

Nature of the transient BaF₂-related phases in the “BaF₂” processing of Ba₂YCu₃O_{7-x} superconductors

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Transient BaF₂-based oxyfluoride phases are thought to play a critical role in the formation of the *c*-textured Ba₂YCu₃O_{7-x} layers of coated conductors. *In situ* high-temperature x-ray diffraction from the precursor films containing pure BaF₂ as well as pseudobinary BaF₂-Y, BaF₂-Cu, and Y-Cu mixtures and heat treated in water vapor under reduced conditions revealed that the transient BaF₂-based superstructures, similar to those observed during formation of Ba₂YCu₃O_{7-x}, develop even from the pure BaF₂ precursor. These superstructures result from the dissolution of oxygen in BaF₂ leading to formation of the oxyfluoride phase, Ba(F_{2-2x}□_x)O_x, with an ordered arrangement of O, F, and F vacancies. © 2006 American Institute of Physics. [DOI: 10.1063/1.2184757]

The *ex situ* “BaF₂” process,^{1,2} which is one of the most successful processes for manufacturing of long-length Ba₂YCu₃O_{7-x} (Y-213) coated conductors, involves a low-temperature deposition of precursor layers onto a substrate using either a fast rate *e*-beam deposition or solution methods. High quality films/tapes have been produced using both SrTiO₃ substrates and rolling-assisted biaxially textured substrates.³⁻⁶ Detailed understanding of the phase formation sequence during the *ex situ* “BaF₂” conversion process is important for producing homogeneous tapes with reproducible properties.

The overall process of formation of the Y-213 phase from the (BaF₂+Y+Cu) amorphous mixture can be expressed as $(2\text{BaF}_2 + \text{Y} + 3\text{Cu})(\text{amorphous}) + 2\text{H}_2\text{O}(\text{g}) + (2\frac{1}{2} - \frac{1}{2}x)\text{O}_2(\text{g}) \rightarrow \text{Ba}_2\text{YCu}_3\text{O}_{7-x}(\text{s}) + 4\text{HF}(\text{g})$,^{7,8} that is, the process consists of a series of oxidation/hydration reactions involving BaF₂, Y, and Cu. The cubic BaF₂-like (BF) oxyfluoride Ba(F_{2-2x}□_x)O_x ($a_{\text{BF}} \approx 6.2 \text{ \AA}$)⁹ crystallizes from the amorphous precursor around $T=300 \text{ }^\circ\text{C}$. Further heating above $T=550 \text{ }^\circ\text{C}$, produces a BaF₂-related superstructure (SS) having lattice parameters ($a_{\text{ss}} \approx a_{\text{BF}}\sqrt{6/2}$, $b_{\text{ss}} \approx a_{\text{BF}}\sqrt{2/2}$, and $c_{\text{ss}} \approx a_{\text{BF}}\sqrt{3}$)¹⁰⁻¹² and a signature x-ray diffraction reflection at $2\theta \approx 25^\circ$. Wu *et al.*¹⁰ attributed the formation of this superstructure to the dissolution of Y in the BaF₂ with the 2:1 ordering of Ba and Y. Based on the similarity between the c_{ss} and the *c* parameter of Y-213 phase, Wu *et al.*^{10,12} suggested that the (Ba₂Y)F_yO_x superstructure provides a template for the nucleation of Y-213 phase and is therefore essential for the epitaxial growth of the superconducting phase. The goal of the present work is to clarify the origin of the transient BaF₂-based superstructure through *in situ* studies of phase formation in the precursor systems BaF₂-Y, BaF₂-Cu, BaF₂-Cu, and BaF₂.

