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The Production of Complex Metal Oxides Using Single-Source Mixed-Metal Precursors

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ABSTRACT

Transparent conductive materials, super capacitors, and battery parts are examples of contemporary uses. Complex metal oxides are used in a variety of applications because they can contain many metals, phases, or do pants. This feature article explores the use of mixed-metal single-source precursors in the production of complex metal oxides. It is discussed how various precursors disintegrate and interact, including mixed-metal alkoxides, complexes with chelating legends, clusters, polyoxometallates, and metal-organic frameworks. Examining the advantages of using a single source precursor method and emphasizing those advantages

INTRODUCTION

One of the largest and most versatile families of solid materials, metal oxides come in a wide range of compositions, structures, and properties. Metal oxides are widely employed in a wide range of products, including gas sensors, super capacitors, superconductors, ferroelectric and multiferroic materials, batteries, transistors, solar cells, photo catalysts, and luminous materials. By adding hetero-metals as dopants or stoichiometric components, metal oxides' characteristics can be improved. This makes synthesis more difficult. The use of molecular single-source precursors (SSPs) to obtain metal oxide materials containing at least two included metals is explored in this article. Oxides (CMOs) comprise hetero-metal doped metal oxides (B: AxOy), composite metal oxides with a mixture of oxide phases (AwOx/ByOz), and mixed-metal oxides (AxByOz). SSPs can be used to access a variety of mixed-metal oxides, such as perovskites (ABO3) and pyrochlores (A2B2O7).

Traditional Synthesis of Complex Metal Oxides

Due to difficulties in precisely controlling the final species' stoichiometry, structure, and homogeneity, the synthesis of CMOs is frequently difficult. The severe temperatures frequently needed for classic "ceramic" solid-state synthesis does little to ease these difficulties. Solid-state reactions involving oxide, carbonate, or nitrate precursors are common in conventional ceramic methods. Processing at high temperatures is frequently necessary, especially when highly crystalline products are desired. The stoichiometry and phase purity may be difficult to manage using these methods. High temperatures have the potential to cause phase separation, only access thermodynamic products, and release volatile components that can change the intended stoichiometries. High temperatures further limit the ability to create particular application qualities by dictating the crystalline, particle size, and porosity of the generated materials. For these reasons, bottom-up molecular soft chemistry approaches have been helpful in streamlining CMO synthesis, increasing productivity, and opening the door to novel material characteristics (such as kinetically controlled products). Many CMOs can be produced from a mixture of monometallic molecular precursors, or multi-source precursors. However, this straightforward method can be challenging if the various precursors have dissimilar physical characteristics, such as solubility or reactivity. Different solubility's could cause phase separation during a drying step when using a solution-based deposition procedure (like drop-casting), causing the multi-source precursors to crystallize separately and creating an uneven layer before calcination. Different single-metal species' reactivity during hydrolytic reaction pathways, including sol-gel procedures, might result in phase separation and is likely to produce an improperly mixed product.

Opportunities Using Mixed-Metal Precursors

As an alternate synthetic method to access CMOs, mixed-metal (heterometallic), complexes or frameworks, which include more than one metal, can be used as SSPs. Using an SSP has been said to have benefits such simplifying material synthesis, providing access to uncommon or otherwise unavailable products, or producing materials with improved performance. By combining all of the necessary metals into a single precursor, the stoichiometry is established at the molecular level. Following the elimination of the supporting organic groups in the SSPs and reconstruction of the molecular connectivity, sometimes requiring hydrolysis, CMOs may then be obtained. Pre-existing bonds in the precursor molecules, particularly M-O connections, have been hypothesised to lower the nucleation barrier to produce solid-phase materials and hence may provide access to CMOs at lower temperatures. The mixed-metal precursors at least lessen the diffusion distances necessary to put the CMO structure together, regardless of any prefabricated M-O bonding. CMOs can be created with tiny particle sizes and high surface areas, or they can be deposited onto more sensitive substrates, by utilising lower syn- thesis temperatures. The creation of high surface-area nanoporous structures at relatively low reaction temperatures is made possible by the significant heat emitted during the breakdown of organic molecules, which is otherwise not possible at higher temperatures. This process also helps pure-phased oxides crystallise more easily. Mixed-metal complexes frequently provide a significantly more accurate stoichiometry and greater homogeneity of the target metals than (multi-source) single-metal molecular precursors because the component elements are accurately dispersed inside the molecular precursor. An SSP might have the ideal inter-metal stoichiometry needed to transform it into a pure phase mixed-metal oxide. Alternatively, may consist of a combination of metals that undergoes transformation into two or more (interpenetrated) oxide phases (previously classified by Veith as a type 3SSP). The primary mixed-metal species that have been described as SSPs for the synthesis of CMOs are summarised in this feature article (Fig. 1), ranging from the well-known mixed-metal alkoxides to more recent techniques such employing metal-organic frameworks as precursors or using multimetallic species.

