Thermal decomposition of yttrium(III) hexanoate in argon

J.-C. Grivel^{1}, M.J. Suarez Guevara¹, F. Attique¹, Y. Zhao^{1,4}, X. Tang^{1,4}, P.G.P.A. Pallewatta¹, A. Watenphul^{2,3}, and M. v. Zimmermann²*

¹Department of Energy Conversion and Storage, Technical University of Denmark,
Frederiksborgvej 399, DK - 4000 Roskilde Denmark

²Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22603 Hamburg, Germany

³Institute of Mineralogy and Petrography, University of Hamburg, Grindelallee 48, 20146
Hamburg, Germany

⁴Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, 20146 Hamburg,
Germany

Abstract

The thermal decomposition of yttrium(III) hexanoate ($\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$) in argon was studied by means of thermogravimetry, differential thermal analysis, IR-spectroscopy, X-ray diffraction at a laboratory Cu-tube source and in-situ experiments at a synchrotron radiation source as well as hot-stage optical microscopy. Dehydration occurs between 40°C and 110°C and is accompanied by a transition from solid to liquid crystalline state. At the onset of the main decomposition stage of the anhydrous $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3$, solidification takes place in the 315°C – 335°C range. $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3$ decomposes in a single step into $\text{Y}_2\text{O}_2\text{CO}_3$ with release of CO_2 and 6-undecanone between 280°C and 490°C. A side reaction appears to yield elemental carbon and volatile decane ($\text{C}_{10}\text{H}_{22}$). $\text{Y}_2\text{O}_2\text{CO}_3$ is converted to Y_2O_3 with release of CO_2 between 500°C and 975°C.

Keywords: Yttrium hexanoate, thermal decomposition, simultaneous TG-DTA, FTIR, alkanoates

***Corresponding author:** email: jean@dtu.dk
tel: +45 4677 4739
fax: +45 4677 5758

1. Introduction

Yttrium sesquioxide (Y_2O_3) is a versatile compound that can be applied to various devices including sensors [1], catalysts [2], bioimaging probes [3], infrared converters [4], lasers [5] and scintillators [6]. Among various manufacturing techniques for processing functional ceramic thin films, chemical solution deposition is attractive owing to its low cost, ease of up-scalability and ability to coat surfaces with various shapes. Furthermore, solutions with high homogeneity can be prepared and dense sintered films can be obtained using relatively low processing temperatures. Various types of Y_2O_3 -based thin films have been recently manufactured using Y-metallorganic precursors [7-10], successful thin film preparation of more complex yttrium-containing compounds like $(\text{Y,Yb})\text{MnO}_3$ [8] and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [11-16] was also reported. Only few different yttrium precursor carboxylates including acetylacetonate [7], isopropoxide [8], citrate [9,10], propionates [11,12] and acetates [13-16] appear to have been used so far. Yttrium acetate ($\text{Y}(\text{CH}_3\text{CO}_2)_3$) and yttrium propionate ($\text{Y}(\text{C}_2\text{H}_5\text{CO}_2)_3$) are short chain alkanoates. As reported in Severin and Ledford [17] in the case of titanium, zirconium and hafnium-based functional thin films, longer chain alkanoates may yield higher quality films. In order to optimize the processing parameters in view of Y-based film preparation and optimization, a detailed knowledge of the thermal decomposition course of relevant potential precursor salts is very useful. We recently reported on the thermal behavior of yttrium butyrate ($\text{Y}(\text{C}_3\text{H}_7\text{CO}_2)_3$) and yttrium valerate ($\text{Y}(\text{C}_4\text{H}_9\text{CO}_2)_3$) [18,19]. In the present work, we report on a detailed investigation of the thermal behavior of yttrium hexanoate ($\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3$), which involves the next member of the linear chain carboxylate series and draw parallels with other yttrium as well as lanthanide alkanoate salts that are used or could be used as promising precursors for functional coatings.

2. Experimental

500 mg of $\text{Y}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$ ($x \approx 3$) powder with 99.9% purity (rare earth basis) from Alfa Aesar was dissolved at room temperature in 4 ml of hexanoic acid ($\text{C}_5\text{H}_{11}\text{COOH}$, common name: caproic acid; Alfa Aesar, 98+ %) with the addition of 1 ml H_2O . After slow evaporation of the excess solvent and drying at 40°C during 2 months without stirring, a solid translucent mass of yellow-orange color that could be easily crushed into powder was obtained and used without further treatment for characterization and for the thermal decomposition studies.

Thermogravimetry (TG) and differential thermal analysis (DTA) measurements were conducted in a simultaneous **TG-DTA** device from Netzsch (model STA 449C) using a heating rate of $5^\circ\text{C}/\text{min}$ up to 1200°C . The carrier gas consisted of argon with a flow that was fixed to $40\text{ mL}/\text{min}$. The runs were made at atmospheric pressure. A sample mass of $11.5 \pm 0.2\text{ mg}$ was used for the measurements. The powders were loaded without compaction in alumina crucibles with 6 mm diameter and 3 mm depth. $\alpha\text{-Al}_2\text{O}_3$ powder (48 mg) was used as reference. Buoyancy corrections were made on the basis of data recorded on empty crucibles before each measurement. In order to check the reproducibility of the results 9 runs were made. The temperature of the DTA peaks and **mass** losses were constant within 3°C , whereas the value of mass losses at all decomposition stages were reproducible within 0.7 %.

