

Tailoring Molecular Precursors for Multicomponent Oxides

Liliane G. Hubert-Pfalzgraf

Universite de Lyon 1, IRC, UPR-CNRS
2 avenue A. Einstein, 69626 - Villeurbanne Cédex (France)
(Received September 23, 1998)

Simple ways to build up mixed-metal molecules which can act as potential single-source precursors to multicomponent oxides are reviewed. Emphasis is given to Lewis acid-base reactions between metal alkoxides $M(OR)_n$, and between metal alkoxides and more accessible oxide precursors, carboxylates $M(O_2CR)_n$ and β -diketonates $M(\beta\text{-dik})_n$. Characterization of the precursors is achieved in the solid state (single crystal X-ray diffraction, FT-IR) and by multinuclear NMR in solution. The reactions proceed toward the formation of aggregates in which the different metals display their usual coordinations numbers, often six for transition metals, as shown. Strategies for fixing the stoichiometry between the metals are developed. The reactivity of the MM species (dissociation, effects of chemical modifiers, of other metallic species, hydrolytic or non-hydrolytic condensation, etc.) will be indicated. Transformations into oxides are illustrated on precursors for titanates or niobates.

Key words : Precursor, Alkoxide, Mixed-metal Species, Carboxylate, Sol-gel, Lanthanides, Ferroelectrics

I. Introduction

Simple or multicomponent oxide ceramics represent an important class of advanced materials.¹⁾ Traditional routes based on reactions between solids at high temperature met severe limitations such as poor control of the properties (microstructure, surface area, etc.) and only body shaped ceramics are accessible. Molecular chemistry opens up new alternatives. Going from a molecular precursor to a ceramic corresponds to an inorganic polymerization reaction. The latter can be induced in solution by an appropriate reactant-(water for the sol-gel process)-or in the vapor phase by heat, thus featuring the MOCVD process (Metal Organic Vapor Phase Deposition).²⁾ The most obvious precursors for oxides are molecules having already metal-oxygen bonds, namely metal alkoxides $M(OR)_n$ or oxoalkoxides $MO(OR)_n$, β -diketonates $M(\beta\text{-dik})_n$ ($\text{dik}=\text{RCOCHCOR}'$) and metal carboxylates $M(O_2CR)_n$. Basic requirements of precursors are solubility for the sol-gel process, as well as for "wet MOCVD" techniques (which place less demand on the precursor than classical MOCVD), volatility and a pyrolysable character for conventional MOCVD. In terms of transformation into the materials, high ceramic yields and controlled conversion are desired. This implies to control the hydrolysis rates, access to a suitable rheology (stable sols, homogeneous gels, viscosity...) especially for coatings and, for the materials required in their crystalline form, low temperatures of crystallization.

Metal alkoxides are the most used oxide precursors due to an easy commercial availability and to the high lability of the M-OR bond allowing facile tailoring in situ during processing.³⁾ Multicomponent oxides are accessible by using

mixture of precursors or "single-source" precursors in which the metals-generally two- are incorporated in an unique molecule in a ratio matching that of the desired material.^{4,6)} Such molecules are expected to overcome the insolubility of some precursors (alkoxides of dn metals such as copper), to provide a better control of the microstructure of the final material, and, for MOCVD, to facilitate the transport of poorly volatile metal derivatives, barium for instance.⁷⁾ They can improve stability toward moisture and/or oxidation (for instance for barium) or stabilize unusual oxidation states (for instance Ce(III) as $\text{CeAl}_3(\text{OPr})$).¹²⁾

The paper will present some of our results on the synthesis and use of single-source precursors for access to multicomponent oxides via sol-gel routes.

1. Mixed-metal species vs mixtures of precursors: toward homogeneity at a molecular level ?

Homogeneity can be seen as the absence of insoluble species in a medium, or as homogeneity at a molecular level, this involving an intimate mixing of the metals in an unique molecule. Molecular design of precursors implies concern of the latter aspect. How can one obtain processible mixed-metal species ? Different strategies can be envisioned. They are based on simple Lewis acid-base reactions or on substitution reactions.

1.1. Lewis acid- base reactions

Such reactions are based on the mixing of alkoxides and of other oxide precursors of different metals. They are largely used for wet chemical routes (sol-gel, aerosol assisted CVD) for their convenience since no isolation of the effective precursor is required. With the exception of silicon alkox-

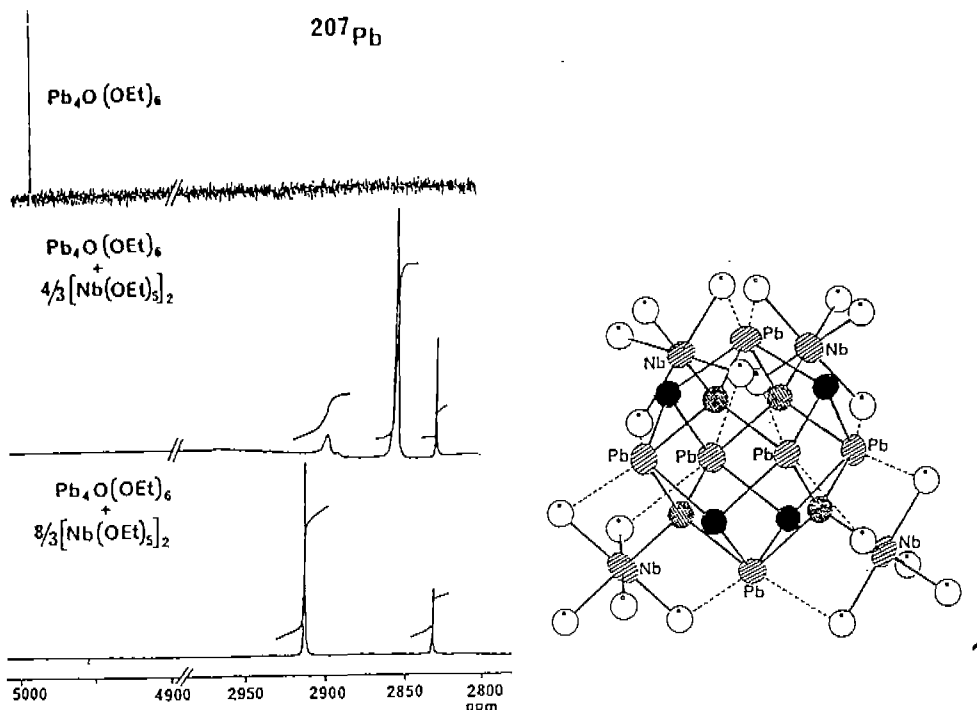
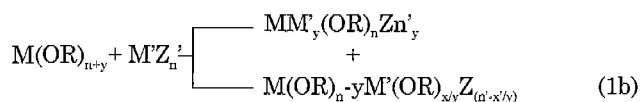


Fig. 1. $^{207}\text{Pb}\{^1\text{H}\}$ NMR as a tool for studies of multimetallic systems. The $\text{Pb}_4\text{O}(\text{OEt})_6\text{-Nb}(\text{OEt})_5$ system in toluene.

ides (which are inert and must be prehydrolysed as $\text{R}_3\text{Si}(\text{OH})$ species for formation of M-O-Si bonds), all reactions between metal alkoxides were considered to lead to heterometallic alkoxides, generally more soluble than the starting materials, via dissolution of insoluble homometallic alkoxides. However data on molecular composition of solutions derived from simple mixing remain limited. The stoichiometry of the reaction is determined a posteriori after isolation and characterization of the compounds. The distribution of products of such reactions is at the mercy of thermodynamic control. This is a drawback when stoichiometric control is important as for some electroceramics, that criteria is less important when only atomic scale mixing of the metals has to be reached. Reactions between metal alkoxides and more accessible oxide precursors namely acetates, β -diketonates or nitrates⁹ are alternative routes to mixed-metal species (eq 1a) or, if the latter are unstable, to heteroleptic (mixed ligands) homometallic species (eq 1b)



where $\text{Z} = \text{OAc}$, β -dik, NO_3

The difficulty of the reactions involving only metal alkoxides is to get insight into the system. FT-IR data provide little information. Multinuclear NMR appears as one of the most powerful tool if the metal is active and sensitive. Nuclei having spin $I=1/2$ and thus offering high resolution spectra have been used. ^{29}Si NMR and the less common ^{207}Pb NMR illustrate the potential.

