Synthesis, crystal structure modeling and thermal decomposition of yttrium propionate [Y$_2$(CH$_3$CH$_2$COO)$_6$·H$_2$O]·3.5H$_2$O

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ABSTRACT

An yttrium propionate complex was synthesized and characterized for its application as precursor for Y$_2$O$_3$ based oxide thin films deposition and YBa$_2$Cu$_3$O$_{7-x}$ superconducting thin films. The TG–DTA and FT-IR analyses have revealed the formation of an yttrium propionate complex with the formula [Y$_2$(CH$_3$CH$_2$COO)$_6$·H$_2$O]·3.5H$_2$O. The molecular structure of the yttrium propionate complex was determined by modeling the FT-IR spectra. The coordination numbers for the yttrium ions are eight and nine, respectively being coordinated by bridging bimetallic triconnective and chelating bidentate propionate groups.

The thermal decomposition of yttrium propionate has been investigated by thermogravimetric (TG) and differential thermal analysis (DTA) coupled with quadrupole mass spectrometry (QMS), X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) techniques.

1. Introduction

Yttrium propionates have become very promising precursors to obtain yttrium oxide (Y$_2$O$_3$) nanopowders and both polycrystalline and epitaxial thin films by chemical solution deposition (CSD) [1]. Y$_2$O$_3$ is a very interesting material for electronic and optical applications because of its high refractive index (1.7–1.9) and dielectric constant (10–17), high melting point (∼2439 °C) and large optical band gap (∼5.5 eV) [2,3]. Y$_2$O$_3$ is considered as a potential gate dielectric material for the replacement of silicon dioxide in complementary metal oxide semiconductor devices [4].

Recently, yttrium propionate precursors have gained a special interest in coated conductors fabrication for the low fluorine chemical route of YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) superconducting epitaxial thin film growth [5]. Apart from the YBCO film deposition, the as obtained yttrium propionates can be used for the deposition of epitaxial Y$_2$O$_3$ buffer layers in a coated conductor multilayer architecture and to develop in situ nanosized Y$_2$O$_3$ artificial pinning centers in the YBCO films to increase the critical current density [6,7].

The understanding of the decomposition mechanisms of the precursor plays a crucial role in the optimization process of the yttrium propionate precursor conversion into the final products [8]. This aspect is very important, especially for the deposition of epitaxial thin films where both morphological and structural properties have to be controlled simultaneously by pyrolysis and crystallization processes, in order to obtain a high quality epitaxial film [5,9].

In the present work we present the results on the synthesis and characterization of an yttrium propionate complex used as precursor for the fabrication of YBCO coated conductor. The decomposition process of the yttrium propionate complex to Y$_2$O$_3$, in the temperature range from room temperature to 700 °C, both in air and nitrogen atmosphere, is also presented.

For modeling the structure it was used Spartan ES, a powerful molecular modeling software, to build the molecular geometries, measure bond distances and determine the vibrational frequencies necessary to generate the FT-IR spectra and to compare them with the experimental data based spectra.

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2. Experimental

2.1. Powder synthesis

The yttrium propionate solution was prepared at room temperature starting from commercially available (Alfa Aesar) yttrium acetate Y(CH$_3$COO)$_3$·4H$_2$O (99.99%), methanol CH$_3$OH (99.9%) and propionic acid C$_2$H$_5$–COOH (99.9+%). The yttrium acetate was dispersed in methanol, treated with an excess of propionic acid. The concentration of the metal ion in the final solution is 0.02 M. The

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precursor powder has been obtained by drying the coating solution at 80 °C.

2.2. Molecular modeling

Since no single crystalline sample suitable for single crystal diffraction was obtained, we have considered the computational molecular modeling alternative, based on the FT-IR spectroscopic data, to determine the molecular structure of the yttrium propionate complex. The molecular modeling was performed by using the SPARTAN 10 software, version 1.0.1 (Wavefunction, Inc.) [10]. In the final geometry optimization and properties calculations, the PM3, method available in the Spartan software [11], was used. This method was developed since it can reproduce bonds with good geometry accuracy and create spectra, which can be compared with the experimental ones. The parameters for the PM3 method for complex are based only on reproducing the equilibrium geometries. Semi-empirical models have proven to be successful for the calculation of the equilibrium geometries, including the geometries of the complex.

2.3. Characterization techniques

The thermal decomposition behavior of the precursor powder was investigated using termogravimetric-differential thermal analyses (TG–DTA) performed from ambient temperature up to 700 °C both in air, and dry nitrogen, at a heating rate of 10 °C/min in platinum crucibles, using α-Al$_2$O$_3$ powder as reference.

The TG–DTA equipment was coupled with a QMS 200 atmospheric sampling quadrupole spectrometer with an ionization potential of 70 eV in the m/z = 10–90 range (m/z represents the ratio between the mass of the ion (m) and the number of the elementary charges (e)).

For a better understanding of the role of each reactant in the reaction sequence, the reagents were step-wise added and analyzed by FT-IR analyses. The FT-IR absorption spectra of the samples in the 400–4000 cm^{-1} spectral range were obtained with a Perkin Elmer FT-IR spectrometer. The spectra were collected with a 2 cm^{-1} spectral resolution and 30 scans.

The precursor powder was investigated by X-ray diffraction measurements performed at room temperature using a Bruker diffractometer operating with a Cu K$_\alpha$ radiation (λ = 1.54 Å).

