1. Introduction

The development of superconducting Ba$_2$YCu$_3$O$_{6.5}$+$_x$ based tape is continuing at an accelerated pace, with the promise of substantial cost-reductions and performance enhancements in a variety of high temperature superconductor (high $T_c$) applications, such as transformer-, magnet-, and motor-windings and power transmission cables. This technology, the “second generation” of high $T_c$ materials, depends upon the fabrication of superconducting layers deposited on flexible metallic substrates [1-4]. Generally the metallic substrates require deposition of intermediate buffer layers to serve as diffusion barriers at the metal interface, while
promoting textured growth of the overlying oxide superconductor phase. One of the leading processes for producing highly textured second generation “coated conductors” is the “BaF$_2$ ex situ” method [5-7], a process which consists of two principal steps. In the first step, amorphous films having (2 BaF$_2$ + Y + 3 Cu) stoichiometry are deposited on the buffer layer by physical vapor deposition (PVD) or metal/organic deposition (MOD) techniques. The second step (shown diagrammatically in Fig. 1) involves the conversion of the amorphous film to superconducting material, nominally according to the following overall reaction:

\[
(2\text{ BaF}_2 + \text{Y} + 3\text{ Cu})(\text{amorphous}) + (2\text{ H}_2\text{O} + 2.25\text{ O}_2)(\text{g}) \rightarrow \text{Ba}_2\text{YCu}_3\text{O}_6.5 + x(s) + 4\text{ HF}(\text{g}).
\]

Typically, the reaction takes place at $\approx 730 \, ^\circ\text{C}$ to $750 \, ^\circ\text{C}$. The principal advantages of the ex situ process are that the first step is a relatively simple, rapid operation completed without the necessity of substrate heating, and that the second, more time-consuming step can be completed separately from the deposition process, without the need for vacuum conditions. The exact nature of the conversion process remains controversial. Indirect evidence has been presented for the formation of an amorphous intermediate phase (possibly a liquid) during the conversion [8].

2. Previous Work

Research has previously been conducted in our laboratory to determine the nature of low-melting-temperature liquids involved in the BaF$_2$ ex situ conversion [9-11]. The relevant phase equilibria can be discussed with reference to the Ba,Y,Cu/O,F quaternary reciprocal system, portrayed in Fig. 2a as a trigonal prism in compositional phase space. Initially, the relative thermodynamic stabilities of Table I were used to subdivide the trigonal prism of Fig. 2a into its constituent tetrahedra, shown in Fig. 2b. The phase stabilities defining these tetrahedra have since been confirmed experimentally, and hence the tetrahedra serve as a valid outline for discussion of the conversion process. In traversing along a compositional vector from the oxides at the base of the trigonal prism, to the fluorides at the top, the three constituent tetrahedra encountered are: BaF$_2$-BaO-$\frac{1}{2}$Y$_2$O$_3$-CuO$_x$, BaF$_2$-YF$_3$-$\frac{1}{2}$Y$_2$O$_3$-CuO$_x$, and BaF$_2$-YF$_3$-CuF$_2$-CuO$_x$. The first two tetrahedra share the very stable BaF$_2$-$\frac{1}{2}$Y$_2$O$_3$-CuO$_x$ compositional plane, where the ideal compositions of PVD precursor films would be plotted. In terms of fluoride/oxide ratio, the progression of such films during ex situ conversion to superconductor would ideally follow the path shown in the lower tetrahedron of Fig. 2b. Yet, melting temperatures below 815 °C were not found in this tetrahedron, even in the presence of

![Fig. 1. Schematic illustration of the “BaF$_2$ ex situ” process for fabrication of Ba$_2$YCu$_3$O$_{6.5+x}$ coated conductors, showing conversion of precursor film (top), as deposited on substrate/buffer layer. Precursor is converted starting at buffer/precursor interface by reaction with water vapor entering from top. Superconductor layer (dark) grows and is then annealed at lower temperatures under dry conditions in oxygen.](image-url)
H₂O-containing gas mixtures with reduced P\textsubscript{O₂}. Locally, it is possible that PVD compositions might deviate from the BaF\textsubscript{2}-½Y\textsubscript{2}O\textsubscript{3}-CuO plane in the fluoride-direction. Also, MOD films initially have compositions with more fluoride than would correspond to compositions in this plane. Therefore our search for low-melting liquids was also extended into the fluoride-rich regions of Fig. 2. Our experimental investigation of the BaF\textsubscript{2}-YF\textsubscript{3}-½Y\textsubscript{2}O\textsubscript{3}-CuO tetrahedron has shown that melting temperatures in that tetrahedron are in excess of 800 °C, even in the presence of H₂O, or with reduced P\textsubscript{O₂}.