A Bruker Tensor 27 spectrometer coupled to the exhaust line of the **simultaneous TG-DTA** device by a transfer line heated to 200°C was used for Fourier transform infra-red (FTIR) evolved gas analysis. FTIR spectra were also recorded on samples heated in the **simultaneous TG-DTA** instrument at a rate of $5^\circ\text{C}/\text{min}$ and air quenched by opening the machine (up to 600°C) or cooled at a rate of $50^\circ\text{C}/\text{min}$ (from above 600°C) in order to examine the evolution of the decomposition products. X-ray diffraction (XRD) patterns were collected on the fast cooled

samples in a STOE diffractometer using CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). In-situ high-temperature hard x-ray (synchrotron) diffraction measurements up to 500°C were conducted at the Wiggler beamline BW5, located at the storage ring DORIS at DESY in Hamburg (Germany). The photon energy of the incident beam was 77.8 keV, corresponding to a wavelength $\lambda = 0.1593 \text{ \AA}$. The diffraction patterns were recorded during a temperature ramp of 5 °C/min in an Ar-filled furnace. Details on the experimental setup and data analysis can be found in previous publications [20,21]. The evolution of microstructural features was observed in-situ at low magnification (50x) by hot-stage optical microscopy in a HCP901 chamber from INSTEC Ltd under Ar flow during heating at 5 °C/min up to 760°C.

3. Results and discussion

The XRD pattern of the as-prepared sample is plotted in Fig. 1. The compound appears to be well crystallised. The presence of a high intensity reflection at low angle is typical for rare-earth alkanoates [24-29]. Assuming a structure similar to that of long chain cerium, lanthanum or neodymium carboxylates, i.e. lamellar bilayer structure with two stretched alkyl chains in *all-trans* conformation, the expected maximum lamellar spacing for yttrium hexanoate can be calculated using the following relation [29]:

$$d_{\max} = 2d_{\text{C-H}} + 2(n-1)d_{\text{C-C}} \sin 55^\circ + 2d_{\text{C-O}} + 2r_{\text{Y}^{3+}}$$

Where n is the total number of C atoms in a ligand, $d_{\text{C-H}} = 1.09 \text{ \AA}$, $d_{\text{C-C}} = 1.54 \text{ \AA}$, $d_{\text{C-O}} = 1.36 \text{ \AA}$ and $r_{\text{Y}^{3+}} = 1.215 \text{ \AA}$ (coordination number 9) [30]. The resulting value of $d_{\max} = 19.95 \text{ \AA}$ corresponds well to an interplane spacing of 19.96 Å calculated with the lowest angle reflection of the XRD pattern at $2\theta = 4.417^\circ$. Furthermore, regularly spaced reflections with lower intensity at $2\theta = 8.875^\circ$, 13.325° and 17.841° correspond to 1/2, 1/3 and 1/4 d-spacing and support a

layered structure. Further detailed studies are however needed to fully determine the structure of this compound.

The FTIR spectrum (inset in Fig. 1) shows the typical absorption bands of an hexanoate salt as evidenced by comparison with previously published data for Cu-hexanoate [22]. The *all-trans* conformation assumed for the X-ray structural analysis, is supported by the presence of $n/2 = 3$ (n being the total number of carbon atoms in the chain) clear CH_2 wagging progression bands ($\text{w}(\text{CH}_2)$) between 1250 cm^{-1} and 1350 cm^{-1} [24]. The strongest absorption band of hexanoic acid due to $\text{C} = \text{O}$ stretching vibrations at 1711 cm^{-1} [31] is not visible, showing that the excess solvent has been evaporated. The broad $\nu_s(\text{OH})$ absorption band at $3200 - 3400\text{ cm}^{-1}$ and the $\delta(\text{H}_2\text{O})$ band at 1640 cm^{-1} show that the as-prepared compound is in a hydrated state. The strong band at 1542 cm^{-1} is due to the asymmetric carboxyl stretching ($\nu_{\text{as}}(\text{COO}^-)$) vibrations, whereas the symmetric carboxyl stretching band ($\nu_s(\text{COO}^-)$) occurs at 1424 cm^{-1} . The $\Delta\nu = \nu_{\text{as}}(\text{COO}^-) - \nu_s(\text{COO}^-)$ value is 118 cm^{-1} for yttrium hexanoate and thus smaller than for Na-hexanoate [32]. According to the study of Deacon and Phillips [33], it could be concluded that bidentate chelating or bridging coordination is present in Y-hexanoate, similarly to the case of Y-valerate [19].