Chemical routes to lead oxide materials have special value

in material science due to the high volatility of lead oxide resulting in a difficult control of the stoichiometry for solid state routes. Monitoring of the reaction between lead oxoalkoxide $\text{Pb}_4\text{O}(\text{OEt})_6$ and $\text{Nb}(\text{OEt})_5$ by ^{207}Pb NMR gave evidence for a reaction (shift to higher frequencies, increase of the solubility) and suggested a stoichiometry around 2 : 3 (Fig. 1). However the lack of well characterized compounds which can be used as references for lead limits structural conclusions during association as well as subsequent transformation by hydrolysis-polycondensation. More information was obtained by isolation and characterization by single crystal X-ray diffraction of the species, namely $\text{Pb}_6\text{-Nb}_4(\mu_4\text{-O})_4(\text{OEt})_{24}$ (1).⁹ An interesting point is that the ratio between the metals matches that required by the PNM ceramic, $\text{PbNb}_{2/3}\text{Mg}_{1/3}\text{O}_3$. 1 can be considered as a complex between $\text{Pb}_6\text{O}_4(\text{OEt})_4$, derived from $\text{Pb}_4\text{O}(\text{OEt})_6$, and the niobium alkoxide via the peripheral oxo ligands. Similar spontaneous generation of oxo ligands affords the Pb-Ti species, $\text{Pb}_2\text{Ti}_2\text{O}(\text{OiPr})_{10}$ (2) starting from the non-oxo alkoxides $[\text{Pb}(\text{OiPr})_2]^\circ$ and $\text{Ti}(\text{OiPr})_4$.¹⁰ These reactions are facile since lead displays an extensive oxoalkoxide chemistry. By contrast, no reaction was observed between titanium or niobium isopropoxides and the insoluble bismuth or zinc isopropoxides (see 2.1.2).

1.1.1. Can oxoalkoxide clusters form MM' species ?

Many metal alkoxides are actually oxoalkoxide clusters, such as $\text{Pb}_4\text{O}(\text{OEt})_6$. Can they undergo formation of mixed-metal species and provide homogeneity at a molecular level. Lanthanide derivatives offer a large variety of oxoalkoxide clusters. Compounds of type $\text{Ln}_4\text{Ti}(\mu_5\text{-O})(\text{OPr})_{14}$ can be ob-

tained by mixing of lanthanide oxoisopropoxides $\text{Ln}_3(\mu_3\text{-O})(\text{OPr})_{13}$ ($\text{Ln}=\text{Y}, \text{Nd}, \text{Sm}, \dots$) and titanium isopropoxide at room temperature. Zirconium analogs $\text{Ln}_4\text{ZrO}(\text{OPr})_{14}$ are obtained in similar conditions but their formation is less favored probably as a result of the dimeric nature of zirconium isopropoxide. These species can be seen as adducts between $\text{M}(\text{OR})_4$ and $\text{Ln}_4\text{O}(\text{OR})_{10}$ via the central oxo ligand.^{11,12} They could give access to homogeneous dispersions of the rare earth metal oxide into an inorganic MO_2 oxide matrix. One can notice that the stereolability of metal alkoxides or oxoalkoxides allows easy access to mixed-metal species. Oxoalkoxide clusters do not hinder the formation of MM' species but might actually offer an anchoring site for the other metal via the oxo ligand.

1.1.2. How can one promote the formation of mixed-metal species ?

Bismuth based electrooptical materials are currently of high interest due to their lower fatigue, by comparison to PLZT for instance.¹³ Bismuth acetate is rather inert. No reaction was observed between titanium or tantalum isopropoxides and the insoluble bismuth isopropoxide, illustrating the fact that formation of MM' species by mixing metal alkoxides is not as general as stated, especially when polymeric and/or insoluble metal alkoxides are involved.

Thermal activation is precluded due to the tendency of bismuth alkoxides to decompose into colloidal metal. The formation of Bi-Ti species can however be induced by microhydrolysis. $\text{BiTi}_2(\mu_3\text{-O})(\text{OiPr})_9$ can be obtained but the use of ethoxides is a better choice since a species whose formula, $\text{Bi}_4\text{Ti}_3\text{O}_4(\text{OEt})_{16}$, is directly related to the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ electroptic, is formed.¹⁴ One can emphasize that for many insoluble alkoxides, depolymerization cannot be achieved by other metal alkoxides in anhydrous conditions, dissolution and thus depolymerisation is promoted by the presence of water. Such a situation is encountered, by accident, in material science where commercial and thus non-anhydrous solvents are used. For many systems involving homoleptic alkoxides of different metals, oxoalkoxides are actually the true reactive species for access to MM' species.

The Ta-Zn system is another example illustrating the low reactivity of some alkoxides toward formation of heterometallic species. Generation of the oxo ligands, required for assembling the different metals can here be generated by ultrasonic activation. $\text{Ta}_4\text{Zn}_2(\mu_2\text{-O})_2(\mu_3\text{-O})_2(\text{OiPr})_{16}$ (3) results from the reaction of $[\text{Zn}(\text{OPr})_2]$ (and $\text{Ta}(\text{OPr})_5$). Its structure based on two triangular units shows that important reorganization-generation of four oxo ligands has occurred and is presumably the origin of the need for activation for the Ta (or Nb)-Zn system.¹⁵ It also shows, that by contrast with most oxoalkoxides, the oxo ligands have a small connectivity-doubly and triply bridging-in order to decrease the coordination number (CN) of the pentavalent tantalum centre to its usual value, namely six.

Absence of homogeneity at a molecular level was also observed by mixing cerium isopropoxide $\text{Ce}_2(\text{OPr})_8(\text{PriOH})_2$

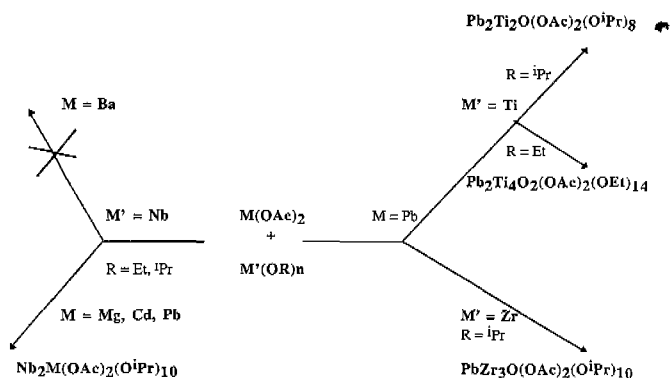
and barium, titanium or niobium isopropoxides. The use of ancillary ligands such as β -diketones,¹⁶ pinacol¹⁷ promoted the formation of mixed-metal species and thus homogeneity at a molecular level. Addition of acetic acid to a mixture of titanium and zirconium alkoxides in isopropanol afforded $\text{Zr}_2\text{Ti}_4\text{O}_4(\text{OPr})_8(\text{OPr})_2(\text{OAc})_4$ and $\text{Zr}_6\text{Ti}_3\text{O}_6(\text{OPr})_{16}(\text{OAc})_8$ respectively as established by X-ray diffraction.¹⁸ The latter reactions are quite complex since water is generated by esterification and the assembly between the metals is actually ensured by oxo and acetato ligands.

