A low-fluorine solution with a 2:1 F/Ba mole ratio for the fabrication of YBCO films

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Abstract

In previously reported low-fluorine MOD-YBCO studies, the lowest F/Ba mole ratio of the precursor solution was 4.5. Further lowering the F/Ba ratio would bring benefits for the environment, thick film deposition, and an understanding of the heat treatment process. On the other hand, the F/Ba ratio must be at least 2 for full conversion of the Ba-precursor to BaF2 to avoid the formation of BaCO3, which is detrimental to the superconducting performance of YBCO films. In this study, a solution with a 2:1 F/Ba mole ratio was developed, and the fluorine content of this solution was approximately only 10.3% of that used in the conventional TFA-MOD method. Attenuated total reflectance-Fourier transform-infrared spectra (ATR-FT-IR) revealed that BaCO3 was remarkably suppressed in the as-pyrolyzed film—and eliminated at 700 °C. Thus, YBCO films with a critical current density (Jc) of over 5 MA cm−2 (77 K, 0 T, 200 nm thickness) could be obtained on lanthanum aluminate single-crystal substrates. In situ FT-IR spectra showed that no obvious fluorinated gaseous by-products were detected in the pyrolysis step, which indicated that all F atoms might remain in the film as fluorides. X-ray diffraction θ/2θ scans showed the presence of BaF2—but not of YF3 or CuF2—in films quenched at 400–800 °C. The formation priority of BaF2 over YF3 and CuF2 was interpreted by examining the chemical equilibrium of the potential reactions. Our study could enlarge the synthesis window of precursor solutions for MOD-YBCO fabrication, and serve as a foundation for continuously and systematically studying the influence of fluorine content in the precursor solutions.

Keywords: YBCO film, low-fluorine, F/Ba ratio, phase evolution, chemical equilibrium

(Some figures may appear in colour only in the online journal)

1. Introduction

Trifluoroacetate metal organic deposition (TFA-MOD), which was first reported by Gupta et al [1], is one of the most popular methods of fabricating high-performance YBa2Cu3O7−δ (YBCO) superconducting films [2–5]. The fluorine content in the precursor solution of the TFA-MOD method is of great significance, because the formation of BaCO3,
which is very stable during heat treatment and impairs the critical current density ($J_c$) of the final YBCO films, can be avoided by the formation of BaF$_2$ [1, 2]. The fluorine content of BaF$_2$ can subsequently be easily removed, accompanied by the generation and release of HF gas [6].

However, the conventional TFA-MOD method requires a pyrolysis step that usually takes more than 10 h to complete [5]. Such a slow process constitutes a serious barrier to industrial production. Lowering the fluorine content of the precursor solution is considered to be effective in shortening the time required for the pyrolysis step [7]. This idea has been realized in many groups by substituting fluorine-free salt(s) for one or two specific trifluoroacetate(s) in the precursor solution. To the best of our knowledge, there are three main routes of metal salt substitution(s): (1) Cu salt [7], (2) Cu and Y salts [8, 9], (3) Cu and Ba salts [10]. Relative to the conventional TFA-MOD solution (100% fluorine content), the fluorine contents of these precursor solutions could be evaluated as 53.8%, 30.8% (or 23.1% if the poor-Ba stoichiometry is used [11]) and 23.1%, respectively. In these studies using the route of metal salt substitution(s), the F/Ba ratio was limited to a narrow range, with a lowest value of 4.5. To obtain a F/Ba ratio in a wider range, especially lower than 4.5, a more flexible synthesis method should be employed. Thus, in the present work, we directly use Y, Ba and Cu acetates as the precursors while trifluoroacetic acid was added as the fluorine source.

Using a solution with a lower fluorine content to prepare YBCO films would be beneficial. First, environmentally harmful fluorine-containing by-products could be reduced. Second, a greater understanding of the heat treatment process could be obtained. Third, the F/Ba ratio in the as-pyrolyzed films could also be lowered, which might have important consequences for YBCO thick film fabrication. In multi-coated MOD-YBCO thick film research by Li et al [12] and Feenstra et al [13], a modification to lower the F/Ba ratio prior to the crystallization step was proposed, based on the hypothesis of a transient liquid phase during crystallization [14, 15]. They lowered the F/Ba ratio by altering the water partial pressure and heating rate [12], or by introducing a medium-temperature anneal (<650°C, 60 min), called the ‘F-Module’, between pyrolysis and crystallization [13].