As shown in Fig. 2, heating results in several mass loss steps (TG curve) and endothermic peaks (DTA trace). The first endothermic event (I in Fig. 2) takes place between 40°C and 110°C and is associated to a relative mass loss of 4.7 %. The FTIR spectrum of the evolved gas (98°C in Fig. 3) shows evidence for the release of H_2O . Dehydration is further confirmed by the FTIR spectrum of a sample quenched from 120°C , in which the $\nu_s(\text{OH})$ absorption band due to the presence of H_2O in the as-prepared sample has disappeared (Fig.4). This indicates that the whole H_2O content has been released and that the starting compound had a composition corresponding

approximately to $\text{Y}(\text{C}_5\text{H}_{11}\text{COO})_3 \cdot 1.2\text{H}_2\text{O}$. On the other hand, besides the disappearance of the H_2O absorption bands, the FTIR spectrum of the 120°C -quenched sample is nearly unchanged compared to that of the starting powder, showing that dehydration does not induce a decomposition of the Y-hexanoate framework.

Hot stage microscopy observations (Fig.5) show that melting takes place during dehydration between 40°C and 100°C . *In-situ* XRD diffraction patterns (Fig.6) reveal that the original structure disappears during the dehydration-melting process. It must be noted that the wavelength of the incident X-ray beam used for the *in-situ* high-temperature studies is much shorter than that used for collecting XRD patterns at room temperature on the as-prepared and quenched samples. For this reason, the same reflections appear at significantly smaller 2θ values. The 2θ scale of Fig.6 corresponds in fact to a $4.84^\circ \leq 2\theta \leq 15.5^\circ$ range in Fig.1. The sharp intensity drop at $2\theta < 0.6^\circ$ in Fig.6 is due to the Pb beam-stop preventing saturation of the two-dimensional detector by the direct beam, whereas the increasing background intensity at $2\theta > 1.2^\circ$ results from the furnace assembly. Between 40°C and 110°C , a broad diffraction peak appears and growth at a position corresponding to a d-spacing of $13.93 \pm 0.15 \text{ \AA}$, which is compatible with a partial melting of the alkyl chains, while the lamellar bilayer structure is retained [25]. This peak is visible up to 270°C but then vanishes within 30°C . This last temperature range corresponds to the onset of DTA peak II and to the beginning of the associated mass loss (Fig.2). There is no evidence for a clearing peak in the DTA trace in this temperature range so that it seems that the thermal decomposition of $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3$ takes place from the liquid crystalline phase, without prior transition to an isotropic liquid state. During this thermal event, CO_2 and 6-undecanone are released as gas educts as shown in Fig. 3 (340°C). The release of CO_2 in association with a symmetrical ketone during the main decomposition stage of Y-

alkanoates has previously been reported for Y-acetate [37], Y-propionate [18,38,39], Y-butyrate [18] and Y-valerate [19], where the symmetrical ketone consisted in acetone, 3-pentanone, 4-heptanone and 5-nonanone respectively. Following a similar free-radical mechanism [40] in the case of Y-hexanoate, it can be assumed that alkyl and acyl radicals are released during the decomposition of $Y(C_5H_{11}CO_2)_3$ as:

Recombination of the alkyl and acyl units would naturally lead to the formation of 6-undecanone without need for further rearrangement:

Whereas the other decomposition educts can result in the formation of a monoxycarbonate and the release of gaseous CO_2 :

The assignment of the evolved gas FTIR absorption bands to 6-undecanone is not straightforward. The spectrum of 5-undecanone, which has the same composition but a slightly different configuration, is very similar to that of 6-undecanone [31]. Only the minor skeletal vibrations in the $1180\text{ cm}^{-1} - 1318\text{ cm}^{-1}$ wavenumber range present sensible differences, which allow determining the released gas species as 6-undecanone. 4-, 3- and 2-undecanone can be ruled out although their C=O stretching, symmetric and asymmetric stretching methyl and methylene modes occur at the same wavenumber and similar intensity than for 6-undecanone, but clear differences occur between 900 cm^{-1} and 1200 cm^{-1} . In the case of Y-propionate, Nasui et al. [39] reported that, besides a main contribution from the symmetrical 3-pentanone molecule, the unsymmetrical ketone 2-pentanone was also released, although in a significantly lower relative proportion. Although we cannot totally exclude that some 5-undecanone was also present in the

gas educts of Y-hexanoate in the present case, it can be safely assumed on the basis of the FTIR evolved gas analysis, that 6-undecanone is the major constituent. Nevertheless, a careful examination of the “340°C” spectrum in Fig. 3 reveals that the intensity of the two bands marked with symbol * is enhanced compared in particular to the band centered at 1420 cm⁻¹ (● in Fig. 3), which should in principle only be slightly less intense than its two neighbors [31]. A possible explanation for this feature is that two alkyl or two acyl radicals could combine with each other instead of following reaction (2).

