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# **Corrigendum: An advanced low-fluorine solution route for fabrication of high-performance YBCO superconducting films**

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Figure 3 on page 3 was incorrect. The corrected figure is shown below.



**Figure 3.** HRTEM image of a YBCO film derived from the advanced low-fluorine solution. The inset shows the TEM-SAD of the cross section between YBCO and the LAO substrate.

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# RAPID COMMUNICATION

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# An advanced low-fluorine solution route for fabrication of high-performance YBCO superconducting films

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#### Abstract

We have developed a new low-fluorine solution consisting of non-fluorine (F-free) barium and copper salts, and fluorine-containing yttrium trifluoroacetate. Using this new low-fluorine solution, the BaCO<sub>3</sub> phase was avoided in the pyrolyzed precursor films. Instead, CuO, Y and Ba fluorides (YF<sub>3</sub> and BaF<sub>2</sub>) were formed in the precursor films pyrolyzed at 450 °C, which was the same as when an All-TFA solution (prepared using Y, Ba, Cu trifluoroacetates as precursors) or other fluorine-reduced solutions were used. This new kind of low-fluorine solution has only 23% of the fluorine content in an All-TFA solution, and the fluorine content was lower than any other fluorine-reduced solution. Thus, rapid production of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (YBCO) films can be easily realized. Using a heating rate of 10 °C min<sup>-1</sup> in the pyrolysis process, a high critical current density ( $J_c$ ) of 5 MA cm<sup>-2</sup> (at 77 K, 0 T) was obtained in YBCO films fabricated on LaAlO<sub>3</sub> (LAO) single crystal substrates from the new starting solution.

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

### 1. Introduction

The metal-organic deposition (MOD) method, using a starting solution containing trifluoroacetate (TFA) salts of yttrium, barium and copper, is one of the most promising methods for fabricating of long YBCO tapes. However, the traditional TFA-MOD method using the All-TFA solution requires more than 10 h for the pyrolysis process for each single-coated film, resulting in a low production rate for thicker YBCO-coated conductors [1, 2]. For practical production, high-efficiency deposition of YBCO films is necessary. In the recent decades, many investigations have been carried out to shorten the pyrolysis time [3–6].

The heating rate of the pyrolysis process leads to gas generation due to decomposition of the compounds, and thus affects the film quality (bulk density, uniformity, etc) [7]. In the TFA-MOD method, the large pores (low bulk density) and non-uniform distribution of metal elements in the precursor film lead to degradation of crystallinity and, hence, the  $J_c$ of YBCO films [8, 9]. The rate of the gas generation is determined by the amount of fluorine element, the molecular weight, the heating rate, and the film thickness of each single coating. An improvement in processing time and the thickness of the precursor films can be achieved by reducing the fluorine-reduced solution developed by ISTEC (Japan) provided YBCO film with a high critical current of 470 A cm<sup>-1</sup> W<sup>-1</sup> after multiple coating and calcination [10].

In our previous work, we developed a low-fluorine solution that consisted of barium trifluoroacetate and flourinefree copper and yttrium salts. The duration of the pyrolysis process using this low-fluorine route was shortened to several

#### Supercond. Sci. Technol. 25 (2012) 062001

hours [11, 12]. During the preparation of the low-fluorine solution, the yttrium acetates should be dissolved in methanol, with the help of complexing agents containing amine groups such as diethylenetriamine (DETA) or NH<sub>4</sub>OH [13–15]. Although the introduction of amine groups in the solution can also suppress the release rate of HF gas, and hence lead to a high heating rate of the pyrolysis [16], it induces the formation of Cu<sub>2</sub>O or even metallic Cu grains at 300–350 °C, resulting in aggregated CuO particles left in the final film [17]. Thus an accurate stoichiometry of Y:Ba:Cu = 1:2:3 is difficult to realize at atomic level inside the film, which degrades the film superconductivity.

