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Synthesis and thermal decomposition of a novel zirconium acetato-propionate cluster: [Zr12]

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ABSTRACT

This work reports a novel Zirconium acetato-propionate complex herein called [Zr12] obtained by reaction of zirconium acetylacetonate $Zr(acac)_4$ with propionic acid. The molecular structure has been determined by X-ray diffraction on single crystals and proposed to be $[Zr_{12}(\mu_3\text{-}O)_{16}(CH_3CH_2CO_2)_{12}(CH_3CO_2)_8(\mu_2\text{-}CH_3CH_2CO_2)_4]$. This cluster involves oxo/hydroxo bonds in the direct surrounding of the metallic center. The decomposition of [Zr12] has been studied by thermal analysis and compared to $Zr(acac)_4$. Its temperature of decomposition is much lower than for acetylacetonate derivative. In consequence, the formation of ZrO_2 is easier from [Zr12] than from $Zr(acac)_4$. This phenomenon highlights the influence of the molecular structure on the process of decomposition. The local surrounding of Zr in [Zr12] and in ZrO_2 are very close, while it is markedly different in $Zr(acac)_4$.This difference of environment of the metallic ions is at the origin of the huge difference of thermal behavior of both compounds.

1. Introduction

Metal-organic decomposition (MOD) is one of the less expensive methods to produce thin oxide films. MOD needs liquid precursors which are deposited then dried as a film on a substrate. This film is then pyrolyzed to get an oxide film well crystallized [1]. Numerous oxide films have been made with success by this simple, economic and scalable processing. For example, MOD is extensively used to produce high temperature superconducting tapes of $YBa_2Cu_3O_7$ (YBCO) [2–4], where $La_2Zr_2O_7$ (LZO) is often used as an efficient buffer layer with great benefit [5–7]. $La_2Zr_2O_7$ concerns many other fields of applications: radiation tolerance, ionic conductivity in doped compositions and thermal barrier coating. Therefore great interest is devoted to precursors of Zirconium and Lanthanum usable in MOD.

Among the wide panel of available precursors, the most currently used for MOD are carboxylates, alkoxides or β-diketonates. Metal carboxylates present a wide variety of bonding arrangements and offer considerable opportunities to develop precursor's chemistry [7–9]. In that context, propionates derivatives are friendly compounds. Indeed, they are generally stable in air contrary to acetates or alkoxides which are often reactive with moisture. However propionates derivatives are not commercially available and must be prepared specially.

Syntheses of carboxylates by various methods have already been described such as interchange of carboxylic acid in the case of manganites [10] or reaction of alkoxides with carboxylic acids [11]. Up to date, several papers have reported the use of “Zr and La propionates”, for the preparation of LZO thin films by chemical routes (MOD) [6,12–14]. The authors explain that the solutions of precursors are conveniently obtained by dissolving stoichiometric quantities of La and Zr acetylacetonates (acac) in propionic acid. Note that “acac” ligands are often used [15,16] as precursors and supposed not to be modified during their solubilization. Only recently, at least for Lanthanum and Zirconium precursors, Yu et al. and Knoth et al. have shown that the real deposited metal precursors should be in fact metal-propionate derivatives and not simply the “acac” derivatives dissolved in propionic acid [6,14]. However, structure and composition of propionate derivatives are poorly known although these parameters are expected to play a crucial role in the transformation of the precursor into an oxide, a key stage of the MOD process. Indeed, the molecular structure and

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particularly the atomic arrangement of the precursor is very important. It imposes the local composition and is probably a major factor of the transformation and crystallization of the oxide. These factors greatly impact the temperature of formation and the final microstructure of the oxide. In the case of precursors obtained by dissolving acetylacetonates derivatives in propionic acid, the local composition, thermal decomposition and chemical properties are expected to differ from the initial one. Until now, few efforts were made to correlate the nature of the precursors (acetylacetonate, acetate, propionate…) with the final oxide, here we want to contribute to this topic [1].

In this paper, we focus on a zirconium acetato-propionate [Zr12] prepared from $Zr(acac)_4$. Its composition and structure have been established by structural determinations on single crystals and confirmed by thermal analysis. Finally, this study shows that structure and atmosphere are crucial to control the stage of pyrolysis.

2. Experimental section

Zirconium(IV) acetylacetonate (Zirconium(IV) 2,4-pentanedionate, or $Zr(acac)_4$), were commercial products of Aldrich grade. The purity of $Zr(acac)_4$ was controlled by elemental analysis and corresponded within 4 wt % to the stoichiometric $Zr(acac)_4 = Zr(C_5H_7O_2)_4$. Complementary X-ray analysis proved that the compound was well crystallized and had to the expected structure. No adsorbed H_2O was detected by FT-IR spectroscopy. Propionic acid (99.5%) (also from Aldrich grade) was used as received without any special precaution, except when specified. All reactions and manipulations were performed under aerobic conditions.