In order to develop a new solution with a lower fluorine content, two points should be noted in the conventional TFA-MOD method [16, 17] and the low-fluorine MOD studies [10, 18, 19]: First, the phases involved in the formation of YBCO are CuO, BaF$_2$ (or its partially oxidized phase) and Y$_2$Cu$_2$O$_5$ (or Y$_2$O$_3$). This is also found in the ex situ ‘BaF$_2$ process’ [20], which is considered to be the origin of the TFA-MOD method [5]. Clearly, Y and Cu do not require to be fluorinated during YBCO formation. Second, the fluorine-containing phase in the as-pyrolyzed films is a solid solution of BaF$_2$ and YF$_3$. During the intermediate phase evolution before YBCO formation, YF$_3$ converts to an oxide, indicating its lower stability than BaF$_2$. It could be assumed that BaF$_2$ may form prior to YF$_3$. Thus, the fluorine content of a precursor solution with a 2:1 F/Ba mole ratio might be adequate for full conversion of the Ba-precursor to BaF$_2$.

In the present work, a precursor solution with a 2:1 F/Ba mole ratio (hereafter denoted as ‘F/Ba-2’) was developed.

Table 1. The detailed reagent quantities utilized to synthesize the solution F/Ba-2 (20 ml, 1.2 mol l$^{-1}$).

| Reagent | Quantity |
|---------|----------|
| $\text{Y(CH}_3\text{COO)}_3\cdot\text{4H}_2\text{O}$ (Sigma-Aldrich) | 0.004 mol |
| $\text{Ba(CH}_3\text{COO)}_2$ (Alfa Aesar) | 0.008 mol |
| $\text{Cu(CH}_3\text{COO)}_2\cdot\text{H}_2\text{O}$ (Alfa Aesar) | 0.012 mol |
| $\text{CuF}_3\text{COOH}$ (Alfa Aesar) | 0.0054 ± 0.0003 mol |
| $\text{CH}_3\text{H}_2\text{COOH}$ (Alfa Aesar) | Excess |
| $\text{CH}_3\text{OH}$ (Sigma-Aldrich) | 10 ml |
| $\text{NH}_3\cdot\text{H}_2\text{O}$ (Alfa Aesar) | 3.3 ml |

The fluorine content of this solution was approximately only 10.3% of that used in the conventional TFA-MOD solution, which could allow a greater understanding of the heat treatment process and also be more environmentally friendly. YBCO thin films with favorable superconducting performance could be consistently obtained using this solution. The behavior of the precursor during heat treatment was also studied by multiple characterization methods and analyses of the chemical equilibrium.

2. Experimental details

2.1. Sample preparation

To synthesize the F/Ba-2 solution, Y, Ba and Cu acetates with a stoichiometric ratio of 1:2:3, trifluoroacetic acid, deionized water, and propionic acid were directly mixed. The quantity of trifluoroacetic acid was 10.3 mol%, of the total $\text{CH}_3\text{COO}^-$ anion, with an uncertainty estimated to be 0.5%. After stirring for 1 h, the obtained solution was refined in a BUCHI Rotavapor R-210 rotary evaporator under decompression for 2 h. Methanol and ammonia water were then added to the gel-like product to obtain a transparent solution. After repeating the refinement under decompression and adding methanol, a precursor solution with pH 6.8 could be obtained. Details of the reagents used to synthesize the solution F/Ba-2, which had a molar concentration of total metal ions of 1.2 mol l$^{-1}$, are summarized in table 1. Polyelectrolyte glycol (PEG) 1500, which can help alleviate stress generation and prevent buckling during a rapid pyrolysis step [21], was used as an additive in the precursor solution. To obtain thicker films, a solution of F/Ba-2 with a concentration of 1.6 mol l$^{-1}$ was also prepared. For convenience, these two solutions were named ‘F/Ba-2-1.2M’ and ‘F/Ba-2-1.6M’, respectively. Unless expressly noted, the results in this paper were based on the solution F/Ba-2-1.2M. According to the measurements using a rotational viscometer (NXS-11B), the viscosity of solution F/B-2-1.2M was about 3.0 mPas, and that of solution F/B-2-1.6M was about 9.2 mPas.

