

PAPER • OPEN ACCESS

On the thermodynamics of Barium Oxyfluoride precursor in YBCO growth via the MOD process

To cite this article: M De Angelis and M Tomellini 2024 *J. Phys. D: Appl. Phys.* **57** 465301

View the [article online](#) for updates and enhancements.

You may also like

- [The damage property of oxyfluoride glasses irradiated by a 351 nm high fluence laser](#)
Chaoqi Hou, Weinan Li, Pengfei Wang et al.
- [Fabrication of dense yttrium oxyfluoride ceramics by hot pressing and their mechanical, thermal, and electrical properties](#)
Ryuki Tahara, Toru Tsunoura, Katsumi Yoshida et al.
- [Iron Oxyfluorides as High Capacity Cathode Materials for Lithium Batteries](#)
N. Pereira, F. Badway, M. Wartelsky et al.



PRIME
PACIFIC RIM MEETING
ON ELECTROCHEMICAL
AND SOLID STATE SCIENCE

HONOLULU, HI
October 6-11, 2024

Joint International Meeting of
The Electrochemical Society of Japan (ECSJ)
The Korean Electrochemical Society (KECS)
The Electrochemical Society (ECS)

Early Registration Deadline:
September 3, 2024

**MAKE YOUR PLANS
NOW!**

On the thermodynamics of Barium Oxyfluoride precursor in YBCO growth via the MOD process

M De Angelis^{1,2,*}  and M Tomellini¹ 

¹ Department of Chemical Sciences and Technologies, Tor Vergata University, Via della Ricerca Scientifica 1, 00133 Rome, Italy

² Department of Fusion and Technologies for Nuclear Safety and Security, ENEA, Superconductivity Laboratory, Via E. Fermi 45, 00044 Frascati (Rome), Italy

E-mail: michele.deangelis.01@alumni.uniroma2.eu

Received 10 April 2024, revised 31 May 2024

Accepted for publication 8 July 2024

Published 22 August 2024



Abstract

Barium Oxyfluoride plays an important role, as a precursor species, in the nucleation and growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) via the low fluorine metal organic decomposition (MOD low-fluorine) route. In this contribution, we present a study on the thermodynamics of oxyfluoride by processing experimental data on YBCO growth on LaAlO_3 (LAO) substrates. The analysis allows one to determine the standard enthalpy and the standard entropy changes for oxyfluoride formation from barium oxide and barium fluoride. To identify the thermodynamically more favorable route to oxyfluoride formation in the MOD low-fluorine process, the free energy change for the formation of the precursor, through reactions involving gas water, has been determined. The free energy of formation via fluoride and water indicates higher stability of oxygen rich oxyfluoride for $\frac{P_{\text{HF}}^2}{P_{\text{H}_2\text{O}}} < 10^{-6}$. In the framework of nucleation theory, the present results are needed to study the effect of precursor composition on film orientation.

Keywords: YBCO crystal growth, fluorine based MOD process, thermodynamics of oxyfluoride precursor

1. Introduction

During the last decades the chemical solution decomposition technique has been applied, with success, in the growth of thin film of high temperature superconductors, YBCO, by employing the metal organic decomposition (MOD) approach with precursor solutions made of Y, Ba, and Cu metal organic salts,

usually trifluoroacetates (TFA) or a mixture of trifluoroacetates and acetates (in this case called MOD low-fluorine), dissolved in an organic solvent [1–4]. In the first YBCO synthesis, made with yttrium stearate, barium, and copper naphthenate, the formation of BaCO_3 during the processing step significantly affected the film superconducting properties [5, 6]. Hence, by taking inspiration from the physical BaF_2 process [7–9], metal TFAs were adopted with the aim of promoting BaF_2 nucleation, instead of BaCO_3 , at the end of the pyrolysis step [3]. In fact, BaF_2 decomposes more easily and at lower temperatures than the stable BaCO_3 [6, 10] forming the oxyfluoride responsible for the nucleation and growth of highly epitaxial YBCO film. The formation of oxyfluoride has also been observed in BaF_2 *ex-situ* process studied in [11, 12].

In TFA synthesis, pure YBCO low fluorine solution is prepared with yttrium(III) acetate (or trifluoroacetate) hydrate,

* Author to whom any correspondence should be addressed.



Original content from this work may be used under the terms of the [Creative Commons Attribution 4.0 licence](https://creativecommons.org/licenses/by/4.0/). Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

barium(II) trifluoroacetate (or acetate) hydrate and copper(II) acetate. A small excess of copper acetate was used in consideration of the copper loss possibly occurring during the pyrolysis step [13]. The MOD low-fluorine process consists of three main steps, they are as follows: (i) precursor solution preparation; (ii) substrate coating; (iii) a first low temperature treatment (pyrolysis) for the removal of the organic matrix and (iv) a high temperature treatment (firing) to promote the YBCO nucleation and growth followed by its oxygenation, where YBCO converts from the tetragonal to orthorhombic superconducting phase [14, 15].

Many aspects of thermal treatment have been experimentally investigated by several research groups with the purpose of optimizing the MOD process. The effect on YBCO synthesis of some parameters, such as the rate of temperature increasing (the so-called ramp rate), the composition of the gaseous phase in the furnace, with particular attention to the oxygen and water content, the annealing temperature and the duration of the crystallization or oxygenation steps have been studied in detail, as witnessed by the vast literature devoted to the topic [16–19]. For a comprehensive presentation of the physical-chemistry of YBCO nucleation and growth mechanisms in the fluorine-based MOD route, the readers may refer to the excellent topical reviews reported in [1, 20].

After pyrolysis, the sample consists of an amorphous heterogeneous mixture of oxide and oxyfluoride compounds [15, 21] which are further converted by the presence of water during the high temperature treatment. This stage is particularly important as it determines the crystal orientation during the growth. Indeed, optimal transport properties of YBCO films have been observed for crystal growth along the *c*-axis [22]. These results have triggered a series of studies on the early stages of YBCO crystal formation, namely the nucleation process, aimed at understanding the role of deposition parameters, such as partial pressure of water, $P(\text{H}_2\text{O})$, and temperature, T , on the fraction of *c*-oriented crystals [23, 24]. The classical nucleation theory is at the basis of these approaches where the free energy for nucleation is given by the sum of volume and surface terms [24, 25]: the first is linked to the free energy change for the reaction of YBCO formation in the precursor matrix, the second term is due to the excess free energy of the YBCO-substrate, YBCO-vacuum and YBCO-precursor interfaces. Specifically, in the MOD low-fluorine route the precursor has been identified with a barium–oxyfluoride (OF) that is one of the components entering the chemical reaction for YBCO nucleation and growth [1, 2, 26–30].

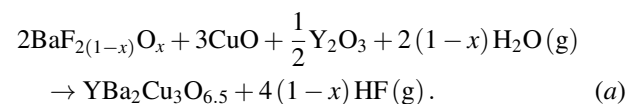
As reported in [30, 31] (MOD process) and [12] (*ex-situ* BaF_2 process), only the OF is observed prior to the formation of the YBCO because the presence of yttrium–oxyfluoride was not detected. In fact, as reported in [30], the yttrium–barium fluoride transforms into OF which leads to YBCO formation.

