A new phase is detected within 100µm of 24 DEG ab grain boundary (GB) in YBa$_2$Cu$_3$O$_{7-δ}$ 50 nm films on SrTiO$_3$ by enhanced (001) anomalous scattering. Site identification and temperature dependence is interpreted using crystallographic weights to distinguish enhanced scattering from total electron yield and fluorescence spectra. The c-axis, $c_0$ indicates that only ortho-I phase is present far from GB, both ortho-I and II phases are present near GB. The phase $c_0$ is constant versus temperature across the transition to superconductivity.

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**EXPERIMENTAL**

Synchrotron X-ray absorption spectra (XAS) of layered cuprates, YBCO$_{6.5}$ to 6.9 where superconducting planes are intercalated between ionic and perhaps magnetic layers are compared at the O:K, Cu:L$_{2,3}$ and Ba:M$_{4,5}$ edges. The film oxygen composition is obtained from the variation in the c-axis, $c_0$ that determines the (001) enhanced scattered amplitude.

![Diagram](image)

**FIG. 1:** Sample: (a) Measurement geometry determined by the fixed horizontal incident beam $k_i$, its position and angle $θ$ by the sample displacement and rotation about the x-axis, and $k_s$ by the detector angle $2θ$ to $k_s$. (b) BC02/03 (001) XRD versus s-s 005 $0.024_{-0.012}^{+0.024}$ $θ$ moves across the GB. A new phase is induced within 100µm at the Ba:M$_{4,5}$ edges. 

![Figure 2](image)

**Figure 2:** Phases detected by $I_s/I_0$ as incident beam position $x$ moves across the GB. A new phase is induced within 100µm of GB ($Δa$) detected by enhancement peak at $ΔE_{Bragg}/ΔE_{Bragg}$ = $Δc_0/c_0$ from the original $c_0$(ortho-I phase) $≈ 11.6Å$ to $c_0$(ortho-II phase) $≈ 11.7Å$.

![Figure 3](image)

**Figure 3:** Effect of $E_{Bragg}$ (2) on $I_s/I_0$ near the Ba:M$_{4,5}$ edges (BC02/03; BC04/04). Lifetime broadening and distortion due to some Ba, commonly occupying Y sites is observed. Broadening is evident in the integrated intensities, I from 730eV and the fit to A (4) with different WHHH at the M$_4$ and M$_5$ WL, but the integrated intensities remain equal even as the lines narrow.
The Thomson amplitude \( f_j(k, k_s, E) = f_0(k_j, k_s, E) + \Delta f_j(k_j, k_s, \hat{e}_i, \hat{e}_s, E) \). (1)

The anomalous amplitude:

\[
\Delta f_j(k_j, k_s, \hat{e}_i, \hat{e}_s, E) = f_j(E) - f_0(E) = f_j(E) - f_0(E) \approx \sum \frac{\Sigma_{[\hat{e}_j - \mu_\text{HWHH}]}(E_j, E) \sin(n_{\text{p}}r_j)}{1 + y^2} = \frac{A_j}{\text{I}_0 + F} \text{if} \quad E \approx E_{\text{Bragg}} - E_{\text{nn}} \approx 18\text{eV} \text{disappears at } 10^3\text{eV.} \]

**DISCUSSION**

The YBCO (001) diffraction enhancement is the only one accessible by soft X-rays. The scattering amplitude \( f_j(E) \) depends on the incident and scattered photon momenta \( k_i, k_s \) (fig. 1a), polarization \( \hat{e}_i, \hat{e}_s \) and \( E^4 \). (6)

\[
\Delta f_j(k_j, k_s, \hat{e}_i, \hat{e}_s, E) = f_j(E) - f_0(E) = f_j(E) - f_0(E) \approx \sum \frac{\Sigma_{[\hat{e}_j - \mu_\text{HWHH}]}(E_j, E) \sin(n_{\text{p}}r_j)}{1 + y^2} = \frac{A_j}{\text{I}_0 + F} \text{if} \quad E \approx E_{\text{Bragg}} - E_{\text{nn}} \approx 18\text{eV} \text{disappears at } 10^3\text{eV.} \]