To overcome the shortcomings in the low-fluorine solution consisting of Ba-TFA and fluorine-free yttrium and copper salts, a new starting solution, using fluorine-free barium and copper salts and flourine-containing yttrium salt as precursors, is proposed in this paper. The total content of fluorine in the precursor solution is only 23% of that in the conventional All-TFA solution. One may think that in using this solution  $YF_3$  rather than  $BaF_2$  will be formed in the precursor film. On the contrary, our results indicated that both  $YF_3$  and  $BaF_2$  were formed inside the precursor film. Also, YBCO films with high-performance were achieved through a rapid heat-treatment process.

#### 2. Experiments

The precursor solution was prepared by mixing three solutions in a controlled stoichiometry of Y:Ba:Cu=1:2:3. Yttrium acetate (Y(OAc)<sub>3</sub>) was dissolved in de-ionized water in a stoichiometric quantity of trifluoroacetic acid at room temperature, and then water and acetic acid were removed by vacuum evaporation at 75 °C. A transparent glassy residue, namely Y-TFA, was obtained. Solution 1 was prepared by dissolving this glassy residue in methanol (MeOH). Solution 2 was prepared by dissolving barium acetate  $(Ba(OAc)_2)$  in MeOH with the help of a certain quantity of lactic acid. Solution 3 was prepared by dissolving the copper acetate (Cu(OAc)<sub>2</sub>) in a small amount of hot methacrylic acid, which was then diluted with MeOH. The stable precursor solution was produced after solutions 1, 2 and 3 were mixed and stirred at room temperature. The synthesized precursor solution was then condensed to control the viscosity and the total metallic ion concentration (1 mol  $l^{-1}$ ). For convenience, we call the new low-fluorine YBCO precursor solution the 'advanced low-fluorine solution'.

The YBCO gel films were produced by dip-coating on single crystal LAO substrates. The gel films were heat-treated using two standard steps, which is similar to the other low-fluorine solution route reported elsewhere [11]. First, they were decomposed by increasing the temperature from room temperature to  $450 \,^{\circ}$ C in a humid oxygen gas atmosphere. Then, the  $450 \,^{\circ}$ C-pyrolyzed precursor films were heated to the maximum temperature of  $800 \,^{\circ}$ C ( $T_{max}$ ) in a O<sub>2</sub>/N<sub>2</sub> gas flow for 70 min. The partial pressure of oxygen in the mixed gas was 1.3%. After holding at  $T_{max}$  for 70 min, the gas was switched to a dry mixture gas and the films were held at  $T_{max}$  for another 20 min. Next, the furnace was cooled



Figure 1. XRD pattern of a YBCO film derived from the advanced low-fluorine solution.

down to 450 °C, at which temperature the films were finally post-annealed in dry oxygen for 2 h. The typical thickness of a single-coated YBCO film is 230–250 nm.

A 7000S-type x-ray diffractometer (XRD) with Cu K $\alpha$ radiation was used to detect the phase in the films. Scanning electron microscopy (SEM) experiments were performed on a JEM-6700F. No conductive coating was applied. The critical transition temperature  $(T_c)$  of the YBCO film was measured through a standard four-probe method. Film thickness was measured by a Sufcorde-SE3500 surface roughness analyser. Fourier transform infrared (FT-IR) spectra of the gel films and pyrolyzed films coated on the silicon wafer were obtained with a FT-IR spectrophotometer (Shimadzu: FT-IR800). A 3010-F-type high-resolution transmission electron microscope (HRTEM) was employed to confirm the epitaxial growth of the films. A multi-function vibrating sample magnetometer (VersaLab-VSM) was adopted to measure the superconducting properties of the films at varying applied magnetic field and temperature.  $J_c-H$  curves were obtained from the M-H curves using a calculation according to the Bean model [18], as given by equation (1):

$$J_{\rm c} = 20\Delta M / [a(1 - a/3b)V]$$
(1)

where  $\Delta M$  is calculated according to the vertical width of M-H loops at zero field, and a and b are the length and the width of the film. The size of the sample used in the magnetic  $J_c$  measurement was 2 mm × 2.5 mm. The applied field, with magnetic strengths of 0–3 T, was perpendicular to the film surface during the magnetization measurement.