In that case, decane (C₁₀H₂₂) is expected to be formed and released as a gas species. The FTIR spectrum of decane can indeed account for the enhancement of the two absorption bands at 1463 cm⁻¹ and 1361 cm⁻¹ as shown in Fig. 3. Simultaneously, more CO₂ as well as elemental carbon would be formed by reaction (4'). The presence of carbon in the samples is strongly suggested by the dark coloration of the powders quenched between 325°C and ≈1025°C, providing support to reaction (4'), which naturally imply that reaction (4) is also at play due to balance considerations as each pair of acyl radicals that follow reaction (4') leaves a pair of supernumerary alkyl radicals.

The FTIR spectra recorded on quenched samples (Fig.4) show that the absorption bands due to the hexanoate ligands progressively disappear upon heating, whereas a pattern corresponding to an yttrium oxycarbonate [36,37,41] remains at 500°C as expected from reaction (3).

As shown in Fig.7, which depicts the time evolution of the intensity of the strongest absorption band of 6-undecanone (ν_{as}(CH₃)), the release of this gas species is finished at 490 ± 5 °C. At this temperature, the overall mass loss amounts to 70.3 %, which is in very good agreement with the

expected value (70.4 %) for decomposition from $\text{Y}(\text{C}_5\text{H}_{11}\text{COO})_3 \cdot 1.2\text{H}_2\text{O}$ to $\frac{1}{2}\text{Y}_2\text{O}_2\text{CO}_3$. The completion of this transformation is supported by the FTIR spectrum of a sample quenched from 500°C (Figs. 4 and 8), which only shows absorption bands of the oxycarbonate. The XRD pattern of the same sample (Fig.9) reveals the appearance of a broad peak centered around $2\theta = 28.8^\circ$, which could be ascribed to both the Y_2O_3 ((2 2 2) reflection) and the $\text{Y}_2\text{O}_2\text{CO}_3$ ((1 0 2) reflection) [39]. However, Y_2O_3 is not clearly detected by FTIR spectroscopy at this temperature as illustrated in Fig. 8, which shows no clear evidence for the Y_2O_3 absorption band at 560 cm^{-1} [42].

The decomposition of $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3$ to $\text{Y}_2\text{O}_2\text{CO}_3$ extends over two endothermic peaks (II and III in the DTA trace – Fig. 2). Peak III, which has a much lower intensity, occurs in parallel with a decrease of the mass loss rate as evidenced in the TG and DTG traces (Fig.2). The origin of this behavior is not clear but could be related to the formation of intermediate yttrium oxycarbonate products like $\text{Y}_2(\text{CO}_3)_3$ or $\text{Y}_2\text{O}(\text{CO}_3)_2$ as reported during the thermal decomposition of yttrium acetate [37]. The transient presence of such compounds could however not be evidenced in our samples neither by XRD, due to the amorphous state of the powders, nor by FTIR, owing to the similarities of the various yttrium carbonate and oxycarbonates modifications [36]. Nevertheless, the continuous release of CO_2 from the onset of stage II allows to exclude an $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3 \rightarrow \text{Y}(\text{CO}_3)_3 + \text{C}_5\text{H}_{11}\text{COC}_5\text{H}_{11}$ stage as main decomposition route, because this would suppress the evolution of CO_2 during the initial part of the $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3$ decomposition process.

Above 500°C and up to about 975°C, a broad endothermic peak appears in the DTA trace (IV in Fig. 2), while the mass of the sample continues to decrease by a few percent until it reaches a constant value from $980 \pm 10^\circ\text{C}$. During this step, CO_2 is the only gas species detected as educt

by FTIR (653°C in Fig.3). Simultaneously, the absorption bands of $\text{Y}_2\text{O}_2\text{CO}_3$ disappear from the FTIR spectra of quenched samples, whereas the absorption band of Y_2O_3 emerges from the background and becomes more and more intense (Fig.8). The XRD patterns of samples fast cooled from above 550°C also provide evidence for the formation of Y_2O_3 (Fig.9). The last decomposition step can thus be written as follows:

The total mass loss amounts to 73.5 %, which is in reasonable agreement with the 75.2 % theoretically expected for the decomposition of $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3 \cdot 1.2\text{H}_2\text{O}$ to $\frac{1}{2}\text{Y}_2\text{O}_3$. The difference might be partly due to the presence of a minor amount of yet unburned carbonaceous residue [39].

Melting prior to decomposition occurs neither in the short chain length yttrium alkanoates $\text{Y}(\text{CH}_3\text{CO}_2)_3$ and $\text{Y}(\text{C}_2\text{H}_5\text{CO}_2)_3$ [18,37-39] nor in the heptanoate $\text{Y}(\text{C}_6\text{H}_{13}\text{CO}_2)_3$ [43]. However, $\text{Y}(\text{HCO}_2)_3$ and several compounds with alkyl chain length longer than in yttrium propionate studied up to now show evidence for melting, which takes place at 182°C (formate) [41], 105°C (butyrate) [18], 88°C (valerate) [19], 85°C (dodecanoate) [44]. The fact that dehydration proceeds before melting in $\text{Y}(\text{C}_3\text{H}_7\text{CO}_2)_3$ [18] and simultaneously with melting in $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3$ is reminiscent of observations made on some hydrated light lanthanide alkanoates [24,27].