In the BaF\textsubscript{2}-YF\textsubscript{3}-CuF\textsubscript{x}-CuO\textsubscript{x} tetrahedron, fluoride-rich liquids melting as low as 580 °C were found; possibly these could be involved in the early stages of MOD
film conversion. However, for low-melting liquids to be generally operative in conversion of both PVD and MOD films, they would need to lie closer in phase space to the BaF₂-½Y₂O₃-CuO plane. Consequently, our search for low-melting liquids has turned to the possible presence of Ba(OH)₂, a compound known to melt much lower (at ≈ 408 °C)\(^{[12]}\) than the other phases and components of the Ba,Y,Cu/O,F system. Under suitable \(p_{\text{H}_2\text{O}}\) and temperature, Ba(OH)₂ could proxy for the BaO component.

3. Possible Presence of Ba(OH)₂ During Ex Situ Conversion

Reaction (1) may be rewritten as the sum of several constituent reactions, based in part on high temperature powder x-ray diffraction (HTXRD) observations in our laboratory \([10,13]\) and in other laboratories \([14,15]\). Moreover, under sufficiently high \(p_{\text{H}_2\text{O}}\) the BaO component of Fig. 2 could effectively be replaced by Ba(OH)₂, resulting in the following conversion steps:

\[
3 \text{Cu(amarhophous)} + 1.5 \text{O}_2(\text{g}) \rightarrow 3 \text{CuO(s)} \quad (2)
\]

\[
\text{Y(amarhophous)} + \text{CuO(s)} + 0.75 \text{O}_2(\text{g}) \rightarrow 0.5 \text{Y}_2\text{Cu}_2\text{O}_5(s) \quad (3)
\]

\[
2 \text{BaF}_2(\text{amarhophous}) \rightarrow 2 \text{BaF}_2(s) \quad (4)
\]

\[
2 \text{BaF}_2(s) + 4 \text{H}_2\text{O}(g) \rightarrow 2 \text{Ba(OH)}_2(\text{liq}) + 4 \text{HF}(g) \quad (5)
\]

\[
2 \text{Ba(OH)}_2(\text{liq}) + 0.5 \text{Y}_2\text{Cu}_2\text{O}_5(s) + 2 \text{CuO(s)} \rightarrow \text{Ba}_2\text{YCu}_3\text{O}_{6.5+\text{x}}(s) + 2 \text{H}_2\text{O}(g). \quad (6)
\]

Reactions (5) and (6) indicate the presence of Ba(OH)₂ liquid as an intermediate step.

4. Goal and Approach of Present Investigation

The primary goal of this paper is to evaluate the possible presence of Ba(OH)₂ liquid during the ex situ conversion process, using a combination of experimental and calculative methods. Demonstrating the presence of liquids at high temperature is of course not possible by HTXRD, and so we must rely on less direct methods. Also, maintaining the high \(p_{\text{H}_2\text{O}}\) and low \(p_{\text{F}_2}\) thought necessary to form Ba(OH)₂ liquids from BaF₂ at high temperature in a controlled experimental environment is in itself a daunting task. For this purpose, we constructed a special high-flow steam furnace, as described below. We have completed extensive equilibrium calculations on the stability of Ba(OH)₂ liquids using available thermodynamic data, including the effect of CO₂ contamination. Based on the calculated stabilities, we designed experiments using the high-flow steam furnace to test for the formation Ba(OH)₂(liquid) according to its predicted stability field. As a background for this work, differential thermal analysis (DTA) experiments were completed on carefully chosen compositions.

5. Experimental Procedure\(^1\)

BaO was synthesized from 99.99 % purity (metals, by mass) BaCO₃ by vacuum-calcining at 1300 °C for 10 h, followed by transfer to a glovebox. Complete decarbonation and conversion to BaO were verified by x-ray powder diffraction (XRD) in a sealed x-ray mount \([16]\). Powder XRD was completed on a Philips 20 diffractometer\(^2\) using Cu Kα radiation and a graphite monochromator. Diffractometer control and data acquisition were achieved using the JADE software system.