1.1.3. Can one modify the stoichiometry MM' between the metals ?

While the reactions between lithium and niobium alkoxides or lead and titanium isopropoxides proceed toward the formation of only one MM' species, which interestingly displays the stoichiometry needed for applications, the situation can be less ideal as observed for the Ti-Ba or Ti-Sr systems. Mixing barium and titanium alkoxides ($\text{R}=\text{Et}, \text{Pr}$) in a 1 : 1 stoichiometry, as required for BaTiO_3 gives several MM' species but not the expected one $[\text{BaTi}(\text{OR})_6]_m$,¹⁹ since this stoichiometry is unable to satisfy the high CN required for barium. Oxo ligands can permit to adjust the stoichiometry leading to $\text{Ti}_4\text{Ba}_4\text{O}_4(\text{OPr})_{16}(\text{PriOH})_4$ but homogeneity at the atomic scale is lost upon redissolution.¹⁹

Chelating ligands such as β -diketonates or carboxylates should also achieve high CN for barium. Barium acetate, however, is inert. By contrast, the reaction between titanium ethoxide and barium tetramethylheptanedionate affords $\text{Ba}_2\text{Ti}_2(\text{thd})_4(\text{OEt})_8(\text{EtOH})_2$ 4 ($\text{thd}=\text{tBuCOCH}_2\text{COtBu}$) by self-assembly.²⁰ Each metal bears a chelating β -diketonate, additional ethanol molecules allow barium to be seven-coordinate. The insoluble barium acetylacetonate can be used as well for access to Ba-Ti species of 1 : 1 stoichiometry but the structure of the resulting species is different. Titanium ethoxide and isopropoxide behave differently and a Ba-Ti species of 1 : 1 stoichiometry is no longer obtained for isopropoxide. Sr-Ti species of 1 : 1 stoichiometry are accessible by a similar route independently of the alkoxide, isopropoxide or ethoxide.²¹ The structure of $\text{Sr}_2\text{Ti}_2(\text{thd})_4(\text{OiPr})_8$ is related to that of the BaTi species but strontium is only 6-coordinated since no alcohol is present in its coordination sphere.

Reactions between metal alkoxides and β -diketonates are prone to formation of homometallic species as a result of redistribution reactions (eq 1b). The Ba-Ti and Sr-Ti examples show that a convenient set of ligands can stabilize mixed-metal β -diketonatoalkoxides. The structure of the Ba-Ti species is retained in non-polar solvents. However as a general feature, mixed-metal β -diketonatoalkoxides are more sensitive toward Lewis bases than homoleptic mixed-metal alkoxides owing to the rich coordination chemistry of the β -diketonates as compared to that of metal alkoxides.²² Segregation of 4 is for instance promoted in diglyme giving $\text{Ba}(\text{thd})_2(\text{diglyme})$ and $\text{Ti}(\text{OEt})_4$.



Scheme 1. Reactivity of $M(\text{OAc})_2$ toward group 5 and group 4 metal alkoxides.

1.1.4. Use of carboxylates as associated oxide precursors?

Sol-gel techniques use often 2-ethylhexanoates as soluble carboxylates. Acetates are better in terms of ceramic yield and they could leave less carbonaceous residues but they have been neglected due to their poor solubility. Are these oxide precursors without value for solution routes or can one take advantage of acetates as bridging ligands for assembling different metals?

The reactions between niobium alkoxides $\text{Nb}(\text{OR})_5$ ($R = \text{Et}, \text{iPr}$) and anhydrous acetates $M(\text{OAc})_2$ ($M = \text{Mg}, \text{Ba}, \text{Pb}, \text{Cd}$) were investigated (Scheme 1). With the exception of barium, the reactions proceed smoothly at room temperature in solvents such as hydrocarbons and are evidenced by the dissolution of the acetates giving $\text{Nb}_2M(\mu\text{-OAc})_2(\text{OR})_{10}$.²³ The formulation of **5** corresponds to simple adducts (no ester ROAc) is eliminated at room temperature) since hexacoordination of the metals is achieved without the need of an oxo ligand. Isopropoxides are more reactive than ethoxides due to the presence of monomeric moieties. The choice of the solvent might be crucial since it can act as a competing ligand toward the metal carboxylate. Barium acetate remains inert even under refluxing or in the presence of acetic acid.

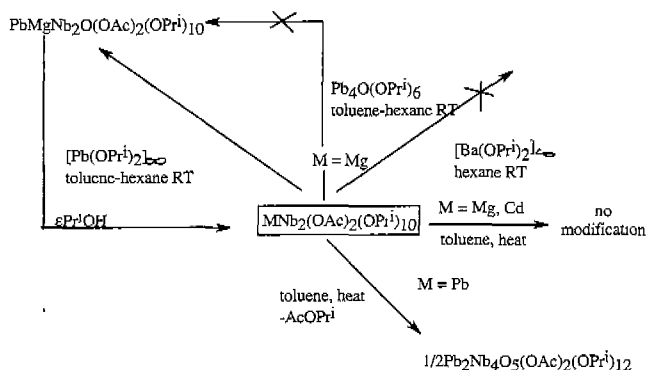
The reactions are more diverse when anhydrous lead acetate is reacted with group 4 metal alkoxides. Mixed-metal species having oxo ligands are formed in all cases even at room temperature, their MM' stoichiometry is function of the metal, titanium or zirconium, and of the R group. $\text{Pb}_2\text{Ti}_2\text{O}(\text{OiPr})_8(\text{OAc})_2$ only, matches the stoichiometry of PbTiO_3 .¹⁰ The non-formation of Pb-Zr species of 1 : 1 stoichiometry by mixing zirconium isopropoxide with lead isopropoxide²⁴ or lead acetate ($\text{PbZr}_3\text{O}(\text{OAc})_2(\text{OPri})_{10}$ is formed in the latter case) accounts for the tendency to metal segregation for solution routes to PbZrO_3 . FT-IR data and especially the difference in the $\nu_{\text{as}}\text{CO}_2$ and $\nu_{\text{s}}\text{CO}_2$ stretching frequencies (< to 200 cm^{-1} in all cases) suggests that the acetate ligands are in bridging or chelating positions for all derivatives.

What is the origin of the different behaviour between niobium and titanium alkoxides with respect to $\text{Pb}(\text{OAc})_2$ adducts for the former, oxo derivatives for the latter? X-ray

structural data provide some explanation while they also establish unequivocally the heterometallic nature of the species. Acetate ligands clamp the different metals together; the transition metals, niobium or titanium are both 6-coordinate having thus the coordination number required for the perovskites. This usual coordination number is easily achieved for the pentavalent niobium but requires an additional multidentate ligand for group 4 metals. The oxo ligand O^{2-} which is generated spontaneously from alkoxide ligands at room temperature (via the elimination of RCOMe esters at higher temperatures giving then different, more condensed Pb-Ti products)^{10,25} and which assembles here four metals allows to attain hexacoordination.