2.1. Synthesis

Crystals named [Zr12] were obtained by dissolution of 10.25 mmol of $Zr(acac)_4$ in a large excess of distilled propionic acid (270 mmol, 20 mL) at room temperature. After few minutes of stirring, the dissolution was still uncompleted. This mixture was heated at 160 °C for 1 h in order to obtain a stable yellow solution. The excess of propionic acid was evaporated under vacuum. Removal of the solvent left a crude product (2.42 g). This product was dried at 60 °C and resulted in a white powder. Considering the final product as $Zr(prop)_4$ i.e. $= Zr(CH_3CH_2COO)_4$, the yield would be 70%. Colorless cubic shaped crystals suitable for X-ray diffraction were obtained after dissolution of the crude product into propionic acid and slow diffusion of added acetone. The crystals were cubic and stable in air. Further X-ray diffraction revealed that these crystals were built with units involving 12 Zr atoms surrounded by O, C and H atoms and called hereafter [Zr12].

2.2. Single crystal X-ray diffraction

Crystal structure of compound [Zr12] was obtained by X-ray diffraction (MoKα radiation) at room temperature using a Nonius Kappa CCD diffractometer by means of the collect program Nonius [17]. More than 16,000 reflections were collected. Lorentz-polarization correction, peak integration and background determination were carried out with the *Denzo* program [18]. Frame scaling and unit-cell parameters refinements were made through the "*scalepack program*" [18]. No absorption corrections were applied to the data set. All structures were solved by direct methods using the *SIR97* program [19] combined with Fourier difference calculations and refined against F using reflections with $[I/\sigma(I) > 3]$ with the *crystals* program [19]. All atomic displacements parameters for non-hydrogen atoms have been refined anisotropically. The hydrogen atoms were located on the basis of the conformation of the supporting molecule.

2.3. Powder X-Ray diffraction

Powder X-Ray diffraction (XRD) experiments were carried out on a Siemens D5000 diffractometer (θ–2θ Bragg-Brentano geometry) with CuKα radiation. Patterns were recorded over a range of 5–30°, using a step-scanning mode (0.01° step, 8 s of counting time).

2.4. Thermogravimetric analysis and differential thermal analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of test samples were performed on a coupled SETARAM TAG 16 system (Lyon-France). The system has two symmetrical furnaces requiring only very small Archimede corrections of the weight variations. TGA and DTA measurements were carried out in dense alumina crucibles. The heating device allows to make measurements of thermal behavior (TGA/DTA) on heating up to 1600 °C at various rates (2–20 °C min^{-1}), in a dynamic atmosphere of Ar or Ar-20%O_2 (10 L h^{-1}). Samples of 10–40 mg were typically used.

2.5. Elementary chemical analysis

Chemical analyses of test samples were performed on small quantities (10–100 mg) at the Central service of analysis of CNRS (CNRS-Vernaison Lyon, France). Zr element was determined by ICP in solution (with a relative error of 2%), C and H were quantified by catharometric detection (relative error 0.3%), O was determined by measuring CO_2 produced by reaction of the pyrolyzed products on an active C.

3. Results and discussion

3.1. Elemental analysis

Analytical data of [Zr12] are summarized in Table 1. Experimental values obtained for the cluster [Zr12] were compared with the calculated values for $Zr(prop)_4$ i.e. $= Zr(CH_3CH_2COO)_4$. The comparison with experimental values shows that the re-crystallized product is consistent with the formulas $Zr_{12}C_{74}H_{122}O_{72}$ and not with $Zr(prop)_4$ as we thought initially. Note that the observed yield i.e. 93% is close to 100% while only 70% would be received if one assumes the formation of $Zr(prop)_4$. The small differences between theoretical and experimental values obtained for [Zr12] can be accounted to the presence of solvent within the crystalline structure (propionic or acetic acid) and in the final product (residual solvent of reaction).

3.2. Structure of [Zr12] crystals

The structure of the herein called compound [Zr12] was established by single crystal X-ray diffraction. The crystallographic data and structure refinement parameters for [Zr12] are summarized in Table 2.

This compound is centrosymmetric and crystallizes in the monoclinic space group, $P2_1/c$. Its structure consists of dodecanuclear clusters made of hexanuclear $[Zr_6(\mu_3\text{-}O)_8(CH_3CH_2CO_2)_6(CH_3CO_2)_4]$ sub-units (Zr6), linked by four propionate ligands in a bidentate mode (Fig. 1).

Table 1
Elemental analysis of [Zr12] compared to $Zr(prop)_4 = Zr(CH_3CH_2COO)_4$.

	C	H	Zr
[Zr12][a]	**30.54**	**4.67**	**28.8**
	27.27	*3.77*	*33.59*
$Zr(prop)_4$	*37.58*	*5.25*	*23.78*

Bold measured data, italic from stoichiometric formulas.
[a] From composition of [Zr12] (see section Structure of [Zr12]).