For melting studies, a Ba(OH)₂/BaO mixture was prepared by controlled hydration of BaO. Melting and annealing experiments with simultaneous differential thermal analysis/thermogravimetric analysis (DTA/TGA) were completed in a Mettler TA1 thermoanalyzer outfitted with Anatech digital control and data acquisition electronics. DTA was completed at a ramp rate of 10 °C/min. The DTA apparatus was calibrated against the α/β quartz transition (571 °C) and the NaCl melting point (801 °C); DTA temperatures are estimated to have \(< ± 3 °C\) standard uncertainty. DTA crucibles were of dense slip-cast MgO.

To enable experiments at high \(p_{\text{H}_2\text{O}}\), a furnace capable of operation up to \(p_{\text{H}_2\text{O}} = (0.1 \text{ MPa})\) at temperatures above 800 °C was constructed, as shown schematically in Fig. 3. The special features of this furnace are: 1. a 3 kW steam generator provides an approximately constant-pressure source of steam for the furnace; 2. the steam generator uses a water feedstock with reduced CO₂ (discussed below); 3. all areas of the furnace and supply lines are maintained at \(>100 °C\); 4. a type S thermocouple is positioned in the base of

\(^1\) Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
6. Calculative Procedure

Solid-liquid-gas equilibria in the system Ba(OH)$_2$-BaO-BaF$_2$-H$_2$O-HF (and also with CO$_2$) were calculated as a function of temperature using the Janaf thermochemical database [17] and the FactSage software suite [18]. The latter uses a Gibbs energy minimization algorithm to calculate equilibrium concentrations of species in the gas phase, and to calculate activities of liquid and solid phases. The calculative procedure involves minimizing the total stoichiometric summation of terms:

$$G(i,T) = \Delta_f H^{\circ}_{m}(i,298) + \int_{298}^{T} C_p(i) dT$$

$$-T \left( S^a(i,298) + \int_{298}^{T} C_p(i)/T dT \right)$$

for the collection of phases being considered, where $G(i,T)$ = Gibbs energy function for phase i, $\Delta_f H^{\circ}_{m}(i,298)$ = standard molar enthalpy of formation for phase i, $S^a(i,298)$ = absolute molar entropy for phase i, $C_p(i) = molar heat capacity of phase i at constant pressure (0.1 MPa)$, and $T$ = temperature kelvin. For solution phases, appropriate mixing terms must be added to Eq. (7), including terms of the form $RT \ln(p_j)$, where $R$ = gas constant and $p_j$ = activity or partial pressure of species j. Species considered in the calculations are shown in Table 2. For the present calculations, gaseous species were considered to mix ideally. As described...
below, for purposes of calculation we assume there is negligible solubility of BaO and BaF$_2$ in Ba(OH)$_2$ liquids at the eutectic. Therefore to a first approximation the liquids are simple liquids, essentially pure. With regard to solid phases, there is evidence for solid solution of BaO in BaF$_2$ [19], although a quantitative determination has not been made, and the extent is not known. Also, existence of a compound intermediate between BaF$_2$ and Ba(OH)$_2$ has been proposed [15]. As yet, there has been no definitive proof of such a compound, and there is no published x-ray diffraction pattern in the Powder Diffraction File [20]. However, it is clear that refinements in the calculations will need to be made, if additional data become available. For the present, the calculations give an approximate idea of the Ba(OH)$_2$(liq) stability field. It is expected that solubility of BaF$_2$ or BaO in Ba(OH)$_2$(liq) would expand the liquid field of stability, whereas existence of an intermediate compound would have the opposite effect.