Four different films, 0.7 μm thick, were used in these studies: Film No. 1 (BaF₂+Y[Ba:Y=2:1]), Film No. 2 (BaF₂+Cu[Ba:Cu=2:3]), Film No. 3 (Y+Cu[Y:Cu=1:3]), and Film No. 4 (BaF₂). The cation ratios were selected according to Ba:Y:Cu=2:1:3. The precursors were

deposited at ~100 °C by electron beam evaporation of Cu (metal), Y (metal), and BaF₂ on single crystal SrTiO₃ substrates.³ The compositions were derived from calibrated readings of the evaporation rate monitors and inductively coupled plasma (ICP) analysis. The details of the experimental setup for the *ex situ* conversion anneal were reported previously.⁷ X-ray diffraction confirmed that two of the as-deposited films were amorphous (Film Nos. 1 and 3), whereas two others (Films Nos. 2 and 4) contained a crystalline BaF₂ phase. The films were relatively stable in air;² however, as a precaution, the films were kept in a dry box prior to the high-temperature x-ray diffraction experiments.

In situ studies of phase formation were conducted in a Siemens D5000 θ - θ x-ray diffractometer¹³ equipped with a high-temperature furnace, a position sensitive detector, and a custom-designed gas flow apparatus.⁷ Cu K_α radiation was used. The sample, mounted on a Pt heating band using alumina paste, was ramped from room temperature to 700 °C and the x-ray diffraction patterns were collected every 50 °C in the 14°–40° 2θ range for 6 min per scan. Finally, the temperature was elevated to 735 °C and multiple x-ray scans, each 6 min long, were collected until no further changes in the diffraction patterns could be observed. The experiments were conducted under a flow of (He +0.1% O₂) bubbled through the saturated aqueous NaCl solution (9.9 mol % NaCl at 22 °C) to avoid condensation. Selected samples were examined in a transmission electron microscope operated at 200 kV. The cross-sectional specimens were prepared by conventional sectioning, polishing and dimpling (both sides) to a thickness of 25 μm. The thinning was continued in a Gatan PIPS (5 kV, 4.5°)¹ until perforation occurred.

In the BaF₂-Y-H₂O system (Film No. 1, Fig. 1), the onset of crystallization for the BaF₂-like phase occurs around 250 °C as inferred from the appearance of the 111_{BF} reflection. The formation of a BaF₂-related superstructure, similar to that observed in the BaF₂-Cu-Y precursors at $T \approx 600 \text{ }^\circ\text{C}$, is evident from the signature diffraction peak at $2\theta \approx 25^\circ$; this peak is present through 735 °C. At 700 °C, the peaks indicated in Fig. 1 as 2' and 2 can be indexed according to the pseudo-orthorhombic ($\beta \approx 90^\circ$) cell with

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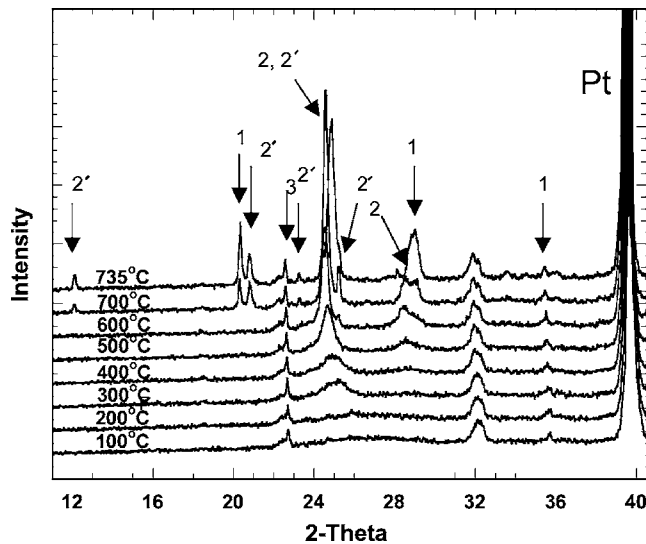


FIG. 1. X-ray diffraction pattern of Film No. 1 ($\text{BaF}_2\text{-Y-H}_2\text{O}$) as a function of temperature (1- Y_2O_3 , 2-cubic BaF_2 -like $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$, 2'- $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$ superstructure, 3- SrTiO_3).