**Figure 4**: Effect of \( E_{\text{Bragg}} \) on \( I/\text{I}_0 \) near the Cu:L_{2,3} edges compared to \( F/I_0 \) and fitted to relation (4) \( A(L_j)/A(L_j)=3, \alpha_\text{Cu} \) is constant to \( 1\% \) in 40eV interval. 100eV broad background at \( E(Cu:L_j) - E_{\text{Bragg}} \approx 18\text{eV} \) disappears at 10^3eV. Insert shows reversible 24th cycle of \( I/\text{I}_0 \) versus \( T \) (red \( T>T_c \), blue \( T<T_c \)) with \( E_{\text{Bragg}}-E(Cu:L_3)>10^3\text{eV} \).

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**DISCUSSION**

The yields obtained on YBCO transitions: O:1s^2 \( \leftrightarrow 0:1s.n_{\text{p}}z, n>2 \) and O:1s^2 \( \leftrightarrow 0:1s.n_{\text{p}}z, n>2 \) when \( \hat{e}_i \) is in the ab plane is according to relation (1). Comparison of enhancement at \( E_{\text{Bragg}}=545 \) and 2*10^3eV (Table I, fig. 5 #37, 28) identifies the site contributions. \( I/\text{I}_0 \) are a mixture of real, R and imaginary, I terms in \( \Delta f \). The data (fig. 2-5) are analyzed with the purpose to ascertain the properties of films with GB for proper industrial use:

(i) A mixture of real and imaginary components is observed in the WL at the Cu:L_{2,3} and Ba:M_{5,4} (fig. 3, 4) for BC and SC films where TEY/I_0 and F/I_0 show a Lorentzian shaped WL with an edge jump weaker than 1% of WL amplitude. Thus if the f^0 tail is linear, the enhanced scattered amplitude minus a base line may be compared to:

\[
A_j = I_j/I_0 = \langle y_0 \cos(\phi) - \sin(\phi) \rangle [1 + y^2] \quad (4)
\]

where \( y=(E-E_0)/\text{HWHH} \), \( E_0 \) is the edge energy and HWHH is the WL half width at half height. The fitted A indicate that the film rotates the plane polarized beam by \( \phi(Cu:L_3) \approx 3\pi/4 \pm \pi \) at \( E(Cu:L_3) - E_{\text{Bragg}}=18 \) to 10^2eV, and \( \phi \approx I/I_0(E_{\text{Bragg}}) \) (fig. 4) agrees with theory \( \phi \approx 0^\circ \). The observed lifetime broadening \( \Delta \) narrows to HWHH=0.7 from 1.7eV when \( E_{\text{Bragg}} < E(Cu:L_3)=10^3 \) and 18eV, respectively. WL transitions at L_{2,3} edges (fig. 4) depend on the Cu valence:

\[
\begin{align*}
\text{Cu}^{1+}(2p^6) & \Rightarrow \text{Cu}^{1+}(2p^53d^{10}) \quad \text{Cu}^{1+}(2p^53d^{9}) \\
\text{Cu}^{1+}(2p^53d^{9}) & \Rightarrow \text{Cu}^{1+}(2p^63d^{9}) \quad \text{Cu}^{1+}(2p^53d^{9}) \\
\text{Cu}^{1+}(2p^53d^{9}) & \Rightarrow \text{Cu}^{1+}(2p^63d^{9}) \quad \text{Cu}^{1+}(2p^63d^{9}) \\
\end{align*}
\]

The crystal field splitting (different at the L_{2,3} and L_{1} edges) and orientation \( \phi \) making it difficult to assign spectral features to the Cu sites in YBCO. Site identification is made by the variation in \( \alpha Cu_2/\alpha Cu_1 \approx 1-1.4 \) the enhanced shoulders ~ 6eV above the main signal, but of opposite sign amplitude may be due to the Cu:1 site contribution. The exact cancellation expected for \( E_{\text{Bragg}}=1083\text{eV} \), \( \alpha Cu_2/\alpha Cu_1 \approx 1 \), if the second order matrix elements in \( \Delta f \) for both sites is of the same order of magnitude, is not observed, indicating that Cu:1 and Cu:2 appear at different E, with a different Cu valence and \( \phi(Cu:2) \approx 3\pi/4 \).

