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MOCVD Precursors for the Deposition of NaREF 4 (RE = Y, Gd) Films**

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Heterobimetallic sodium rare-earths complexes: “third-generation” MOCVD precursors for the deposition of NaREF₄ (RE = Y, Gd) films

Sergio Battiato,^{†,§} Patrizia Rossi,[‡] Paola Paoli[‡] and Graziella Malandrino^{†,*}

[†]Dipartimento di Scienze Chimiche, Università di Catania and INSTM UdR Catania, V.le A. Doria 6, 95125 Catania, Italy.

[‡]Dipartimento di Ingegneria Industriale, Università di Firenze, Via Santa Marta 3, 50136 Firenze, Italy.

KEYWORDS. MOCVD, Single source, Precursors, Heterobimetallic, Upconversion.

ABSTRACT: We report the synthesis of novel heterobimetallic precursors of formula [RE(hfa)₄]⁻[Na•tetraglyme]⁺ [RE=Y, Gd; Hhfa= 1,1,1,5,5,5-hexafluoro-2,4-pentanedione and tetraglyme= 2,5,8,11,14-pentaoxapentadecane], which can be efficiently used as single-sources for the metalorganic chemical vapor deposition of NaREF₄ films.

During last years, sodium rare earth tetrafluorides (NaREF₄, RE = Gd, Y, Lu) phases have been reported to be the ideal matrices for upconversion (UC) processes when doped with Ln³⁺ ions such as Yb³⁺/Er³⁺ (Tm³⁺, Ho³⁺).¹⁻⁶ NaREF₄ exists in two polymorphic forms at ambient pressure and temperature: the cubic (α) and the hexagonal (β), the latter phase in particular being the most efficient host matrix for UC emissions.

Up to now, great efforts have been made on the synthesis and applications of NaREF₄ crystals or powders suitably doped for upconversion applications,⁷⁻⁹ and in particular, hydro- and solvo-thermal methods have been applied.¹⁰⁻¹³

However, photonic applications require the upconversion materials in thin film form and so far, the fabrication of NaYF₄ and NaGdF₄ materials in thin film form has been scarcely investigated. In particular, electrodeposition,¹⁴ thermal evaporation¹⁵ and sol-gel/spin-coating approaches¹⁶ have been applied to synthesize UC NaYF₄ and/or NaGdF₄ films.

Nevertheless, a more simple and straightforward process easily scalable in view of potential industrial applications is highly required. Compared to physical vapor deposition techniques, the metalorganic chemical vapor deposition (MOCVD) takes advantage, in particular for complex phases such as the ternary phases of these NaREF₄ systems, of a simple process, a ready scalability and a higher throughput.

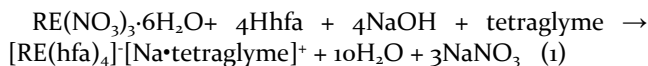
In the perspective of the synthesis of multicomponent films, the availability of suitable precursors is of crucial importance. In conventional MOCVD, the metal sources of multimetal films, such as NaREF₄, must be not only thermally stable, but also compatible in terms of volatility to easily adjust the film stoichiometry. In this context, it is highly desirable the availability of a single-source heterometallic precursor, containing all the required elements

(Na,RE,F) in a single molecule, which would not only ensure greater homogeneity at atomic levels and the absence of unnecessary contaminating ions, but it would also allow a better control of the process.

Recently, some heterobimetallic complexes containing sodium and rare-earth metals have been synthesized and applied to the fabrication of NaREF₄ nanomaterials via solution or decomposition routes.¹⁷⁻²¹ In a few cases their thermal behavior makes them potentially applicable to MOCVD processes, since quantitative sublimation was observed in an evacuated, sealed ampule at 150 °C for 24 h.²¹

In this communication, we report for the first time on the synthesis and comprehensive investigation (single crystal X-ray structure, NMR and FT-IR characterization, thermal behavior) of novel single-source heterobimetallic precursors of formula [RE(hfa)₄]⁻[Na•tetraglyme]⁺ [RE = Y (1), Gd (2)]. Their potentiality as MOCVD sources has been assessed through their applications to the deposition of NaREF₄ films. The final results proclaim these complexes as the “third-generation” precursors of MOCVD processes. In fact, they present better behavior vs. the “first-generation” precursors, i. e. simple β-diketonates, which are not very stable, giving problems of reproducibility,²² and the “second-generation” ones, i.e. polyether β-diketonate adducts, which are volatile and thermally stable but supply only one metal ion.^{22,23} Overall, these “third-generation” precursors are volatile, thermally stable and simultaneously supply all the elements required for the target phase, namely two metal ions and fluorine.