Lanthanide acetates can also react with alkoxides such as zirconium isopropoxide but heating is required. $[\text{GdZr}_3(\mu_4\text{-O})(\text{OAc})_3(\text{OPri})_{10}]_2$ is formed. Its structure is based on the assembly via acetates of two tetranuclear $\text{GdZr}_3\text{O}(\text{OAc})_2(\text{OPri})_{10}$ units,¹¹ analogous to $\text{PbZr}_3\text{O}(\text{OAc})_2(\text{OPri})_{10}$. One can thus notice that the structure of mixed-metal species involves some *basic building blocks*. Zirconium 2-methoxyethoxide is more reactive and dissolution of the lanthanide acetate is achieved at room temperature in a 1 : 1 stoichiometry. Scheme 2 collects some of the basic building blocks observed for mixed-metal species. One can notice that the alternating hexacoordinated metals $M = \text{Mg}, \text{Pb}, \text{Cd}$ and niobium in **5** preform the columbite network.

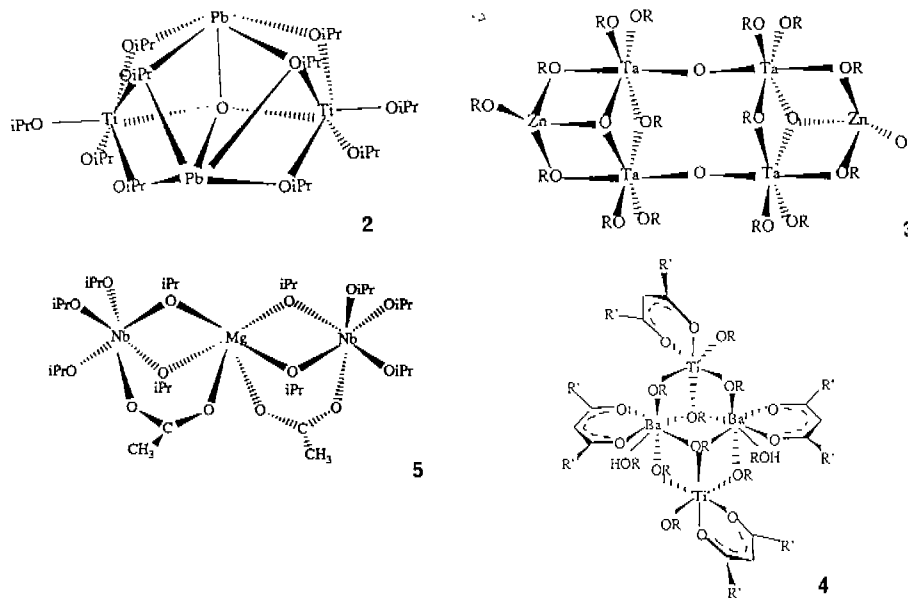
NMR data (^1H , ^{13}C , ^{207}Pb , ^{113}Cd) indicate that the solid state structures of all preceding species are retained in non-polar solutions. ^{207}Pb NMR data of the Pb-Ti and Pb-Nb species indicate a decrease in the chemical shifts with respect to the lead derivatives. This corresponds to an increase in the coordination number of lead, from four to five or six in the single-source precursors.



Scheme 2. Reactivity of the $\text{MNb}_2(\text{OAc})_2(\text{OPri})_{10}$ ($M = \text{Mg}, \text{Cd}, \text{Pb}$) species.

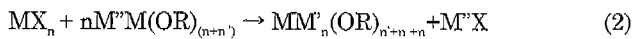
2. How to control the stoichiometry between the metals? Use of metalloligands

For all reactions based on Lewis acid-base interactions, the stoichiometry of the MM' species is determined a posteriori. *Rational construction* of MM' species requires control of the stoichiometry between the metals. This can be achieved by synthetic routes based on metathesis reactions

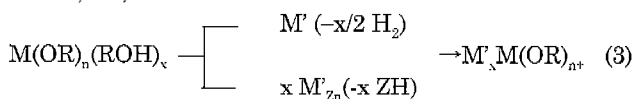


Scheme 3.

(eq. 2), or on strategies using the reactivity of coordinated ligands, the most common being alcohols (eq. 3). The driving force of these reactions is the elimination of insoluble or volatile by-products.^{5,6)} The latter reactions can be used directly during the processing.

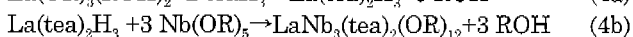
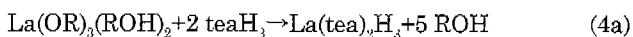


$M' = \text{Li, Na, K}$



with $Z = \text{H, R, NR}_2$

These reactions rely on the availability of appropriate synthons, namely heterometallic alkoxides for instance based on alkali metals (eq. 2) or alcohol solvates²⁶⁾ (eq. 3). The acidity of alcohol is enhanced by coordination but stable alcohol solvates are not always available with usual alcohols. Hydroxyl functionalities can generally be introduced in the coordination sphere by reacting metal alkoxides with polyols such as triethanolamine, pinacol, etc. These species act as metalloligands. The formation of $\text{LaNb}_3(\text{tea})_2(\text{OR})_{12}$ ($\text{R} = \text{Pr}^i$, $\text{teaH}_3 = \text{triethanolamine}$)²⁷⁾ and of the cerium (IV)-titanium pinacolate $\text{Ce}_2\text{Ti}_2\text{O}_2(\text{pin})_2(\text{pinH})_2(\text{OiPr})_6$ [$\text{pinH}_2 = \text{pinacol} = \text{Me}_2\text{C}(\text{OH})\text{C}(\text{OH})\text{Me}_2$]²⁸⁾ illustrates this strategy,¹⁷⁾ the parent alcohol being eliminated in the process. For the La-Nb species, the central atrane acts as a *template* as well as an assembling ligand.²⁷⁾ Some degree of *topological control* can thus be exerted by use of metalloligands based on an appropriate polyfunctional organic fragment.



where the H in the polyol and complex formulation stand for the hydroxyles

2.1. What reactivity can be expected for mixed-metal species ?

Chemical modification of homoleptic mixed-metal alkoxides may also give access to single-source precursors as well as tailor their properties. A basic question is: does the reaction proceed with conservation or modification of the stoichiometry between M and M' ? Data remain scarce but we have observed a trend for the modification of the stoichiometry via the extrusion of insoluble species usually based on main group elements. The reaction between $\text{Pb}_2\text{Ti}_2\text{O}(\text{OiPr})_{10}$ and controlled amounts of acetic acid or acetylacetonone giving $\text{Pb}_2\text{Ti}_2(\mu_4\text{-O})\text{Z}_2(\text{OPri})_8$ ($\text{Z} = \text{OAc, acac}$) is a rare example of chemical modification with retention of the stoichiometry since only small structural variations occur by introduction of the bidentate ligands (all metals are assembled around a central μ_4 -oxo ligand).¹⁰⁾

The structure of MM' species is usually retained in non-polar solvents. Hydrolysis-polycondensation reactions are mostly performed in polar media, the parent alcohol. This is not always the best choice especially for MM' species based on classical OR ligands only or for β -diketonatoalkoxides. Alcohol can promote dissociation if stable solvates $\text{M}(\text{OR})_n(\text{ROH})_x$ or $\text{MZ}_2(\text{ROH})_y$ can be formed, precipitation of insoluble species is another possible drawback. Precipitation of barium isopropoxide was observed by dissolution at room temperature of a Ba-Ce isopropoxide, $\text{Ce}_4\text{Ba}_2(\text{OPr})_{20}$, in isopropanol.¹⁶⁾ Addition of a common modifier, 2-methoxyethanol, to a solution of $\text{Nb}_4\text{Pb}_6\text{O}_4(\text{OEt})_{24}$ promotes the precipitation of insoluble, polymeric lead methoxyethoxide and thus change in the stoichiometry. These examples show that some knowledge about basic chemistry of a system is desirable in order to select appropriate solvents and/or additives.