(ii) Data at the O:K edge indicate that a displacement of the 100m wide beam, across the GB detects a new enhancement peak, associated with a higher \( \alpha \text{O} \) phase. The relative amplitude (fig. 2, #50, 51) in the XAFS region centered at 538eV (\( \alpha \text{O}=11.7\) A\#) identifies it with the ortho-II phase (YBCO_{6.5}) relative to that at 546eV (\( \alpha \text{O}=11.6\) A\#) for the ortho-I phase (YBCO_{6.5}) in agreement with the XRD data. The width of the GB is comparable to the beam width since full enhancement, at \( E_{\text{Bragg}}=538\text{eV} \) appears only within \( x \approx 4.87\text{±0.05}\text{A} \), while that at 546eV decreases very little across the GB. Comparison to \( \alpha \text{O} \) data versus O composition indicates that the GB has a ~5% discontinuous O decrease induces the ortho-II phase which releases the film strain, by creating the \( \kappa \) p dimeric lattice distortions (PLD) observed in XRD for the film. (10c, 8c).
near 528, 538eV is identified with O:2 by the doubling of \( \alpha(O:2) \) and orientation independent amplitude maximum in F/I\(_0\) expected in a nearly local octahedral field. I/I\(_0\) near 530eV is identified with O:1 by the relative amplitudes \( \alpha(O:1) = 0.8 \) and 1.9, and I/I\(_0\) near 531eV to 536eV is identified with O:3A,B by \( \alpha(O:3A,B) \) sign changes:

\[
I/I_0(\alpha(O:3A,B)) \approx -2.7 < 0 \quad \text{while} \quad I/I_0(\alpha(O:3A,B)) \approx 3.5 > 0.
\]

Assignments made by a single diffraction with soft X-rays using the variation of \( \alpha \) versus \( E_{\text{Bragg}} \) are similar to those made by different measurements\(^8\) for de-twinned single crystals YBCO\(_x\), and may be correlated to the chemical valence: The most negative ionic valence is associated with the lowest energy for site O:2 in the BaO layer, the next higher energy with site O:1 in the CuO chains and the highest valence is assigned to sites O:3A,B where molecular orbital calculations show that the CuO\(_2\) layer in YBCO nano-particles is covalent with a Mulliken atomic charge at the O:3A,B sites of \(-1.3\) and 0.8 at the Cu:2 sites\(^8c,9\).

### Table 1: Assignment of the YBCO\(_x\) unit cell sites, Hanzen notation\(^5a\) by correlation of I/I\(_0\) to crystallographic diffraction weights \( \alpha \) when \( E = E_{\text{Bragg}} \) and \( E 
eq E_{\text{Bragg}} \) (fig. 2-5).

| YBCO\(_x\) | \( D_{2h}^{\beta} \) | Site: | O:1 | O:2 | O:3A,B | Cu:1 | Cu:2 | Ba | Y |
|---|---|---|---|---|---|---|---|---|
| YBCO\(_x\) | (001) enhancement | \( Z' \) | 0 | \( + \) | 0.8 | 0 | 1.9 | 3.4 | 1 | -1.9 | 0.6 |
| \( I/I_0 \) Peak | \( E \) (eV) | \( \alpha(E) \) | \( I/I_0 \) | Site Contribution to Signal |
| 528 | + | + | yes | yes |
| 530 | + | + | yes | yes |
| 531-535 | - | + | yes | yes |
| 531-535 | + | + | maybe | yes |
| 538 | + | + | yes | yes |
| 545 | + | + | yes | yes |
| 779 | + | + | yes | yes |
| 793 | + | + | yes | yes |
| 932 | ± | ± | yes | yes |
| 950 | ± | ± | yes | yes |
| 936 | ± | ± | yes | yes |
| 934 | ± | ± | yes | yes |
| 945 | ± | ± | yes | yes |

Temperature dependence measurements indicate that \( c_0 \) is unchanged across \( T_c \) by the constant enhancement peak observed at \( E_{\text{Bragg}} \approx 546eV \) in the ortho-I phase. \( \phi(Cu:2.3L_3,3) \approx 3\pi/4 \) in (4) is constant across \( T_c \), but a reversible 0.5eV edge shift below \( T_c \) observed at the Cu:2:L3,2 edges in a 24 h, T cycle (fig. 4 insert) is assigned to an increased Cu:2 site valence below \( T_c \).