$a \approx a_{\text{BF}}\sqrt{6/2} \approx 7.3 \text{ \AA}$, $b \approx a_{\text{BF}}/\sqrt{2} \approx 4.3 \text{ \AA}$, and $c \approx a_{\text{BF}}/3 \approx 10.9 \text{ \AA}$, ($\mathbf{k}_1=1/6[1\bar{1}2]^*$, $\mathbf{k}_2=[1\bar{1}0]^*$, and $\mathbf{k}_3=1/3[111]^*$, where the asterisk refers to a reciprocal space). The 111_{BF} reflection is indexed as the 003 reflection of the superlattice. The barium oxyfluoride can be described using the general formula $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$, where \square denotes F vacancies that are generated to maintain charge balance. The formation of $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$ occurs via an overall reaction: $\text{BaF}_2 + \text{Y} + \frac{3}{4}\text{O}_2 + x\text{H}_2\text{O} \rightarrow \text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x + \frac{1}{2}\text{Y}_2\text{O}_3 + 2x\text{HF}\uparrow$.

The $\text{BaF}_2\text{-Cu}$ films, as deposited, contained a crystalline BaF_2 -like phase. Heating these films above 600°C in the presence of H_2O produced a $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$ superstructure similar to that observed in the $\text{BaF}_2\text{-Y}$ system (see peaks 2' in Fig. 2). At $T \approx 700^\circ\text{C}$, BaCuO_2 forms. Interestingly, the low angle diffraction peak at 2θ around 12° is missing in the $\text{BaF}_2\text{-Cu}$ film (Fig. 2) at 735°C and occurs at $700\text{--}735^\circ\text{C}$ for the $\text{BaF}_2\text{-Y}$ system (Fig. 1). The overall reaction in this system can be described as $2\text{BaF}_2 + 2\text{Cu} + 3/2\text{O}_2 + x\text{H}_2\text{O}$

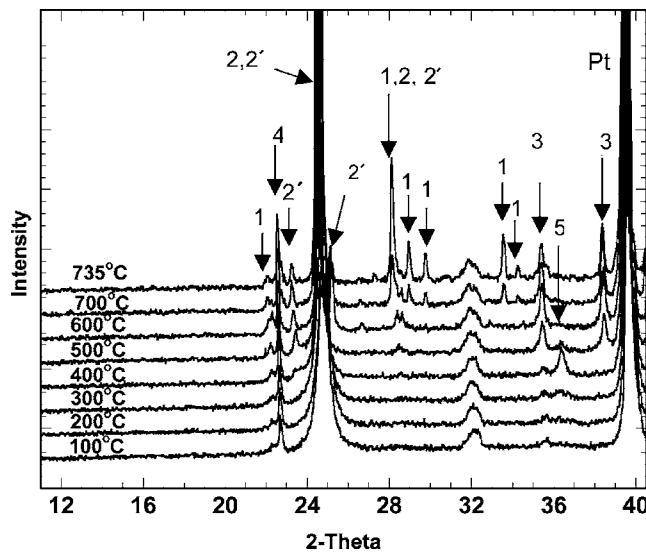


FIG. 2. X-ray diffraction pattern of Film No. 2 ($\text{BaF}_2\text{-Cu-H}_2\text{O}$) as a function of temperature (1- BaCuO_2 , 2-cubic BaF_2 -like $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$, 2'- $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$ superstructure, 3- CuO , 4- SrTiO_3 , 5- Cu_2O).

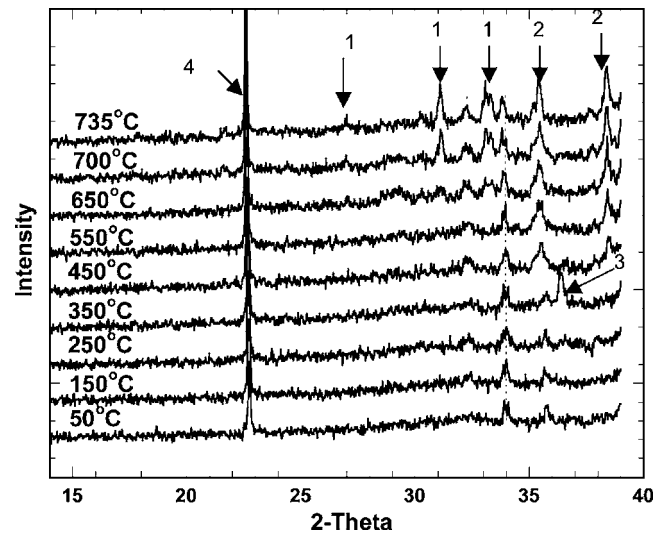


FIG. 3. X-ray diffraction pattern of Film No. 3 ($\text{Y-Cu-H}_2\text{O}$) as a function of temperature (1- $\text{Y}_2\text{Cu}_2\text{O}_5$, 2- CuO , 3- Cu_2O , 4- SrTiO_3).