Another important quantity that can influence the growth mechanism of YBCO is the oxygen content in the atmosphere during the heat treatment. The oxygen effect has been extensively studied and has significant importance on the oriented growth process where, during the heat treatment, oxygen is supplied to the reagents by water decomposition and by the gas in the reaction environment [2, 16, 32]. Molecular oxygen

in the gas phase can saturate fluorine vacancies, thus changing the *x* value, although this process requires both oxygen dissociation and charge transfer from the OF to obtain O^{2-} , whose energetics are not completely known. Further studies are therefore needed to improve the description of the free energy for nucleation in terms of oxygen content, i.e. oxygen partial pressure during heat treatment.

The OF is formed by substitution of fluorine ions with oxygen ions in the BaF_2 fluorite structure, that is $\text{BaF}_{2(1-x)}\text{O}_x$ where the insertion of substitutional O^{2-} implies the formation of single charged fluorine vacancies to ensure charge balancing³. The growth of the OF at the substrate surface, as a precursor phase in the MOD process for YBCO, has been ascertained by several experimental studies. The OF has been identified by XRD and TEM analyses and surface sensitive spectroscopies as well [9, 28–30]. The role of OF in the nucleation process at the SrTiO_3 (STO) substrate has also been discussed in [1, 9, 26, 30]. It has been shown how the nucleation process takes place within the OF matrix, where the OF plays the role of an intermediate structure which acts as a template for the nucleation of YBCO crystal at high temperature (973 – 1073 K) as a tetragonal phase, with oxygen content about ~ 6.5 . When it is cooled down in oxygen atmosphere (853 – 873 K), a tetragonal-orthorhombic phase transition occurs and by further treatment at a lower temperature (e.g. 723 – 823 K) the oxygenation is completed to the level of ~ 6.95 related to a film with good superconducting properties [33]. In fact, for thick films, microscopy analysis does show that the (111) plane of the OF is aligned to the (001) plane of the YBCO and with the (001) of the STO substrate [26]. Owing to the similarity between the STO and LAO perovskite structures, it is expected that the same mechanism should be operative at the LAO substrate. It is also hypothesized that this intermediate phase may affect the interfacial energies entering the nucleation work and, therefore, the nucleation rate for *c*-axis or *a*-axis oriented growth of crystals [24]. It is hypothesized that the content of gas water during the high temperature treatment affects the composition of the OF, *x*, which seems to influence the orientation of crystal growth [24].

Based on these studies, the reaction describing the conversion of oxides and OF in YBCO is written according to [1, 27]:



Although scarce in the literature, it is worth pointing out that information on the thermodynamics of this reaction have been obtained through experimental studies on the kinetics of YBCO growth, as presented in [1, 27, 34]. On the other hand, to the best of the authors' knowledge, information on the thermodynamics of the formation of the OF are absent in the

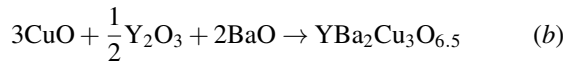
³ To simplify the notation throughout the text we set: $\text{BaF}_{2(1-x)}\text{O}_x \equiv \text{BaF}_{2(1-x)}(\text{V}_\text{F})_x\text{O}_x$, with V_F and O fluorine vacancy and substitutional oxygen respectively.

literature, despite being important for a quantitative description of the nucleation and growth kinetics [24]. This information is also important in deeming whether other reaction routes can efficiently compete with reaction (a).

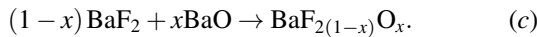
Based on these considerations, the purpose of this work is to provide some insights into the thermodynamics of OF formation by interpreting, through a thermodynamic approach, the experimental data of reaction (a).

2. Results and discussion

As anticipated, the standard free energy of reaction (a) has been determined in [1, 27] using experimental data on the growth rate of YBCO as a function of temperature and partial pressure of H₂O and HF. The outcome of this study does show that, in the temperature interval 973 K < T < 1073 K, the standard free energy of reaction (a) (at x = 1/2) is in the range 180–220 KJ mol⁻¹ YBCO. Figures of the same order of magnitude have also been measured in [34]. On the other hand, the free energy of formation of YBa₂Cu₃O_{6.5} from oxides can be determined by exploiting the *compound energy model* [35, 36]. Specifically, for the reaction



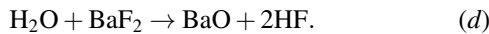
this model gives the standard free energy value $\Delta G_b^0 = -86.287 + 0.00246 T$ (kJ mol⁻¹). By employing these results and the experimental data quoted above, it is possible to estimate the standard free energy of the formation of the OF from barium fluoride and barium oxide:



In fact, expressing the free energy change of reactions (a)–(c) in terms of the free energies of formation of the components, the standard free energy of reaction (c), $\Delta G_c^0 \equiv \Delta G_{\text{OF}}^0$, is derived as follows:

$$\Delta G_{\text{OF}}^0 = \frac{1}{2} [\Delta G_b^0 - \Delta G_a^0 + 2(1-x)\Delta G_d^0], \quad (1)$$

where ΔG_j^0 is the standard free energy change of reaction j, with j = a, b, d, and ΔG_d^0 the standard free energy change of reaction (d) below:



By employing the experimental data [1, 27] for reaction (a) and the thermodynamic data for reactions b–d available in the literature [37], use of equation (1) gives the temperature dependence of the standard free energy change of reaction (c). As mentioned in the introduction, during the last step of the MOD, i.e. the firing, the mixture of compounds involved in the reaction is converted into oxides by the presence of water. Therefore, reaction (c) for the formation of the OF from oxides and reaction (d) is closely connected. In fact, as reported in [28], a possible reaction for OF formation is $\text{BaF}_2 + x\text{H}_2\text{O} \rightarrow$

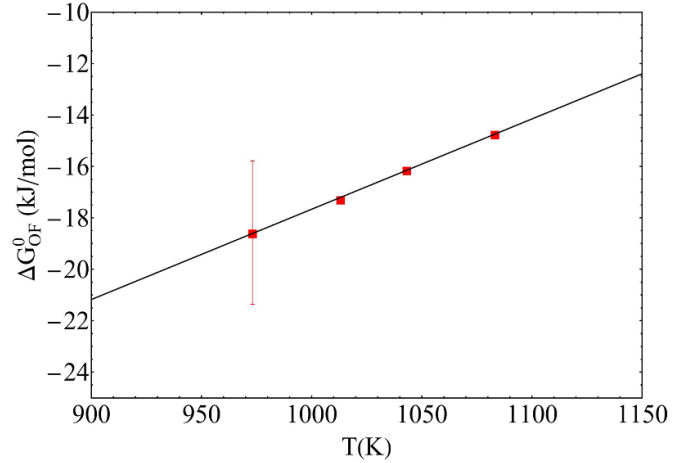


Figure 1. Free energy for the formation of OF in the range of 973 K < T < 1073 K at x = 1/2. Solid squares are the computational output of equation (1) obtained using experimental data from reference [1]. The error bar was evaluated on the basis of the data reported in [1] and is equal to 15% of the measurement for each data point.

$\text{BaF}_{2(1-x)}\text{O}_x + 2x\text{HF}$ that can be obtained from reactions (c) and (d) as discussed below.