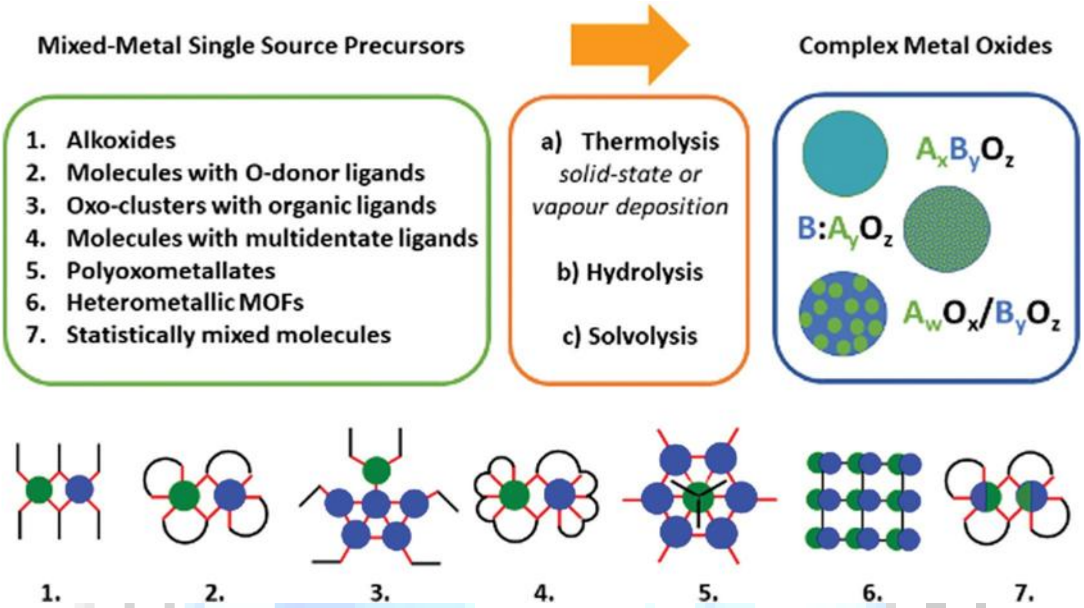

Fig. 1 Routes to Convert a Mixed-Metal Single-Source Precursor into the Different Varieties of Complex Metal Oxide

General Methods to Access Cmos from Single-Source Molecular Precursors

1.1 Thermal Decomposition

A) Solid-state thermolysis. Making CMOs is simple when using thermal decomposition of a mixed-metal SSP in the solid phase. The formation of CMOs results from the precursors' high-temperature breakdown, which also causes any organic components to disappear or break down. Controlling the heating rate is crucial because it can prevent melting or vaporisation of the molecular species, which can happen under rapid heating. The benefit of a solid-phase transition is the preservation of the elemental composition, as determined by the molecular precursor, with only the loss of volatile decomposition products, allowing for perfect stoichiometric control of the inter-metal ratio in the CMO products.

SSPs may be made to have good solubility, which enables the production of thin (microcrystalline) films of the SSP that are ready for thermal breakdown to a thin layer using simple solution deposition processes as drop, spin, or spray coating. The chemistry involved in the deposition and drying of precursors can be extremely complicated and can have a significant impact on the material that results from further calcinations.

Modern methods provide temperature-controlled powder X-ray diffraction studies for in situ assessment of the breakdown and calcinations process. It has been demonstrated that the outcomes of these reactions depend on the maximum heating temperature (and the rate of temperature increase). There are numerous instances when SSPs can break down and form CMOs at significantly lower temperatures than with conventional solid-state ceramic techniques.

The release of gaseous organic breakdown products (and possibly solvent molecules) is necessary for the decomposition of metal-organic compounds. The particle size and porosity of the generated oxide may change as a result of releasing these gases. Due to more gas escape during thermolysis, precursors with higher organic content produce breakdown products with larger porosity and smaller particle sizes. In order to preserve the precisely calculated inter-metal ratio in the SSP, attention should be taken while selecting the maximum heating temperature during annealing. For example, volatile metal compounds, such as Li_2O or PbO, can also be lost. The internal heating of the sample and the promotion of crystallization are two additional benefits of an SSP's combustible component. However, an excessive amount of organic material may result in carbon impurities in the finished product and/or the reduction of metals (like Bi(III) to metallic Bi).

B) Chemical Vapour Deposition. A thin film deposit of CMO product is typically left behind when the liquid precursors used in the (metal-organic) Chemical Vapour Deposition (CVD) process are volatilized at an intermediate temperature (200^0C) and quickly decomposed on a high-temperature substrate. Due to the various components' various physical properties, stabilities, and decomposition traits, using a mixture of mono-metallic precursors can be challenging. In order to overcome these challenges, extremely high temperatures may exacerbate lattice imperfections in the deposited film. By using a single precursor molecule rather than a variety of species with different volatilities, a CVD process may be made simpler. To preserve the uniqueness of the precursor, any SSPs must endure evaporation without degrading.

A careful selection of legends is necessary during CVD operations to ensure no carbon is retained because carbon impurities can be detrimental to the use of CMOs. In order to create thin films of FeSnOx from Fe-Sn SSPs or mixes of CdTiO3/TiO_2 from Cd-Ti_2 SSPs, aerosol-assisted CVD (AACVD) is a beneficial technique. AACVD lowers the need for extremely volatile precursors.

1.2 Hydrolysis

When Brnsted basic metal-organic compounds (such as organometallics, metal amides, or metal alkoxides) come into contact with water molecules, either within the solution or when exposed to outside air, they are susceptible to hydrolysis and polycondensation by elimination of small or volatile molecules (such as alkanes, arenes, amines, or alcohols). Water molecules give out H+ to remove ligands and O_2— to create metal oxides during hydrolysis. In order to create oxide materials, sol-gel methods are frequently used. In sol-gel processes, small metal oxide particles are produced by hydrolysis and grow and connect with one another through condensation to form a gel of nanostructures that are shielded by leftover ligands and hydroxides. To increase the homogeneity of the gel phase, more multidentate ligands or polymers may be used. The bulk oxide phase that results from calcinations of this amorphous gel can have a variety of product compositions depending on the temperature at which it is cooked. Although they may need careful control of several parameters (e.g., temperature, solvent, concentration), sol-gel processes are preferred for their simplicity and ability to affect the final particle morphology. Water serves as both a ligand and a solvent in aqueous processes, making it challenging to regulate the pace and degree of hydrolysis, condensation, and aggregation. This makes it challenging to regulate the crystalline, shape, and repeatability of the CMOs formed.

