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Thermal decomposition of barium trifluoroacetate thin films

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ABSTRACT

The thermal decomposition of barium trifluoroacetate thin films under different atmospheres is presented. Thermogravimetry and evolved gas analysis have been used for this *in situ* analysis. We focus our attention on the different behavior exhibited by films when compared to powders. The decomposition of barium trifluoroacetate is altered due to the faster out-diffusion of the product reaction:CF_2. After barium trifluoroacetate decomposition a stable intermediate, barium fluoride, is formed. The decomposition of barium fluoride is diffusion controlled and depends on water partial pressure.

1. Introduction

Chemical solution deposition (CSD) is an efficient, flexible, low cost and scalable method for the fabrication of functional oxide films [1–3]. CSD involves solution preparation, solution deposition, a low temperature thermal treatment to remove the organic species and a high temperature thermal treatment to crystallize the amorphous films. Thermal analysis (TA) is especially suited to analyzing the low temperature treatment due to its ability to monitor *in situ* the processes that take place during precursor decomposition as well as their dependence on the treatment conditions: temperature program and oxygen and water partial pressures [4–9]. Knowledge of the transport mechanism that affects the thermal decomposition of the organic precursor is essential for CSD processing [10–12].

Although CSD is used to synthesize films, TA is routinely performed on powders, TA analysis on films is very scarce. In general, the main reason for this is that the signal measured by TA techniques is proportional to the sample mass. For instance, typical sample masses for thermogravimetric measurements on powders are around 10 mg whereas film masses are, at best, one order of magnitude smaller. In addition, precursor decomposition usually involves solid-gas reactions that strongly depend on transport phenomena: in-diffusion of reactants, out-diffusion of products or heat dissipation in exothermic processes. As a result, the behavior of powders may strongly differ from the actual behavior of films [13–16].

In this paper we will analyze the thermal decomposition of barium trifluoroacetate, $Ba(CF_3COO)_2$ ($Ba(TFA)_2$), in the form of films. $Ba(TFA)_2$, combined with yttrium and copper precursors, is the most common precursor in the fabrication of high-performance $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconducting films [12,17,18]. Thermogravimetry (TG) is used to monitor the decomposition process. A mass spectrometer (MS) is used to perform the evolved gas analysis (EGA) of volatiles formed during decomposition. Intermediate and final products are characterized using scanning electron microscopy (SEM), energy dispersive X-ray micro-analysis (EDX) and X-ray diffraction (XRD). Different atmospheres have been tested. We will show that $Ba(TFA)_2$ films decompose differently to powders [19–21] and that BaF_2 decomposition kinetics is controlled by HF diffusion.

2. Experimental

The synthesis of barium trifluoroacetate $Ba(CF_3COO)_2$ powders is described in Ref. [21]. A solution 0.56 M of $Ba(TFA)_2$ in anhydrous methyl alcohol was obtained at room temperature by manually shaking the mixture for less than 1 min. Films were prepared by manually freely spreading microdrops (~2 μL) on the

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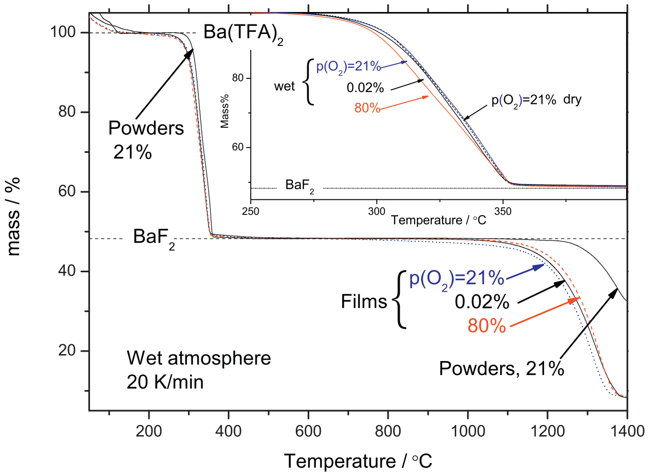

Fig. 1. TG curves for thermal decomposition of $Ba(TFA)_2$ films heated at 20 K/min in wet atmospheres with different oxygen partial pressures: air (21%), nitrogen and oxygen mixture (80% O_2) and argon (0.02%) and powders in wet air. Precursor masses per unit surface of a single film, m_S, are 1.14, 1.15 and 1.19 mg/cm^2 respectively. The initial sample mass of powders was 18 mg. The mass has been normalized to the mass after dehydration. Inset: detail of the precursor film decomposition for wet and dry atmospheres and for different oxygen partial pressures.