The result of the computation of equation (1) is displayed in figure 1 where the free energy for the formation of OF, from barium oxide and Fluoride, lies in the range –25, –10 kJ mol⁻¹ for 973 K < T < 1073 K. Furthermore, the standard enthalpy and entropy change of reaction (c) is estimated from the data of figure 1 through the relationships $\Delta S_{\text{OF}}^0 = -\frac{\partial \Delta G_{\text{OF}}^0}{\partial T}$ and $\Delta H_{\text{OF}}^0 = \frac{\partial(\Delta G_{\text{OF}}^0/T)}{\partial(1/T)}$. The results of this elaboration provides $\Delta S_{\text{OF}}^0 = -35 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta H_{\text{OF}}^0 \cong -53 \pm 8 \text{ kJ mol}^{-1}$, nearly constant in the explored interval of temperature. The reaction to the formation of OF from oxides is found to be exothermic in the whole interval of temperature.

To begin with, we discuss the data for the entropy change of reaction (c). The entropy splits in the vibrational (v) and configurational (c) contributions, the latter being related to the OF, provided structural disorder is present. We get $\Delta S_{\text{OF}}^0 = \Delta S_{v,\text{OF}}^0 + \Delta S_{c,\text{OF}}^0 = S_{v,\text{OF}}^0 - (1-x)S_{v,\text{BaF}_2}^0 - xS_{v,\text{BaO}}^0 + S_{c,\text{OF}}^0$ with the configurational entropy ($S_{c,\text{OF}}^0 = \Delta S_{c,\text{OF}}^0$) depending on the adopted model for the defective structure [24]. The vibrational entropy of the OF is therefore given by $S_{v,\text{OF}}^0 = \Delta S_{\text{OF}}^0 + (1-x)S_{v,\text{BaF}_2}^0 + xS_{v,\text{BaO}}^0 - S_{c,\text{OF}}^0$.

Regarding the configurational entropy, we consider the following cases: (i) according to [29], disorder occurs in planes along the [111] direction of the BaF₂ cell that host vacancies and fluorine (substitutional oxygen being ordered in the structure); (ii) vacancies and substitutional oxygen are randomly distributed in the fluorine sub-lattice with both contributing to the configurational entropy. For case (i) $S_{c,\text{OF}} = R \ln \frac{M!}{n!(M-n)!}$ with n number of vacancies and M total number of fluorine sites in the layer hosting fluorine and vacancies (V_F[•]), i.e. 2 – x moles of sites per mole of OF. Since the mole fractions of V_F[•] and F_F are $\frac{x}{2-x}$ and $\frac{2-2x}{2-x}$, respectively, use of Stirling’s expression provides:

$$S_{c,OF}^0 = -R \left[x \ln \frac{x}{2-x} + 2(1-x) \ln \frac{2-2x}{2-x} \right]. \quad (2)$$

On the other hand, for case (ii) $S_{c,OF} = R \ln \frac{M_0!}{n_O! n_V! (M_0 - n_O - n_V)!}$ where n_O is the number of substitutional, $n_V = n_O$ the number of vacancies and M_0 the total number of fluorine sites (i.e. 2 moles of sites per mole of OF), since $\frac{n_O}{M_0} = \frac{x}{2}$ the entropy is equal to:

$$S_{c,OF}^0 = -R \left[2x \ln \frac{x}{2} + 2(1-x) \ln (1-x) \right]. \quad (3)$$

In equations (2) and (3) the entropy is per mole of OF. Figure 2 shows the vibrational contribution $S_{v,OF}^0$, as a function of temperature at $x = 1/2$, for complete ordered (i.e. $S_{c,OF}^0 = 0$) and disordered OF structures according to cases (i) and (ii).

To describe the behavior of the vibrational entropy with temperature, we employ both Einstein and Debye models of a harmonic solid. The former approach provides,

$$S_v^0(T) = S_E(\theta_E/T) = 3mR \left[\frac{\theta_E}{T} \frac{1}{(e^{\theta_E/T} - 1)} - \ln(1 - e^{-\theta_E/T}) \right]$$

and the latter

$$S_v^0(T) = S_D(\theta_D/T) = 9mR \left(\frac{T}{\theta_D} \right)^3 \times \int_0^{\theta_D/T} \left[\xi (e^\xi - 1)^{-1} - \ln(1 - e^{-\xi}) \right] \xi^2 d\xi,$$

where θ_E and θ_D are the Einstein and the average Debye temperatures, respectively, and m the number of oscillators (ions) per molecule of compound. From the fit of the data of figure 2(a), we obtain the Einstein and the Debye temperatures of OF together with those of BaO and BaF₂ (see table 1 and figure 2(b)).

The S_D and S_E functions describes the entropy data of both BaF₂ and BaO well. The θ_D value obtained by fitting the entropy data in the high temperature region is noteworthy, since the $S_D(\theta_D/T)$ function is in good agreement with the entropy data in an extended temperature range (inset of figure 2(b)). By inspection of the $S(\theta_{D(E)}/T)$ functions the relationship $\theta_D = \theta_E e^{1/3}$ is verified in the high temperature limit. The values of θ_D obtained for BaO and BaF₂ are in agreement with those reported in [38, 39]. We recall that, at a given temperature and in the high temperature regime, the greater the Debye temperature, the lower the vibrational entropy. An increase of the Debye temperature for a given number of oscillators implies a larger dispersion of the density of vibrational states. This occurs in defective solids by increasing the number of components and/or the concentration of defects.

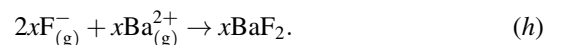
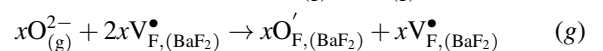
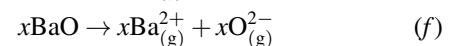
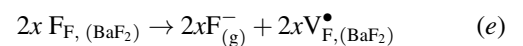
As far as the enthalpy change of reaction (c) is concerned, by considering as a first approximation $\Delta H_{OF}^0 \cong \Delta U_{OF}^0$, where H and U are, respectively, the enthalpy and internal energy, the relation holds:

$$\begin{aligned} \Delta H_{OF}^0 &= xU_{BaO} + (1-x)U_{BaF_2} - U_{OF} - \frac{\partial \Delta \ln Q_v}{\partial \beta} \\ &= xU_{BaO} + (1-x)U_{BaF_2} - U_{OF} + \int_0^T \Delta c(T') dT', \end{aligned} \quad (4)$$

where U_i (positive definite) is the lattice energy of the ionic compound, $\Delta \ln Q_v = \ln \frac{Q_{v,OF}}{Q_{v,BaO}^x Q_{v,BaF_2}^{1-x}}$ with $Q_{v,n}$ vibrational partition function of compound n , Δc the change in specific heats of reaction (c) and $\beta = 1/k_B T$. Considering harmonic lattice vibrations in the high temperature regime, where the fluorine process takes place ($T > 973$ K), the temperature dependent term can be approximated by the equipartition of energy. For instance, at $T = 1000$ K the thermodynamic data for BaO and BaF₂ (in [37]) provides $\int_0^T [c_{BaF_2}(T') - c_{BaO}(T')] dT' = 24.8$ kJ mol⁻¹ to be compared with $3\gamma RT = 24.9$ kJ mol⁻¹, where $\gamma = 1$ is the difference between the number of oscillators (ions) between BaF₂ and BaO. Consequently, since the number of oscillators is conserved in the reaction, as a first approximation we neglect the last term in equation (4). The data of figure 1 gives a $\Delta H_{OF} < 0$, i.e. the lattice energy of OF is lower than the mean value of the lattice energies of BaF₂ and BaO (with weights x and $(1-x)$).

