

## Modulus study of microcracks in single domain $\text{YBa}_2\text{Cu}_3\text{O}_x$ with $c$ -axis pressure during oxygen anneal

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### Abstract

As the modulus is a quantitative measure of the bulk mechanical properties, it can serve as a sensitive probe for the crack propagation kinetics inside the materials. The  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (YBCO) single domain with a tetragonal phase was pressed under a uniaxial pressure along the  $c$ -axis. The pressed sample was oxygenated at 400 °C for various time intervals up to 188 h. For each oxygenation interval, Young's modulus was measured to study the effects of  $c$ -axis pressure on  $ab$ -plane crack propagation in single domain YBCO. The measurement was repeated along two directions:  $ab$ -plane (S) and  $c$ -axis (T), on the same sample annealed in flowing oxygen for various times. The experimental results showed that the modulus values of both directions remained unchanged for the entire oxygenation period, indicating that the  $ab$ -plane crack propagation was effectively suppressed. In contrast, it was found that, without the  $c$ -axis pressure, the modulus experienced a rapid fall when the sample had undergone a massive tetragonal-to-orthorhombic (T-to-O) transition.

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### 1. Introduction

$\text{YBa}_2\text{Cu}_3\text{O}_x$  (YBCO) exhibits a tetragonal (T) to orthorhombic (O) phase transformation as oxygen content exceeds 6.4 [1–5]. In large domain YBCO prepared by seeded melt growth methods [6] it has been found that  $ab$ -plane cracks are often formed due to volume changes that occur during the T-to-O phase transition. These microcracks are highly undesirable in both fundamental studies and engineering applications. For instance, in RF filter design; these cracks are detrimental to the surface properties. On the other hand, these internal cracks interrupt the integrity of the materials, making the measurement of intrinsic properties difficult for basic research. Therefore,

seeking for ways to remove, or reduce the micro cracks in bulk YBCO is of great importance. In our previous study [6], we employed a unique method that effectively reduced the  $ab$ -plane cracks. This was achieved by applying a  $c$ -axis uniaxial pressure on polished  $ab$ -plane surfaces during oxygenation. Both surface optical microscopy and X-ray study showed that no micro cracks were observed in the YBCO single domain samples oxygenated in this fashion. However, in this previous study, the observation was limited on the polished sample surfaces. Although the surface optical microscopy revealed no obvious cracks, the information on the internal  $ab$ -plane crack propagation was unknown. In another parallel study of  $ab$ -plane cracks, we used a modulus measurement to probe the crack propagation in the similar single domain YBCO samples [7,9]. As the samples were annealed in flowing oxygen, it was found that the modulus values experienced a rapid fall, corresponding to the T-to-O phase transition, which was

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confirmed by X-ray diffraction. This experiment showed a close relationship between the crack propagation kinetics and mechanical properties (modulus) in the YBCO single domains. In this follow-up research, we present the data from modulus measurements on the YBCO single domain samples under a  $c$ -axis uniaxial pressure during the oxygen anneal. The results are consistent with optical observations from the previous works. The crack formation mechanism under  $c$ -axis pressure is discussed.

## 2. Experimental

The single domain YBCO was grown by a variety of methods developed for large-scale engineering applications [8,10–19]. In this research, the single domain samples were disc shaped pellets (20 mm in diameter and 15 mm in height). We used precursors of 70 wt.%  $\text{YBa}_2\text{Cu}_3\text{O}_x$ , 30 wt.%  $\text{Y}_2\text{BaCuO}_5$ , and 0.15 wt.% Pt. These powders were thoroughly mixed and uniaxially pressed at 100 MPa into a disc shaped green pellet of 35 g. The green pellet was sintered in air at 930 °C for 24 h. A  $\text{SmBa}_2\text{Cu}_3\text{O}_x$  single domain was used as seed having a dimension of  $2 \times 2 \times 1.5 \text{ mm}^3$ . The seed was on the top of the green pellet before the growth process. The green pellet was placed on an alumina plate with an intermediate layer of  $\text{Y}_2\text{O}_3$  powder to avoid liquid spreading on the interior surfaces of the furnace. A sintered thin plate consisting of a mixture of  $\text{YbBa}_2\text{Cu}_3\text{O}_x$  and  $\text{YBa}_2\text{Cu}_3\text{O}_x$  was also used between the green pellet and the  $\text{Y}_2\text{O}_3$  layer. This substrate was found necessary to avoid parasitic grain growth from the bottom. After the completion of the domain growth, the sample was cooled in nitrogen gas to prevent the phase transformation from the tetragonal to orthorhombic structure. In this way, the sample is free of  $ab$ -plane crack formation. The details about the YBCO single domain growth can be found in Refs. [20–22].