### 7. Effect of $p_{CO_2}$ on Ba(OH)$_2$ Equilibria

One of the reasons for the relative success of the BaF$_2$ ex situ method is the elimination of carbonate (usually present as BaCO$_3$) from the processing route. Carbonate not only affects the kinetics of Ba$_2$YCu$_3$O$_6.5+x$(s) formation due to the relative stability of BaCO$_3$(s), but also affects the equilibrium phase assemblage by favoring formation of oxycarbonate phases such as Ba$_2$Y$_2$O$_5$·$x$CO$_2$ and Ba$_2$Y$_2$O$_5$·$x$CO$_2$ [21,22]. Formation of these phases interferes with Ba$_2$YCu$_3$O$_6.5+x$(s) formation and complicates the decarbonation reactions which must take place for formation of Ba$_2$YCu$_3$O$_6.5+x$(s) from BaCO$_3$-containing precursors. Furthermore, presence of carbon in the superconductor phase has been shown to adversely affect properties [23].

Calculations have been performed to estimate the effect of CO$_2$ on Ba(OH)$_2$ equilibria, by adding CO$_2$(g), three polymorphs of BaCO$_3$(s), and BaCO$_3$(liq) to the list of species considered in Table 2. These calculations have been completed to determine the values of $p_{H_2O}$ and $p_{CO_2}$ which are in equilibrium with coexisting Ba(OH)$_2$ and BaCO$_3$, as shown in Fig. 4. From the curves in Fig. 4, at 500 ºC, a $p_{CO_2}$ of $< 10^{-4}$ Pa is required to avoid formation of BaCO$_3$, while a $p_{H_2O}$ of $> 10^{1.5}$ Pa is necessary to stabilize Ba(OH)$_2$. At 900 ºC, $p_{CO_2}$ must be $< 10^{1.4}$ Pa to avoid formation of BaCO$_3$, and $p_{H_2O}$ of $> 10^{4.5}$ Pa is required to stabilize Ba(OH)$_2$. For comparison, at 25 ºC, water in equilibrium with air ($p_{CO_2} = 10^{1.5}$ Pa) contains $10^{-7}$ mol fraction dissolved CO$_2$. Water of this composition, if vaporized, would be within the BaCO$_3$ stability field up to $≈ 625$ ºC. At 99 ºC, water in equilibrium with air contains $10^{-9}$ mole fraction CO$_2$, and if vaporized, would fall below the BaCO$_3$ stability line above $≈ 525$ ºC. From these calculations it is clear that water used to generate $p_{H_2O}$ must be heated to reduce CO$_2$ content if formation of BaCO$_3$ is to be avoided. This is especially critical in experiments involving the formation of Ba(OH)$_2$, such as those discussed below.

### 8. Ba(OH)$_2$/BaO

The melting of a Ba(OH)$_2$/BaO mixture was investigated by DTA to estimate the effect of BaO solubility on the melting temperature. A lowering of $= 3$ ºC was found, which lies within the estimated uncertainty of the DTA measurements. It is therefore concluded that the solubility of BaO in Ba(OH)$_2$ liquids is negligible, and that Ba(OH)$_2$ liquid can be modeled for calculational purposes as essentially pure Ba(OH)$_2$.

Accordingly, equilibria between solid and liquid Ba(OH)$_2$ and BaO(s) were calculated and are presented in the phase diagram of Fig. 5. At $p_{H_2O} = 0.1$ MPa, Ba(OH)$_2$(liq) is stable up to $= 1051$ ºC. At lower temperatures, the Ba(OH)$_2$(s) stability field extends to
very low values of $p_{H_2O} (< 10^{-10} \text{ Pa})$. The Ba(OH)$_2$(liq) stability field is confined to a relatively narrow slice of the phase diagram above $p_{H_2O} \approx 10 \text{ Pa}$, lying between the phase fields of BaO(s) and Ba(OH)$_2$(s). The most abundant gaseous species in equilibrium with Ba(OH)$_2$(liq) along the Ba(OH)$_2$(liq)/BaO(s) equilibrium curve are shown for selected temperatures in Table 3. While $p_{H_2O}$ is several orders of magnitude above the other partial pressures, it is noteworthy that at 900 °C, $p_{Ba(OH)_2}$ reaches $\approx 1 \text{ Pa}$. A partial pressure of this magnitude is sufficient to cause significant mass transport of Ba(OH)$_2$ in the gas phase. At 25 °C (not shown in Fig. 5 or Table 3), the calculated $p_{H_2O}$ over coexisting Ba(OH)$_2$(s) and BaO(s) is estimated to be $10^{-14} \text{ Pa}$, an indication of the difficulty in storing and handling BaO.