2.1.1. What about reactions with other metallic species?

Investigation of a number of systems has indicated that formation of terheterometallic species in processing conditions (without the driving force of precipitation of alkali metal halides (i.e. eq. 2), although accessible, requires a special set of ligands. Thus if three or more different metals are involved, the medium is likely to be a mixture of heterometallic species based on two different metals only. Scheme 3 summarizes the reactivity trends of $MNb_2(OAc)_2(OPri)_{10}$. Species involving lead are more sensitive to thermal condensation via elimination of isopropylacetate (ν_{CO_2} 1759 cm^{-1}) than those based on other divalent metals such as magnesium or cadmium. This is probably related to the stereochemical versatility of the lead centres which, by contrast to the other metals can adopt a variety of CN and display a lone pair.²³⁾

Knowledge of the intermediates on the way to the material remains scarce: does the hydrolysis-polycondensation reactions proceed via heterometallic M-O-M' or via homometallic M-O-M and M'-O-M' species? Getting insight is difficult in general, as a result of the lack of appropriate techniques for studies in situ or of amorphous intermediates. Studies are essentially limited to M-O-Si²⁹⁾ or M-O-Al systems.³⁰⁾ Investigations of the first steps of hydrolysis polycondensation reactions have indicated conservation of the stoichiometry between the metals for the $LiNb(OEt)_6$ species directly related to $LiNbO_3$.²⁾ The Ba-Ti system, by contrast, illustrates the complexity which can be encoun-

tered for heavy metals displaying a variety of CN and/or alkoxide ligands having numerous coordination modes. Hydrolysis of Ba and Ti 2-methoxyethoxides leads to the isolation of $Ba_4Ti_3O_{18}(OC_2H_4OMe)_6$. Segregation is also favored here by slow processing (about 2 months).³⁾

3. Condensation reactions: Processing into materials

Various mixed-metal species based on niobium or titanium and having a MM' stoichiometry related to materials can be available easily and in high yields (>80%). Are these precursors useful for material science? Is control of the stoichiometry between the metals enough? what is the benefit of mixing of the metals on the molecular scale?

Table 1 collects the results of the hydrolysis polycondensation of species with different MM' stoichiometries. The value of a mixed-metal species with respect to a mixture of precursors can be illustrated by the Ta-Zn or Bi-Ti systems. Hydrolysis of $Bi_4Ti_3O_6(OEt)_{16}$ in THF offers directly $Bi_4Ti_3O_{12}$ which crystallizes at 470°C. This temperature is ~200°C lower than that for other solution routes to $Bi_4Ti_3O_{12}$,¹⁴⁾ using $Ti(OR)_4$ associated to bismuth acetate or nitrate, since no pyrochlore is formed as intermediate. Indeed, solutions containing $Bi(OAc)_3$ and $Ti(OEt)_4$ (4 : 3 stoichiometry) in 2-methoxyethanol and in which no molecular homogeneity exists, lead to a multiphased material, $Bi_2Ti_2O_7$ and $Bi_4Ti_3O_{12}$ at 500°C requiring temperatures up to 700°C for conversion into the pure perovskite.³¹⁾ $Bi_4Ti_3O_{12}$ is obtained as a powder starting from the ethoxide but the rheology can be tailored by using 2-meth-

Table 1. Conversion of Mixed-Metal Species by Hydrolysis-Polycondensation

Compound	Hydrolysis conditions (RT)	Onset of crystallisation	T°C	Crystalline material (XRD)
A) Niobates and tantalates				
$MgNb_2(OAc)_2(OPri)_{10}$	THF (0.1 M)	600		$MgNb_2O_6$
$MgNb_2(OPri)_{12}$	PriOH (0.06 M)	850		$MgNb_2O_6$
$MgNb_2(OEt)_{12}(EtOH)_2$	EtOH (0.02 M)	650		$CdNb_2O_6$
$CdNb_2(OAc)_2(OPri)_{10}$	THF (0.1 M)	600		$PbNb_2O_6$
$PbNb_2(OAc)_2(OPri)_{10}$	Pri OH (0.1 M)	600	800	$PbNb_2O_6 + PbNb_4O_{11}(\epsilon)$
$[PbNb_2O(OPri)_{10}]_m$	Pri OH (0.1 M)	600		$Pb_3Nb_4O_{13}$
$Zn_2Ta_4O_4(OPri)_{16}$	THF (0.02 M)	750	750	$Pb_3Nb_4O_{13} + PbNb_4O_{11}(\epsilon)$
$Zn_2Ta_4I_2(OPri)_{14}$	Pri OH (0.05 M)			$ZnTa_2O_6$
$Zn(OEt)_2 + 2Ta(OEt)_5$	EtOH	800	1,000	$ZnTa_2O_6 + Zn_3Ta_2O_8(\epsilon) + Ta_2O_5(\epsilon)$
B) Titanates and zirconates				
$Pb_2Ti_2O(OPri)_{10}$	Pri OH (0.1 M)	475		$Ta_2O_5(\epsilon) + ZnO$
$Pb_2Ti_2O(OAc)_2(OPri)_8$	THF (0.01 M)	600	700	$Pb_2Ti_2O_6 + PbTiO_3$
	PriOH+acetone	500		$PbTiO_3$
$Pb_2Ti_4O(OAc)_2(OEt)_{14}$	THF (0.01 M)	600	1,000	$PbTiO_3$
$PbZr_3O(OAc)_2(OPri)_{10}$	THF (0.01 M)	600		$PbTi_3O_6 + red PbO$
				$PbTiO_3 + TiO_2$ (rutile)
$PbTi_2O(OEt)_8$	EtOH (0.05 M)	650	800	cubic ZrO_2 + amorphous material
				$PbZrO_3 + cubic ZrO_2$
$Gd_2Zr_6O_2(OAc)_6(OPri)_{20}$	THF (0.01 M)	600		$PbTiO_7 + red PbO$
$Bi_4Ti_3O_6(OEt)_{16}$	THF (0.01 M)	470		cubic $ZrO_2 + Gd_2O_3$ (solid solution)
	THF (0.01 M)			$Bi_4Ti_3O_{12}$

