Rare earth $\beta$-diketonate and carboxylate metal complexes as precursors for MOCVD of oxide films

To cite this version:
N. Kuzmina, L. Martynenko, Z. Tu, A. Kaul, G. Girichev, et al.. Rare earth $\beta$-diketonate and carboxylate metal complexes as precursors for MOCVD of oxide films. Journal de Physique IV Colloque, 1993, 03 (C3), pp.C3-385-C3-390. <10.1051/jp4:1993353>. <jpa-00251410>

HAL Id: jpa-00251410
https://hal.archives-ouvertes.fr/jpa-00251410
Submitted on 1 Jan 1993

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Rare earth β-diketonate and carboxylate metal complexes as precursors for MOCVD of oxide films


Department of Chemistry, Moscow State University, Moscow 119899, Russia

Abstract - Volatile and thermostable complexes of lanthanide acetylacetonates and pivalates were obtained and investigated by different methods. These compounds were used for lanthanide oxide containing film producing and for fabrication of silica optical fibers doped by lanthanide oxide. The properties of these and already known volatile precursors are compared.

It is well recognized that rare earth containing films have many applications in microelectronics. Metal Organic Chemical Vapour Deposition (MOCVD) has become one of the most effective methods for producing of thin films. This technique needs volatile and thermostable lanthanide compounds. There are two groups of volatile lanthanide compounds which can be sublimated at relatively low temperature (120-400°C) - chelate complexes with organic ligands (with M-O or/and M-N bonds) and organometallics (with M-C bonds). The organolanthanides are air- and moisture-sensitive that is a specific property of M-C bond. These sensitive compounds have been used only for doping semiconductors of rare earth by MOCVD[1].

The volatile lanthanide chelate complexes with organic ligands such as 1,3-diketonates have been successfully used to produce lanthanide containing oxide films, f.e. yttrium aluminium garnet and high temperature superconductors[2,3]. Lanthanide complexes with organic O-donor ligands are compounds with mainly ionic bonds and with high value of central rare earth ion coordination number. These properties are attributable to associated structure of lanthanide β-diketonates. Only bulky ligands are capable
to inhibit association and promote volatility. Bulky 2,2,6,6,-tetramethyl-3,5-heptanedione ligand (Hthd, also termed dipivalolymethane) is the most useful for preparing volatile lanthanide β-diketonates. The main idea of our work is search for new volatile lanthanide compounds and the comparison of their behavior with that of known volatile compounds in CVD processes. It was found that such accessible and inexpensive lanthanide β-diketonates as acetylacetonates (acac, also termed pentane-2,4-dionate) and pivalates (Piv, also termed trimethylacetates) can be sublimated and used for film producing.

1. **Volatile lanthanide acetylacetonates.**

It is known that lanthanide acetylacetonates Ln(acac)₃ are of oligomeric structure and due to this are practically nonvolatile. Usually these compounds are synthesized as hydrates Ln(acac)₃·3H₂O:

\[ 
\text{LnX}_3 + 3\text{Hacac} + 3\text{NH}_3\cdot\text{aq} \rightarrow \text{Ln(acac)}_3\cdot3\text{H}_2\text{O} \quad (\text{H}_2\text{O}, \text{pH 7}) 
\]

Hydrolysis and decomposition of these compounds occur when heated:

\[ 
\text{Ln(acac)}_3\cdot3\text{H}_2\text{O} \rightarrow \text{Ln}_x(\text{acac})_y(\text{OH})_z + \text{H}_2\text{O} + \text{Hacac} 
\]

As an example, thermal decomposition of Y(acac)₃·3H₂O was shown to give Y₄(acac)₁₀(OH)₂[4].

The mixed ligand complex formation have been used for modification acetylacetonate volatility. The volatile and thermostable forms of lanthanide acetylacetonates were prepared by reactions of nonvolatile acetylacetonate hydrates and O- or N-donor neutral ligands (Q):

\[ 
\text{Ln(acac)}_3\cdot3\text{H}_2\text{O} + n\text{Q} \rightarrow \text{Ln(acac)}_3\cdot n\text{Q} + 3\text{H}_2\text{O} 
\]

where Q is o-phenantroline(Phen)[5], HMPA[6], acetylacetonimine (HAcim)[7], \( n = 1, 2 \).

The adducts Ln(acac)₃·nQ were investigated in solid state and in gaseous phase by IR and thermal analysis, mass spectrometry, photoelectron spectroscopy. It was found that addition of the neutral donor ligands Q was accompanied by formation of adducts which did not hydrolyse when heated. Three different modes of adducts MAA₃·nQ sublimation were demonstrated:

(1) \[ 
\text{M(acac)}_3\cdot n\text{Q}_1(s) \rightarrow \text{M(acac)}_3(s) + n\text{Q}_1(g) \rightarrow \text{M(acac)}_3(g) 
\]
The volatility of \( \text{MAA}_3 \cdot nQ \) depends on nature of the lanthanide ion and the donor ligand and can be varied. Data of table 1 illustrate these dependencies for typical elements of cerium and yttrium groups of lanthanides.