An attempt to estimate the enthalpy of formation of the OF can be done by employing a Born–Haber (BH) cycle for the solubility of ionic species in a solid matrix [40]. The reaction for the formation of one mole of OF, that is for the insertion of x moles of substitutional oxygen, is given by reaction (c)⁴ where the OF with composition x is made up of x substitutional oxygen ions and x fluorine vacancies in the BaF₂ structure.

To study the energetics of reaction (c) let us consider the following cycle for the insertion of x moles of oxygen ions into the fluorite structure:



The first process (e) is the abstraction of fluorine ions ($F_{F,(BaF_2)}$) from BaF₂ with the formation of fluorine vacancies ($V_{F,(BaF_2)}^\bullet$) into the solid and fluorine ions in the gas phase ($F_{(g)}^-$). The second process (f) is the oxide decomposition into gaseous ions. The third process (g) leads to the formation of oxygen (substitutional) at the F site ($O'_{F,(BaF_2)}$), where the substitutional negative defect is single charged. The last reaction (h) is the formation of stoichiometric BaF₂ cells at the surface of the solid. This process can be envisaged as the formation of a Schottky defect (*lattice molecule*), increasing the number of lattice cells by a unit.

⁴ Based on the BH cycle reactions (e)–(h), the process should be better written as the formation of one mole of OF within a ‘reservoir’ of $(N-1)$ moles of BaF₂: $(N-x)BaF_2 + xBaO \rightarrow BaF_{2(N-x)}O_x + (N-1)BaF_2$.

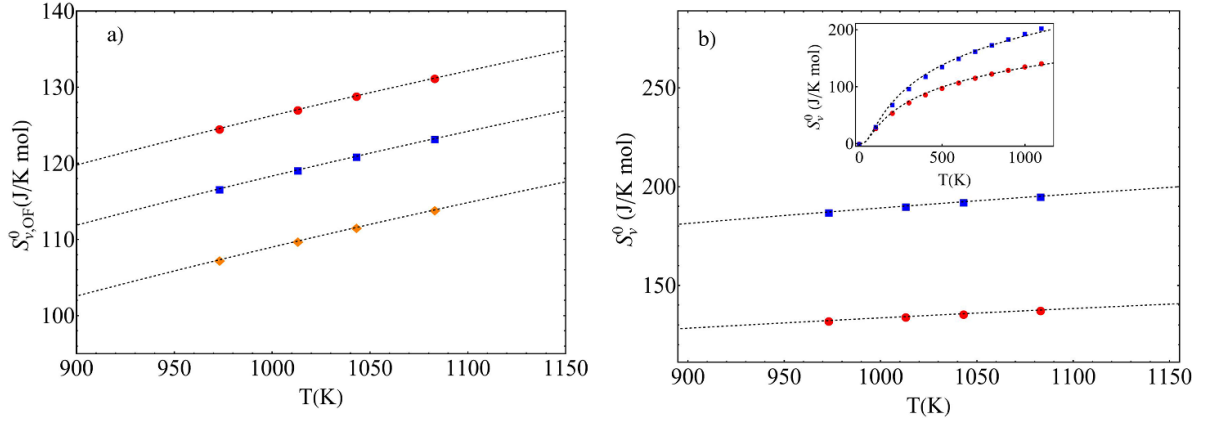


Figure 2. Panel (a): Vibrational entropy of OF in the range $973 \text{ K} < T < 1073 \text{ K}$ at $x = 1/2$. Solid circles: vibrational entropy of the OF assuming complete ordering of the OF structure. Solid squares and diamonds refer to the vibrational contributions to the entropy for cases (i) and (ii), respectively (see text). Dashed lines are the best fits of Debye's model of harmonic solid to the data points. Panel (b): behavior of the standard entropy of BaO and BaF₂, from [37] (symbols), in the same temperature range of the data reported in panel a. The dashed lines are the best fits of Debye's model for $m(\text{BaF}_2) = 3$ and $m(\text{BaO}) = 2$, which provides the θ_D values of table 1. These values were used to compute the $S_D(\theta_D/T)$ function in a wider temperature domain and compared to the thermodynamic data of [37] in the inset of figure (b) (symbols).

Table 1. For each compound the Einstein and Debye temperatures (θ_E, θ_D) and the number of oscillators (m) have been reported. OF represent a complete ordered structure, i.e. when the entropy variation of reaction (c) is only given by the vibrational contribution. OF (i) and OF (ii) refer to the cases of partially ordered OF, i.e. the standard entropy variation of reaction (c) also includes configurational contributions due to either vacancies (case i) or both vacancies and substitutional (case ii) (see also the text).

Compound	θ_E (K)	m	θ_D (K)
BaO	187 ± 28	2	261 ± 39
BaF ₂	217 ± 33	3	303 ± 45
OF	360 ± 54	2.5	503 ± 76
OF (i)	410 ± 62	2.5	573 ± 86
OF (ii)	477 ± 72	2.5	667 ± 100

The energetics of the cycle is computed for the model case of a dilute defective solid solution. Under these circumstances, in the processes that leave charge defects in the solid (i.e. processes *e* and *g*) the defects are assumed to be non-interacting. In other words, the relative distance between them is large. For the enthalpy of formation of the solid solution, ΔH_{sol} , we get (at 0 K):

$$\Delta H_{\text{sol}} = x[2E_V + U_{\text{BaO}} - E_O - U_{\text{BaF}_2}]. \quad (5)$$

In equation (5), U_i (positive definite) is the lattice energy of the ionic compound and E_V is the energy of abstraction of fluorine ions that is equal to the Coulomb interactions of F⁻ with the ionic lattice, given by the Madelung series. This contribution cancels out with the energy (E_O) gained by inserting an O²⁻ ion into the vacant site since the vacancy left in the lattice does not interact with the substitutional in the unrelaxed

lattice, as mentioned above. Equation (5) becomes,

$$\Delta H_{\text{sol}} \cong x[U_{\text{BaO}} - U_{\text{BaF}_2}]. \quad (6)$$

The evaluation of ΔH_{sol} as a function of T can be done through the expression of the internal energy $\Delta U(T) = \Delta U(0) + \int_0^T \Delta c(T') dT'$, with $\Delta U(0)$ internal energy change at $T = 0\text{K}$ and Δc the difference between the specific heats of the compounds. However, as reported above (see equation 4), since in the sequence of steps (*e* – *h*) the number of oscillators is conserved, as a first approximation, and at high temperature, the temperature-dependent term can be neglected.