The precursor solution was coated on lanthanum aluminate (LAO) single-crystal substrates (5 × 5 mm$^2$) using a spin coater under <30% relative humidity. The rotation speed was 8000 rpm for solution F/Ba-2-1.2M, and 4000 rpm for solution F/Ba-2-1.6M. The acceleration time was 1 s. Heat treatment was conducted in an MTI GSL-1500X tube furnace. First, the
samples were pyrolyzed, starting at room temperature (RT) to 400 °C at a heating rate of 3 °C min⁻¹, in a humid O₂ gas atmosphere. Then, the pyrolyzed samples were crystallized at 800 °C for 2 h in a 400 ppm O₂/N₂ atmospheric mixture. The YBCO superconducting films were then obtained after 2 h of annealing in a dry O₂ gas atmosphere. The entire heat treatment process is illustrated in figure 1. To trace the chemical reaction path between the pyrolysis and crystallization steps, a series of samples was quenched at 400–800 °C in this profile.

2.2. Characterization and measurements

Optical microscopy (OM) observation was conducted on the pyrolyzed films with a Nikon ME600 polarized optical microscope under bright-field conditions. The quality of the pyrolyzed film was evaluated by OM observation. Scanning electron microscopy (SEM) characterization was performed in a LEO 1530 with an in-lens detector (EHT = 10 keV). The surface morphology and cross-sectional structure of the YBCO film could be observed, and the film thickness was estimated according to the cross-sectional images.

Attenuated total reflectance-Fourier transform-infrared spectra (ATR-FT-IR) were taken with a PerkinElmer Spectrum GX FTIR system to detect the presence of BaCO₃. This sensitive technique allows the detection of BaCO₃ at a level as low as 2 wt% [22].

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out using a Netzsch STA 449C thermal analyzer in a humid oxygen atmosphere from RT to 400 °C, at a heating rate of 3 °C min⁻¹. Samples for the DSC-TGA measurement were in the form of bulk gels, prepared by slowly evaporating the free solvent in the precursor solution at 70 °C for 12 h. FT-IR spectra of the gaseous by-products generated in the decomposition reactions were simultaneously recorded with a BRUKERER Tensor 27 FT-IR spectrometer connected to the thermal analyzer. The background carbon dioxide signal was subtracted. To account for the presence of water in the atmosphere, water signals from the background and the product were always subtracted to reveal the signals from other gaseous products.

The identification of the phases present in the films quenched at 400–800 °C and in the final YBCO films were performed with x-ray diffraction (XRD) θ/2θ scans in a BRUKER D8 diffractometer, using a Cu Kα source and a four-circle sample holder. The scan speed was 3 s/step with an increment of 0.02°/step. In our study, it should be noted that when the alignment of the sample was perfect, many undesirable peaks of the LAO single-crystal substrate ascribed to the x-ray source impurity appeared. To avoid them and reveal the relatively weak signals from some intermediate phases, XRD θ/2θ scans were conducted while the sample was slightly deviated from perfect alignment. XRD φ scans were performed to study the in-plane texture of the highly aligned phases in the films. The scan speed was 0.6 s/step with an increment of 0.02°/step.

The superconducting properties of YBCO films were measured in a CRYOGENIC cryogen-free measuring system. The critical temperature (Tc) was determined by AC susceptibility measurements with a magnetic field amplitude of 0.1 mT and a frequency of 21 Hz. A four-probe method system with a fixed current of 10 mA was utilized to record the resistance–temperature curves of the YBCO films. Magnetization hysteresis loops of the YBCO films were recorded by a vibrating sample magnetometer (VSM) at 77 K, under a magnetic field perpendicular to the surface of the LAO substrate. The critical current density (Jc) was calculated using equation (1), which is based on the extended Bean critical state model [23]:

$$J_c = \frac{2\Delta m}{V(a(1-a/3b))}$$

where a, b, V and Δm are the width, length (a ≤ b), volume of the film and the opening of the magnetization hysteresis loop at a certain magnetic field, respectively.
3. Results

3.1. Feasibility study of YBCO film fabrication

An as-pyrolyzed film, previously coated with the solution F/Ba-2, was obtained by quenching the film at the end of the 400 °C stage in figure 1. Its typical surface morphology observed by OM is shown in figure 2(a). The surface of the as-pyrolyzed film was flat and smooth, without undesirable features such as cracks, bubbles or buckling. Thus, high-quality as-pyrolyzed films could be obtained within 2.5 h using the solution F/Ba-2—a duration much shorter than that of the conventional TFA-MOD method [5].