#### 3. Results and discussion

Using the advanced low-fluorine solution, YBCO singlecoated films were deposited on LAO substrates. Figure 1 shows a typical  $\theta$ -2 $\theta$  XRD pattern of a YBCO film on a LAO single crystal substrate. As shown in this figure, only the (00*l*) reflections could be detected in the pattern of this film. Also, no polycrystalline YBCO peaks were observed at 32.5°, 32.8°, and 58.2° corresponding to (013), (103), and (213)



**Figure 2.** Surface morphology of a YBCO film derived from the advanced low-fluorine solution.



**Figure 3.** HRTEM image of a YBCO film derived from the advanced low-fluorine solution. The inset shows the TEM-SAD of the cross section between YBCO and the LAO substrate.

planes, respectively. Moreover, peaks located at 23.26° and 47.55° respectively corresponding to (010) and (020) planes, were not observed. All these factors indicate that the film has c-oriented growth on the LAO substrate without a-oriented or randomly oriented YBCO grains. Figure 2 shows the surface morphology of the single-coated YBCO film. A small number of pores with diameter less than 1  $\mu$ m were observed on the film surface, which was similar to the microstructure of YBCO films derived from the All-TFA solution [19]. However, the same as detected by the XRD pattern, no a-oriented grains were observed on the film surface, which contributed to the high critical current density of the film. Figure 3 shows the HRTEM image and the selected-area electron diffraction (SAED) pattern of a YBCO film on the LAO substrate. It can be seen from figure 3 that the film was epitaxially grown on the LAO substrate along the c-axis orientation, and that there was no diffusion between YBCO and the LAO substrate.

The critical transition temperature  $T_c$  of the YBCO film was measured through a standard four-probe method. Figure 4 shows the *R*-*T* curve for the YBCO film. The film showed a

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Figure 4. *R*–*T* curve of a YBCO film deposited on a LAO substrate.



**Figure 5.**  $J_c$ –H curve of a YBCO film deposited on a LAO substrate.

high  $T_c$  of 91 K, with a sharp transition width of  $\Delta T = 0.7$  K. Figure 5 shows the  $J_c$ -H curve of the YBCO film. As can be seen, at a temperature of 50 K, the  $J_c$  of the film exceeded over 10 MA cm<sup>-2</sup> at 0 T, and showed a smaller decrease with increasing magnetic field. At 77 K, the YBCO film also showed a high  $J_c$  of 5.4 MA cm<sup>-2</sup> (at 0 T). However, with an increase of the magnetic field, the  $J_c$  at 77 K decreased drastically. When H = 2 T, the  $J_c$  of the film dropped to  $10^5$  A cm<sup>-2</sup>. For applications under a magnetic field at liquid nitrogen temperatures, it is necessary to introduce flux pinning into the YBCO film so as to improve its  $J_c$  under high magnetic field.

The high  $J_c$  value of the YBCO film can be ascribed to its phase-pure quality and well-crystallized structure. A quasiliquid model was suggested by Araki *et al* in [20], which could be used to explain the well-crystallized and high-performance YBCO films derived from the All-TFA solution. The quasiliquid phase can be formed below 800 °C when the molar ratio of F/Ba > 2. A molar ratio of F/Ba > 2 can be realized by formation of YF<sub>3</sub> and BaF<sub>2</sub> phases in the precursor film. One may think, since the advanced low-fluorine precursor solution contains only Y salts as TFA salts, that the formation of YF<sub>3</sub> together with BaF<sub>2</sub>