The U_{BaO} and U_{BaF_2} contributions can be obtained by performing Born-Haber cycles for BaO and BaF₂ and are equal, respectively, to:

$$-U_{\text{BaF}_2} = \Delta_f H_{\text{BaF}_2}^0 - \Delta_s H_{\text{Ba}}^0 - I_{\text{Ba}} + 2A_{\text{F}^-} - D_{\text{F}_2} \quad (7)$$

$$U_{\text{BaO}} = -\Delta_f H_{\text{BaO}}^0 + \Delta_s H_{\text{Ba}}^0 + I_{\text{Ba}} - A_{\text{O}^{2-}} + \frac{1}{2}D_{\text{O}_2}, \quad (8)$$

where $\Delta_f H^0$ and $\Delta_s H^0$ are, respectively, standard enthalpies of formation and sublimation, I_{Ba} the double ionization energy of Barium, A and D are, respectively, the electron affinity and dissociation energy of oxygen. By using equations (7), (8) and (6) this is rewritten as:

$$\Delta H_{\text{sol}} = x \left[\Delta_f H_{\text{BaF}_2}^0 - \Delta_f H_{\text{BaO}}^0 - 2\Delta_f H_{\text{F}^-}^0 + \frac{1}{2}D_{\text{O}_2} - A_{\text{O}^{2-}} \right], \quad (9)$$

where standard enthalpies values are available from the literature [36, 40] and provide⁶:

$$\Delta H_{\text{sol}} = x717 \text{ kJ mol}^{-1}. \quad (10)$$

⁵ Strictly speaking a small difference arises owing to the difference in ionic radii between F and O.

⁶ $\Delta_f H_{\text{BaF}_2}^0 = -1207.475$, $\Delta_f H_{\text{BaO}}^0 = -546.83$, $\Delta_f H_{\text{F}^-}^0 = -250$, $D_{\text{O}_2} = 493.58$, $A_{\text{O}^{2-}} = -631$ in kJ mol^{-1} and $T = 0 \text{ K}$.

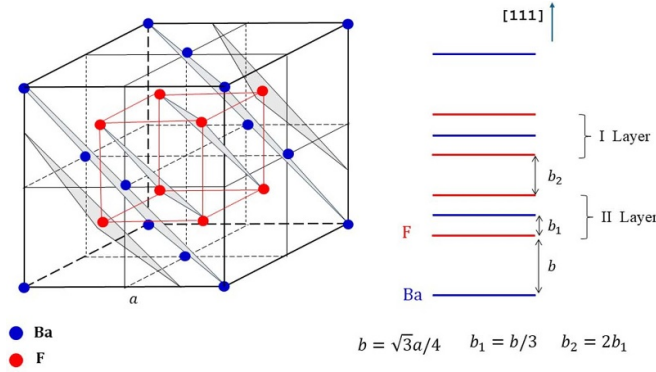


Figure 3. Pictorial view of the conventional cell of barium fluoride. The drawing has been done to enhance the correspondence between lattice points and stacking planes along the [111] direction. The second neighbors of a Fluorine ion are located on the same (111) plane and the first neighbors on adjacent planes. The sequence of (111) stacking planes is such that the distance between two successive Ba-planes equals $b + b_1 = b_2 + 2b_1 = \sqrt{3}a/3$ that is one third of the length of the cell along the [111] direction (diagonal), where b is the distance between the first two successive planes containing Ba and F in the conventional cell of the Fluoride; b_1 and b_2 are, respectively, the distances between F-Ba planes in one layer and F-F planes of two successive layers. In turn, $\sqrt{3}a \approx 11 \text{ \AA}$ is close to the lattice spacing of the YBCO cell along the [001] direction (11.7 \AA). This is the reason why the OF plays the role of a template for YBCO nucleation [26].

So far, we have dealt with a dilute solution of vacancy and substitutional in an unrelaxed lattice. However, the detailed studies on the OF precursor [9, 26, 28, 29, 41] do show that the OF has a rather ordered structure where substitutional and vacancies are placed in a sequence of double layers along the [111] direction of the fluorite structure. By considering undistorted fluorite cells, vacancies and oxygen occupy the tetrahedral sites of fluorine and are located at distance $a/2$ ($a = 6.2 \text{ \AA}$), i.e. they are next neighbors in a square lattice made up of F-sites (figure 3). It is expected that the formation of $O'_F - V_F^\bullet$ complexes lead to an ordered and more stable structure owing to the coulomb interaction between V_F^\bullet and O'_F . Consequently, to get ΔH_{OF} , an extra energy term (ΔE) should be considered in equation (6) that is related to the formation of these complexes and to the lattice relaxation owing to defects insertion:

$$\Delta H_{OF} = \Delta H_{sol} + \Delta E = x[U_{BaO} - U_{BaF_2} + E_{O,V} + \delta e], \quad (11)$$

where $E_{O,V}$ is the extra energy term that takes into account both the interaction between defects and their ordering and δe the relaxation term. It is worth pointing out that the important role played by the interactions among charged defects in ionic solids has already been addressed by C. Wagner in his celebrated work [42]. In fact, it has been found that interactions between defects lead to stabilization of solid structures *via* spontaneous ordering of point defects [43, 44]. It is worth noticing, in passing that equation (4) and equation (11) provides, $U_{OF} = U_{BaF_2} - xE_{O,V} - x\delta e$ which shows that the difference between the lattice energies of fluoride and OF

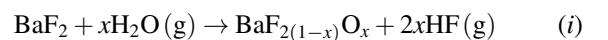
is due to the *interaction-order* and relaxation terms. Using equation (11) and the ΔH_{OF}^0 value derived from the data of figure 1, an energy term $(E_{O,V} + \delta e) = -823 \pm 16 \text{ kJ mol}^{-1}$ was also estimated.

The $E_{O,V}$ contribution can be envisaged as the energy gained when O'_F and V_F^\bullet are brought, from infinite separation, into cells of the square lattice with $O'_F - V_F^\bullet$ as next neighbors. As a crude approximation this term is estimated to be [44], $E_{O,V} \cong -M \frac{e^2}{r_{O-V}} = -M \frac{e^2}{(\frac{a}{3})}$, with $M \cong 1.75$ Madelung's constant that gives $E_{O,V} \cong -784 \text{ kJ mol}^{-1}$.

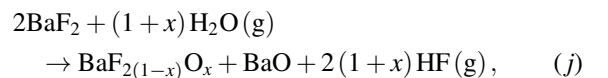
The $E_{O,V}$ value above has to be considered a lower bound since it holds for an extended ordered structure with cells containing only substitutional and vacancies. In this case, owing to the 1:1 ratio between O_F and V_F , the OF is composed by a mixture of 'BaF₂ cells' and 'BaO_FV_F cells' in the ratio $(1-x) : x$. On the other hand, with reference to the structure proposed in [28], the (111) planes of the fluorite are occupied, alternatively, by oxygen ions and either fluorine ions or vacancies. In this case, the presence of fluorine ions in the layers close to those containing O_F , is expected and this makes $E_{O,V}$ less negative. For instance, because of the 1:1 ratio between O_F and V_F , at $x = 1/2$ two substitutional, two vacancies and four fluorine ions are present in the Fcc unit cell. From the lower bound of $E_{O,V}$ and the ΔH_{OF}^0 attained from the experimental data, it is possible to estimate the upper bound of the relaxation energy, namely $\delta e < -39 \text{ kJ mol}^{-1}$. A partial ordering would imply a lower value of the relaxation term: for instance, in the hypothetical case of a 1D array of $O'_F - V_F^\bullet$ defect pairs⁷, this relaxation term should decrease to -190 kJ mol^{-1} .