The ATR-FT-IR spectrum of the as-pyrolyzed sample (denoted as ‘F/Ba-2, 400 °C’) is shown in figure 2(b). For comparison, the as-pyrolyzed films prepared with a non-fluorine solution (denoted as ‘F/Ba-0, 400 °C’) and an conventional 100% fluorine-containing solution (denoted as ‘all TFA, 400 °C’) were also measured. As expected, the characteristic IR-absorption bands of BaCO$_3$ centered at 1415, 1059 and 860 cm$^{-1}$ were detected in the non-fluorine sample but not
in the sample ‘all TFA, 400°C’ . The characteristic bands of BaCO$_3$ were also identified in sample ‘F/Ba-2, 400°C’. However, they were much weaker than those in the non-fluorine sample, indicating that BaCO$_3$ was strongly suppressed by the fluorine content introduced into the precursor solution. It is also worth noticing that BaCO$_3$ was totally eliminated when sample ‘F/Ba-2, 400°C’ was further heated to 700°C, as indicated by the ATR-FT-IR spectrum marked ‘F/Ba-2, 700°C’. In contrast, BaCO$_3$ signals were still strong in the sample ‘F/Ba-0, 700°C’, and remained undetected in the sample ‘all TFA, 700°C’.

Figure 3(a) shows the SEM morphology of the final YBCO film. This sample was composed of plate-like c-axis oriented grains with a small number of nanoscale pores and Cu-rich surface particles. The dominance of the c-axis oriented grains was confirmed by XRD $\theta/2\theta$ characterization, as shown in figure 3(b). The in-plane texture of the film was examined by a $\phi$ scan of the YBCO (102) crystallographic plane. Figure 3(c) shows four sharp peaks with an average full width at half-maximum (FWHM) of 0.67°, corresponding to the typical four-fold symmetry of well-textured YBCO.

The final YBCO films prepared by solution F/B-2-1.2M and F/B-2-1.6M were 200 and 450 nm thick, respectively. Figure 4 shows the cross-sectional SEM images of both the samples. It can be observed that the thicker film was more porous than the thinner one. Thus a lower $J_c$ in the thicker film could be expected. As shown in figure 5, $J_c$ (77 K, 0 T) of the former film was 5.1 MA cm$^{-2}$, and that of the latter film was 2.3 MA cm$^{-2}$. When the applied magnetic field $B$ was increased to 3 T, their $J_c$ values rapidly decreased to 0.1 and 0.01 MA m$^{-2}$, respectively.

As shown in the AC susceptibility–temperature ($\chi–T$) curve of figure 6(a), two main contributions existed in the signal of the film prepared by the solution F/Ba-2-1.2M, indicating its non-uniformity. Multi-peak fitting revealed that the stronger fitted peak (representing the majority of this YBCO film) had a $T_{c\text{, onset}}$ of about 91.5 K, which was similar to the resistance–temperature ($R–T$) curve result of about 91.9 K. The minority region of this sample had a $T_{c\text{, onset}}$ of about 93.5 K, but the reason for this high value was not clear. For the sample prepared by the solution F/Ba-2-1.6M, the value of $T_{c\text{, onset}}$ obtained from the $\chi–T$ curve was about 90.1 K, also similar to that of about 89.4 K obtained from the $R–T$ curve, as shown in figure 6(b). The above results of this section indicate the feasibility of fabricating high-performance YBCO films using our low-fluorine solution.

3.2. In situ study of gaseous by-products produced during the pyrolysis step

In studies on conventional 100% fluorine-containing TFA-MOD solutions, fluorine-containing gaseous by-products were always detected during the pyrolysis step, indicating the loss of F atoms [24–27]. In the present study, the fluorine content of the precursor solution was approximately the minimum requirement for the complete conversion of Ba content to BaF$_2$. Therefore, investigating whether or not fluorine content loss occurred during the pyrolysis step, due to the generation of fluorinated gaseous by-product(s), was necessary.