**Figure 6.** Grazing incidence x-ray diffraction patterns of precursor films: (a) pyrolyzed at  $300 \,^{\circ}$ C for 15 min, (b) pyrolyzed at  $350 \,^{\circ}$ C for 15 min, (c) pyrolyzed at  $450 \,^{\circ}$ C for 15 min, and (d) annealed at  $800 \,^{\circ}$ C for 15 min.

in the pyrolyzed film is almost impossible. However, the truth is far more complicated than first thought. To check the products in the pyrolyzed film, grazing incidence x-ray diffraction was performed on a series of precursor films. The XRD results are shown in figure 6. At 300 °C, the precursor film was almost non-crystalline. At 350° and 450°, peaks corresponding to Ba-Y-F, CuO and BaF2 phases were observed. No peaks corresponding to the BaCO<sub>3</sub> phase were detected. The Ba-Y-F is actually an extensive solid solution formed by BaF<sub>2</sub> and YF<sub>3</sub>. That is to say, using the advanced low-fluorine solution, although the chemical reaction path during the pyrolysis process was different from that of other TFA solution routes, the same products of BaF<sub>2</sub> and YF<sub>3</sub>, and CuO phases were obtained after the pyrolysis process. Thus the same chemical reaction path will be experienced in the following high-temperature annealing stage. From the XRD pattern (d) in figure 6, one can also see that  $Y_2Cu_2O_5$ ,  $BaF_2$ , and CuO phases were formed after the precursor film was annealed at 800 °C for 15 min. Thus, it can reasonably be concluded that with the help of water gas, the decomposition of YF<sub>3</sub> (inside the Y-Ba-F solid) leads to the formation of  $Y_2O_3$ , as shown by equation (2). The formed  $Y_2O_3$  can react with CuO to form  $Y_2Cu_2O_5$ , as indicated by equation (3). Finally, YBCO is formed by the reaction with  $Y_2Cu_2O_5$ , BaF<sub>2</sub>, CuO and water gas, as indicated by equation (4). This mechanism of formation of the YBCO phase is completely the same as that in the All-TFA solution route.

 $2YF_3 + 3H_2O = 6HF + Y_2O_3$ (2)

$$Y_2O_3 + 2CuO = Y_2Cu_2O_5$$
(3)

$$2BaF_{2} + 0.5Y_{2}Cu_{2}O_{5} + 2CuO + 2H_{2}O$$
  
= YBa\_{2}Cu\_{3}O\_{6.5} + 4HF  $\uparrow$  . (4)

During the annealing process, due to the molar ratio of F/Ba > 2, a liquid or quasiliquid phase can be formed. Thus, YBCO films with high performance such as that derived from the All-TFA solution can be realized.

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**Figure 7.** FT-IR spectra of as-deposited gel film (a), and precursor films pyrolyzed at (b) 250 °C, (c) 300 °C, (d) 350 °C, and (e) 450 °C.

From the XRD patterns (b) and (c) of the precursor film shown in figure 6, we can also conclude that when the TFA species combined with the Y ion were decomposed, the F ions were 'absorbed' not only by the Y ions themselves to form YF<sub>3</sub>, but also by the Ba ions to form the  $BaF_2$  phase. This indicates that, compared with the All-TFA solution route, in the advanced low-fluorine solution route the amount of HF gas generated during the pyrolysis stage was greatly reduced. Taking a precursor solution with a stoichiometry of Y:Ba:Cu = 1:2:3, for example, the fluorine content in the advanced low-fluorine solution is only 23.1% of that in the All-TFA solution. During the pyrolysis stage, considering all the Y ions and Ba ions react with CF<sub>3</sub>COO<sup>-</sup> species to form their corresponding fluorides, in the advanced low-fluorine solution route the amount of corrosive fluourine-containing gas released is only 6.2% of that in the All-TFA solution route. Thus, to obtain a precursor film with a smooth surface, a high heating rate can be realized during the pyrolysis stage.