The [RE(hfa)₄]⁻[Na•tetraglyme]⁺ adducts have been prepared through a one-pot reaction from rare earth (yttrium, gadolinium) nitrate source, sodium hydroxide, hexafluoroacetylacetone and tetraglyme in dichloromethane (eqn.1)



The reaction has been conducted in a single step under simple laboratory conditions. In particular, the $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was first suspended in dichloromethane. Tetraglyme was added to the suspension. NaOH and Hhfa were added after 10 min and the mixture was refluxed under stirring for 1 h. Colorless crystals were obtained after partial evaporation of the solvent. The crystals were collected, washed with pentane, filtered, and dried under vacuum.

A slight excess of NaOH (10%) has been used in both cases. NaOH exerts a double effect: it serves as a base able to deprotonate the acidic hydrogen of Hhfa and it is the source of the sodium ion. The procedure yields reproducibly, under open bench manipulations, a clean source adduct in high yield. It has a very low melting point and evaporates quantitatively at low temperature under vacuum and even under atmospheric pressure.

The FT-IR transmittance spectra of complexes **1** and **2** (Figure S1, Supporting Information) show the absence of any band around 3500 cm^{-1} , usually due to OH stretching, thus indicating the anhydrous nature of the complexes. For adduct **1**, the peaks at 1657 , 1557 and 1530 cm^{-1} are associated with the C=O and C=C stretching vibration, typical of the β -diketonate framework. Peaks observed in the 1000 - 1300 cm^{-1} range are characteristic of the polyether C-O bending and/or stretching overlapped with the C-F stretching features. In addition, the glyme modes appear at 949 , 852 and 796 cm^{-1} .²⁴ Data for adduct **2** are commented in the SI. The FT-IR hypothesis, *i.e.* the anhydrous nature of the two complexes, was confirmed by the single crystal X-ray diffraction analysis performed on **1** and **2**. In the asymmetric unit of the two compounds (that are isomorphous and isostructural²¹) just one $[\text{Na} \cdot \text{tetraglyme}]^+$ cation and one $[\text{RE}(\text{hfa})_4]^-$ anion (RE = Y and Gd in **1** and **2**, respectively) are present. The rare earth cations [Y(III) in **1** and Gd(III) in **2**] are octa-coordinated by the oxygen atoms of four hfa anions (see Table S2). The resulting coordination polyhedron is a distorted bicapped trigonal prism with the oxygen atom O(4) and O(8) capping the O(1)-O(2)-O(3)-O(6) and O(2)-O(5)-O(6)-O(7) faces, respectively (see Figures 1, S5 and S6 for the atom labelling). The Na cation is coordinated by the five oxygen atoms of one tetraglyme molecule and by two fluorine atoms of two different hfa anions (see Figure 1 and Table S2). The resulting coordination polyhedron may be described as a pentagonal bipyramid with the five oxygen atoms defining the base. Due to the coordination around the sodium cation (one fluorine atom belongs to a symmetry related hfa anion) a 1D chain polymer, which propagates along the a-c diagonal, arises (see Figure S7). A similar propensity to form chain polymer has already been observed in other two salts (CSD refcodes = CYSFAC10²⁵ and EQUXOF²¹) having $[\text{Y}(\text{hfa})_4]^-$ as anion and an alkaline metal as cation (Cs and Na in CYSFAC10 and EQUXOD, respectively), although in these previous cases due to the absence of ancillary ligands (as in our structures the

tetraglyme molecule) the coordination of the alkaline cation is completed by the donor atoms (oxygen and/or fluorine atoms) of the hfa anion and this forces the RE and alkaline metal to stay closer (see Figures S8 and S9). In fact, in CYSFAC10 the Y \cdots (alkaline metal) shortest distance is about 4.5 \AA , while it is 3.7 \AA in EQUXOF. In **1** and **2** the Y \cdots Na shortest distance are $6.632(5)$ and $6.600(7)\text{ \AA}$, respectively.

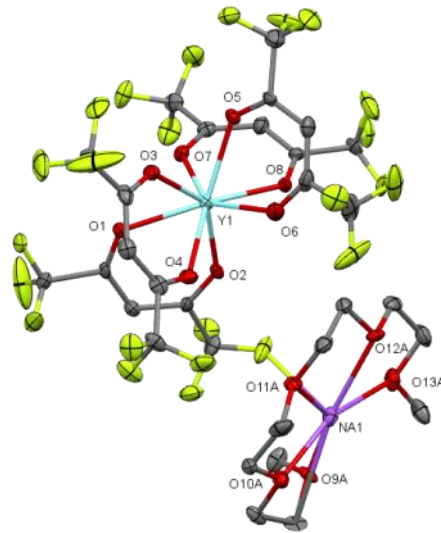


Figure 1. Ball and stick view of the $[\text{Y}(\text{hfa})_4]^- [\text{Na} \cdot \text{tetraglyme}]^+$ complex. Hydrogen atoms have been omitted for sake of clarity. Just one model for the tetraglyme molecule and for the fluorine atoms of the hfa anions are reported (see Supporting Information).