While SSPs start out as mixed-metal species, solution-based hydrolysis processes do not ensure that the intermediate species during a reaction retain the inter-metal ratio. In fact, it is generally believed that in solution-phase reactions, where molecules can quickly equilibrate, there is no "memory" of the previous step, as indicated by the partial hydrolysis of mixed-metal alkoxide precursors. It is probable that the addition of covalently bound bridging oxo groups will create an energy barrier for rearrangement, but that bond redistribution will still be necessary to create the final oxide product. Therefore, using SSPs in sol-gel syntheses may not result in uniformly mixed oxide products but rather may generate biphasic composites more frequently. Connecting metals with a bifunctional ligand is one approach that could be used to maintain closeness despite different rates of hydrolysis.

1.3 Solvolysis

Even though aqueous sol-gel methods are frequently employed to create metal oxides, other non-aqueous reaction methods utilizing organic solvents have also been developed. In order to obtain metal oxides with high crystallinity and a limited size distribution at low temperatures, they can be used to control the condensation rate. The oxygen for metal oxides in the majority of non-aqueous processes comes from the precursors' O-containing elements or the solvent's O-containing component. Depending on the structures of the precursor and, solvolysis condensation reactions can result in the formation of M-O-M bonds and elimination of an ester, ether, or alkyl halide, C-C bond formation, or aldol or ketimine condensation reactions (Fig. 2). However, they also have a big impact on the size, shape, morphology, and even surface composition of the metal oxides produced. Solvent molecules play significant roles in condensation mechanisms.

Mixed-metal SSPs for the Synthesis of CMOs

1.4 Synthetic Strategies

Mixed-metal precursors can be created in a variety of ways (Fig. 3). Initial research concentrated on synthesising mixed-metal alkoxides, and then these systems were derived to include chelating O-donor legends. A more reliable method may be utilised to create a covalent bridge between metals because structures based on straightforward adducts of mono-metallic components can be vulnerable to segregation. The reaction of (basic) organ metallic complexes with (acidic) metal hydroxides can produce oxy-bridged M-O-M0 structures. Similar to this, multidentate ligands' pendant acidic OH groups can react with organometallic reagents. As demonstrated in Zn-Ti SSP (Zn $(POBC)_2Ti(OiPr)_{32}$) (POBC-H = p-carboxy-benzaldehyde oxime), bifunctional (bidentate) linker ligands with separate coordination sites might enable stepwise attachment of two different metals (one at either location). Similar to this, the coordination of benzene rings to the $Cr(CO)_3$ fragment allows the creation of the Zn-Cr precursors $[MeZnOCH_2PhCr(CO)_3]_4$ and $[MeZnOCH(PhCr(CO)_3)_2]_2$, which are necessary for the synthesis of $ZnCr_2O_4$. Fe-Sn precursors $(C_5H_5)Fe(C_5H_4)C_6H_4CO_2SnR_3$ are two examples of useful ferrocene units for incorporating Fe into molecules. Another flexible method for incorporating secondary and tertiary metals into isostructural compounds is to include extra metals within counter ions. This method results in a perfect distribution of the metals when crystallised in an ionic lattice. The polymeric $Cp(CO)_2Fe\text{-}BiCl_2$ molecule, important for the production of the photocatalyst $BiFeO_3$ utilising AACVD techniques, is one of the rare examples of mixed-metal precursors that may even comprise direct M-M0 bonding.

A further synthetic technique is the partial transmetallation of a monometallic cluster precursor before the introduction of a secondary metal. This is an example of combining metals in a statistical mixture into a well defined structural motif. At this point, I refer to these antecedents as "imprecise SSPs," and at the end of this section, I go into further detail about them.

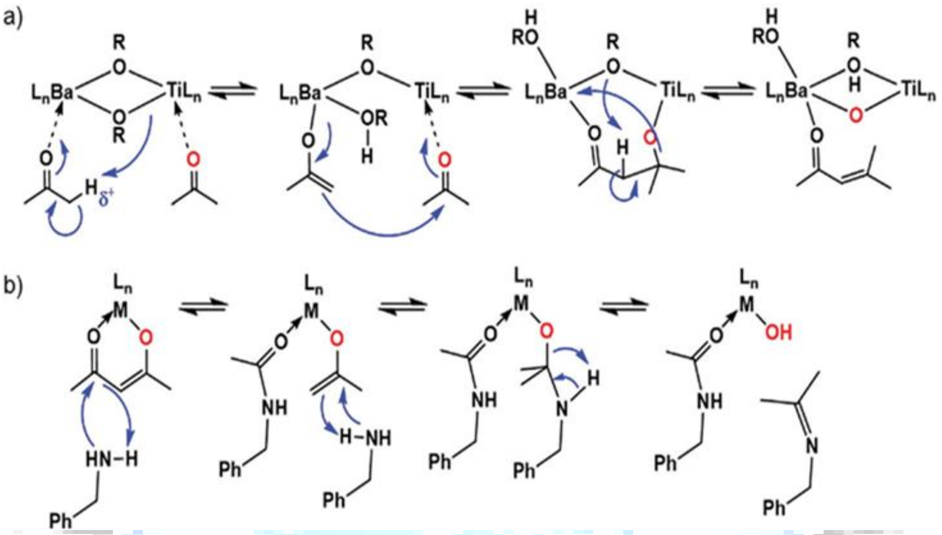

Fig. 2 Metal oxo or metal hydroxide functionalities are introduced through solvothermal mechanisms (O depicted in red), eventually resulting in the condensation of a metal oxide. A typical mechanism for ketamine condensation from an acetylacetonate ligand and benzylamine; (a) aldol condensation in the formation of $BaTiO_3$ from BaTiO $(OiPr)_4$ in dry acetone.