The effect of HF(g) ex situ conversion product on Ba(OH)$_2$(liq)/BaO(s) equilibria must also be considered. As shown in Fig. 6, the log $p_{H_2O}$ values for the Ba(OH)$_2$(liq)/BaO(s) equilibrium remain constant and independent of log $p_{HF}$ for any given temperature. However the maximum value of log $p_{HF}$ to which the Ba(OH)$_2$(liq)/BaO(s) equilibrium is stable increases with increasing temperature. Above this value, indicated by the dashed parts of the equilibrium lines at any given temperature, the Ba(OH)$_2$(liq)/BaO(s) equilibrium is metastable. Gas phase compositions for selected points near the centers of the equilibrium boundaries in Fig. 6 are given in Table 4. Comparison of Table 3 and Table 4 reaffirms the constancy of the equilibrium $p_{H_2O}$ in the presence of HF.

### Table 3. Gas phase partial pressures (Pa) in equilibrium with Ba(OH)$_2$(liq)/BaO(s)

| $T$(°C) | $p_{H_2O}$ | $p_{H_2}$ | $p_{Ba(OH)_2}$ | $p_{O_2}$ | $p_{OH}$ |
|---------|-------------|------------|----------------|-----------|---------|
| 500     | $10^{1.8}$  | $10^{6.3}$ | $10^{6.4}$     | $10^{6.6}$ | $10^{8.2}$ |
| 600     | $10^{7.7}$  | $10^{4.4}$ | $10^{4.2}$     | $10^{4.7}$ | $10^{6.0}$ |
| 700     | $10^{7.5}$  | $10^{2.8}$ | $10^{2.5}$     | $10^{3.2}$ | $10^{4.3}$ |
| 800     | $10^{6.0}$  | $10^{1.7}$ | $10^{1.2}$     | $10^{2.0}$ | $10^{2.9}$ |
| 900     | $10^{5.5}$  | $10^{0.7}$ | $10^{0.1}$     | $10^{1.0}$ | $10^{1.8}$ |

### Table 4. Gas phase partial pressures (Pa) in equilibrium with Ba(OH)$_2$(liq)/BaO(s) in the presence of HF

| $T$(°C) | $p_{H_2O}$ | $p_{HF}$ | $p_{H_2}$ | $p_{Ba(OH)_2}$ | $p_{O_2}$ | $p_{OH}$ |
|---------|-------------|----------|------------|----------------|-----------|---------|
| 500     | $10^{1.8}$  | $10^{6.3}$ | $10^{6.3}$ | $10^{6.4}$     | $10^{6.6}$ | $10^{8.2}$ |
| 600     | $10^{7.7}$  | $10^{5.5}$ | $10^{4.4}$ | $10^{4.3}$     | $10^{4.7}$ | $10^{6.0}$ |
| 700     | $10^{7.5}$  | $10^{4.0}$ | $10^{2.9}$ | $10^{2.5}$     | $10^{3.2}$ | $10^{4.3}$ |
| 800     | $10^{6.0}$  | $10^{4.3}$ | $10^{1.7}$ | $10^{1.2}$     | $10^{2.0}$ | $10^{2.9}$ |
| 900     | $10^{5.5}$  | $10^{3.9}$ | $10^{1.7}$ | $10^{0.1}$     | $10^{1.0}$ | $10^{1.3}$ |

9. **Ba(OH)$_2$/BaF$_2$**

Due to the formation of Ba(OH)$_2$-hydrates, it was not possible to prepare pure Ba(OH)$_2$ from BaO during this investigation, and therefore the melting point lowering of Ba(OH)$_2$/BaF$_2$ mixtures was not investigated experimentally. For calculational purposes it is therefore...
assumed that the solubility of BaF$_2$ in Ba(OH)$_2$(liq) at the eutectic is small, a reasonable assumption, given the much higher melting point of BaF$_2$ (> 1300 °C).