In this experiment, the sample was sliced into  $2.0 \times 0.5 \times 0.24 \text{ mm}^3$  bars from the pellet for the oxygenation anneal under a uniaxial pressure along the  $c$ -axis. The pressure vise was a commercial flange made of stainless steel as shown in Fig. 1. The flange diameter was 34 mm with a thickness of 7.2 mm. As shown in Fig. 1,

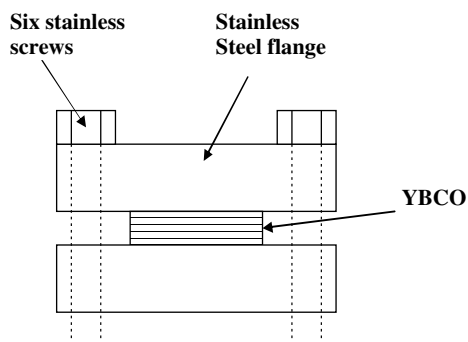


Fig. 1. A schematic diagram showing the application of uniaxial pressure along the  $c$ -axis of the YBCO crystal.

the disc sample was sandwiched between two flanges tightened with screws. Before tightening the screws, the flanges were placed in a hydraulic press for achieving a uniform force along  $c$ -axis. As the hydraulic pressure reached 15 MPa, six 4.2 mm screws were hand-tightened. To ensure a uniform pressure, the top and bottom surfaces of the disc sample were polished by a special device making these surfaces parallel to each other. This procedure was identical to that used in the previous pressure-oxygenation experiment. It was after this parallel surface polishing; the disc sample was sliced into bars of the dimensions described above for heat treatment and modulus measurements.

It should be noted that during origination at 400 °C, expansions of both metallic parts (the flanges and the screws) and the ceramic sample would take place. While the four screws may equally elongate leading to dilatation, the flanges in fact would expand at the same time. Meanwhile, the ceramic sample could also experience expansion, however, maybe at a smaller magnitude. These expansions at the annealing temperature would ultimately result in changes in the overall compressive pressure on the YBCO sample in the  $c$ -axis. Although in present and the previous experiments [6], no direct *in situ* stress measurement was conducted; the results from Ref. [6] show clear effects of the uniaxial pressure on  $ab$ -crack formation and propagation. With the uniaxial pressure applied during oxygenation up to 72 h, no  $ab$ -plane cracks were observed on the polished surfaces under optical microscope. This sharp microscopic contrast is the convincing evidence that, despite of possible dilatation, the uniaxial pressure is still effectively applied and the formation of  $ab$ -plane cracks is suppressed due to this pressure. Furthermore, it was found that the removal of the screws became substantially more difficult after the annealing process indicating an increased compressive stress due to thermal expansion. Nonetheless, at this point, it has been difficult to precisely experimentally determine the dilatation of the screws and related pressure changes at 400 °C.

To study the kinetics of crack behaviors inside the YBCO samples, optical observation may not be ideal since it requires the interruption of the annealing process and destruction of the samples. To observe a continuous crack formation and propagation, we employed a standard test method for dynamic Young's modulus for advanced ceramics. As is well known, the mechanical properties of a ceramic bulk sample are directly connected to the internal cracks. Young's modulus is a typical mechanical property that is reflective of internal crack behaviors. In this experiment, the Grindo Sonic MK5 "Industrial" Instrument was used to determine the Young's modulus [23]. The procedures used to determine Young's modulus can be found in Refs. [7,9]. Dynamic modulus is measured using a resonant vibration that propagates through the interior of the specimen. The formation and propagation of micro cracks can sensitively affect the vibration frequency, based on which the modulus is calculated. The flexure frequency was recorded at each annealing interval. To study the

anisotropic behaviors, the input mechanical resonant wave was sent along two directions: along the *ab*-plane (S) and parallel to the *c*-axis (T). As micro cracks propagated in the matrix of the YBCO, the vibration frequency would change sensitively leading to a reduced modulus of the materials. Therefore, the modulus measurement could be used as an effective tool to study the crack formation and propagation.

In this experiment, the virgin sample had a tetragonal phase as it was cooled in nitrogen gas. These bar samples were annealed in flowing oxygen at 400 °C between 8 h and 188 h. These samples were under uniaxial pressure along the *c*-axis during oxygen annealing. At each annealing interval, the samples were furnace-cooled to room temperature and used for modulus measurement. After each modulus measurement, the very sample was used for a prolonged oxygenation under the same condition. This procedure was repeated for the entire oxygenation process up to 188 h. Two samples with identical geometry were used for parallel study.