3. Results and discussion

3.1. Infrared spectroscopy

In Fig. 1, the FT-IR spectra of the step-wise addition of the reagents are presented. In the FT-IR spectrum of the initial dispersion Y(CH$_3$COO)$_2$·4H$_2$O + CH$_3$OH (Fig. 1b), the vibration modes between 4000 and 3000 cm^{-1} are due to the O–H stretching vibrations corresponding to water and methanol. The vibration modes at 2983–2832 cm^{-1} are attributed to νCH-belonging to the CH$_3$-group.

The consequence of the addition of propionic acid on the yttrium acetate dispersed in methanol (Fig. 1c) results in the appearance of a new vibration mode at 1717 cm^{-1} for the carboxylate group C=O. The three bands at 1552, 1417 and 1279 cm^{-1} assigned to the asymmetric and symmetric stretching vibration of the COO$^-$ and CH$_2^-$ groups, characteristic for the propionates can be also observed.

The difference between the two COO$^-$ vibrations $\Delta\nu = \nu_{as} - \nu_s$ indicates that the coordination type of the metal ion by the carboxylate group is chelating bidentate and bridging bimetallic triconnective [12–14]. In our case $\Delta\nu$ = 135 cm^{-1}, which indicates

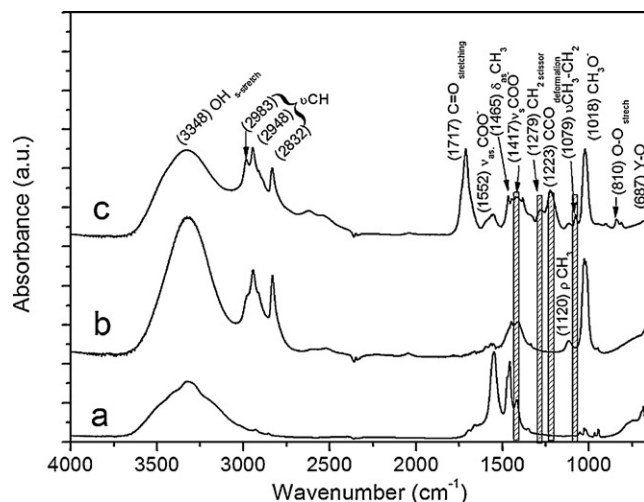**Fig. 1.** FT-IR spectra: (a) powder Y(CH$_3$COO)$_3$·4H$_2$O; (b) Y(CH$_3$COO)$_3$·4H$_2$O + CH$_3$OH; (c) Y(CH$_3$COO)$_3$·4H$_2$O + CH$_3$OH + CH$_3$CH$_2$COOH.

a mixed coordination mode. The characteristic peak for the free acetate ion is not observed in Fig. 1c.

The IR spectrum of the yttrium acetate is presented in Fig. 1a. The characteristic peaks for the acetate ion are: 1461 and 1548 cm^{-1} (Fig. 1a), corresponding to the COO$^-$ asymmetric and symmetric vibration mode, respectively. By comparing the IR spectra of yttrium acetate and yttrium propionate, one can readily identify the $\Delta\nu$(COO$^-$). The value for $\Delta\nu$ is 87 for the acetate ligand and 135 cm^{-1} for the propionate one, respectively. The lower value ($\Delta\nu$) for the acetate should be assigned to the COO$^-$ groups of the monodentate spheric acetate ion [15].

3.2. Molecular and crystal structure

The computed model presented in Fig. 2 has been created by moving the individual atoms and recalculating the position using the MP3 method by taking into consideration the corresponding minimum energy when generating a complex FT-IR vibration spectrum similar to the experimental one. The molecular structure, as determined from the FT-IR spectra by molecular modeling, is Y$_2$(CH$_3$CH$_2$COO)$_6$·H$_2$O (YProp$_3$) (Fig. 2a).

The bond distances for the molecular structure extracted from Fig. 2a are given in Table 1. An error limit of 1–2% was used for the bond length data to create a visual representation of the theoretical IR spectra (Fig. 2b) that best fit the experimental data.

Table 1
Bond distances (Å) determined from the theoretical FT-IR spectra (by modeling study).

Atoms 1	Atoms 2	d 1,2 [Å]	Atoms 1	Atoms 2	d 1,2 [Å]
Y(1)	O(4)	2.324	C(7)	O(4)	1.233
Y(1)	O(5)	2.346	O(2)	C(1)	2.161
Y(1)	O(1)	2.346	O(2)	C(2)	2.408
Y(1)	O(8)	2.374	O(2)	Y(1)	2.491
Y(1)	O(2)	2.374	C(11)	C(12)	2.495
Y(1)	O(3)	2.404	C(1)	O(2)	1.232
Y(1)	O(13)	2.462	C(1)	O(3)	1.275
Y(1)	O(14)	2.491	C(8)	C(9)	1.522
Y(1)	O(12)	2.346	Y(2)	O(7)	2.325
C(13)	C(14)	1.523	Y(2)	O(4)	2.326
C(14)	C(15)	1.521	Y(2)	O(8)	2.325
C(1)	C(2)	1.520	Y(2)	O(11)	2.334
C(2)	C(3)	1.523	C(10)	O(11)	1.304
C(19)	C(20)	1.524	Y(2)	O(10)	1.835
C(20)	C(21)	1.552	Y(2)	O(19)	2.176
O(12)	C(13)	1.232	C(19)	C(20)	1.558