The study of the thermal properties of the $[\text{Y}(\text{hfa})_4]^- [\text{Na} \cdot \text{tetraglyme}]^+$ and $[\text{Gd}(\text{hfa})_4]^- [\text{Na} \cdot \text{tetraglyme}]^+$ adducts is a crucial step for successful applications of these precursors to MOCVD processes. The thermogravimetric (TG) measurements of **1** and **2** derivatives have been carried out at atmospheric pressure under purified nitrogen flow. The TG curve of the adduct **1**, reported in Figure 2, indicates that the β -diketonate adduct evaporates almost quantitatively in the 180 - 300°C temperature range, with a low residue ($\approx 8\%$) left at 350°C , thus indicating a clean vaporization of the precursor. The derivative curve of TG (DTG) consists of a single peak, which confirms that the complex evaporation occurs in a single step, without any-side decomposition.

In regard to the complex **2** (Figure 2), the adduct evaporates in a single step in a narrow temperature range (190 - 290°C) with a residue of 13% left at 350°C . A single step evaporation occurs also in this case, as inferred by the single peak of the derivative curve of the adduct.

From thermal analysis we can conclude that both the heterobimetallic precursors $[\text{Y}(\text{hfa})_4]^- [\text{Na} \cdot \text{tetraglyme}]^+$ and $[\text{Gd}(\text{hfa})_4]^- [\text{Na} \cdot \text{tetraglyme}]^+$ show good mass transport properties as requested for MOCVD applications, and thus

they are expected to be suitable precursors for the deposition of Na-Y-F and Na-Gd-F films, respectively.

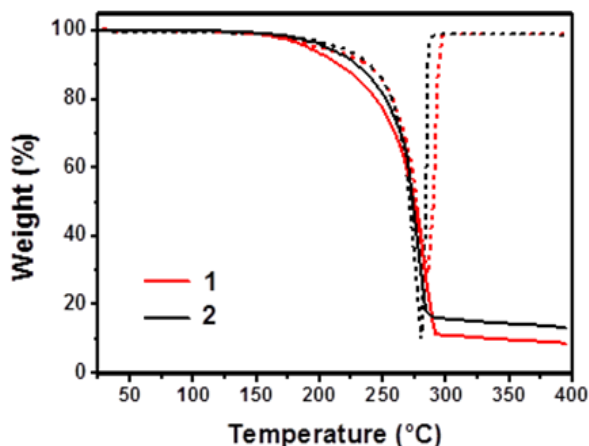


Figure 2. TG (solid lines) and their derivative curves (dashed lines) of the $[Y(hfa)_4]^- [Na\bullet tetraglyme]^+$ (1) and $[Gd(hfa)_4]^- [Na\bullet tetraglyme]^+$ (2) complexes under N_2 flow at atmospheric pressure in the 30–400 °C temperature range.

It is interesting to compare the thermal properties of these $[RE(hfa)_4]^- [Na\bullet tetraglyme]^+$ compounds with its $Na(hfa)$ tetraglyme relative, which decomposes upon heating leaving a residue of NaF .^{16a} Therefore, Y^{24b} or Gd ,²⁶ which are very volatile compounds as single metal polyether hexafluoroacetylacetonate adducts, act as a vehicle for the alkaline sodium ion from solid to vapor phase.

Hence, the validation of the $[RE(hfa)_4]^- [Na\bullet tetraglyme]^+$ heterobimetallic adducts to act as single sources of Na-RE-F elements has been assessed by applying both complexes to the MOCVD syntheses of sodium-yttrium and sodium-gadolinium fluoride films on silicon substrates (see SI for experimental details).

Film characterization from a structural point of view has been assessed by XRD analysis in a grazing incidence mode. The XRD pattern of the $NaGdF_4$ film grown at 500°C nominal deposition temperature (Figure 3a) shows peaks corresponding to 111, 200, 220 and 311 reflections of the cubic $NaGdF_4$ lattice (ICDD n° 27-0697). Similarly, the θ - 2θ pattern of the $NaYF_4$ film deposited at 500°C (Figure 3c) may be associated with the cubic phase of $NaYF_4$ (ICDD n° 06-0342). The nature of the polymorphic phase formed deserves a comment. In fact, even though the α phase is usually the less thermodynamically stable phase, it must be considered that an MOCVD deposition is a dynamic process where kinetic factors may compete with thermodynamic stability of a system. Therefore, it is evident that under the presently applied conditions the kinetic factors are predominant, yielding the α phase. In this context it is worth to note that the focus point of the present manuscript is the formation of the $NaREF_4$ phases, thus indicating that the adducts show a good behavior as MOCVD precursors, allowing to overcome many drawbacks related to the use of multisource adducts.