$\rightarrow \text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x + \text{BaCuO}_2 + \text{CuO} + (2+2x)\text{HF}\uparrow$.

As expected, annealing the Y-Cu precursors under water vapor (Film No. 3) produced $\text{Y}_2\text{Cu}_2\text{O}_5$ at $T \approx 650^\circ\text{C}$ (Fig. 3). No x-ray reflections at $2\theta \approx 25^\circ$ were observed in the Y-Cu films, which suggests that the superstructure giving rise to this reflection in the two previous precursors is associated with the BaF_2 -based phase.

Annealing the pure BaF_2 precursor film in water vapor (Film No. 4) yielded a similar superstructure with the same signature diffraction peak at $\approx 25^\circ 2\theta$ (Fig. 4). These results confirm that the BaF_2 -based superstructure observed in the $\text{BaF}_2\text{-Cu-Y}$, $\text{BaF}_2\text{-Cu}$, and $\text{BaF}_2\text{-Y}$ films is associated with the ordering of F, O, and anion vacancies in the oxyfluoride phase $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$ rather than with the ordering of Ba and Y/Cu. The representative electron diffraction pattern for the BaF_2 film quenched from 600°C is shown in Fig. 5. This pattern was recorded from a single grain along the $\langle 110 \rangle_{\text{BF}}$ zone axis orientation. The superlattice reflections at $k = \frac{1}{3}[111]_{\text{BF}}^* \approx 10.7 \text{ \AA}$ are indicated. The diffraction can be

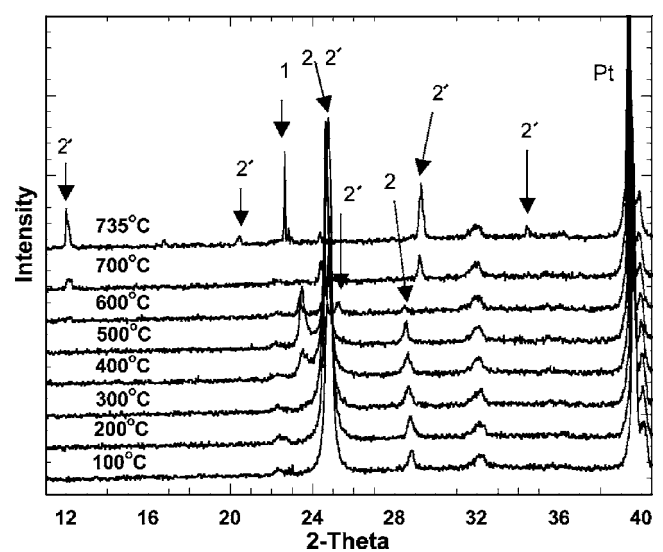


FIG. 4. X-ray diffraction pattern of Film No. 4 ($\text{BaF}_2\text{-H}_2\text{O}$) as a function of temperature (1- SrTiO_3 , 2-cubic BaF_2 -like $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$, 2'- $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$ superstructure).