To identify the gaseous by-products, their in situ FT-IR spectra were simultaneously collected as the DSC-TGA measurement was being conducted. As illustrated in the DSC curve of figure 7, exothermic peaks indicating the decomposition of the PEG additive and metal salts were observed between 190 and 325°C. The TGA curve could be divided into six typical regions, labeled by their representative temperatures in figure 7. The FT-IR spectra of the gaseous by-products collected at these representative temperatures are shown in figures 8(a) and (b). Unless expressly referenced, the bands were assigned according to the FT-IR data from the NIST Chemistry Web Book [28]. Some unidentified bands (VI) were recognized to be the decomposition products of PEG1500, according to the FT-IR measurement of pure PEG1500 shown in figure 8(b).
At 150 °C, only weak signals ascribed to the presence of gaseous propionic acid (I) and ammonia (II) that was previously trapped in the gel matrix were detected. No signals of CO$_2$ (III), which could indicate the decomposition of organic compounds [24, 18], were detected until 217 °C. At 217 °C, the emerging absorption bands at 1599 and 3442 cm$^{-1}$ were assigned to the scissoring vibration and the symmetric stretching vibration of N–H in propanamide (IV) respectively [29, 30]. Between 253 and 281 °C, the characteristic bands corresponding to CO (V) and the decomposition products of PEG1500 (VI) appeared. At the same stage, the signals of CO$_2$ (III) were much stronger, indicating that more organic compounds began to decompose. When the temperature was raised to 325 °C, the emerging absorption bands at 1599 and 3442 cm$^{-1}$ could indicate the decomposition of trifluoroacetate (1153 and 1378 cm$^{-1}$ [28]) nearly overlapped with those of propionic acid (I); thus, determination of its presence needs other techniques such as mass spectrometry. However, no other fluorine-containing gaseous by-products reportedly observed during the decomposition of trifluoroacetates [24–27] were found in our study, including CF$_3$COOH (1200, 1123, 1830 cm$^{-1}$), CF$_3$COF (1097, 1200, 1333, 1897 cm$^{-1}$), COF$_2$ (1957, 1928, 1269, 617 cm$^{-1}$) [31, 32], HF (3920, 3877, 3383, 3788 cm$^{-1}$), C$_2$F$_4$ (1338, 1186 cm$^{-1}$), C$_2$F$_6$ (1250, 1115 cm$^{-1}$) [33].

### 3.3. Intermediate phase evolution between pyrolysis and crystallization steps

To study the evolution of the intermediate phases between the pyrolysis and crystallization steps, film samples previously quenched at 400–800 °C were characterized by XRD $\theta$/2θ scan, as shown in figure 9. For samples quenched at 400 and 500 °C, only broad peaks due to nanocrystalline BaF$_2$ could be detected. When the temperature increased to 600 °C, peaks corresponding to the Y$_2$Cu$_2$O$_5$ and CuO phases emerged, and the crystallinity of the BaF$_2$ markedly improved. At temperatures higher than 700 °C, the crystallinity of the BaF$_2$ phase was further enhanced, and the YBCO signal was detected. Also, the (103) and (013) peaks of YBCO could be observed in figure 9. However, the intensity ($I$) was very weak in the final YBCO films: $I_{(103)}/I_{(005)} = 0.8\%$ for the thinner film and $I_{(103)}/I_{(005)} = 0.9\%$ for the thicker film. The peaks at the positions of BaF$_2$ might also be attributed to its partially oxidized form (denoted as OF), which was difficult to distinguish from BaF$_2$ in the XRD measurements [16, 34]. BaCO$_3$ ($2\theta \sim 23.9^\circ$), which could impair the superconducting performance of the resulting YBCO films [35], was not detected in any of the samples.

Figures 10(a) and (b) show the $\phi$ scan patterns of the (202) crystallographic plane of the (111) and (001) oriented OF phases, respectively. The former phase had a twelve-fold symmetry with an average FWHM of 0.60°, and the first peak was centered at 0°; the latter phase had a four-fold symmetry with an average FWHM of 0.82°, and the first peak was centered at 45°. Thus, it could be inferred that these two OF phases were highly textured, exhibiting epitaxial relationships with the (001)-LAO substrate: (001)OF$\parallel$(001)LAO, [110]OF$\parallel$(100)LAO and (111)OF$\parallel$(001)LAO, [110]OF$\parallel$(100)
LAO. Such relationships were in agreement with a study of the conventional TFA-MOD method [16]. XRD measurements with a rotating sample holder were conducted to quantitatively study the OF phases. In the sample quenched at 800°C, the volume portion of the (111) oriented OF phase could be estimated as over 80%, which was larger than those reported in some conventional TFA-MOD studies [16, 17].