Solidification of the melt has been systematically observed not only in other yttrium alkanoates undergoing melting [18,19] but in other rare-earth alkanoates as well [45,46]. Based on the DTA trace for $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3$, solidification is finished between 330°C and 335°C. At this point, the TG curve and FTIR spectra of quenched samples show that the decomposition to $\text{Y}_2\text{O}_2\text{CO}_3$ is far from complete. As a consequence, a part at least of the $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3$ decomposition process must take place in the solid state.

As discussed above, the release of a symmetrical ketone during the decomposition of $Y(C_5H_{11}CO_2)_3$ can in principle be explained on the basis of a free-radicals model [40]. This is in agreement with previous reports on the thermal decomposition of rare earth valerates [19], butyrates [18,46], propionates [47-49] and acetates [50-51], for which the release of respectively 5-nonanone, 4-heptanone, 3-pentanone and acetone had been observed.

The formation of $Y_2O_2CO_3$ during the thermal decomposition process has already been reported for several of Y-based alkanoate compounds including yttrium formate [41], acetate [37], propionate [18,38,39], butyrate [18] and valerate [19]. This compound thus appears as an intermediate stage that will be difficult to avoid, when aiming at producing Y_2O_3 nanoparticles by thermal treatment of Y-based metalorganic precursors.

The decomposition of $Y_2O_2CO_3$ into Y_2O_3 takes place with a slow but steady decrease of the sample mass, which suggests no intermediate stages contrary to some heavy rare-earth alkanoates [47,48,52,53] but in agreement with other yttrium alkanoates [18,19,37-39,41].

4. Conclusions

The thermal behaviour of $Y(C_5H_{11}CO_2)_3 \cdot 1.2H_2O$ was studied during heating in Ar atmosphere at a rate of 5 °C/min and can be summarised as follows:

(a) Melting and dehydration of $Y(C_5H_{11}CO_2)_3 \cdot 1.2H_2O$ (40°C – 110°C)

(b) Solidification of molten $Y(C_5H_{11}CO_2)_3$ (315°C – 335°C)

(c) Decomposition of $Y(C_5H_{11}CO_2)_3$ with release of CO_2 and $C_{11}H_{22}O$ (6-undecanone) according to the overall reaction: $2Y(C_5H_{11}CO_2)_3 \rightarrow Y_2O_2CO_3 + 3C_5H_{11}COC_5H_{11} + 2CO_2$ (280°C – 490°C)

(d) Decomposition of yttrium monoxycarbonate: $Y_2O_2CO_3 \rightarrow Y_2O_3 + CO_2$ (500°C – 980°C)

Melting takes place from a solid crystalline phase to a liquid crystalline state. Decomposition occurs without evidence for the formation of an isotropic liquid phase.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Acknowledgements

This work was supported by the Department of Energy Conversion and Storage, (project nr. 49605 E-5). The authors also acknowledge financial support from DANSCATT as well as DESY (project I-20110113 EC) for granting beamtime.

References

- [1] R. Sundaram and K.S. Nagaraja, Solid state electrical conductivity and humidity sensing properties of $\text{WO}_3\text{-Y}_2\text{O}_3$ composites, *Physica Status Solidi A* 201 (2004) 529 – 535
- [2] G.B. Sun, K. Hidajat, X.S. Wu and S. Kawi, A crucial role of surface oxygen mobility on nanocrystalline Y_2O_3 support for oxidative steam reforming of ethanol to hydrogen over $\text{Ni/Y}_2\text{O}_3$ catalysts, *Applied Catalysis B* 81 (2008) 303 – 312
- [3] G.K. Das and T.T.Y. Tan, Rare-earth-doped and co-doped Y_2O_3 nanomaterials as potential bioimaging probes, *J. Phys. Chem. C* 112 (2008) 11211 – 11217
- [4] D.Y. Li, Y.X. Wang, X.R. Zhang, H.X. Dong, L. Liu, G. Shi and Y.L. Song, Effect of Li^+ ions on enhancement of near-infrared upconversion emission in $\text{Y}_2\text{O}_3\text{:Tm}^{3+}/\text{Yb}^{3+}$ nanocrystals, *J. Appl. Phys.* 112 (2012) 094701
- [5] Y.L. Kopylov, V.B. Kravchenko, A.A. Komarov, Z.M. Lebedeva and V.V. Shemet, $\text{Nd:Y}_2\text{O}_3$ nanopowders for laser ceramics, *Opt. Mater.* 29 (2007) 1236 – 1239
- [6] A. Fukabori, T. Yanagida, J. Pejchal, S. Maeo, Y. Yokota, A. Yoshikawa, T. Ikegami, F. Moretti and K. Kamada, Optical and scintillation characteristics of Y_2O_3 transparent ceramic, *J. Appl. Phys.* 107 (2010) 073501 (6pp)
- [7] E.O. Oh, C.M. Whang, Y.R. Lee, J.H. Lee, K.J. Yoon, B.K. Kim, J.W. Son, J.H. Lee and H.W. Lee, Thin film yttria-stabilized zirconia electrolyte for intermediate-temperature solid oxide fuel cells (IT-SOFCs) by chemical solution deposition, *J. Eur. Ceram. Soc.* 32 (2012) 1733 – 1741
- [8] K. Suzuki, K. Tanaka, K. Nishizawa, T. Miki and K. Kato, Investigation of electrical properties for $(\text{Y,Yb})\text{MnO}_3/\text{HfO}_2/\text{Si}$ and $(\text{Y,Yb})\text{MnO}_3/\text{Y}_2\text{O}_3/\text{Si}$ structures, *Integrated Ferroelectrics* 75 (2005) 17 – 25