In regard to morphology, the FE-SEM images of the $NaGdF_4$ samples present homogenous surfaces with 100 nm grains (Figure 3b). Analogously, the $NaYF_4$ films evidence a homogeneous surface with grains having dimensions of 150 nm (Figure 3d). The root mean square (RMS) roughness, evaluated through AFM measurements (Fig. S9) on a $5\ \mu m \times 5\ \mu m$ surface of the $NaYF_4$ film is about 21 nm.

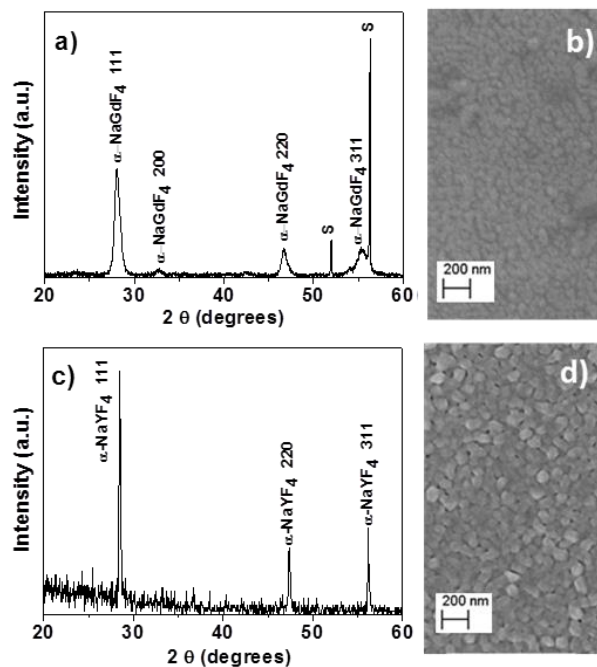


Figure 3. XRD pattern (a) and plane-view FE-SEM image (b) of the $NaGdF_4$ film and XRD pattern (c) and plane-view FE-SEM image (d) of the $NaYF_4$ film grown on Si through MOCVD. S labels indicate the peaks of silicon substrate.

In regard to the film purity, the energy dispersive X-ray (EDX) analyses point to a 0.95:1 and 1:1.06 ratio for the $NaYF_4$ and $NaGdF_4$ stoichiometries, respectively, over $10\ mm \times 10\ mm$ area. This information combined with the XRD data indicate that no minority or amorphous phases are present.

In summary, the present study is the first MOCVD synthetic report on the fabrication of $NaREF_4$ films. In addition, this challenging goal has been achieved through the use of two novel heterobimetallic $[RE(hfa)_4]^- [Na\bullet tetraglyme]^+$ adducts, which have been synthesized and successfully applied as single-source precursors for the deposition of $NaREF_4$ thin films through MOCVD processes. The thermal properties of the synthesized precursors point to their optimal characteristics for the MOCVD application in terms of volatility and thermal stability. To our knowledge, these complexes represent the first ever example of single-sources of three different elements, namely sodium, rare-earth metal and fluorine, with thermal properties suitable for MOCVD applications, thus going beyond traditional issues related to the use of separated sources.

Work is in progress on the optimization of the MOCVD process to stabilize the hexagonal phase, through a systematic variation of the deposition temperature and precursor saturation, since it is likely that both factors play a key role in the delicate balance between kinetic and thermodynamic factors affecting phase formation. Another future development of the present work is the deposition of suitably doped (Yb^{3+} , Er^{3+} or Yb^{3+} , Tm^{3+}) NaREF_4 films for up-conversion applications.

Finally, the straightforward one-pot nature of the presently reported synthetic route envisages the possibility to synthesize novel adducts with new metals, making this approach a wide-ranging strategy for the synthesis of novel "third-generation" MOCVD precursors.

ASSOCIATED CONTENT

Supporting Information. The supporting information is available free of charge via the Internet at <http://pubs.acs.org>.

Experimental details, FT-IR and NMR spectra, vaporization rates, crystallographic data of the adducts. FE-SEM cross-section images, Bragg-Brentano patterns, AFM image, EDX spectra of films (pdf file).

AUTHOR INFORMATION

Corresponding Author

* (G.M.) E-mail: gmalandrino@unict.it.

ORCID

Sergio Battiato: 0000-0002-5456-3058
Patrizia Rossi: 0000-0002-6316-338X
Paola Rossi: 0000-0002-2408-4590
Graziella Malandrino: 0000-0001-7483-3070

Present Address

§ S.B. present address is CEA-Liten 17 Avenue des Martyrs 38000 Grenoble France.

Author Contributions

All authors have given approval to the final version of the manuscript.

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