In the XRD patterns of figure 9, two facts concerning the intermediate phase evolution could be noticed. First, Cu- and Y-related phases were not detected at temperatures < 600°C. Second, no evident peak shift was observed in the peaks of BaF$_2$ (or OF). This result indicated that YF$_3$, which always formed a solid solution with BaF$_2$ [17], was not involved in the intermediate phase evolution in our study. This observation was different from the results of previously reported MOD studies that used a conventional TFA-MOD or low-fluorine precursor solution [19, 10, 36].

4. Discussion

The ATR-FT-IR characterization of BaCO$_3$ and the intermediate phases found by the XRD $\theta/2\theta$ scan (figure 9) revealed that nearly all YBCO formed via reaction (2), as was also reported in studies on the conventional TFA-MOD method [3, 17], the ex situ ‘BaF$_2$ process’ [20] and some low-fluorine MOD studies [7, 10]. The small amount of BaCO$_3$, which was detected in the as-pyrolyzed film and then disappeared at 1700°C, we propose may proceed via two possible paths in the further heat treatment: converting to be a part of the OF phase and therefore involved in reaction (2), or producing YBCO via the reaction proposed in the study of the non-fluorine precursor solution [37, 38].

$$\frac{1}{2}Y_2Cu_2O_5 + 2BaF_2 + 2CuO + 2H_2O(g) \rightarrow YBa_2Cu_3O_{6.5} + 4HF(g). \quad (2)$$

It could be also inferred that BaF$_2$ formed prior to YF$_3$ and CuF$_2$, according to the above study. Some chemical equilibrium analyses were carried out to investigate this formation priority, which was equivalent to this proposition: once YF$_3$ or CuF$_2$ coexisted with Ba-related phases other than BaF$_2$ (usually BaCO$_3$, Ba(OH)$_2$ or BaO), they would keep reacting to form BaF$_2$ until one of them ran out. Therefore, the potential chemical reactions shown in equations (3)–(8) were studied.
at 1800–1800 °C. The XRD θ/2θ scan patterns of films quenched at 400–1800 °C.

Figure 9. XRD θ/2θ scan patterns of films quenched at 400–1800 °C.

Table 2. The molar standard Gibbs free energy for the formation ($\Delta G^0_{f,T}$, kJ mol$^{-1}$) of the concerned phases at 700–1000 K (427–727 °C) [40].

| Phase       | $\Delta G^0_{f,700}$ | $\Delta G^0_{f,800}$ | $\Delta G^0_{f,900}$ | $\Delta G^0_{f,1000}$ |
|-------------|----------------------|-----------------------|----------------------|------------------------|
| BaCO$_3$    | −1033                | −1007                 | −981                 | −956                   |
| BaF$_2$     | −1092                | −1076                 | −1060                | −1044                  |
| BaO         | −487                 | −478                  | −468                 | −458                   |
| Ba(OH)$_2$  | −746                 | −722                  | −697                 | −673                   |
| Y$_2$O$_3$  | −1699                | −1671                 | −1643                | −1615                  |
| YF$_3$      | −1540                | −1516                 | −1492                | −1468                  |
| CuO         | −92                  | −83                   | −75                  | −66                    |
| CuF$_2$     | −431                 | −416                  | −402                 | −389                   |
| CO$_2$(g)   | −395                 | −396                  | −396                 | −396                   |
| H$_2$O(g)   | −209                 | −204                  | −198                 | −193                   |

Table 3. The molar standard Gibbs free energy changes ($\Delta G^0_T$, kJ mol$^{-1}$) for the potential reactions involving the conversion of BaF$_2$ at 700–1000 K (427–727 °C).

| Reaction | $\Delta G^0_{200}$ | $\Delta G^0_{400}$ | $\Delta G^0_{600}$ | $\Delta G^0_{1000}$ |
|----------|-------------------|-------------------|-------------------|-------------------|
| (3)      | 5.55              | −10.7             | −26.8             | −42.7             |
| (4)      | −116              | −131              | −146              | −161              |
| (5)      | −94.4             | −104              | −113              | −122              |
| (6)      | −216              | −225              | −233              | −241              |
| (7)      | −145              | −145              | −145              | −145              |
| (8)      | −266              | −265              | −264              | −263              |

Table 3. The molar standard Gibbs free energy changes ($\Delta G^0_T$, kJ mol$^{-1}$) for the potential reactions involving the conversion of BaF$_2$ at 700–1000 K (427–727 °C).