- [9] Jun Yeol Cho, Ki-Young Ko and Young Rag Do, Optical properties of sol-gel derived $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ thin film phosphors for display applications, *Thin Solid Films* 515 (2007) 3373 – 3379
- [10] M.L. Pang, J. Lin, Z.Y. Cheng, J. Fu, R.B. Xing and S.B. Wang, Patterning and luminescent properties of nanocrystalline $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor films by sol-gel soft lithography, *Mater. Sci. Eng. B* 100 (2003) 124 – 131
- [11] H. Tomita, T. Goto, S. Shimada and K. Takahashi, Solution spinning of a high- T_c oxide superconductor: 5. The influence of yttrium and barium ions on the poly(vinyl alcohol)-copper(II) complex, *Polymer* 37 (1996) 1071 – 1077
- [12] L. Ciontea, A. Angrisani, G. Celentano, T. Petrisor Jr., A. Rudolfoni, A. Vannozzi, A. Augieri, V. Galuzzi, A. Mancini and T Petrisor, Metal propionate synthesis of epitaxial $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films, *J. Phys. Conf. Ser.* 97 (2008) 012302 6pp
- [13] P. Vermeir, I. Cardinael, J. Schaubroek, K. Verbeken, M. Bäcker, P. Lommens, W. Knaepen, J. D'haen, K. De Buysser and I. Van Driessche, Elucidation of the mechanism in fluorine-free prepared $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ coatings, *Inorg. Chem.* 49 (2010) 4471 – 4477
- [14] D.L. Shi, Y.L. Xu, H.B. Yao, Z. Han, J. Lian, L.M. Wang, A.H. Li, H.K. Liu and S.X. Dou, The development of $\text{YBa}_2\text{Cu}_3\text{O}_x$ thin films using a fluorine-free sol-gel approach for coated conductors, *Supercond. Sci. Technol.* 17 (2004) 1420 – 1425
- [15] X. Tang, D. He, Y. Zhao and J.-C. Grivel, Characterization of microstructure and performance of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films synthesized through sol-gel aqueous precursors with DEA/TEA addition, *J. Supercond. Nov. Magn.* 26 (2013) 1883 – 1886

- [16] X. Tang, Y. Zhao and J.-C. Grivel, Influence of initial pH on the microstructure of YBa₂Cu₃O_{7-x} superconducting thin films derived from DEA-aqueous sol-gel method, *Ceramics International*, 39 (2013) 7735 – 7741
- [17] K.G. Severin and J.S. Ledford, Characterization of titanium and zirconium valerate sol-gel films, *Chem. Mater.* 6 (1994) 890 – 898
- [18] J.-C. Grivel, Thermal decomposition of yttrium(III) propionate and butyrate, *J. Anal. Appl. Pyrolysis* 101 (2013) 185 – 192
- [19] J.-C. Grivel, Y. Zhao, X. Tang, P.G.P.A. Pallewatta, A. Watenphul and M.v. Zimmermann, Thermal decomposition of yttrium(III) valerate in argon, *J. Anal. Appl. Pyrolysis* 106 (2014) 125 – 131
- [20] J.-C. Grivel, N.H. Andersen, P.G.A.P. Pallewatta, Y. Zhao and M. von Zimmermann, Influence of Bi, Se and Te additions on the formation temperature of MgB₂, *Supercond. Sci. Technol.* 25 (2012) 015010 (6pp)
- [21] J.-C. Grivel, A.C. Wulff, Y. Zhao, J. Bednarčik and M. V. Zimmermann, In situ study on the formation of FeTe, *J. Mater. Sci.* 46 (2011) 4540 – 4544
- [22] J.A.R. Cheda, M.V. García, M.I. Redondo, S. Gargani and P. Ferloni, Short chain copper(II) *n*-alkanoate liquid crystals, *Liquid Crystals* 31 (2004) 1 – 14
- [23] Y. Maréchal, The molecular structure of liquid water delivered by absorption spectroscopy in the whole IR region completed with thermodynamics data, *J. Mol. Struct.* 1004 (2011) 146 – 155
- [24] L. Jongen, K. Binnemans, D. Hinz and G. Meyer, Mesomorphic behavior of cerium(III) alkanoates, *Mater. Sci. Eng. C* 18 (2001) 199 – 204