Fig. 3 Possibilities for Synthesis of Heterometallic Compounds

1.5 Heterobimetallic

During the CMO synthesis, SSPs can also be created in situ by mixing monometallic reagents directly. Make that a mixed-metal SSP is emerging and not just a collection of precursors. However, this strategy does enable a simple synthetic procedure. Although it is generally believed that excluding halide ligands from precursors is beneficial for the formation of clean oxide materials, several examples have now demonstrated that post-calcination washing steps can remove any halide contaminants (which are frequently highly soluble) from the desired oxide phase. Although it is challenging to simply group the wide variety of SSPs into predetermined categories, in the sections that follow, we have made an effort to divide the literature examples into five main categories of molecular SSPs, as well as a group of extended framework precursors and a final section on statistically mixed metal species. Alkoxides of mixed metals.

A class of compounds known as mixed-metal alkoxides is one in which alkoxy groups connect several metals. The first composition in this family was $Na[Al(OR)_4]$, which was created in 1929. Typically, they are created by mixing homometallic alkoxides in a Lewis acid-Lewis base process. However, in some circumstances, a metathesis reaction involving metal chlorides and a group 1 metal alkoxide has also been effective. Nuclear magnetic resonance (NMR) spectroscopy at a changing temperature may be able to detect the rapid exchange of alkoxide ligands. There have been many reported mixed-metal alkoxides, and those with similar oxidation states and inter-metal ratios typically have equivalent and foreseeable structures. However, experimental factors, such as the solvent or the makeup of the alkoxide group, can affect how these compounds are synthesised. As a result, precursors with various intermodal ratios, such as $PbZr(OtBu)_6$ and $Pb2Zr_4(OiPr)_{20}$, may be obtained. When the monometallic alkoxides are insoluble polymers, as is frequently the case for MII(OR)2 compounds, problems may occur. Alkoxides with pendant donor groups, such as those with the formulas OC2H4OMe or $—OC_2H_4NMe_2$, can improve stability and solubility as well as provide access to a variety of precursors. Another strategy is to construct volatile precursors for CVD operations by using alkoxide ligands with a-substituents that prevent oligomerization.

A statistical mixture of the metals inside the alkoxide structures might occasionally result by mixing various metal alkoxides that have the same molecular geometries. This process, known as isomorphism substitution, might nevertheless result in molecular homogeneity. Despite the prevalence of bimetallic alkoxides, only a few number of trimetallic alkoxides have been synthesised, such as $[Cd(OiPr)_3MM0_2(OiPr)_9]_2$ (M = Ba, Sr; M0 = Sn, Ti, Zr, Hf), and $[Al(OiPr)_4(HOiPr)BaM_2\text{-}(OiPr)_9]$. (M = Hf or Zr) (Fig. 4) that were synthesised by kinetically controlled stepwise assembly.

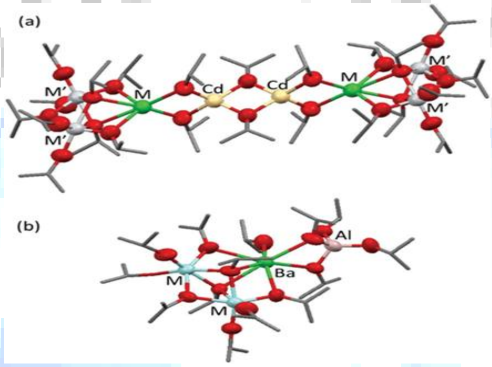

Fig. 4 Solid-State Structures of (A) $[\{Cd(Oipr)_3\}M\{M02(Oipr)_9\}]_2$ (M = Ba, Sr; M0 = Sn, Ti, Zr, Hf) And (B) $[\{Al(Oipr)_4\}\{(Hoipr)Bam2(Oipr)_9\}]$ (M = Hf Or Zr)

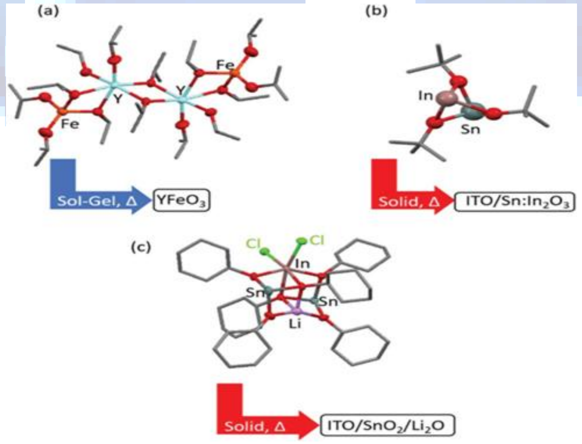

Fig. 5 Heterometallic Alkoxide Ssps (A) $[Yfe(O\ Pr)_6(\ Proh)]_2$ (B) In S- $Nii(Otbu)_3$ (C Cl2In$\{Lisnii(Ocy)_6\}$ And Their Decomposition Products.