However, the reason why no BaCO<sub>3</sub> phase was formed in the precursor film remains unclear. Moreover, the decomposition of other organic species may result in the carbon residue in the pyrolyzed film. To investigate these problems, infrared spectra were also examined on gel films and precursor films pyrolyzed at different temperatures, as shown in figure 7. We pay attention to the stretching vibration modes of the COO<sup>-</sup> bond at 1680 cm<sup>-1</sup> and C-O bond at 1144 and 1202  $\text{cm}^{-1}$ . In the gel film IR spectrum shown in figure 7(a), the COO<sup>-</sup> and C-O bonds were related to carboxyl absorption, which not only could be ascribed to the TFA species [21], but also to lactic acid or methacrylic acid. Another absorption at 1434-1455 cm<sup>-1</sup>, corresponding to the vibration mode of C-H should also be noted, which could only be ascribed to lactic acid or methacrylic acid, since in that TFA no C-H bond exists.

All the vibrations of COO<sup>-</sup>, C–O, and C–H were also observed in the 250 °C-decomposed precursor film, as shown in figure 7, indicating the TFA, lactic acid or methacrylic acid groups might not be totally decomposed at 250 °C. However, in spectrum (b) of figure 7 the relative peak intensity of C–H was decreased, while the relative peak intensity of COOwas increased, compared with that in curve (a). Moreover, in spectrum (b) the peak of C-H mode was shifted from 1434 to 1455  $\text{cm}^{-1}$ . These indicate that the TFA group is decomposed after the lactic acid or methacrylic acid group. In addition, it is reported that the complete decomposition of TFA salts at 250 °C required about 500 min [22]. In our experiments, only 15 min was involved at 250 °C. Thus, the peak located at 1680 cm<sup>-1</sup> in spectrum (b) of figure 7 is mainly ascribed to the TFA salts, not the lactic acid or methacrylic acid species. Therefore, it is reasonable to deduce that the decomposition in the precursor films follows this sequence: firstly, fluorine-free copper or barium salts were decomposed into an amorphous phase; next, the Y-TFA was decomposed and the decomposed  $F^-$  ions were captured not only by Y ions to form YF<sub>3</sub>, but also by Ba ions inside the amorphous Ba compounds to form BaF<sub>2</sub>. During the decomposition, even if the Ba salt was decomposed into BaCO3 or BaO, due to their amorphous state and the acetic condition in the pyrolyzed film matrix, the Ba ions were highly active and could be easily captured by F ions to form a more stable BaF<sub>2</sub> phase. Thus, this decomposition scheme finally leads to the formation of YF<sub>3</sub>, BaF<sub>2</sub> and CuO phases in the precursor film, as detected by XRD and shown in figure 6, and can avoid the formation of carbon-related phases such as BaCO<sub>3</sub> inside the film. The FT-IR spectra also indicate that a 15 min decomposition at 350 or 450 °C can completely expel the carbon-related species in the precursor film, as indicated by spectrum (d) and (e) in figure 7. This carbon-free phenomenon in the precursor film also contributes to the high  $J_c$  of the final YBCO films.

#### 4. Conclusions

We have invented a novel low-fluorine solution (advanced low-fluorine solution) consisting of fluorine-free (F-free) barium and copper salts, and fluorine-containing yttrium trifluoroacetate. This solution has only 23% of the fluorine content of an All-TFA solution. Using this advanced low-fluorine solution, the BaCO<sub>3</sub> phase was avoided in the pyrolyzed precursor films. The fluorine-free Ba and Cu salts were first decomposed at around 250 °C, followed by decomposition of Y-TFA. Also, CuO and the Y and Ba fluorides (YF<sub>3</sub> and BaF<sub>2</sub>) were formed in the precursor films solution routes. Using a heating rate of 10 °C min<sup>-1</sup> in the pyrolysis process, a high  $J_c$ , over 5 MA cm<sup>-2</sup> (at 77 K, 0 T), was obtained in YBCO films fabricated on LAO single crystal substrates using the advanced low-fluorine solution.

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