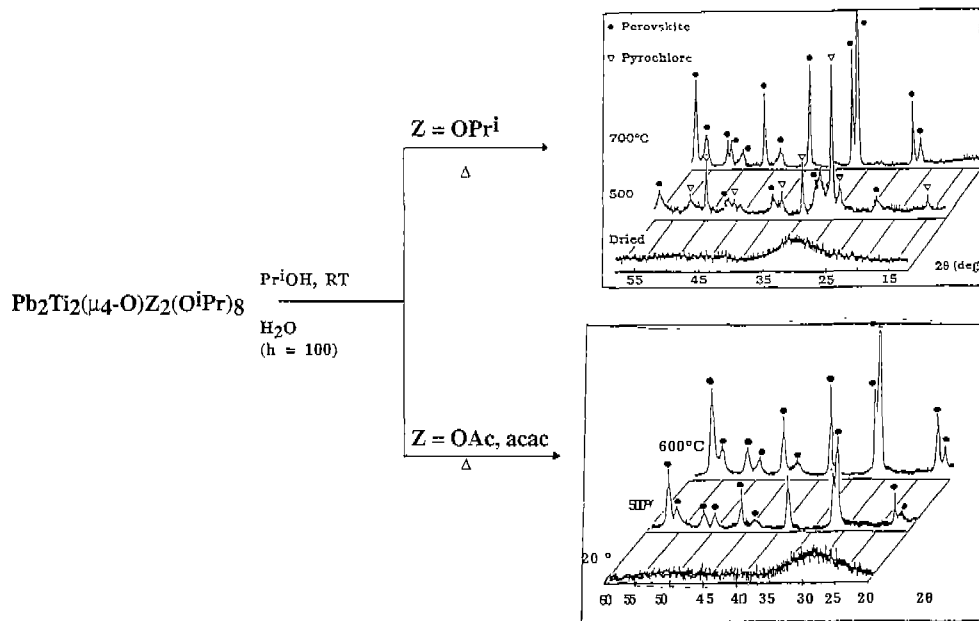


Fig. 2. Hydrolysis-condensation of various lead-titanium precursors.

oxyethoxides in the parent alcohol. Hydrolysis affords physical gels easily converted into sols which can be spread on silica wafers by spin-coating techniques. Coatings up to 150 nm thickness can be built up.¹⁴⁾ Crystallization of the perovskite is observed at 500°C.

3.1. What is the effect of the ancillary ligands ?

The various $\text{Pb}_2\text{Ti}_2(\mu_4\text{-O})(\text{OiPr})_8\text{Z}_2$ species ($\text{Z}=\text{O}^i\text{Pr}$, OAc, acac) allow to estimate the effect of ancillary ligands Z. Hydrolysis was achieved in similar conditions ($[\text{PrOH}]$, 0.01 M.l^{-1} , hydrolysis ratio $h=[\text{H}_2\text{O}]/[\text{Pb}_2\text{Ti}_2\text{O}(\text{OiPr})_8\text{Z}_2]=100$). Amorphous powders are obtained but they have different characteristics.⁹⁾ The FT-IR spectra of the powders resulting from the acetate or acetylacetonate derivatives show νCO absorptions bands ($1600\text{-}1400\text{ cm}^{-1}$) indicating differential hydrolysis (chelating ligands are less susceptible to water). These ligands are eliminated below 400°C as shown by TGA and leave no carbonates residues. They allow a controlled transformation into the material and PbTiO_3 is obtained directly at 500°C. By contrast, crystallization of the powders derived from $\text{Pb}_2\text{Ti}_2\text{O}(\text{OiPr})_{10}$ (Fig. 2) gives $\text{Pb}_2\text{Ti}_2\text{O}_6$, heating to 700°C is needed for pure PbTiO_3 .¹⁰⁾

The effect of ancillary ligands can also be seen with the Ba-Ti precursors. The β -diketonate preclude extensive polymerization and sols are formed by hydrolysis. However, the structure of the Ba-Ti acetylacetonate in which the β -diketonates are all on barium favours segregation and a multiphase material (BaTiO_3 , BaTi_2O_5 and BaO) is crystallized at 800°C. By contrast pure BaTiO_3 results from the hydrolysis of $\text{Ba}_2\text{Ti}_2(\text{thd})_4(\text{OEt})_8(\text{EtOH})_2$.²⁰⁾

3.2. Effect of the solvent: Non-hydrolytic condensation

An undesirable effect of a solvent is to promote segregation between the metals. A more attractive aspect is to change the condensations mechanism. Use of acetone as a solvent for $\text{Pb}_2\text{Ti}_2\text{O}(\text{OAc})_2(\text{O}^i\text{Pr})_8$ for instance leads to a precipitate having spectroscopic characteristics similar to those obtained by addition of water, namely broad absorption bands around 800 cm^{-1} accounting for M-O-M bonds. Is the formation of these M-O-M bonds the result of accidental hydrolysis or of a reaction with acetone? Proton NMR monitoring indicates a reaction leading to a precipitate and mesityl oxide. Acetone can induce non hydrolytic sol-gel condensation.³²⁾ Its extent is related to the basicity of metal alkoxides. From a molecular chemistry point of view, these reactions proceed via the formation of an enolate. This was confirmed by the isolation of $\text{Ti}_3(\mu_3\text{-O})_2(\text{O}^i\text{Pr})_5(\text{OCMe}=\text{CH}_2)_3$ ($^i\text{PrOH}$) obtained by condensation of $\text{Ti}(\text{O}^i\text{Pr})_4$ in neat acetone. This titanium species is a precursor to organic-inorganic materials via polymerisation with organic moieties.³³⁾ From a material science point of view, the use of acetone associated to isopropanol (1/4 in volume) for the hydrolysis medium of $\text{Pb}_2\text{Ti}_2\text{O}(\text{OAc})_2(\text{OiPr})_8$ allows a decrease in the particle size (from 9800 nm to 235 nm) and of the temperature of crystallization of lead titanate. Use of acetone allows also to control the nature of the crystalline phase, it avoids the formation of pyrochlore in the transformation of $\text{Pb}_2\text{Ti}_2\text{O}(\text{O}^i\text{Pr})_{10}$. Acetone can thus be a handle in sol-gel chemistry.³⁴⁾ Fig. 3 illustrates the effect of acetylacetonate on the particle size.

IV. Conclusion

A large range of mixed-metal species is accessible in mild conditions, often at room temperature, by mixing metal

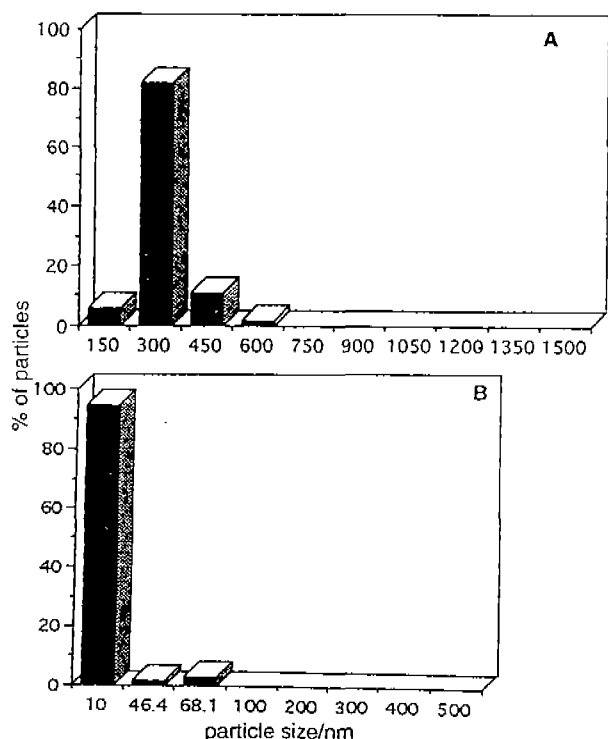


Fig. 3. Comparison of the particle size (in nm) of the sols resulting from hydrolysis of $\text{Pb}_2\text{Ti}_2\text{O}(\text{OiPr})_8\text{Z}_2$ Z=acac (a) Z=OAc (b) in acetone: isopropanol (1 : 4) for $h=100$.