### 3. Results and discussion

To investigate the internal crack propagation along the *ab*-planes, we employed a modulus measurement on these

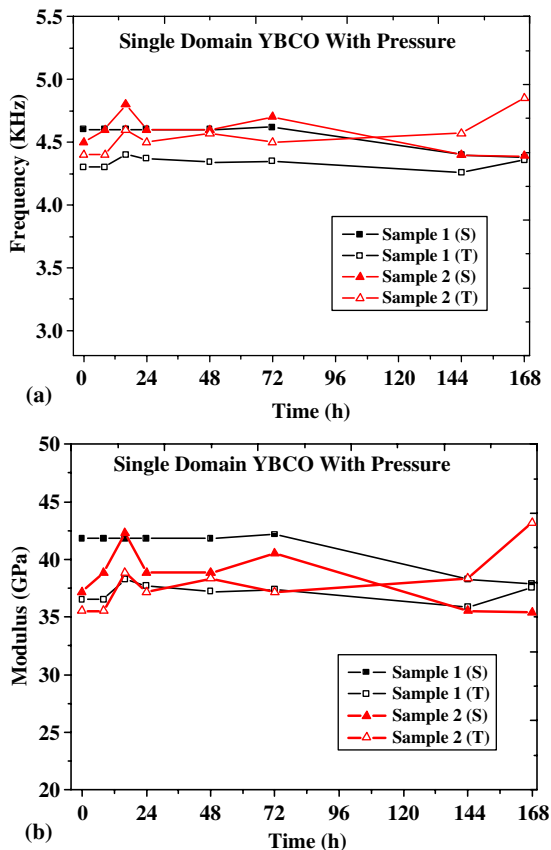


Fig. 2. (a) Flexure frequency versus annealing time, and (b) modulus versus annealing time for samples annealed under the *c*-axis pressure for both S and T directions.

samples. The data are shown in Fig. 2. Both flexure frequency and modulus data along *ab*-plane (S) and *c*-axis (T) for both samples (S1, T1, S2, T2) are shown in Fig. 2a and b, respectively. The reason for using both S and T modes was to ensure that there was no anisotropic effect in modulus. In Fig. 2a, the frequency values in both S and T directions remain more or less the same indicating no significant microstructural changes during oxygenation. The similar behaviors were observed in modulus as can be seen in Fig. 2b. Fig. 2b shows that the modulus values obtained from these two directions are on the same order of magnitude for both samples, and this behavior remains unchanged for the entire annealing time up to 188 h. In this work, we also studied the crack propagation kinetics in the similar samples oxygenated for the same length of time. However, these samples were annealed without uniaxial pressure along the *c*-axis. For comparison, we show both frequency and modulus data for two YBCO single domain samples oxygenated without pressure in Fig. 3. Note that, in the oxygenation experiment without uniaxial pressure, the modulus data were taken only along the *ab*-plane (S) since anisotropy in mechanical properties was observed to be not significant. As can be seen in Fig. 3a, the frequency values remain a plateau up to 48 h. They experience

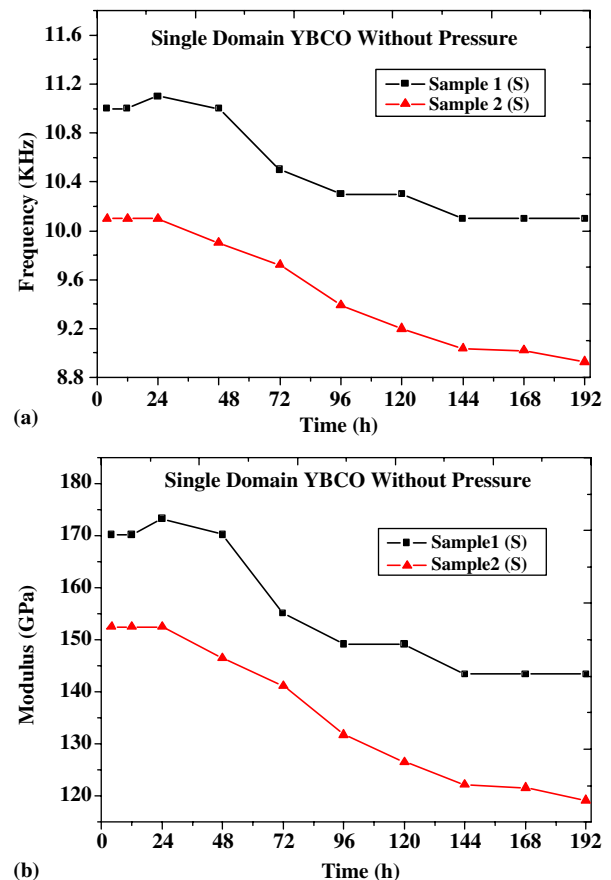


Fig. 3. (a) Flexure frequency versus annealing time, and (b) modulus versus annealing time for samples annealed without the *c*-axis pressure for the S direction.