To describe the equilibrium between Ba(OH)$_2$(liq) and BaF$_2$(s), it is necessary to consider $p_{\text{HF}}$ as well as $p_{\text{H}_2\text{O}}$. Figure 7 shows calculated curves for the Ba(OH)$_2$(liq)/BaF$_2$(s) equilibrium at several temperatures. As the temperature increases, the maximum $p_{\text{HF}}$ value to which the Ba(OH)$_2$(liq) stability field extends increases. As temperature increases, the minimum $p_{\text{H}_2\text{O}}$ value to which the Ba(OH)$_2$(liq) stability field extends also increases. Below this value, the Ba(OH)$_2$(liq)/BaF$_2$(s) equilibrium is metastable. Gas phase compositions at selected points on the curves in Fig. 7 are given in Table 5. At higher temperatures, as for the Ba(OH)$_2$(liq)/BaO(s) equilibrium, the values of $p_{\text{Ba(OH)O}_2}$ become significant. From the slopes of Fig. 7 and the data in Table 5, a given increase in $p_{\text{H}_2\text{O}}$ results in a proportionately much larger increase in the equilibrium $p_{\text{HF}}$. For example, an order-of-magnitude increase in $p_{\text{H}_2\text{O}}$ produces a two orders-of-magnitude increase in $p_{\text{HF}}$. The requirements for HF(g) removal during the conversion of BaF$_2$(s) to Ba(OH)$_2$(liq) are significantly reduced by maintaining increased $p_{\text{H}_2\text{O}}$ as well as by maintaining higher temperatures.

| $T$(°C) | $p_{\text{H}_2\text{O}}$ | $p_{\text{HF}}$ | $p_{\text{H}_2}$ | $p_{\text{Ba(OH)O}_2}$ | $p_{\text{O}_2}$ | $p_{\text{OH}}$ |
|-------|----------------|--------------|----------------|----------------|----------------|----------------|
| 500   | $10^4$        | $10^{-3.6}$  | $10^{-5.2}$    | $10^{-6.4}$    | $10^{-5.5}$    | $10^{-7.2}$    |
| 600   | $10^4.0$      | $10^{-2.1}$  | $10^{-3.6}$    | $10^{-4.2}$    | $10^{-3.9}$    | $10^{-5.2}$    |
| 700   | $10^4.3$      | $10^{-1.1}$  | $10^{-2.3}$    | $10^{-2.5}$    | $10^{-2.6}$    | $10^{-3.7}$    |
| 800   | $10^4.6$      | $10^{-0.2}$  | $10^{-1.3}$    | $10^{-1.2}$    | $10^{-1.6}$    | $10^{-2.6}$    |
| 900   | $10^4.7$      | $10^{-0.4}$  | $10^{-0.6}$    | $10^{-0.1}$    | $10^{-0.8}$    | $10^{-1.6}$    |

10. Ba(OH)$_2$/BaO/BaF$_2$

Treatment of equilibria involving the three phases Ba(OH)$_2$, BaO, and BaF$_2$ is facilitated by the use of the 3-D plot shown in Fig. 8, where the three-phase Ba(OH)$_2$/BaO/BaF$_2$ equilibrium is represented as a function of $p_{\text{H}_2\text{O}}, p_{\text{HF}}$, and temperature. The three-phase equilibrium is actually a curve in $\log p_{\text{HF}} - \log p_{\text{H}_2\text{O}}$-temperature parameter space, as illustrated by its projection onto the base of the plot. Table 6 gives gas phase compositions at selected points along the three-phase equilibrium.

![Fig. 8. Three-phase Ba(OH)$_2$/BaO/BaF$_2$ equilibrium as a function of $\log p_{\text{H}_2\text{O}}, \log p_{\text{HF}}$, and temperature. Dashed lines indicate orthogonal projection of the equilibrium curve onto the sidewalls of the 3-D plot.](image)

The data in Fig. 8 can also be conveniently represented through the use of isothermal sections, as shown in Fig. 9. Here the three-phase Ba(OH)$_2$/BaO/BaF$_2$ equilibrium plots as a point at the juncture of the areas...
corresponding to the Ba(OH)$_2$, BaO, and BaF$_2$ stability fields. With increasing temperature, the stability field of Ba(OH)$_2$ shrinks to higher $p_{H_2O}$, but simultaneously expands to higher $p_{HF}$.

On the basis of Fig. 9, a steam furnace experiment was designed to test for the formation of Ba(OH)$_2$(liq) from BaF$_2$(s). Using the steam furnace, $p_{H_2O}$ of 0.1 MPa at temperatures of 800 °C or above can be maintained for extended periods of time. These are the optimum conditions for formation of Ba(OH)$_2$(liq) according to reaction (5), provided $p_{HF}$ can be maintained at < 1 Pa. In practice, the latter requirement can be met by rapidly flowing steam over the sample to remove product HF, thereby reducing $p_{HF}$ to low levels.

