

MOCVD of complex oxide systems: from precursor chemistry to applications

Graziella Malandrino,^{*a} Roberta G. Toro,^b Raffaella Lo Nigro^c and Ignazio L. Fragalà^a

^a Dipartimento di Scienze Chimiche, Università di Catania, and INSTM, UdR Catania, Viale A. Doria 6, 95125 Catania, Italy.

^b INSTM, Centro di Riferimento “Materiali nanodimensionati per microelettronica e settori correlati”, c/o Dipartimento Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy

^c IMM, sezione di Catania, CNR, Stradale Primo Sole n 50, 95121 Catania, Italy.

Among complex oxide systems, perovskites (ABO₃) cover an important role due to their appealing and variegated functional properties. In fact, a wide variety of substitutions at both A and B sites is responsible for the great flexibility of the perovskite structure giving rise to a very large number of derivatives with subtle variations in structure. The synthesis of these complex systems is not an easy task since at least two or even four different precursors have to be applied with a stringent control of vaporization rates to afford materials with the correct stoichiometry, thus the thermal properties of used precursors play a crucial role.

This contribution will focus on the engineering of precursor molecular architectures with specific properties based on an *a priori* tailoring of the coordination environment. A variety of alkaline-, transition, and rare-earth metal β -diketonate complexes coordinated with neutral Lewis bases will be considered.

The success of an MOCVD process depends critically on the availability of volatile, thermally stable precursors that exhibit high and constant vapor pressures, since poor performances affect the film properties. Therefore, an accurate knowledge of relationship between molecular architectures and physical properties/thermal behavior of precursors is of fundamental relevance for the optimization of processes in the perspective of achieving uniform and reproducible MOCVD film growth.

It will be demonstrated that mass transport properties are strictly correlated to coordination spheres and that a fine tailoring of properties of interest for MOCVD applications is possible by adjusting the architectural framework of the complexes. On the other hand, the coordination sphere of any central metal ion crucially depends on the subtle interplay between the ionic radius and the ion charge. Namely, for a given charge, the larger the ion the higher is the coordination number. In the case of the alkaline earth metals, coordination numbers up to 11 have been observed in the case of the large Ba metal.¹ In table 1 the ionic

radii of the alkaline-earth and some selected lanthanide metals are summarized in relation to the most commonly observed coordination.

Metal ion	Ionic radius (Å)	Coordination number	Ref.
Mg(II)	0.65	6	2
Ca(II)	0.99	8	1
Sr(II)	1.13	9	1
Ba(II)	1.35	9-10	1
La(III)	1.15	9-10	3
Gd(III)	1.02	8-9	3
Ho(III)	0.96	8	4

Table 1. Correlation between ionic radii and coordination number for alkaline- and lanthanide metals.

Lanthanides are similarly large in terms of ionic radii but, at difference with the alkaline earth ions, they are 3+ ions. Nevertheless, a six-coordination, due to the “tris” hfa ligation, is usually not sufficient to complete the coordination sphere of lanthanides and a neutral ligand of appropriate length is required to yield complexes with physico-chemical properties suited to MOCVD applications. Polyether ancillary ligands play a crucial role and there is evidence of an intriguing interplay between the polyether chain length and the Ln³⁺ ionic radius in determining the volatility of these adducts, and in some cases a lengthening of the polyether chain parallels a decrease in volatility.

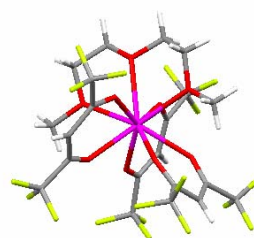


Figure 1. A scheme of lanthanide adducts with a diglyme ancillary ligand showing the most commonly observed coordination of 9 in the lanthanide series.

The relationships involving molecular architectures, thermal and transport properties, decomposition kinetics and mechanisms will be discussed in relation to deposition of advanced materials. It will be shown that applications of these precursors to the MOCVD processes of perovskite systems yield materials of good quality, both in terms of chemical composition and structural characteristics as well as in terms of functional properties.

¹ D. J. Otaway, W. S. Rees, *Coord. Chem. Rev.* **210**, 279, (2000), and references therein.

² M. E. Fragalà, R.G. Toro, P. Rossi, P. Dapporto, G. Malandrino, *Chem. Mater.*, **21**, xxx, (2009).

³ G. Malandrino, I. L. Fragalà, *Coord. Chem. Rev.*, **250**, 1605, (2006) and references therein.

⁴ S. J. Kang, Y. S. Jung, II-H. Suh, *Bull. Korean Chem. Soc.* **20**, 95, (1999).

* E-mail: gmalandrino@dipchi.unict.it