Despite the fact that mixed-metal alkoxides can serve as helpful synthons to produce more mixed-metal compounds, they frequently have low stability and/or are perhaps in equilibrium with their mono-metallic components, which restricts their direct usage as SSPs. Donor solvents may also interfere with adduct coordination, causing the segregation of the metals and the separation of homometallic alkoxides.

Despite their limitations, many examples of mixed metal alkoxides produce useful CMOs. Early studies of SSPs in sol-gel chemistry developed precursors for the useful perovskite $BaTiO_3$ which can be used in capacitors or transducers. This work culminated in using mixed-metal alkoxides, such as $BaTiO(O\textit{n}Bu)_4(\textit{n}BuOH)$, in industrial processes to prepare $BaTiO_3$ films. The related $BaTiO(OiPr)_4 \cdot 7iPrOH$ has also been shown to produce $BaTiO_3$ by non-aqueous routes. This Lewis acidic SSP reacts with dry acetone (or cyclohexanone) *via* an aldol condensation at room temperature, allowing the very low-temperature synthesis of $BaTiO_3$, and avoids multigrain particles which affect the dielectric properties of the perovskite that can occur from high-temperature ceramic synthesis (Fig. 2a). However, the stoichiometry of the SSP may not be precisely reflected in the CMO, as is the case with any solution-sol-gel process. A small excess of Ti in this instance (4% extra) suggests that solution rearrangements may permit some metal segregation. $[YFe(OiPr)_6(iPrOH)]_2$ and $Mg_2Ti_2(OEt)_{12}(EtOH)_4$ are more instances of the utilization of mixed-metal alkoxides as SSPs that provide pure CMO products and prevent impurities. iPrOH, YFe(OiPr)6By low-temperature sol-gel hydrolysis followed by annealing, 2, which is difficult to obtain by other methods as a kinetic product, is transformed into the weak ferromagnetic perovskite YFeO3 (Fig. 5a). By utilizing this procedure, the production of Fe_3O_4 or $Y_3Fe_5O_{12}$ impurities, which are frequently produced when using other techniques, is prevented. At 900°C, $MgTiO_3$ is produced by the solid phase of 15 $Mg_2Ti_2(OEt)_{12}(EtOH)_4$ without the presence of frequent contaminated phases such as $MgTi_2O_5$ or Mg_2TiO_4. $MgTiO_3$ is used in capacitors or resonators in communication devices, but previous studies have noted that it is challenging to produce phase-pure MgTiO3. For example, a solid-state reaction that necessitates a sintering temperature of over 1400 °C results in final materials that contain a certain amount of $MgTi_2O_5$.

The molecule InISnII$(OtBu)_3$, which serves as a precursor for Sn-rich ITO (indium tin oxide), is another intriguing alkoxide compound (Fig. 5b). Although ITO has a low percentage of Sn (B5–15 mol%) and is a significant trans-parent conductor, there is interest in producing it because indium is pricey. materials having a lower indium concentration that are equally transparent and conductive. Thermal decomposition of $InSn(OtBu)_3$ can result in a solid solution of crystalline ITO particles in an amorphous indium oxide matrix. High Sn concentration is possible while still keeping outstanding trans parent conductivity (resistivity 4.1 10—3 O cm) when using the SSP. Alternatively, In $4Sn_3O_{12}$ formation or In2O3/SnO2 segregation is seen when using conventional routes to ITO, which are limited to o15 mol% Sn_2 content. Additionally, mesoporous Sn-rich ITO can be created by combining $InSn(OtBu)_3$ with block-co-polymers. ITO does not need to crystallize in order to have the desired characteristics, hence low formation temperatures can be employed to maintain a high surface area. Trimetallic X_2InIIILiSnII $(OCy)_6$ (X = Cl or Br) makes use of indium in its more reliable +3 oxidation state with lower metal content. Low-temperature thermal deterioration created ITO/SnO_2/Li_2O thin-film field-effect transistors that performed well (with saturation electron mobilities of up to 6.36 10—1 cm2 V—1 s—1), especially when taking into account the low in content (Fig. 5c).

Organ metallic precursors are frequently moisture-sensitive, just like metal alkoxides. Alkyl groups, on the other hand, have a lower propensity than alkoxides to serve as a bridging ligand, which lessens the propensity of a complex to dimerize and may therefore increase volatility. An instance of a mixed alkoxide/alkyl mixed-metal SSP is Mg[(m-OtBu)2AlMe$_2$]$_2$ (Fig. 6). This compound is a great candidate for CVD processes due to its high volatility. At just 400 °C, the SSP converts to $MgAl_2O_4$ films, with perfect stoichiometry, no carbon impurities, and good homogeneity that has been verified by Auger depth profiling. When using separate Mg and Al precursors, however, high temperatures (Z1000^{0}C) are frequently needed to deposit $MgAl_2O_4$ films by CVD; this can lead to an unacceptable stoichiometric deviation, flaws in the lattice and excessive tensile stress. The smooth decomposition of $Mg[(m\text{-}OtBu)_2AlMe_2]_2$ via charge redistribution processes, such as those indicated in Fig. 6, is partially responsible for its clean, regulated decomposition (for example, the hydrocarbons CH4 and CH2QCMe$_2$ are removed as gases as the only by-products). The [R3SnOZnR0]4 cubanes (R = Me, Ph, R0 = Me, Et, tBu) can be used to produce Sn doped ZnO and/or Zn2SnO$_4$ tested as a field-effect or thin-film transistor (Fig. 7a) by replacing alkoxide or amido groups with a tin containing —$OSnR_3$ or —$N(SnR_3)_2$ moieties. Due to the volatility of the SnMe3 fragment beyond 115 °C, it should be noted that thermal degradation causes loss of Sn content when R = Me; nevertheless, Sn loss is almost totally offset by the replacement of Me by Ph, albeit with a minor increase in carbon impurities in the final product. Monometallic Zn cubane precursors can also be mixed in to change the end product's Sn concentration.