Results of a steam furnace experiment in which a single crystal fragment of optical quality BaF$_2$ was held at 815 °C, for 2h, with $p_{H_2O}$ = 0.1 MPa, with a steam flow over the sample estimated at > 0.2 L/s, are shown in Fig. 10a. Fluorine on the surface of the BaF$_2$ has been uniformly replaced by oxygen to a depth of at least 1 µm, as estimated by the lack of a fluorine EDS signal from the underlying BaF$_2$ (Fig. 10b). The full EDS spectrum (not presented) shows Ba and O as the main constituents on the surface of the reacted crystal, with a relatively small C K$_\alpha$ peak (no method was available for detection of hydrogen). The smooth, dense nature of the reacted surface is consistent with the formation of Ba(OH)$_2$ liquid. As discussed above, CO$_2$ in the water feedstock for this experiment was reduced to low levels such that the formation of BaCO$_3$ was minimized. The EDS spectrum of Fig. 10b indicates that BaCO$_3$ was not a major reaction product, as the C K$_\alpha$ intensity is similarly low for both reacted and unreacted crystals. The presence of C in both spectra is an indication of minor hydrocarbon surface contamination. Smaller peaks present in the reacted sample are due to trace contaminants from the steam boiler and transport line (Si, possibly Co), and are not likely to have had a significant effect on the F/O reaction. We conclude that formation of Ba(OH)$_2$(liq) from BaF$_2$(s) according to reaction (5) is the most probable explanation of the results in Fig. 10.

The high-flow experiment at 815 °C, $p_{H_2O}$ = 0.1 MPa may be near the upper limit of conditions useful for practical processing of second-generation coated conductors, due to the thermal limitations of currently available substrate/buffer combinations. From Fig. 9, production of Ba(OH)$_2$ liquids at lower temperatures requires more complete removal of HF from the reaction site. An estimate of the requirements for Ba(OH)$_2$(liq) formation according to reaction (5) at 700 °C can be made as follows. First, it must be noted that, at 700 °C, $p_{HF}$ must be $< 10^{-1}$ Pa for Ba(OH)$_2$(liq) to form. At a steam flow rate of 0.2 L/s over the sample, this gives a maximum HF removal of $10^{-3.8}$ mL/s from the reaction site, assuming equilibrium. The resulting rate of formation of Ba(OH)$_2$(liq) from BaF$_2$(s) according to reaction (5) is the most probable explanation of the results in Fig. 10.

The high-flow experiment at 815 °C, $p_{H_2O}$ = 0.1 MPa may be near the upper limit of conditions useful for practical processing of second-generation coated conductors, due to the thermal limitations of currently available substrate/buffer combinations. From Fig. 9, production of Ba(OH)$_2$ liquids at lower temperatures requires more complete removal of HF from the reaction site. An estimate of the requirements for Ba(OH)$_2$(liq) formation according to reaction (5) at 700 °C can be made as follows. First, it must be noted that, at 700 °C, $p_{HF}$ must be $< 10^{-1}$ Pa for Ba(OH)$_2$(liq) to form. At a steam flow rate of 0.2 L/s over the sample, this gives a maximum HF removal of $10^{-3.8}$ mL/s from the reaction site, assuming equilibrium. The resulting rate of formation of Ba(OH)$_2$(liq) is $10^{-8.1}$ mol/s. If reaction (5) is the rate-limiting step, then Ba$_2$YCu$_3$O$_{6.5+x}$ would be formed by reaction (6) at a rate of $10^{-8.4}$ mol/s. For a 1 cm$^2$ area, this corresponds to a thickness conversion rate of $10^{-2.3}$ µm/s at 700 °C. Thus, formation of Ba$_2$YCu$_3$O$_{6.5+x}$ superconducting films of 1 µm thickness over an area of 1 cm$^2$ could conceivably be achieved in 200 s to 250 s, with potential for scale-up