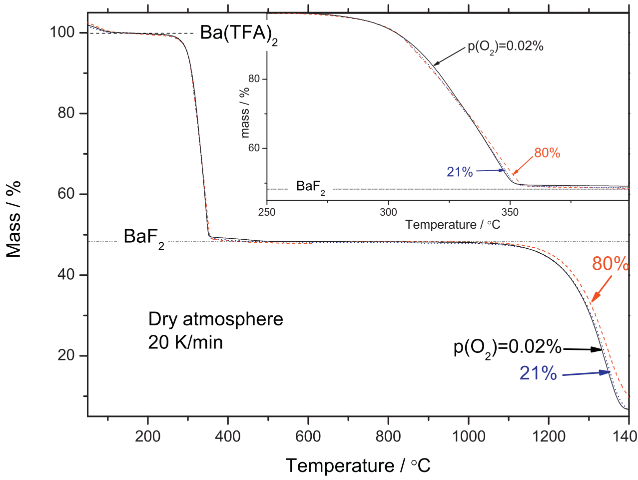

Fig. 2. TG curves for thermal decomposition of $Ba(TFA)_2$ heated at 20 K/min in dry atmospheres with different oxygen partial pressures: air (21%, dotted line), nitrogen and oxygen mixture (80% O_2, dashed line) and argon (0.02%, solid line). Values of m_S are 0.98, 1.44 and 1.29 mg/cm^2 respectively. The mass has been normalized to the mass after dehydration. Horizontal dotted line is the expected final mass for the formation of BaF_2. Inset: detail of the precursor decomposition.

surface of a glass disc (12 mm in diameter) or on a square LAO plate (10 mm × 10 mm). The solvent was removed by heating the substrate at 70 °C for 15 min in a hot plate under vacuum. After solvent evaporation, the masses of the films vary from 0.21 to 2.0 mg.

TG analysis was performed with a Setaram apparatus model, Setsys Evolution 16. To improve the signal-noise ratio, two substrates coated on both sides were analyzed simultaneously. Gas flow was controlled by mass flow meters. High-purity nitrogen, argon, oxygen and synthetic air were used. Water-saturated gases were obtained by bubbling the carrier gas in water at standard temperature and pressure (25 °C, 1 atm). TG curves were corrected by subtracting a consecutive identical second measurement that was performed without opening the furnace to ensure that the differences between the first and second measurements were minimal. In addition, the mass of the final residue was measured at room temperature with an analytical balance that allows us to determine the absolute mass with accuracy better than 5 μg. Then, the TG curve is vertically shifted so that the final mass of the TG curve coincides with that measured at room temperature. Residual oxygen and water partial pressures on the furnace were 0.01% and 0.002%, respectively. Simultaneous TG and EGA analyses were performed with a Mettler Toledo, model TGA851eLF, thermobalance coupled to an MKS quadrupole mass spectrometer (Microvision Plus). Residual oxygen and water partial pressures on the TGA851eLF furnace were 0.2% and 0.04%, respectively. Complementary EGA analyses were performed by placing the samples inside a quartz tube at a pressure of around 10^{-6} mbar. Samples were heated using an external furnace. Thermal analysis experiments were performed at heating rates of 5, 10 and 20 K/min.

XRD experiments were done in a SMART APEX diffractometer from Bruker AXS. The X-ray beam wavelength was 0.710730 Å (Mo-Kα). The X-ray source was operated at a voltage of 50 kV and a current of 3 mA. SEM and EDX observations were performed in a Zeiss DSM 960A scanning electron microscope operated at 20 kV. Samples were coated with a thin gold or carbon films to remove electrostatic charges.

3. Results

In Figs. 1 and 2 we have plotted the mass variation when $Ba(TFA)_2$ films are heated at 20 K/min in dry and wet atmospheres with different oxygen content. The mass loss evolution can be divided into three stages. The first stage (below 150 °C) corresponds to dehydration. The larger mass loss takes place at the second stage, which starts at 220 °C and is related to precursor decomposition. The mass of the solid residue after precursor decomposition remains constant in a wide temperature range and corresponds to the expected mass of BaF_2:

$$\frac{m[BaF_2]}{m[Ba(CF_3COO)_2]} \times 100 = 48.25\%. \qquad (1)$$

The formation of BaF_2 has been confirmed by XRD analysis. Fig. 3 shows that the product, when films are heated up to 400 °C at 20 K/min in dry and wet argon and air atmospheres, is mainly crystalline BaF_2. The formation of BaF_2 instead of BaO or $BaCO_3$ is due to the high electronegativity of fluorine which displaces the oxygen bonded to Ba [18].

SEM analysis of the films obtained under different atmospheres has revealed that the thickness is quite inhomogeneous (see Fig. 4a). This result is not surprising if we take into account that the solution

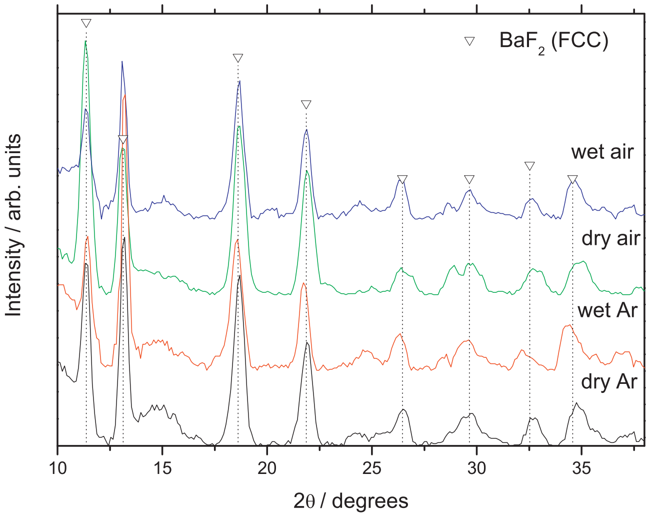

Fig. 3. X-ray powder diffractograms of solid residues after heating the $Ba(TFA)_2$ to 400 °C at 20 K/min in different atmospheres. Triangles: face-centered BaF_2 phase [28].