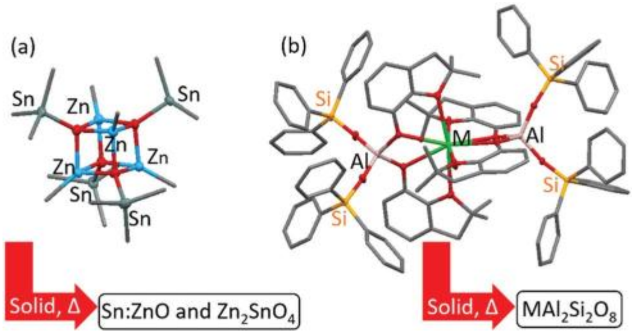

Fig. 7 Solid State Structures of Heterometallic Ssps (A) [(CH3)$_3$snoznch$_3$]$_4$ And (B) [M{(M-Ddbfo)$_2$Al(Osir$_3$)$_2$}$_2$] (M = Ba, Sr) And Their Decomposition Products.

As an alternative to alkoxides, dioxide groups can introduce silicon into the precursors, for example, allowing direct formation of high-melting point $MAl_2Si_2O_8$ feldspar ceramics (useful in aerospace applications) from [M{(m-ddbfo)2-Al(OSiR3)$_2$}$_2$] (M = Ba, Sr, ddbfoH = 2,3-dihydro-2,2-dimethyl- benzofuran-7-ol) (Fig. 7b).

1.6 Mixed-Metal Complexes with Other O-Donor Ligands

It becomes possible to incorporate main group or late transition elements into mixed-metal complexes that would otherwise be difficult to form or unavailable as straightforward mixed-metal alkoxides with the addition of additional oxygen donor ligands, such as bidentate ligands like carboxylates and b-diketo- nates. Multiple ligands and metals can be combined to create a variety of mixed metal/mixed ligand complexes that are useful as SSPs. Heterobimetallic complications may be encouraged by combining ligands with various Lewis facilities. In comparison to straightforward mixed-metal alkoxides, these ligated complexes are more stable against hydrolysis and generally more soluble in common organic solvents, making them more effective precursors for the synthesis of CMOs. However, it should be noted that the use of polar coordinating solvents can result in the formation of homo-metallic precursors supported by the solvent. Importantly, it has been demonstrated repeatedly that the thermal decomposition of carboxylate and acetylacetonate (acac—) ligands proceeds at temperatures comparable to those of alkoxides, enabling uniform thermal decomposition pathways of heteroleptic complexes.76 Long thermolysis processes may be necessary for large, bulky ligands like 2,3-dihydro-2,2-dimethyl benzofuran-7-ol to thoroughly purge organic impurities from the desired oxide products.

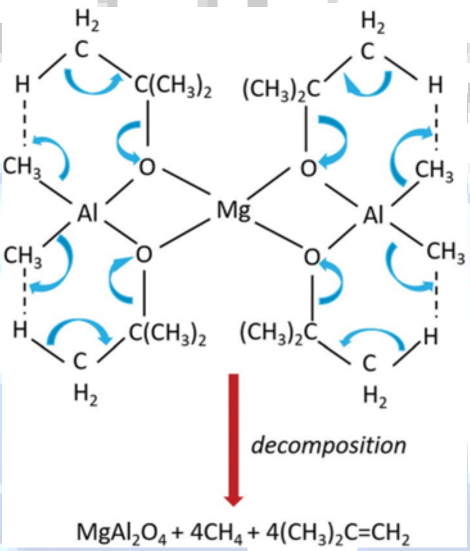

Fig. 6 Schematic Illustration of The Pathway of The Mg[(M-O*t*bu)$_2$alme$_2$]$_2$ SSP To Form Mgal$_2$o$_4$ *Via* The Elimination of Methane And Me_2CCH_2.