alkoxides (or oxoalkoxides) and appropriate other oxide precursors. "Single-source" precursors of MTiO_3 ($M=\text{Pb}, \text{Ba}, \text{Sr}$) are available. The choice of an OR group, of an ancillary ligand Z, acetates or different β -diketonates, is not innocent for access to precursors matching the MM' stoichiometry of materials by using Lewis acid-base reactions. One can notice the importance of an oxo ligand; the versatility of its coordination modes (μ_2 - to μ_6 -) allows to adjust the coordination number of the metals. It can be essential for the reactivity of some metal alkoxides and can be generated by traces of water or of dioxygen,³⁵ from alkoxide ligands or by elimination of esters when carboxylic moieties are involved. Control of the stoichiometry between the metals can be achieved in processing conditions (formation of volatile by-products) by using the reactivity of coordinated ligands, alcohols or polyols especially. From a structural point of view, transition metals display generally their common coordination number, six, in the precursors while the situation is more diverse for the main group metals with the need for barium to proceed to high CN while lead and bismuth have relatively low CN (as compared to solid state chemistry and perovskites related structures) and stereochemically active lone pairs. Important structural changes are thus likely to occur during the passage from the precursor to materials and control of the stoichiometry between the metals is not the only criteria of importance for the transformation. The other ligands (acetates, β -diketonates,...) play an important role which remains to

be fully understood: what is their effect on the stabilization or destabilization of intermediate phases and as a result on the temperature of crystallization? Dissociation processes, promoted either by a poor choice of the solvent or by structural features such as ligation via peripheral oxo ligands, will lead to multiphased materials and thus to higher crystallization temperatures. The use of acetone as cosolvent is a handle which deserves more investigation especially for control of particle size. Better knowledge about the behavior of polyhydroxylated systems is desirable for access to appropriate rheology without the toxic 2-methoxyethanol and for getting homogeneity at a molecular level.

Acknowledgments

The author is grateful to the CNRS for financial support and to the contributions of coworkers whose names are listed in the references.

References

1. G. H. Haertling, *Electrooptical Ceramics*, L. M. Editor, M. Dekker, New York, (1988).
2. L. G. Hubert-Pfalzgraf, "Metal Alkoxides for Electrooptical Ceramics," *Processing of Ceramics*, Ed. B. I. Lee and E. J. A. Pope, M. Dekker, New-York 1995, chap. 2. L. G. Hubert-Pfalzgraf, "Metal Alkoxides and β -Diketonates as Precursors for Oxide and Non-oxide Thin Films," *Appl. Organometal. Chem.*, **6**, 627, (1992). L. G. Hubert-Pfalzgraf, "Alkoxides as Molecular Precursors for Oxide Based Materials: Opportunities for New Materials" *New J. Chem.*, **11**, 663 (1987).
3. D. C. Bradley, R. C. Mehrotra and D. P. Gaur, *Metal Alkoxides*, Academic Press, London, (1968).
4. D. C. Chandler, C. Roger and M. J. Hampden-Smith, "Chemical Aspects of Solution Routes to Perovskite-Phase Mixed-Metal Oxides From Metal-Organic Precursors," *Chem. Rev.*, **93**, 1205-1241, (1993), and references therein.
5. K. G. Caulton and L. G. Hubert-Pfalzgraf, "Synthesis, Structural Principles and Reactivity of Heterometallic Alkoxides," *Chem. Rev.*, **90**, 969-995, (1990).
6. L. G. Hubert-Pfalzgraf, "Mixed-Metal Alkoxides and Oxoalkoxides as Intermediates on Chemical Routes to Materials," *Polyhedron*, **13**, 1181-1195, (1994), and references therein.
7. F. Labrize, L. G. Hubert-Pfalzgraf, J. C. Daran and P. Tobaly, "Synthesis and Characterization of Volatile Mixed-Metal Yttrium-Barium, Barium-Copper and Yttrium-copper β -Diketonatofluoroisopropoxides. Molecular Structure of $\text{Ba}_2\text{Y}_2(\text{thd})_4[\text{OCH}(\text{CF}_3)_2]_4$," *Polyhedron*, **15**, 2207-2218, (1995).
8. H. C. Zeng and S. K. Tung, "Synthesis of Lithium Niobate Gels Using a Metal Alkoxide-Metal Nitrate Precursor" *Chem Mater*, **8**, 2667-2672 (1996).
9. R. Papiernik, L. G. Hubert-Pfalzgraf, J. C. Daran and Y. Jeannin, "Lead(II) Oxoalkoxides as Complex Ligands: Synthesis and Molecular Structure of $\text{Pb}_6\text{O}_4(\text{OEt})_4[\text{Nb}(\text{OEt})_5]_4$,"