An attempt to investigate the dependence of the free energy of reaction (c) with OF composition, x , can be done using equation (11) and a value of $x = 1/2$ for the experimental data of figure 1 [1]. From the definition $\Delta G_{OF}^0 = \Delta H_{OF}^0 - T(\Delta S_{v,OF}^0 + \Delta S_{c,OF}^0)$ and equation (11) one obtains $\Delta G_{OF}^0(x, T) = 2x\Delta G_{OF}^0(\frac{1}{2}, T) - T(\Delta S_{v,OF}^0(x, T) + \Delta S_{c,OF}^0(x, T) - 2x\Delta S_{OF}^0(\frac{1}{2}, T))$ with $x = 1/2$ assigned to data in figure 1 [1]. The Debye temperature is taken independent of x , that is, the vibrational entropy depends upon x through the number of oscillators equal to $3 - x$ per mole of OF. The results of the computation are reported in figure 4 for vibrational entropy in accord with the Debye approach and the configurational term given by equation (2) as suggested in [28].

Before concluding, we consider the formation of the OF, in the MOD process, through reactions between fluoride and water according to



and



⁷ For instance, stabilization of the structure by arrays of $O'_F - V_F^\bullet$ interacting pairs would imply $M = 2 \ln 2 \cong 1.4$ in the $E_{O,V}$ expression above.

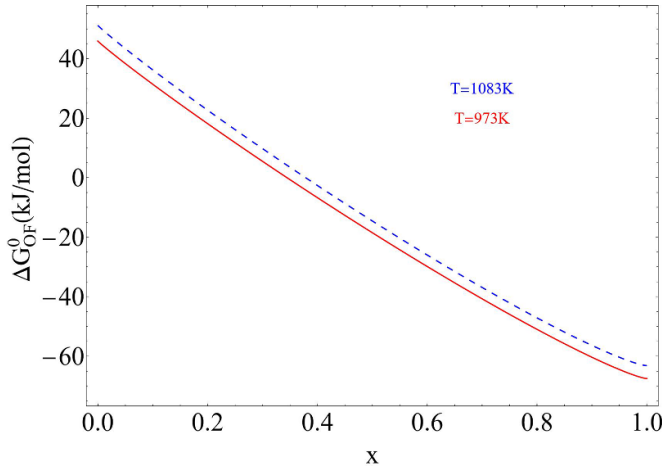


Figure 4. Standard free energy for OF formation from oxide and fluorides as a function of composition at $T = 1083\text{ K}$ (blue dashed line) and $T = 973\text{ K}$ (red solid line). Computations refer to configurational entropy change given by equation (2), i.e. by considering random arrangement of fluorine vacancies and fluorine ions on (111) planes [28].

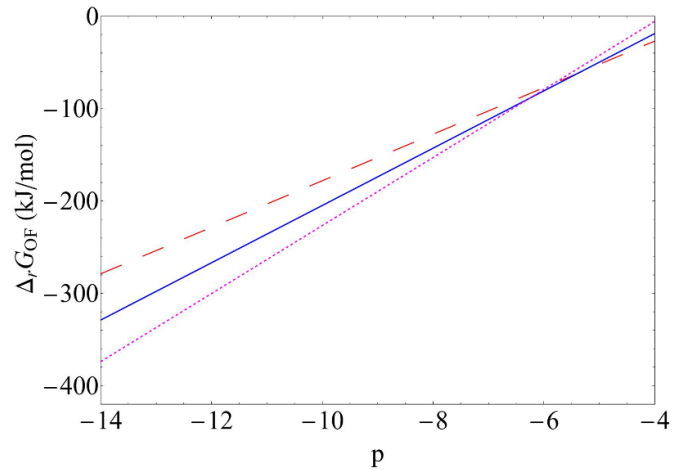


Figure 6. Free energy change of OF formation through barium fluoride and water (reaction (i)) as a function of $p = \log \frac{P_{\text{HF}}^2}{P_{\text{H}_2\text{O}}^2}$, at $T = 1013\text{ K}$ and for several values of OF composition ($x = 0.3$ red, dashed line; $x = 0.6$ blue, full line; $x = 0.9$ purple, dotted-line). The plot indicates that the formation of higher defective OF is favored for lower p values ($p < -6$).

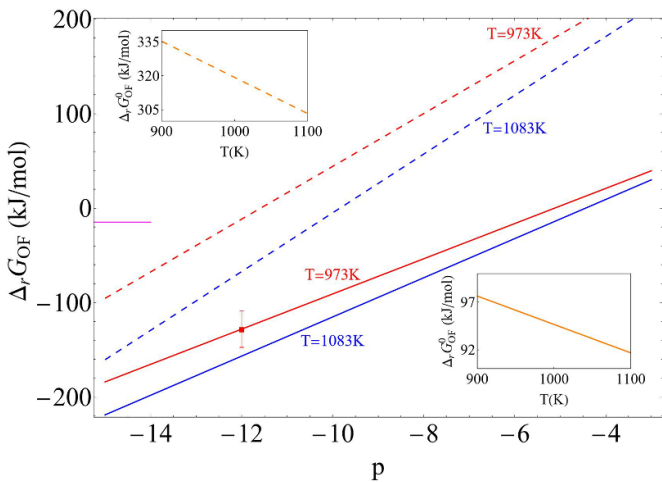


Figure 5. Behavior of the free energy variation for OF formation through barium fluoride and water as a function of $p = \log \frac{P_{\text{HF}}^2}{P_{\text{H}_2\text{O}}^2}$ at constant temperature and $x = 0.5$. Solid lines and dashed lines refer to reactions (i) and (j), respectively, at $T = 973\text{ K}$ and 1083 K . The computation was performed using the data of figure 1. Insets: The standard free energies as a function of temperature of reactions (i) and (j) are shown as solid and dashed lines, respectively. In the figure the standard free energy of OF formation from oxide and fluoride (reaction (c)) at $T = 1083\text{ K}$ is also shown. The curves $\Delta_r G$ vs p shows that the route to OF formation via reaction (i) is thermodynamically favored compared to reaction (j).

where reaction (j) proceeds with an excess of fluoride and water. For these reactions the free energy variation is also a function of partial pressure ratio, $p = \log \frac{P_{\text{HF}}^2}{P_{\text{H}_2\text{O}}^2}$, namely $\Delta_r G(x, T) = \Delta_r G^0(x, T) + RTy \ln 10^p$, with $y = x$ and $y = 1 + x$ for reactions (i) and (j), respectively. The computation is displayed in figure 5 where $\Delta_r G$ is reported as a function of p and for two temperatures. In these calculations, the configurational contribution to OF formation is in accordance

with equation (2). The behavior of the standard free energy variation of these reactions, as a function of temperature, is reported in the inset of the same figure. The negative slope of the lines is due to the entropy variation that is expected to be positive due to the formation of HF gas. The present analysis indicates that the most favorable route for the OF formation is based on reaction (i) for the range of p and T employed in the MOD route. In general, using the $\Delta G_{\text{OF}}^0(x, T)$ function computed above, it is possible to estimate the free energy of these reactions for $0.25 < x < 1$ where YBCO formation is allowed in the MOD process. Figure 5 also shows that at lower temperatures the formation of OF is possible in dependence of the p value. Figure 6 displays the free energy of reaction (i) as a function of p for several values of OF composition at $T = 1013\text{ K}$. The curves intersect at point $p = -6$, and this implies an inversion in the stability of the OF by promoting the OF with higher oxygen content at lower values of $\frac{P_{\text{HF}}^2}{P_{\text{H}_2\text{O}}^2}$