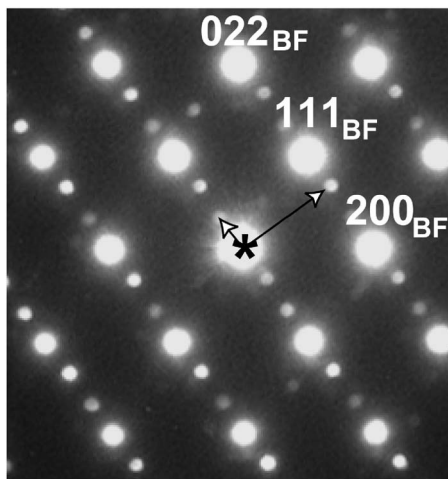


FIG. 5. Representative $(110)_{\text{BF}}$ zone axis electron diffraction pattern recorded from the single grain (Film No. 4) in the BaF_2 film quenched from 600°C after annealing in water vapor. The superlattice reflections at $\mathbf{k} = \frac{1}{3}[111]_{\text{BF}}^*$ (BF represents barium fluoride) are indicated.

described according to a hexagonal unit cell with the lattice parameters $a_{\text{ss}} = a_{\text{BF}}/\sqrt{2}$ and $c_{\text{ss}} = a_{\text{BF}} \times \sqrt{3}$, and $P\bar{3}m1$ (No. 164) symmetry (Fig. 6). The ordering, which occurs along the $[111]_{\text{BF}}$ direction (ordering vector $\mathbf{k} = \frac{1}{3}[111]_{\text{BF}}^*$), can be attributed to the alternating double layers of $[(\text{F}/\square)\text{Ba}_4]$ and $[\text{OBa}_4]$ tetrahedra (a disordered distribution of the F vacancies in the $[(\text{F}/\square)\text{Ba}_4]$ layers is assumed). Similar O/F ordering has been reported previously for a stoichiometric YOF phase;¹⁴ however, in YOF, the 1:1 ratio of O and F required doubling of the c lattice ($c_{\text{ss}} \approx 2 \times a_{\text{dis}} \times \sqrt{3}$; “dis” stands for disordered). Increasing both oxygen and F-vacancy concentrations in $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$ with increasing temperatures likely induces additional ordering of the F vacancies, causing further symmetry reduction from $P\bar{3}m1$ to

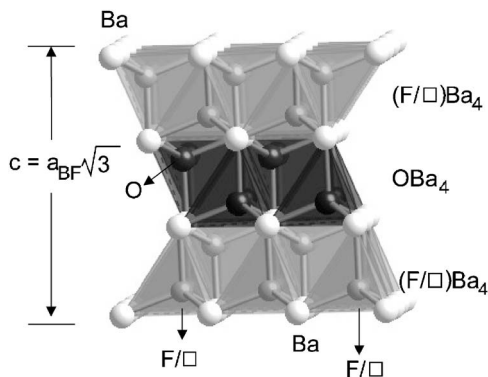


FIG. 6. Structural model of the $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$ phase showing the alternating double layers of $[(\text{F}/\square)\text{Ba}_4]$ and $[\text{OBa}_4]$ tetrahedra. The ordering occurs along the $[111]_{\text{BF}}^*$ direction (ordering vector $\mathbf{k} = \frac{1}{3}[111]_{\text{BF}}^*$). A disordered distribution of the F vacancies is assumed.

$P2_1/m$ ($a_{\text{ss}} = a_{\text{BF}}\sqrt{6}/2$, $b_{\text{ss}} = a_{\text{BF}}/\sqrt{2}$, $c_{\text{ss}} = a_{\text{BF}} \times \sqrt{3}$, $\beta \approx 90^\circ$) or lower.⁷ For example, at 735°C , one observes additional low angle diffraction peaks. The formation of $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$ in this system can be described as $\text{BaF}_2 + x\text{H}_2\text{O} \rightarrow \text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x + 2x\text{HF}\uparrow$.

The $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$ phase is metastable since it cannot be obtained in the bulk form.¹⁵ Our results demonstrate that the formation of the transient BaF_2 -based superstructures during the “ BaF_2 process” is related to the anion ordering in the oxyfluoride $\text{Ba}(\text{F}_{2-2x}\square_x)\text{O}_x$ and occurs even in the absence of Y and Cu. The O/F ratio in this phase increases continuously during processing. The O/F/ \square ordering is similar to that observed in the stoichiometric YOF; however, the periodicities of the resulting superstructures are different due to the different anion ratios in the Ba- and Y-based compounds. The details of anion ordering in the barium oxyfluorides require further investigation, as does their role in the nucleation of the c -textured high- T_c superconductor Y-213 phase.

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