(iii) In the ideal YBCO\(_x\), Ba occupies a unique site but in real crystals it also occupies Y sites. As \( E_{\text{Bragg}} \approx E(Ba:M5) = -38 \) to \( 2*10^3eV \) lifetime broadening is observed when \( \alpha_{Ba}/\alpha_{Y} \approx -0.8 \) but the WL narrow for \( \alpha_{Ba}/\alpha_{Y} \approx 3 \) (Table I, fig. 3 #52 and #33). Amplitudes for WL transitions: \( Ba^{2+} \cdot \text{Ba}^{2+} \cdot (3d^{10}) \approx \text{Ba}^{2+} \cdot (3d^{10} \cdot 4f_{5/2}) \); \( Ba^{2+} \cdot (3d^{10} \cdot 4f_{5/2}) \), are proportional to the initial state multiplicities, \( A_{M5}/A_{M4} = 1.5 \) only for \( E_{\text{Bragg}} \approx E > 2*10^3eV \). The TEY/I\(_0\) for BC04/04 are orientation dependent\(^c,9\).

**CONCLUSION**

The fabricated nano-film YBCO\(_x\) (001) anomalous enhanced scattering analysis, sensitive to phase and O composition characterizes the GB for device applications and theoretical interpretation of transport data.

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**REFERENCES**

[1](a) M. A. Navacerrada, M. L. Lucia and F. Sánchez-Quesada, *Europhys. Lett.* **54**, 387 (2001); (b) M.A. Navacerrada and J.V. Acrivos, *Nanotech* **2003**, 1, 751 (2003); (c) H.S. Sahibudeen, J.V. Acrivos and M.A. Navacerrada, *Nanotech* **2005**, 2, 573 (2005)

[2] J.B. Kortright et al., *J. Magn. Magn. Materials* **207**, 7 (1999)

[3] P.Nachimuthu et al., *Chem. Mater.* **15**, 3939 (2003)

[4] (a) R.W. James, “The optical principles of X-rays”, Ox Bow Press, Woodbridge, Conn. 1962; (b) L.K. Templeton and D.H. Templeton, *Acta Cryst.* A**47**, 414 (1991)

[5] (a) R.M. Hanzen et al., “Physical Properties of High Temperature Superconductors, II” p. 121, D.M. Ginsberg, ed, World Scientific, Singapore (1990); (b) N.H. Andersen, *Physica C* **317-318**, 259 (1999)

[6] (a) L.B. Sorensen et al., “Diffraction anomalous fine structure” North Holland, G. Materlik et al, ed (1994) p.389; (b) Hämäläinen, et al, *ibid* p. 48; (c) J.C. Woicik et al., *Phys. Rev.B* **58**, R4215 (1998)

[7] (a) A. Bianconi et al, *Phys. Rev. B* **38**, 7196 (1988); (b) F.M.F. de Groot et al., *Phys. Rev. B* **42**, 5459 (1990); (c) J.V. Acrivos et al., arXiv, cond-mat/0504369

[8](a) M. Merz, et al, *Phys. Rev. Lett.* **80**, 5192 (1998); (b) J.H. Guo et al., *Phys. Rev. B* **61**, 9140 (2000); (c) E. Bascones et al., *ibid*, 71, 121505 (2005)

[9] (a) J.V. Acrivos, *Solid State Sciences*, 2, 807 (2000); (b) J.V. Acrivos et al., *Microchemical Journal*, 71, 117 (2002); (c) *ibid*, 81, 98 (2005)