When heating heterobimetallic complexes that are unstable to heating, such as $Ba_2Ti_2(thd)_4(OEt)_8(EtOH)_2$ (the = tetramethylheptanedionate) and $Ba_2Ti_2(acac)_4(OEt)_8$, the volatile $Ti(OEt)_4$ or $Ti(acac)_2(OEt)_2$ fragments can be driven off, resulting in segregation of the metals. These two precursors enable the synthesis of $BaTiO_3$ through solution hydrolysis, but the latter precursor also generates $BaTi_2O_5$ and BaO by-products, suggesting that the metals in this complex may be more easily segregated. Other examples also show metal segregation during hydrolytic (sol-gel) treatment, such as the M-Ti (M = Ni, Co, and Mg) precursors M2Ti2(acac)4(OEt)8, which partially hydrolyze to produce 2 $M_5TiO(acac)_6(OEt)_6$ + 8 $Ti(acac)(OEt)_3$. Another example is the precursor CoAl2(acac)3- (OAc)OiPr$_4$ that, when thermal zed in the solid state or by CVD, yields homogenous spinel CoAl2O$_4$; however, sol-gel hydrolytic techniques provide a mixed phase result. Excellent examples of the use of b-diketonate ligands in SSPs are the complexes prepared by Dikarev and co-workers; LiMn2(thd)5 (thd=2,2,6,6-tetramethyl-3,5-heptanedionate) and $[LiM(tbaoac)_3]_2$ (M =Co or Fe, tbaoac = tert-butyl acetoace- tonate) which act as volatile and air-stable SSPs for phase pure LiMn2O$_4$, $LiCoO_2$ or $LiFeO_2$ cathode materials for Li-ion batteries (Fig. 8). LiMn2 (thd) has been demonstrated to be stable in non-coordinating solvents and to undergo direct thermolysis under oxygen at 600°C. The [LiCo(tbaoac)3]2 complex was shown to be solubilised in both coordinating and non-coordinating solvents thanks to the addition of an asymmetric b-diketone ligand, which also prevented polymerization and caused phase-pure LiCoO2 to form at temperatures as low as 280°C. When creating thin-film batteries that require films between nm and mm in thickness, using an SSP is especially advantageous. The trimetallic SSP $LiMnCo(thd)_5$, whose trimetallic structure can be verified in the gas phase by Direct Analysis in Real Time (DART) mass spectrometry and which can be utilised to produce LiMnCoO4, has just been discovered. The Dikarev group has also lately focused on Na analogues of these SSPs, $[NaM(tbaoac)_3]_2$, with the goal of cathodes for Na-ion battery technology. Oxalate anions, [C2O$_4$]$_2$—, have been employed to build numerous 2D or 3D coordination networks which may integrate secon- dary metals as countering, e.g. $[Co(bipy)_3][Mn_2(C2O_4)_3]\cdot H_2O$

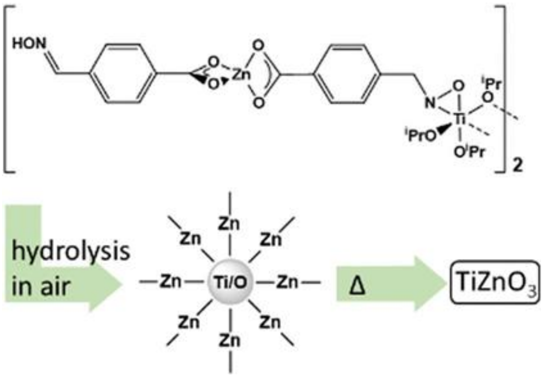

Fig. 7 Hydrolysis of a Ti–Zn SSP Assembled using A Bifunctional Ligand

Ti/O nanostructures covered with Zn-containing ligands undergo hydrolysis and are then transformed into TiZnO$_3$ at 4400 °C. bpy stands for 2,20-bipyridine. These promise easy ligand decomposition into CO2 or CO and thermal decomposition into CMOs, such as CoMn2O$_4$. Ti-Zn SSPs (Zn (POBC)$_2$Ti(OiPr)$_2$; Fig. 9) have been created using a bifunctional carboxyl ate/oxime ligand (POBC), which selectively binds various metal fragments at each site. TiZnO$_3$ is produced using these SSPs. In this instance, the carboxylates completely stabilize the Zn whereas the oxime-coordinated titanium centre retains the reactive alkoxide ligands. Therefore, the Ti site undergoes hydrolysis and condenses upon reaction with moisture (from the air), resulting in the formation of titanium oxide nanoparticles encircled by organic ligands containing encapsulated Zn atoms. The residual organic components can subsequently be broken down by heating, and Zn atoms can then diffuse into the oxide phase. When compared to a control reaction using multiple precursor sources, the final product had more homogeneity and surface area.

1.7 Oxo-Bridged Mixed-Metal Clusters with Organic Ligands

In the presence of minute amounts of water, mixed-metal alkoxides are prone to condensation and hydrolysis, which results in a range of new structures, including mixed-metal oxo-alkoxides, which may serve as appropriate SSPs for CMO production. When oxo ligands are added, alkoxide precursors' solubility may be drastically altered, especially if polymeric alkoxide, which is generally insoluble, is transformed into a molecular oxo-alkoxide cluster. These oxo-bridged species, such as doped-polyoxotitanium cages (POTs), are produced when titanium alkoxides partially hydrolyze and condense in the presence of a dopant metal source (such as metal chlorides). Metal-doped POTs (M-POTs) of different compositions and sizes are accessible using solvothermal synthetic techniques, and a series of M-POTs with the formula [TixOy(OR)zMnXm] (M = main group element, transition metal, or lanthanide metal; X = anion) have been created. By adjusting the ratios of the starting materials MXw and Ti(OR)$_4$ (for example, M = CoII, FeII), the stoichiometry of M and Ti can be adjusted for particular metal species.115 In other situations (such M = CeIII),

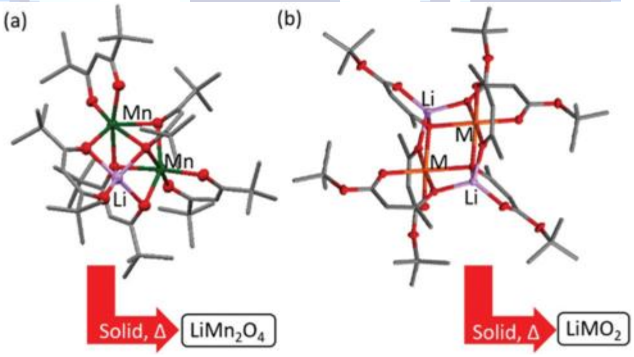

Fig. 8 Heterometallic SSPs (M = Co or Fe) and their decomposition products (a) LiMn2(thd) and (b) [LiM(tbaoac)$_3$]$_2$. Fractional crystallization can be used to separate different products from the process that have different M: Ti ratios.