Table 1.

Results of mixed ligand complexes \( \text{LnAA}_3 \cdot nQ \) sublimation

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass loss (mol.% of RE, ±5%)</th>
<th>Mode of sublimation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NdAA}_3 \cdot \text{Phen} )</td>
<td>100</td>
<td>3</td>
<td>[5]</td>
</tr>
<tr>
<td>( \text{GdAA}_3 \cdot \text{Phen} )</td>
<td>100</td>
<td>3</td>
<td>[5]</td>
</tr>
<tr>
<td>( \text{ErAA}_3 \cdot \text{Phen} )</td>
<td>100</td>
<td>3</td>
<td>[5]</td>
</tr>
<tr>
<td>( \text{YAA}_3 \cdot \text{Phen} )</td>
<td>100</td>
<td>3</td>
<td>[5]</td>
</tr>
<tr>
<td>( \text{NdAA}_3 \cdot \text{HMPA} )</td>
<td>40</td>
<td>2</td>
<td>[6]</td>
</tr>
<tr>
<td>( \text{GdAA}_3 \cdot \text{HMPA} )</td>
<td>60</td>
<td>2</td>
<td>[6]</td>
</tr>
<tr>
<td>( \text{ErAA}_3 \cdot \text{HMPA} )</td>
<td>95</td>
<td>2</td>
<td>[6]</td>
</tr>
<tr>
<td>( \text{YAA}_3 \cdot \text{HMPA} )</td>
<td>90</td>
<td>2</td>
<td>[6]</td>
</tr>
<tr>
<td>( \text{NdAA}_3 \cdot 2\text{HAcim} )</td>
<td>nonvol.</td>
<td>1</td>
<td>[7]</td>
</tr>
<tr>
<td>( \text{GdAA}_3 \cdot 2\text{HAcim} )</td>
<td>nonvol.</td>
<td>1</td>
<td>[7]</td>
</tr>
<tr>
<td>( \text{ErAA}_3 \cdot \text{HAcim} )</td>
<td>80</td>
<td>1</td>
<td>[7]</td>
</tr>
<tr>
<td>( \text{YAA}_3 \cdot \text{HAcim} )</td>
<td>70</td>
<td>1</td>
<td>[7]</td>
</tr>
</tbody>
</table>

The enthalpies of \( \text{NdAA}_3 \), \( \text{HoAA}_3 \), \( \text{ErAA}_3 \) sublimation were calculated from mass spectrometric data (table 2) [8]. The values of \( \Delta H_{\text{sub}} \) for known lanthanide dipivaloylmethanates [9] are given in table 2 in order to compare with the ones for lanthanide acetylacetanates. The comparison shows that \( \Delta H_{\text{sub}} \) of monomeric lanthanide acetylacetanates are quite close to that of dipivaloylmethanates. However the mass spectrometric data demonstrate that
Lnthd₃ decompose in gaseous phase at more high temperature than acetylacetonates. The thermal stability of Ythd₃ have been investigated in vapour[10]. Its stability temperature range extends up to 500-550°C. Lanthanide acetylacetonates decompose in vapour at ~ 400°C.

Table 2
The enthalpy of sublimation of lanthanide acetylacetonates[8] and dipivaloylmethanates [9].

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH_{sub}, kcal/mol</th>
<th>Temperature range, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdAA₃</td>
<td>34.6±1.6</td>
<td>392-408</td>
</tr>
<tr>
<td>HoAA₃</td>
<td>33.2±1.8</td>
<td>385-417</td>
</tr>
<tr>
<td>ErAA₃</td>
<td>31.0±1.8</td>
<td>365-417</td>
</tr>
<tr>
<td>Ndthd₃</td>
<td>37.9±1.2</td>
<td>430-491</td>
</tr>
<tr>
<td>Hothd₃</td>
<td>31.4±1.1</td>
<td>420-458</td>
</tr>
<tr>
<td>Erthd₃</td>
<td>31.8±1.2</td>
<td>410-454</td>
</tr>
</tbody>
</table>