rapid falls after 48 h of oxygen anneal. Exact behaviors of these two samples were observed in the modulus as shown in Fig. 3b. The modulus values for these samples remain at the same level up to 48 h, and thereafter begin to decrease in a quite pronounced fashion indicating significant mechanical and microstructural changes during anneal.

In the previous study [6], we found that, after the sample was treated in flowing oxygen at 400 °C for 18 h, micro cracks formed, which were typically seen in many previous studies [27,28]. These studies showed that the micro cracks provided the paths for efficient oxygen diffusion, without which oxygen diffusion became effectively slowed down. As the oxygen diffused into the sample along the *ab*-planes, these micro cracks also propagated into the interior of the domain structure at a rate that was comparable to that of oxygen diffusion. In our previous study [6], we found that, the sample that was annealed under the *c*-axis pressure exhibited no visible cracks under optical microscopy. Similar crack free surfaces were observed when the annealing time up to 72 h. However, in this previous study, the research was only focused on the *polished surfaces* of the annealed samples with and without pressure.

In another previous experiment [7,9], we found a rapid fall in modulus around 48 h of oxygen anneal. Both XRD and magnetization data showed that this rapid fall in modulus corresponded to the T-to-O transition in the sample at this time period. From Figs. 2 and 3, we can see significant difference in the modulus behaviors from samples annealed with and without *c*-axis pressure. Closely related to the optical observations reported in Ref. [6], the changes in modulus are associated with *ab*-plane crack formation and propagation. Therefore, without *c*-axis pressure, the rapid fall in modulus is a clear indication of crack propagation, while it remains unchanged when a uniaxial pressure is applied, as observed in both present and previous studies [6,7,9].

The T-to-O phase transition has been well observed and studied in early studies [1–5]. As a result of T-to-O phase transition, structural changes will lead to the formation of various lattice defects such as twinning and micro cracks. These defects have significant effects on physical properties including flux pinning and transport critical current density in the YBCO crystals [24–26]. One of the negative consequences of T-to-O phase transition is the formation and propagation of micro cracks along the *ab*-planes. When the phase transition occurs, the *c*-axis will be shortened creating a tensile stress in the outer regions of the sample. This strain profile in the oxygenated layer will cause cracking parallel to *ab*-plane with cracks apparent at the sample surface [27]. The 211 particles in the YBCO single domain can also contribute to the *ab*-plane cracks [28]. The local tensile stress can initiate cracks along *ab*-planes and the level of this stress depends on the size of 211 particles [27,28]. As discussed in Refs. [6,7,9], the contraction of the crystal in the *c*-axis is hindered by the 211 particles since the 211 phase remains unchanged in volume during T-to-O phase transition. If a pressure in this direction can be

pre-applied restricting any expansion or contraction of the YBCO crystal, formation of *ab*-plane cracks maybe suppressed. On the other hand, for an *ab*-plane crack to propagate, a tensile stress must initiate it at the crack tip. However, the applied *c*-axis uniaxial pressure will confine it considerably making crack propagation more difficult. With the confinement of the *c*-axis pressure, not only can the crack initiation be significantly suppressed, but also slow down its propagation kinetics. However, in this initial experiment, it is difficult to quantitatively determine the local crack tip stress and the counter force from the uniaxial pressure applied. More detailed experiments addressing these critical stresses are underway. It should be noted that, due to the suppression of crack propagation, the oxygen diffusion along the *ab*-planes may also be slow down, making the oxygenation more difficult.

#### 4. Summary

By measuring Young's modulus of single domain YBCO, the *ab*-plane crack behaviors are studied during the oxygen anneal at 400 °C. To effectively suppress the *ab*-plane crack formation and propagation, a uniaxial pressure is applied along the *c*-axis by a pressure vise. The experimental results have clearly shown that, the modulus values of the samples experience pronounced falls at annealing time of 48 h, but they remain more or less unchanged in the samples with the uniaxial pressure. These results are consistent with the previous experimental data that these variations in modulus are closely associated with the *ab*-plane crack formation and propagation. The pressure applied along the *c*-axis can significantly compensate the crack tip stresses and in turn resist the propagation of the *ab*-plane cracks.

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