° 2θ range. The patterns were recorded continuously for approximately 12 min each. A significantly wider range of 2θ (14°-62°) could be scanned with a PSD during half that time, while preserving comparable noise level; however, the 2θ range between 40° and 52° (around the strongest 200 peak of SrTiO$_3$) had to be excluded to avoid saturation of the PSD. Four films from three differently processed sets were selected for this report. Film #1 (Set-1) is a 0.3 µm BaF$_2$ film, which was heated from room temperature to 735 °C over a 2 hr period. Film #2 (Set-2), Film #3 (Set-2), and Film #4 (set-3) are 1 µm thick. Film #2 was ramped to 735 °C in 30 minutes, while Films #3 and #4 were ramped to 735 °C in 2 hrs. Films #1, #2 and #3 were studied using a scintillation counter, while Film #4 was studied using PSD.

**RESULTS AND DISCUSSION**

**Phase Evolution**

![X-ray diffraction pattern](image)

Fig. 1. High temperature x-ray diffraction patterns of Film #1 (0.3 µm). The film was heated up to 735 °C in 2 hr.
Figure 1 shows a series of high temperature XRD patterns (12° range 2θ) from the 0.3 µm Film #1. The crystallization of the BaF₂-type phase followed by the development of the Y-213 phase is observed. The intensities of the 00l reflections of Y-123 appear much stronger than those of the h00 reflections.

Figures 2 and 3 illustrate selected XRD patterns of the two 1 um thick films (Films #2 and #3). Phase formation sequence repeats that observed for the thin film. A comparison between the two thick films suggests that slower heating to T=735ºC promotes c- over a-texture. Both thick films featured smaller fraction of the c-textured regions as compared to the thin film (#1); however, more data is needed to test the significance of these observations. Under more optimized conditions, non c-axis growth can be essentially eliminated.

XRD patterns of Film #4 (set 3) recorded at different temperatures upon heating to 735ºC are shown in Fig. 4a, while Fig. 4b displays the patterns subsequently recorded at T=735ºC as a function of time. The phase evolution on heating can be summarized as following: First, the crystallization of both the BaF₂-type and Cu₂O phases occur at ~300ºC. At ~550 ºC, the Cu₂O oxidizes to CuO. Y-213 nucleates at ~700 ºC along with the ‘X’ phase, which is tentatively identified as the Ba₄Y₂Cu₇Oₓ (427) phase. Phases of Ba₂YCu₄Oₓ (214)/427 type have been observed as intergrowths [8, 9]. These phases are stable at temperatures lower than those for Y-213 [10]. The 427-phase disappeared ~70 minutes after the temperature reached 735ºC (Fig. 5b), while the BaF₂-type phase was totally consumed after ~100 min. TEM studies of specimens representing different stages of phase formation are in progress to identify the nature of the intermediary phase and to provide insight into a growth mechanism of the Y-213 phase.

**Texture Analysis**

The software ‘TexturePlus’ (http://www.ceramics.nist.gov/webbook/TexturePlus/texture.htm), developed at NIST, was used to determine the volume fractions of differently textured Y-123 phase in the samples [11]. This program calculates the texture profile of a specimen using two XRD patterns: a θ-2θ scan of the Bragg peak from the textured planes, and a rocking curve with the diffractometer set at the angle of interest.

Quantitative analysis of the distribution of orientation for the a- and c-axis populations for Film #4 was performed. The XRD pattern of the Film #4 cooled to room temperature featured both h00 and 00l reflections. Omega-scans using the 200 and 007 reflections are shown in Figs. 5a and 5b. The FWHM for these peaks is rather narrow, 0.36° and 0.76° for reflections 007 and 200, respectively. Assuming negligible amount of random orientation, the volume fraction ratio Vₐ/Vₐ can be approximately estimated as the ratio of the integrals of the corrected o-scans multiplied by the ratio of the integrated films peak intensities of the random sample. Using the expression: \( V_{200}/V_{007} = [(I_{\text{int}})_{200}/(I_{\text{int}})_{007}] \cdot [(I_{\text{ran}})_{007}/(I_{\text{ran}})_{200}] \), the ratio is estimated to be ~ (0.040/0.086) (3/34), or ~ 2/5.

**Phase Formation Kinetics**

The kinetics of Y-123 growth was estimated for the Film #2 by following the changes in intensities of both BaF₂ 111 and the Y-213 002 reflections as a function of time (Fig. 6). The zero time corresponds to the maximum intensity of the BaF₂ peak. These results indicate that
Fig. 2. High temperature X-ray diffraction patterns of Film #2 (1 µm). The film was heated up to 735 °C in 30 min.

Fig. 3. High temperature X-ray diffraction patterns of Film #3 (1 µm). The film was heated up to 735 °C in 2 hr.
Fig. 4a. X-ray diffraction patterns of Film #4 as a function of temperature (°C).

Fig. 4b. X-ray diffraction patterns of Film #4 (at a fixed 735 °C) as a function of time (min).
Fig. 5a. $\omega$ scan of the 200 reflection of Film #4

Fig. 5b. $\omega$ scan of the 007 reflection of Film #4

Fig. 6. A plot of the integrated intensity of the strongest BaF$_2$ (111) peak and The Y-213 (002) peak for Film #2 as a function of time (min).
both the growth of Y-213 and the consumption of BaF$_2$ are approximately linear. The Y-213 was found to be fully converted in approximately 100 minutes. The linear rate of formation of Y-213 agrees with that reported by Smith et al. [12].

**SUMMARY**

The use of a PSD facilitates analysis of the phase formation sequence from the Ba-Cu-Y-F precursor to the Y-213. Preliminary results indicate that in the 0.3 µm film the c-axis texture is predominant, while the thicker 1 µm films contain a significant amount of a-oriented regions. Detailed analysis of phase formation in this system using combined HTXRD/XRD and TEM techniques is in progress to elucidate the detailed phase formation sequence, as well as the effect of various processing parameters on the growth and texture of Y-213 phase.

**ACKNOWLEDGEMENTS**

Partial financial support from the US Department of Energy (DOE) is acknowledged.

1Certain trade names and company products are mentioned in the text or identified in illustrations in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by National Institute of Standards and Technology.

**REFERENCES**