BaCO$_3$ + 2/3YF$_3$ ⇌ BaF$_2$ + 1/3Y$_2$O$_3$ + CO$_2$(g) (3)
BaCO$_3$ + CuF$_2$ ⇌ BaF$_2$ + CuO + CO$_2$(g) (4)
Ba(OH)$_2$ + 2/3YF$_3$ ⇌ BaF$_2$ + 1/3Y$_2$O$_3$ + H$_2$O(g) (5)
Ba(OH)$_2$ + CuF$_2$ ⇌ BaF$_2$ + CuO + H$_2$O(g) (6)
BaO + 2/3YF$_3$ ⇌ BaF$_2$ + 1/3Y$_2$O$_3$ (7)
BaO + CuF$_2$ ⇌ BaF$_2$ + CuO. (8)

The standard molar Gibbs free energy change ($\Delta G^0_T$) of a chemical reaction can be calculated by equation (9) [39], where the $\nu$ represent the stoichiometric coefficients, and the $\Delta G^0_{f,T}$ are the standard molar Gibbs energy for the formation of a substance involved in the reaction at a temperature $T$. The $\Delta G^0_T$ data [40] of the phases concerned are summarized in table 2. Thus $\Delta G^0_T$ values for each reaction at 700–1000 K (i.e., 427–727 °C) could then be obtained and are summarized in table 3.

$\Delta G^0_T = \sum \nu \Delta G^0_{f,T}$ (products) − $\sum \nu \Delta G^0_{f,T}$ (reactants) (9)

The direction of reactions (3)–(6) depended on the partial pressure of the gaseous product (CO$_2$ or H$_2$O). Table 4 shows the equilibrium pressure of the gaseous product ($P_e,T$) in these reactions at 700–1000 K, as calculated by equation (10) [41] (where $K_p$ is the equilibrium constant). Taking reaction (3) at 700 K as an example, only when the partial pressure of CO$_2$ > 0.385 atm did this reaction proceed towards the left. However, at 400–800 °C, the samples were placed in a flowing...
O₂/N₂ mixture gas and therefore the pressure of CO₂ could not retain such a high value. Consequently, reaction (3) constantly proceeded towards the right, i.e. if BaCO₃ and YF₃ coexisted, they would keep reacting to form BaF₂ until one of them ran out. Concerning reactions (4)–(6), we could draw the same conclusion no matter whether the gaseous product was CO₂ or H₂O. Reactions (7) and (8), which did not involve gaseous reactants or products, had ΔG°₂₉₈ much lower than zero, indicating BaO would also react with YF₃ or CuF₂ to form BaF₂ in a thermodynamically stable state. According to the analyses above, YF₃ or CuF₂ were not stable before all the Ba precursor was converted to BaF₂. Thus, the formation priority of BaF₂ over YF₃ and CuF₂ was verified.

5. Summary

A low-fluorine precursor solution for MOD-YBCO fabrication was developed. The fluorine content of this solution was approximately only 10.3% of that used in the conventional TFA-MOD solution, corresponding to a starting F/Ba mole ratio of 2:1. ATR-FT-IR revealed that BaCO₃ was remarkably suppressed in the as-pyrolyzed film—and eliminated at 700°C. In situ FT-IR spectra showed that no obvious fluorinated gaseous by-products were detected in the pyrolysis step, indicating BaO would also react with YF₃ or CuF₂ to form BaF₂ in a thermodynamically stable state. According to the analyses above, YF₃ or CuF₂ were not stable before all the Ba precursor was converted to BaF₂. Thus, the formation priority of BaF₂ over YF₃ and CuF₂ was verified.

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Table 4. The equilibrium pressure of CO₂ or H₂O (Pₑ,₆) in reactions (3)–(6) at 700–1000 K (427–727 °C). The unit of Pₑ,₆ is atm.

| Reaction | Pₑ,700 | Pₑ,800 | Pₑ,900 | Pₑ,1000 |
|----------|--------|--------|--------|---------|
| (3)      | 0.385  | 5.03   | 36.0   | 170     |
| (4)      | 4.58×10⁸ | 3.80×10⁸ | 3.16×10⁸ | 2.64×10⁸ |
| (5)      | 1.11×10⁷ | 6.42×10⁶ | 3.87×10⁶ | 2.45×10⁶ |
| (6)      | 1.32×10¹⁶ | 4.85×10¹⁴ | 3.40×10¹³ | 3.81×10¹² |
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