ratio ($\frac{P_{\text{HF}}^2}{P_{\text{H}_2\text{O}}^2} < 10^{-6}$). This output is in agreement with results previously obtained in the literature on experimental conditions promoting YBCO nucleation and growth [8, 11, 24, 45]. It follows that an increase in water partial pressure during the firing treatment leads to greater x values, which is valuable for YBCO growth ($x > 0.25$ [11, 46]). However, the composition of oxygen in the OF, and therefore $P_{\text{H}_2\text{O}}$, also has an impact on the fraction of c -oriented crystals in the MOD process [47]. In connection to approaches for heterogeneous nucleation of YBCO, the present computation can be useful to gain insight into the effect of x on film orientation. Indeed, the nucleation rate of c and a oriented crystals strongly depends on the nucleation energy barrier which, in turn, is affected by the free energy of reaction (c) and excess energies of interphases [24]. As anticipated in the introduction, oxygen can influence the YBCO synthesis by MOD low-fluorine route. For example, in non-fluorine MOD processes, oxygen in the gas phase affects

the oriented growth of YBCO as evidenced by the $P_{O_2} - T$ phase diagram [48]. In the framework of the present approach, we hypothesize that the effect of P_{O_2} on reaction (a) is to change the stoichiometry of the OF either via a direct saturation of F-vacancies by oxygen ions or through the formation of vacancy and substitutional oxygen couples, through F_2 formation. However, further studies are needed to assess the feasibility of these reactions.

3. Conclusions

In this work, thermodynamic data on the formation reaction of YBCO by the MOD route (reaction (a)) have been analyzed to estimate the free energy of OF formation from barium oxide and fluoride (reaction (c)). The vibrational entropy of the precursor has been determined, as a function of temperature, for three cases of defect arrangement in the fluorite structure. The model case of a harmonic solid is in good agreement with the data and provides a Debye temperature in the range 500–600 K. The free energy change of OF formation through reaction between barium fluoride and water (reaction (i)) is shown to be thermodynamically favorable when compared to reaction between barium fluoride and oxide (reaction (c)). An estimate of the free energy of the reaction (c) as a function of OF composition, x , indicates the presence of a turning point in the isothermal plot, $\Delta_r G$ vs $p = \log \frac{p_{HF}^2}{p_{H_2O}}$, at $p \cong -6$. This implies thermodynamic stability of the OF with higher oxygen content for $p < -6$.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Acknowledgments

The authors are indebted with Dr V Pinto for the helpful discussions and the critical reading of the paper.

M D A work has been carried out within the framework of the XXXIX Doctoral program in Chemical Sciences, Department of Chemical Science and Technologies, University of Rome Tor Vergata. The PhD grant has been partially funded by ENEA, Italian National Agency for New Technologies, Energy and Sustainable Economic Development.

The authors would like to thank Grant MUR Dipartimento di Eccellenza 2023-27 X-CHEM project ‘eXpanding CHEMistry: implementing excellence in research and teaching’.

ORCID iDs

M De Angelis  <https://orcid.org/0009-0003-6732-8051>
M Tomellini  <https://orcid.org/0000-0002-2625-7096>

References

- [1] Sánchez-Valdés C F, Puig T and Obradors X 2015 *In situ* study through electrical resistance of growth rate of trifluoroacetate-based solution-derived $YBa_2Cu_3O_7$ films *Supercond. Sci. Technol.* **28** 024006
- [2] Obradors X, Puig T, Ricart S, Coll M, Gázquez J, Palau A and Granados X 2012 Growth, nanostructure and vortex pinning in superconducting $YBa_2Cu_3O_7$ thin films based on trifluoroacetate solutions *Supercond. Sci. Technol.* **25** 123001
- [3] Gupta A, Jagannathan R, Cooper E I, Giess E A, Landman J I and Hussey B W 1988 Superconducting oxide films with high transition temperature prepared from metal trifluoroacetate precursors *Appl. Phys. Lett.* **52** 2077–9
- [4] Schneller T, Waser R, Kosec M and Payne D 2013 *Chemical Solution Deposition of Functional Oxide Thin Films* (Springer)
- [5] Kumagai T, Yokota H, Kawaguchi K, Kondo W and Mizuta S 1987 Preparation of superconducting $YBa_2Cu_3O_{7-\delta}$ thin films by the dipping-pyrolysis process using organic acid salts *Chem. Lett.* **16** 1645–6
- [6] Parmigiani F, Chiarello G, Ripamonti N, Goretzki H and Roll U 1987 Observation of carboxylic groups in the lattice of sintered $Ba_2YCu_3O_{7-y}$ high- T_c superconductors *Phys. Rev. B* **36** 7148–50
- [7] Mankiewich P M, Scofield J H, Skocpol W J, Howard R E, Dayem A H and Good E 1987 Reproducible technique for fabrication of thin films of high transition temperature superconductors *Appl. Phys. Lett.* **51** 1753–5
- [8] Solovyov V F, Wiesmann H J and Suenaga M 2005 Nucleation of $YBa_2Cu_3O_{7-x}$ on buffered metallic substrates in thick precursor films made by the BaF_2 process *Supercond. Sci. Technol.* **18** 239–48
- [9] Wu L, Zhu Y, Solovyov V F, Wiesmann H J, Moodenbaugh A R, Sabatini R L and Suenaga M 2001 Nucleation and growth of $YBa_2Cu_3O_x$ on $SrTiO_3$ and CeO_2 by a BaF_2 postdeposition reaction process *J. Mater. Res.* **16** 2869–84
- [10] Gallagher P K, O’Bryan H M, Sunshine S A, Murphy D W, Laboratories T B and Hill M 1987 Oxygen stoichiometry In $Ba_2YCu_3O_x$ *Mater. Res. Bull.* **22** 995–1006
- [11] Solovyov V F, Wiesmann H J and Suenaga M 2001 Growth rate limiting mechanisms of $YBa_2Cu_3O_7$ films manufactured by ex situ processing *Physica C* **353** 14–22
- [12] Wong-Ng W, Levin I, Feenstra R, Cook L P and Vaudin M 2004 Phase evolution of $Ba_2YCu_3O_{6+x}$ films during the BaF_2 process *Supercond. Sci. Technol.* **17** S548–56
- [13] McIntyre P C, Cima M J, Fai Ng M, Chiu R C and Rhine W E 1990 Texture development in $Ba_2YCu_3O_{7-x}$ films from trifluoroacetate precursors *J. Mater. Res.* **5** 2771–9
- [14] Palmer X *et al* 2015 Solution design for low-fluorine trifluoroacetate route to $YBa_2Cu_3O_7$ films *Supercond. Sci. Technol.* **29** 024002
- [15] Piperno L *et al* 2020 Elucidation of the decomposition reactions of low-fluorine $YBa_2Cu_3O_{7-x}$ precursors during film pyrolysis *J. Anal. Appl. Pyrolysis* **148** 104777
- [16] Araki T and Hirabayashi I 2003 Review of a chemical approach to $YBa_2Cu_3O_{7-x}$ coated superconductors—metalorganic deposition using trifluoroacetates *Supercond. Sci. Technol.* **16** R71–94
- [17] Puig T, González J C, Pomar A, Mestres N, Castaño O, Coll M, Gázquez J, Sandiumenge F, Piñol S and Obradors X 2005 The influence of growth conditions on the microstructure and critical currents of TFA-MOD $YBa_2Cu_3O_7$ films *Supercond. Sci. Technol.* **18** 1141–50
- [18] Wesolowski D E, Yoshizumi M and Cima M J 2007 Understanding the MOD process between decomposition