- [25] L. Jongen, K. Binnemans, D. Hinz and G. Meyer, Thermal behavior of lanthanum(III) alkanoates, *Liquid Crystals* 28 (2001) 1727 – 1733
- [26] K. Binnemans, L. Jongen, C. Bromant, D. Hinz and G. Meyer, Structure and mesomorphism of neodymium(III) alkanoates, *Inorg. Chem.* 39 (2000) 5938 – 5945
- [27] L. Jongen, K. Binnemans, D. Hinz and G. Meyer, Mesomorphic 16ormats 16 of praseodymium(III) alkanoates, *Liquid Crystals* 28 (2001) 819 – 825
- [28] L. Jongen, D. Hinz, G. Meyer and K. Binnemans, Induced mesophases in binary mixtures of lanthanide(III) dodecanoates, *Chem. Mater.* 13 (2001) 2243 – 2246
- [29] E.F. Marques, H.D. Burrows and M. da Graça Miguel, The structure and thermal behavior of some long chain cerium(III) carboxylates, *J. Chem. Soc. Faraday Trans.* 94 (1998) 1729 – 1736
- [30] R.D. Shannon, Revised effective ionic-radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Cryst. A* 32 (1976) 751 – 767
- [31] SDBSWeb : <http://sdbb.db.aist.go.jp> (National Institute of Advanced Industrial Science and Technology, 08-2014)
- [32] J. Umemura, D.G. Cameron and H.H. Mantsch, An FT-IR study of micelle formation in aqueous sodium *n*-hexanoate solutions, *J. Phys. Chem.* 84 (1980) 2272 – 2277
- [33] G.B. Deacon and R.J. Phillips, Relationships between the carbon-oxygen stretching frequencies of carboxylate complexes and the type of carboxylate coordination, *Coordination Chemistry Reviews* 33 (1980) 227 – 250
- [34] H. Yamada and W.B. Person, Absolute infrared intensities of the fundamental absorption bands in solid CO₂ and N₂O, *J. Chem. Phys.* 41 (1964) 2478 – 2487

- [35] B. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*, John Wiley & Sons, Ltd, West Sussex, 2004
- [36] J.A. Goldsmith and S.D. Ross, Factors affecting the infra-red spectra of some planar anions with D_{3h} symmetry – III. The spectra of rare-earth carbonates and their thermal decomposition products, *Spectrochimica Acta* 23A (1967) 1909 – 1915
- [37] G.A.M. Hussein, Formation of high-surface area yttrium oxide by the thermal decomposition of different inorganic precursors, *Thermochimica Acta* 244 (1994) 139 – 151
- [38] M. Nasui, C. Bogatan (Pop), L. Ciontea and T. Petrisor, Synthesis, crystal structure modeling and thermal decomposition of yttrium propionate $[Y_2(CH_3CH_2COO)_6 \cdot H_2O] \cdot 3.5H_2O$, *J. Anal. Appl. Pyrolysis* 97 (2012) 88 – 93
- [39] M. Nasui, T. Petrisor Jr., R.B. Mos, A. Mesaros, R.A. Varga, B.S. Vasile, T. Ristoiu, L. Ciontea and T. Petrisor, Synthesis, crystal structure and thermal decomposition of yttrium propionate, *J. Anal. Appl. Pyrolysis* 106 (2014) 92 – 98
- [40] A. Hites and K. Biemann, On the mechanism of ketonic decarboxylation. Pyrolysis of calcium decanoate, *J. Amer. Chem. Soc.* 94 (1972) 5772 – 5777
- [41] Y. Masuda, Thermal decomposition of formates. Part VII. Thermal decomposition of yttrium formate dehydrate, *Thermochimica Acta* 53 (1982) 215 – 223
- [42] N. T. McDevitt and W.L. Baun, Infrared absorption study of metal oxides in the low frequency region ($700 - 240\text{ cm}^{-1}$), *Spectrochim. Acta* 20 (1964) 799 – 808
- [43] W. Brzyska and W. Ożga, Thermal decomposition of rare earth element enanthates, *J. Thermal Anal.* 41 (1994) 849 - 858