### Table 6. Gas phase partial pressures (Pa) in equilibrium with Ba(OH)$_2$(liq)/BaO(s)/BaF$_2$(s)

| T(°C) | $p_{H_2O}$ | $p_{HF}$ | $p_{H_2}$ | $p_{Ba(OH)_2}$ | $p_{O_2}$ | $p_{OH}$ |
|-------|------------|----------|-----------|-----------------|--------|----------|
| 500   | $10^{1.8}$ | $10^{-5.2}$ | $10^{-6.3}$ | $10^{-6.4}$ | $10^{-6.6}$ | $10^{-8.2}$ |
| 600   | $10^{2.7}$ | $10^{-3.3}$ | $10^{-4.4}$ | $10^{-4.2}$ | $10^{-4.7}$ | $10^{-6.0}$ |
| 700   | $10^{3.5}$ | $10^{-5.0}$ | $10^{-6.9}$ | $10^{-5.5}$ | $10^{-3.2}$ | $10^{-4.3}$ |
| 800   | $10^{4.0}$ | $10^{-4.3}$ | $10^{-1.7}$ | $10^{-1.2}$ | $10^{-2.0}$ | $10^{-2.9}$ |
| 900   | $10^{4.5}$ | $10^{-3.9}$ | $10^{-1.7}$ | $10^{-0.1}$ | $10^{-1.0}$ | $10^{-1.3}$ |

Fig. 9. Isothermal sections through three-phase Ba(OH)$_2$/BaO/BaF$_2$ region in Fig. 8.
to much larger production rates. High-performance films with 1 µm or greater superconductor thickness could find immediate application in second-generation high \( T_c \) technology, especially if production costs approach the anticipated \$10/kA-m target [24].

11. Summary and Conclusions

Thermodynamic calculations have outlined a stability field for \( \text{Ba(OH)}_2(\text{liq}) \) as a function of \( p_{\text{H}_2\text{O}}, p_{\text{HF}} \), and temperature, based on presently available data. An experiment at 815 °C, \( p_{\text{H}_2\text{O}} = 0.1 \text{ MPa} \) has provided evidence for the formation of \( \text{Ba(OH)}_2(\text{liq}) \) by defluorination of \( \text{BaF}_2(\text{s}) \), as predicted by the calculations. It is possible that under conditions of high \( p_{\text{H}_2\text{O}} \) and rapid gas flow, the formation of \( \text{Ba(OH)}_2(\text{liq}) \) may occur as an intermediate step in the formation of superconducting \( \text{Ba}_2\text{YCu}_3\text{O}_{6.5+x}(\text{s}) \) from amorphous \( (\text{BaF}_2, \text{Y}, \text{Cu}) \) precursors. The presence of a \( \text{Ba(OH)}_2 \) liquid could be important for \( \text{Ba}_2\text{YCu}_3\text{O}_{6.5+x}(\text{s}) \) processing for several reasons. It is well known that a liquid phase enhances mobility and can aid in local mass transport and the development of oriented microstructures. The presence of a liquid would be expected to improve the kinetics of \( \text{Ba}_2\text{YCu}_3\text{O}_{6.5+x}(\text{s}) \) phase formation, although it may be necessary to limit the presence of the liquid phase at some stages during processing to prevent random growth, as opposed to oriented growth. Clearly, it is essential to
control the amount of liquid in order to fully optimize all aspects of Ba2YCu3O6.5+(s) formation using the BaF2 in situ process. With sufficient data on liquid formation, P\text{\textsubscript{H2O}} provides an additional parameter, along with precursor F/O composition, gas flow, temperature, and P\text{\textsubscript{O2}}, with which to reproducibly control the processing of Ba2YCu3O6.5+(s).

The calculated phase diagrams require further experimental verification to establish the role of BaF2 solubility in the liquid, and the precise boundaries of the Ba(OH)2 stability field. Preliminary experiments have indicated that Ba2YCu3O6.5+(s) is stable in the presence of Ba(OH)2(liq) [25]; it is essential to know the range of conditions under which the Ba2YCu3O6.5+(s) and the Ba(OH)2 stability fields overlap. Based on the extent to which Ba(OH)2-based liquids extend into the phase space of Fig. 2, it may prove possible to design processing routes to control intersection of the PVD and MOD processing paths with the hydroxide liquid phase field. Then the full range of P\text{\textsubscript{H2O}}-temperature processing space can be explored to determine if there are new processing routes which might lead to further optimization of superconductor formation and film properties.

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12. References

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