- and YBCO formation *IEEE Trans. Appl. Supercond.* **17** 3351–4
- [19] Wen Z, Wang Z, Liang S, Yu R and Zhu J 2022 Two-band superconductivity through structural and electronic reconstruction on interface: $\text{YBa}_2\text{Cu}_3\text{O}_7/\text{LaAlO}_3(001)$ *J. Appl. Phys.* **131** 125303
- [20] Solovyov V, Dimitrov I K and Li Q 2013 Growth of thick $\text{YBa}_2\text{Cu}_3\text{O}_7$ layers via a barium fluoride process *Supercond. Sci. Technol.* **26** 013001
- [21] Palmer X *et al* 2016 Solution design for low-fluorine trifluoroacetate route to $\text{YBa}_2\text{Cu}_3\text{O}_7$ films *Supercond. Sci. Technol.* **29** 024002
- [22] Grant P M 1997 Superconductivity and electric power: promises, promises.. past, present and future *IEEE Trans. Appl. Supercond.* **7** 112–33
- [23] Solovyov V F, Wiesmann H J, Li Q, Welch D O and Suenaga M 2006 Three- and four- μm -thick $\text{YBa}_2\text{Cu}_3\text{O}_7$ layers with high critical-current densities on flexible metallic substrates by the BaF_2 process *J. Appl. Phys.* **99** 013902
- [24] Pinto V, Celentano G and Tomellini M 2020 Heterogeneous nucleation of YBCO via fluorine based MOD process: thermodynamic and kinetic approach *Supercond. Sci. Technol.* **33** 115006
- [25] Ichino Y, Sudoh K, Miyachi K, Yoshida Y and Takai Y 2003 Orientation mechanism of $\text{REBa}_2\text{Cu}_3\text{O}_7/\text{Cu}/\text{O}$ thin films prepared by pulsed laser deposition *IEEE Trans. Appl. Supercond.* **13** 2735–8
- [26] Wu L, Solovyov V F, Wiesmann H J, Zhu Y and Suenaga M 2002 Mechanisms for hetero-epitaxial nucleation of $\text{YBa}_2\text{Cu}_3\text{O}_{\sim 6.1}$ at the buried precursor/ SrTiO_3 interface in the postdeposition reaction process *Appl. Phys. Lett.* **80** 419–21
- [27] Chen H, Zalamova K, Pomar A, Granados X, Puig T and Obradors X 2010 Growth rate control and solid–gas modeling of TFA- $\text{YBa}_2\text{Cu}_3\text{O}_7$ thin film processing *Supercond. Sci. Technol.* **23** 034005
- [28] Wong-Ng W, Levin I, Cook L P and Feenstra R 2006 Nature of the transient BaF_2 -related phases in the “ BaF_2 ” processing of $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ superconductors *Appl. Phys. Lett.* **88** 102507
- [29] Gazquez J, Sandiumenge F, Coll M, Pomar A, Mestres N, Puig T, Obradors X, Kihn Y, Casanove M-J and Ballesteros C 2006 Precursor evolution and nucleation mechanism of $\text{YBa}_2\text{Cu}_3\text{O}_x$ films by TFA metal–organic decomposition *Chem. Mater.* **18** 6211–9
- [30] Zalamova K, Pomar A, Palau A, Puig T and Obradors X 2010 Intermediate phase evolution in YBCO thin films grown by the TFA process *Supercond. Sci. Technol.* **23** 014012
- [31] Armenio A A *et al* 2011 Structural and chemical evolution of propionate based metal–organic precursors for superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ epitaxial film growth *Supercond. Sci. Technol.* **24** 115008
- [32] Feenstra R, Lindemer T B, Budai J D and Galloway M D 1991 Effect of oxygen pressure on the synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin films by post-deposition annealing *J. Appl. Phys.* **69** 6569–85
- [33] Wördenweber R 1999 Growth of high-Tc thin films *Supercond. Sci. Technol.* **12** R86
- [34] Qu T, Zhu Y, Feng F, Lin G, Deng S, Lu H, Zhang X, Fu Q, Xiao S and Zeng P 2016 Thermodynamics and kinetics analysis of MOD-YBCO heat treatment process using in situ resistance measurement method *IEEE Trans. Appl. Supercond.* **26** 1–5
- [35] Andersson J-O, Guillermet A F, Hillert M, Jansson B and Sundman B 1986 A compound-energy model of ordering in a phase with sites of different coordination numbers *Acta Metall.* **34** 437–45
- [36] Voronin G F and Degerterov S A 1991 Thermodynamics of superconducting phases in the Y-Ba-Cu-O system *Physica C* **176** 387–408
- [37] Malcolm W and Chase J 1998 *NIST-JANAF Thermochemical Tables* 4th edn (American Chemical Society, American Institute of Physics for the National Institute of Standards and Technology)
- [38] Collocott S J and Collins J G 1983 Low-temperature heat capacity of alkaline-earth fluorides: SrF_2 , BaF_2 *J. Phys. C: Solid State Phys.* **16** 6179–84
- [39] Gmelin E 1969 Thermal properties of alkaline-earth-oxides I. Specific heat measurements 1–3 centre national de recherches sur les tres basses temperatures *Z. Naturforsch. A* **24** 1794–800
- [40] Barsis E and Taylor A 1968 Interstitial conduction in BaF_2 crystals *J. Chem. Phys.* **48** 4362–7
- [41] Levin I, Huang Q Z, Cook L P and Wong-Ng W 2005 Nonquenchable chemical order—disorder phase transition in yttrium oxyfluoride *Eur. J. Inorg. Chem.* **2005** 87–91
- [42] Wagner C 1977 Point defects and their interaction *Annu. Rev. Mater. Sci.* **7** 1–24
- [43] Zhang S B, Wei S-H and Zunger A 1997 Stabilization of ternary compounds via ordered arrays of defect Pairs *Phys. Rev. Lett.* **78** 4059–62
- [44] Runcima W, Srinivasan B and Richardson D 1985 The formation energy of point defects in ionic crystals *Aust. J. Phys.* **38** 741
- [45] Piñol S and Castaño O 2006 Water vapour pressure influence on the kinetics of the superconducting YBCO thin films epitaxial growth by the TFA–MOD method *Physica C* **450** 48–55
- [46] Yoshizumi M, Wesolowski D and Cima M J 2005 Determination of HF partial pressure during ex situ conversion of YBCO precursors *Physica C* **423** 75–82
- [47] De Angelis M, Tomellini M, Pinto V and Celentano G in preparation
- [48] Xu Y, Goyal A, Leonard K J, Specht E D, Shi D and Paranthaman M 2006 Processing dependence of texture, and critical properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films on RABiTS substrates by a non-fluorine MOD method *J. Am. Ceram. Soc.* **89** 914–20