- [44] K. Binnemans, L. Jongen, C. Görller-Walrand, W. D'Olieslager, D. Hinz and G. Meyer, Lanthanide(III) dodecanoates: structure, thermal behaviour, and ion-size effects on the mesomorphism, *Eur. J. Inorg. Chem.* 2000 1429 – 1436
- [45] J.-C Grivel, Thermal decomposition of $\text{Ln}(\text{C}_2\text{H}_5\text{CO}_2)\cdot\text{H}_2\text{O}$ ($\text{Ln} = \text{Dy, Tb, Gd, Eu}$ and Sm), *Journal of Thermal Analysis and Calorimetry* 115 (2014) 1253 - 1264
- [46] J.-C. Grivel, Y. Zhao, X. Tang, P.G.P.A. Pallewatta, A. Watenphul and M.v. Zimmermann, Thermal decomposition of lanthanum(III) butyrate in argon atmosphere, *Thermochimica Acta* 566 (2013) 112 – 117
- [47] J.-C. Grivel, Thermal decomposition of $\text{Ln}(\text{C}_2\text{H}_5\text{CO}_2)_3\cdot\text{H}_2\text{O}$ ($\text{Ln} = \text{Ho, Er, Tm}$ and Yb), *J. Thermal Anal. Calor.* 109 (2012) 81 – 88
- [48] J.-C. Grivel, Thermal decomposition of lutetium propionate, *J. Anal. Appl. Pyrolysis* 89 (2010) 250 – 254
- [49] M. Ogawa and K. Manabe, Formation of dilanthanide monoxide tetrapropionate by thermal-decomposition of propionate monohydrate of rare-earth elements (La, Ce, Pr, Nd), *Nippon Kagaku Kaishi* 5 (1993) 617 – 622
- [50] T. Arii, T. Taguchi, A. Kishi, M. Ogawa and Y. Sawada, Thermal decomposition of cerium(III) acetate studied with sample-controlled thermogravimetric-mass spectrometry (SCTG-MS), *J. Eur. Ceram. Soc.* 22 (2002) 2283 – 2289
- [51] G.A.M. Hussein, Formation, characterization, and catalytic activity of gadolinium oxide. Infrared spectroscopic studies, *J. Phys. Chem.* 98 (1994) 9657 – 9664
- [52] L.S. Lazareva, M.N. Ambrozhi and L.M. Dvornikova, Thermography of europium, gadolinium and terbium valerates, *Zh. Neorg. Khim.* 15 (1970) 2361 – 2364

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

396 [53] L.S. Lazareva and L.M. Dvornikova, Thermal decomposition of thulium, ytterbium and
397 lutecium valerates, Zh. Neorg. Khim. 16 (1971) 2116 – 2119

Figure captions

Figure 1: Main panel: XRD pattern of the as prepared Y-hexanoate. Inset: FTIR spectrum of the same sample with band assignments according to [22,23].

Figure 2: Upper panel: TG trace (main frame) and DTG (inset) trace for a $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3 \cdot 1.2\text{H}_2\text{O}$ powder sample recorded in flowing Ar with a heating rate of 5 °C/min. Lower panel: DTA trace recorded simultaneously on the same sample (exothermic upwards; endothermic downwards). Inset: detail of the DTA trace between 262°C and 370°C.

Figure 3: FTIR spectra of the gas phase evolved from a $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3 \cdot 1.2\text{H}_2\text{O}$ sample at different temperatures during decomposition: □: H_2O , ◆: 6-undecanone ($\text{C}_5\text{H}_{11}\text{COC}_5\text{H}_{11}$), ○ CO_2 . Band assignments according to [34] and [35]. The ● and ★ symbols denote absorption bands discussed in the text. The positions of the absorption bands of decane ($\text{C}_{10}\text{H}_{22}$) are shown by vertical bars below the “340°C” spectrum.

Figure 4: FTIR of the solid residue quenched from various temperatures along a heating ramp of 5 °C/min in an Ar atmosphere. The starting powder (20°C) consisted of $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3 \cdot 1.2\text{H}_2\text{O}$. The band assignments for $\text{Y}_2\text{O}_2\text{CO}_3$ (500°C) are based on ref. [36].

Figure 5: Hot stage optical microscope pictures taken at various temperatures on a $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3 \cdot 1.2\text{H}_2\text{O}$ powder sample heated under Ar flow at 5 °C/min. The striations seen on the right hand side of the images from 200°C upwards are due to the underlying Ag foil substrate.

Figure 6: In-situ high energy (synchrotron) XRD patterns recorded at various temperatures on the $\text{Y}(\text{C}_5\text{H}_{11}\text{CO}_2)_3 \cdot 1.2\text{H}_2\text{O}$ powder during heating at 5 °C/min in Ar flow. The strong decrease of the intensity at $2\theta < 0.6$ degrees is due to the lead absorber beamstop.

Figure 7: Temperature dependence of the intensity of the $\nu_{\text{as}}(\text{CH}_3)$ stretching absorption band of 6-undecanone (wavenumber = 2938 cm^{-1}).

Figure 8: FTIR spectra of the solid residue quenched from various temperatures along a heating ramp of $5\text{ }^{\circ}\text{C}/\text{min}$ in an Ar atmosphere.

Figure 9: XRD patterns recorded on yttrium hexanoate powders heated in Ar at $5\text{ }^{\circ}\text{C}/\text{min}$ up to the indicated temperatures and fast cooled to room temperature. ● Y_2O_3 .

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9