- J. Chem. Soc. Chem. Commun.*, 965-966 (1990).
10. S. Daniele, R. Papiernik, L. G. Hubert-Pfalzgraf, S. Jagner and M. Hakansson, "Single-Source Precursors of Lead Titanate: Synthesis, Molecular Structure and Reactivity of $Pb_2Ti_2O(OPr)_{10}$," *Inorg. Chem.*, **34**, 628-633, (1995). L. G. Hubert-Pfalzgraf, S. Daniele, R. Papiernik, M. C. Massiani and J. Vaissermann, "Solution Routes to Lead Titanate," *J. Mater. Chem.*, **7**, 753-762 (1997).
 11. L. G. Hubert-Pfalzgraf, "Toward Molecular Design of Lanthanides Homo and Heterometallic Precursors of Oxide Based Materials," *New J. Chem.*, **19**, 727-750, (1995).
 12. S. Daniele, L. G. Hubert-Pfalzgraf, J. C. Daran and S. Halut, "Synthesis and Molecular Structure of $Sm_2TiO(OPr)_{14}$, a Novel Framework for Heterometallic Alkoxides with a 1:4 Stoichiometry," *Polyhedron.*, **13**, 927-932 (1994).
 13. J. F. Scott and C. A. Paiz de Araujo, *Science*, **246**, 1400, (1989). K. R. Kendall, C. Navas, J. K. Thomas and H. C. zur Loye, *Chem. Mater.*, **8**, 642, (1996). J. W. Pell, K. M. Delak and H. C. Zur Loye, Sol-Gel preparation of $Bi_2M_xV_{1-x/5}O_{5.5}$ delta (M=Cu, Nb, x=0.1, 0.3) *Chem. Mater.*, **10**, 1764-70 (1998).
 14. R. Papiernik, L. G. Hubert-Pfalzgraf, S. Parola, S. Jagner, F. Soares-Carvalho, P. Thomas and J. P. Mercurio, "Mixed-metal Bismuth-Titanium Species. Chemical Routes to $Bi_4Ti_3O_{12}$," *Better Ceramics Through Chemistry VI*, **346**, 285-290 (1994). "Activation of Bismuth Alkoxides: Synthesis Molecular Structure and Reactivity of the $Bi_2(\mu_3-O)(\mu-OR)_4(OR)_5$ and $[Bi_2(OR)_4(acac)]$ (R=Prⁱ), *J. Chem. Soc. Dalton Trans.*, **23**, 4631-4635 (1997).
 15. S. Boulmaaz and L. G. Hubert-Pfalzgraf, *J. Sol-gel Science Technol.*, **2**, 11, (1994). "Synthesis and Characterization of Tantalum-Zinc Oxoisopropoxides: Molecular Structure of $[ZnTa_2(\mu_4-O)(\mu-O)(\mu-OPr)_3(OPr)_4]_2$ Containing an Unprecedented Tantalum Oxoalkoxide Anion," *J. Chem. Soc. Chem. Commun.*, 601-602 (1994).
 16. L. G. Hubert-Pfalzgraf, C. Sirio and C. Bois, "Chemical Routes to Barium-Cerium Oxides. Molecular Structure of $Ba_4Ce_2(\mu_6-O)(thd)_4(\mu_3-OPr)_8(OPr)_2$," *Polyhedron*, **17**, 821-830 (1998).
 17. L. G. Hubert-Pfalzgraf, "Some Aspects of Functional Homo and Heterometallic Alkoxides," *J. Coord. Chem. Rev.*, **178-180**, 967-997 (1998).
 18. I. Laaziz, A. Larbot, A. Julbe, C. Guizard and L. Cot, "Hydrolysis of Mixed Titanium and Zirconium Alkoxides by an Sterification Reaction," *J. Solid State Chem.*, **98**, 393-403 (1992). I. Laaziz, A. Larbot, J. D. Foulon and L. Cot, "Structure of $Zr_2Ti_4O_4(OiPr)_8(OPr)_2(OAc)_6$," *J. Non Cryst. Sol.* (1993).
 19. A. I. Yanovskii, E. P. Turevskoya, M. I. Yarouskoya, V. G. Kessler and N. Ya Turova, "Synthesis and Structure of Ba-Ti and Ca-Ti Metallic Alcoholates," *Russ. J. Inorg. Chem.*, **40**, 339-356 (1995).
 20. V. G. Kessler, S. Daniele, L. G. Hubert-Pfalzgraf and A. Gleizes, "Single-source Precursors for $BaTiO_3$: Synthesis, Characterization of β -diketonatoalkoxides and Molecular Structure of $Ba_2Ti_2(thd)_4(OEt)_8(EtOH)_2$," *Chem. Mater.*, **6**, 2306-2311 (1994).
 21. L. G. Hubert-Pfalzgraf, S. Daniele and J. M. Decams, "Molecular Design of Single Source $BaTiO_3$ and $SrTiO_3$ Precursors," *J. Sol-gel Science Tech.*, **8**, 49-53 (1997).
 22. R. C. Mehrotra, R. Bohra and D. P. Gaur, "Metal β -diketonates and Allied Derivatives," Academic Press, London (1978).
 23. L. G. Hubert-Pfalzgraf, S. Daniele, S. Boulmaaz and R. Papiernik, "Controlling the Properties of Bulk Metal Oxides at a Molecular Level: Alkoxides vs Carboxylates-Alkoxides Routes", *Better Ceramics Through Chemistry VI*, *MRS*, **346**, 21-28 (1994). S. Boulmaaz, R. Papiernik, L. G. Hubert-Pfalzgraf and J. C. Daran, "Molecular Constitution of Solutions of Niobium Alkoxides and Acetates Synthesis, Molecular Structure and Reactivity of $MNb_2(\mu-OAc)_2(OPr)_{10}$ M=Mg, Cd, Pb. *J. Mater. Chem.*, **7**, 2053-2061 (1997).
 24. D. J. Teff, J. C. Huffman and K. G. Caulton, "Influence of Lead(II) Lone Pairs on the Serpentine Structure for Heterometallic Alkoxides," *Inorg. Chem.*, **34**, 2491 (1995). "Heterometallic Alkoxides of Zirconium with Tin(II) or Lead (II)," *Inorg. Chem.*, **36**, 2981 (1996).
 25. J. Caruso and M. J. Hampden-Smith, "Ester Elimination: a General Solvent Dependent Non-Hydrolytic Routes to Metal and Mixed-Metal Oxides," *J. Sol-Gel Science Technol.*, **8**, 35-39, (1997). T. J. Boyle and R. W. Schwartz, "An Investigation of Group IV Alkoxides as Property Control Reagents in the Synthesis of Ceramics Materials," *Comments Inorg. Chem.*, **16**, 243-278 (1994).
 26. B. A. Vaartstra, J. C. Huffman, P. S. Gradeff, L. G. Hubert-Pfalzgraf, J. C. Daran, S. Parraud, K. Yunlu and K. G. Caulton, "Alcohols Adducts of Alkoxides: Intramolecular Hydrogen Bonding as a General Structural Feature," *Inorg. Chem.*, **29**, 3126-3131 (1990).
 27. V. G. Kessler, L. G. Hubert-Pfalzgraf, S. Halut and J. C. Daran, "Reactions of Coordinated Ligands Topological and Stoichiometric Control for Mixed-Metal Alkoxides. Synthesis and Molecular Structure of $La(tea)_2[Nb(OPr)_{11}]_2$," *J. Chem. Soc. Chem. Commun.*, **705** (1994).
 28. V. Abada, L. G. Hubert-Pfalzgraf and J. Vaissermann, "Formation of Mixed-Metal Alkoxides Mediated by the Reactivity of Coordinated Pinacol. Molecular Structure of Ce-Ti and Ce-Nb Species," *Polyhedron.*, (1999).
 29. F. Babonneau, ²⁹Si, ¹⁷O Liquid NMR and ²⁹Si CP-MAS NMR Characterization of Siloxane-Oxide Materials (Me₂-SiO/TiO₂, MeSiOZrO₂, *Better Ceramics Through Chemistry*, *MRS*, **346**, 949-960 (1994).
 30. J. C. Plouxviel, J. P. Bailot, A. Dager, J. C. Boilot and L. G. Hubert-Pfalzgraf, "Chemical Routes to Aluminosilicate Gels, Glasses and Ceramics," *Better Ceramics through Chemistry II*, *MRS*, **73**, 269 (1986).
 31. M. Toyoda, Y. Tamaji, K. Tomono and D. A. Payne, "Synthesis and Characterization of $Bi_4Ti_3O_{12}$ Thin Films by Sol-Gel Processing," *Jpn J. Appl. Phys.*, **32**, 4158-4162 (1993).
 32. S. C. Goel, M. Y. Chiang, P. C. Gibbons and W. E. Buhro, "New Chemistry for the Sol-Gel Process: Acetone as a New Condensation Reagent," *Better Ceramics through Chemistry V*, *Mater. Res. Soc. Proc.*, **271**, 3-13 (1992).
 33. N. Pajot, R. Papiernik, L. G. Hubert-Pfalzgraf and S. Parraud, "Molecules with Polymerizable Ligands as Precursors to Organic Porous Solids", *Better Ceramics through Chem-*

- istry VII*, **435**, 137-144 (1996).
34. T. Fukui, C. Sakurai and M. Okuyama, "Preparation of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ Powders from Complex Alkoxide and Their Lower Temperature Crystallisation," *J. Mater. Res.*, **7**, 791 (1992).
35. S. Parola, R. Papiernik, L. G. Hubert-Pfalzgraf and J. Vaisermann, Synthesis and Molecular Structure of $\text{Bi}_4\text{Ba}_4(\mu_4\text{O})_2(\mu_3\text{-OEt})_8(\mu\text{-OEt})_4(\mu_2\text{-thd})_4$ an Example of the Formation of a Mixed-Metal Alkoxide Assisted by Dioxygen," *J. Chem Soc. Dalton Trans.*, 737-739 (1998).