2. Volatile lanthanide pivalates.
Lanthanide pivalates belong to the class of complexes with carboxylate organic ligands. It is thought to be unexpected result that lanthanide carboxylates are volatile. These lanthanide compounds are ionic and polymeric and as rule they are non volatile [11]. However pivalates contain bulky alkyl group – t-butyl which promotes decreasing of intermolecular forces and increasing of volatility. Besides that lanthanide pivalates were obtained in form of coordination saturated compounds – LnPiv₃·HPiv (n = 3, 3.5) with coordination number equal 8. The adducts LnPiv₃·nHPiv have been investigated by different methods: IR, TA, x-ray analysis, mass spectrometry and sublimation. A comparison of the IR spectra of LnPiv₃·nHPiv with those of HPiv indicates an coordination between the carboxylic C=O and metal ion: band characteristic of the CO₂H group of HPiv (1710cm⁻¹) shifts to lower frequency (1700-1690cm⁻¹) in the spectra of LnPiv₃·nHPiv. By determining the crystal structure of NdPiv₃·3HPiv was showed that it was a dimer. It is shown that two processes take place when heating LnPiv₃·nHPiv at low pressure (40 torr, N₂): formation of MPiv₃
below 200°C and sublimation of MPiv₃ in temperature range 330-
400°C. The compounds MPiv₃ decompose at 450-550°C with lanthanide
oxide formation. Unlike MPiv₃·nHPiv carboxylates MPiv₃ are air-
and moisture-sensitive. Adducts MPiv₃·nHPiv have excellent stor-
ge characteristics and are used for sublimation study (tabl. 3).

Table 3.
The results of lanthanide pivalates sublimation
(0.01 torr, 90 min, 0.2g)

<table>
<thead>
<tr>
<th>Compound</th>
<th>T, °C</th>
<th>Mass loss, mol. % RE ± 2%</th>
<th>T, °C</th>
<th>Mass loss, mol. % RE ± 2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaPiv₃·3.5HPiv</td>
<td>330</td>
<td>95</td>
<td>390</td>
<td>98</td>
</tr>
<tr>
<td>PrPiv₃·3HPiv</td>
<td>&quot;</td>
<td>95</td>
<td>&quot;</td>
<td>98</td>
</tr>
<tr>
<td>NdPiv₃·3HPiv</td>
<td>&quot;</td>
<td>95</td>
<td>&quot;</td>
<td>95</td>
</tr>
<tr>
<td>GdPiv₃·3HPiv</td>
<td>&quot;</td>
<td>90</td>
<td>&quot;</td>
<td>95</td>
</tr>
<tr>
<td>HoPiv₃·3HPiv</td>
<td>&quot;</td>
<td>45</td>
<td>&quot;</td>
<td>95</td>
</tr>
<tr>
<td>ErPiv₃·2.5HPiv</td>
<td>&quot;</td>
<td>35</td>
<td>&quot;</td>
<td>98</td>
</tr>
<tr>
<td>YbPiv₃·2.5Piv</td>
<td>&quot;</td>
<td>30</td>
<td>&quot;</td>
<td>95</td>
</tr>
<tr>
<td>YPiv₃·2.5HPiv</td>
<td>&quot;</td>
<td>20</td>
<td>&quot;</td>
<td>95</td>
</tr>
</tbody>
</table>

The sublimation experiments have shown that the difference in
volatilities of MPiv₃·nHPiv formed by lanthanides of yttrium and
cerium groups has been attributed to differences in sublimation
kinetics. The kinetic factors strongly effectlanthanide pivalate
sublimation because these compounds have oligomeric structures.
Mass spectroscopy data demonstrate their trimeric or dimeric
structures in vapour: Ln₃Piv₅⁺, Ln₂Piv₄⁺, LnPiv₂⁺ at 654 K. Par-
tial thermal decomposition (3-5%) of LnPiv₃ was found under the
conditions of mass spectrometric experiment. For usual sublima-
tion experiments (40 torr, N₂) partial thermal decomposition of
LnPiv₃ appears only in presence of moisture traces in carrier
gas. The vapor densities of NdPiv₃ and ErPiv₃ were determined by
flow methods in the temperature range of 330-370°C. The obtained
values of density are about 3.10⁻⁴ mol/ml what is close to ones
for lanthanide dipivaloylmethanates but the latters sublimate at
lower temperature (150-200° C). Another advantage of lanthanide pivalates is their accessibility and low price when compared with dipivaloylmethanates.

3. The use of volatile lanthanide acetylacetonates and pivalates for MOCVD

Complexes Ln(acac)$_3$.Phen and Ln(thd)$_3$ are used as dopants in the MOCVD method for fabrication of single-mode and multi-mode silica optical fibers where the core is doped by RE in the level of 0.1-3000 ppm. The fiber preforms are fabricated by MOCVD process with deposition of the glass core as a porous layer. It was demonstrated that the type of RE complex did not change the amount of OH groups in the glass core. The content of OH groups is not higher than 1 ppm without any additional drying [12].

References