M-POT alkoxide cages' surrounding alkoxide groups, which are simple to hydrolyze, enable the deposition and subsequent calcination of M-POTs at low temperatures. The thermodynamically preferred rutile phase of TiO$_2$ may not emerge as a result of low-temperature hydrolysis and condensation, but rather the anatase phase. TiO$_2$ with metal ions can be easily deposited on substrates utilising solution techniques since M-POTs are soluble in organic solvents. Concentrated [Ti17O$_{28}$(OiPr)$_{16]}$Co-(phen) solution hydrolyzed at low temperatures. It has been demonstrated that the chemical compound (phen = phenanthroline), when produced by airborne moisture, results in hollow TiO$_2$ nanospheres that are adorned with leftover Co(phenanthroline) pieces The dopant metal ions in the TiO$_2$ products can be distributed uniformly by using M-POT precursors. For example, both energy-dispersive X-ray spectroscopy (EDS) and X-ray photo- electron spectroscopy (XPS) confirmed that sonication of Ce doped POTs (either $[Ti_{28}O_{38}(OEt)_{38}(EtOH)1.4CeCl]$ or [Ti8O7(OEt)21(EtOH)Ce] (Fig. 10b)) in 50 v% aqueous ethanol followed by calcination at 150^0C in air led to CeIII-doped TiO2 (either amorphous or anabases), with a Ce: Ti ratio matching that of the corresponding precursors (either 1: 28 or 1: 8). Surprisingly, once the same process was applied to $[Ti_2O(OEt)_8(EtOHCeCl)]_2$, TiO2 and Ce2Ti2O7 were produced, an oxide that has previously only been produced using solid-state methods at high temperatures (about 1000 °C). Importantly, it is demonstrated that the CeIIITi O in this mixed-phase product, which would otherwise quickly decompose to CeIV products, is significantly stabilised by the presence of TiO2. The development of multi-functional composite CMOs has also benefited from the usage of M-POTs. For instance, after coating [Ti2(OEt)9(NiCl)]2 or [Ti4O(OEt)15(CoCl)] on photo electrodes made of p-Si, nano WO_3, or $BiVO_4$, the precursors hydrolyzed (under air at ambient temperature) to create composites of amorphous TiO_2 with NiOx or $CoO/Co(OH)_{2,}$ respectively. A protective layer of amorphous TiO_2 is added, and at the electrodes, catalytically active sites for the oxidation of water are introduced by the Co or Ni oxide species. Comparing the composite photo electrodes to those made without the deposition of Ti/M precursors, it was discovered that both their activity and photo stability were significantly increased. Simple alkoxides can be thermolyzed to produce new mixed-metal compounds, which can act as helpful SSPs and encourage the synthesis of m-oxo ligands. For instance, controlled thermolysis of the precursor can create $[MgAl2(m_3\text{- }O)(OiPr)_6]_4$, which functions as a much better SSP for formation of pure phase nanocrystalline spinel $MgAl2O_4$ after sol-gel hydrolysis and annealing at only 475 1C. Sol-gel hydrolysis and annealing at only 475 1C causes phase separation and the formation of MgO and $Al2O_3$ by-products. For starting the production of the (tertiary) spinel without binary oxide impurities, it appears that a certain amount of pre-assembly in the oxo-bridged precursor is advantageous.

REFERENCES

[1]. A. B. Djurisic, Y. H. Leung and A. M. C. Ng, *Mater. Horiz.*, 2014, 1, 400–410.
[2]. Z. L. Mensinger, J. T. Gatlin, S. T. Meyers, L. N. Zakharov, D. A. Keszler and D. W. Johnson, *Angew. Chem., Int. Ed.*, 2008, 47, 9484–9486.
[3]. M. Mehring, *Coord. Chem. Rev.*, 2007, 251, 974–1006.
[4]. Q. L. Dai, M. E. Foley, C. J. Breshike, A. Lita and G. F. Strouse, *J. Am. Chem. Soc.*, 2011, 133, 15475–15486.
[5]. G. A. Seisenbaeva and V. G. Kessler, *Nanoscale*, 2014, 6, 6229–6244. 11 M. Veith, *J. Chem. Soc., Dalton Trans.*, 2002, 2405–2412.
[6]. Y. F. Deng, Q. Y. Lv, S. P. Wu and S. Z. Zhan, *Dalton Trans.*, 2010, 39, 2497–2503.
[7]. P. Sobota, A. Drag-Jarzabek, L. John, J. Utko, L. B. Jerzykiewicz and M. Duczmal, *Inorg. Chem.*, 2009, 48, 6584–6593.
[8]. S. Mathur, M. Veith, R. Rapalaviciute, H. Shen, G. F. Goya,
[9]. W. L. Martins and T. S. Berquo, *Chem. Mater.*, 2004, 16, 1906–1913. 16 A. A. Tahir, M. Mazhar, M. Hamid, K. G. U. Wijayantha and
[10]. K. C. Molloy, *Dalton Trans.*, 2009, 3674–3680.
[11]. L. G. Hubert-Pfalzgraf, S. Daniele, R. Papiernik, M. C. Massiani,
[12]. B. Septe, J. Vaissermann and J. C. Daran, *J. Mater. Chem.*, 1997, 7, 753–762.
[13]. M. A. Dreher, M. Krumm, C. Lizandara-Pueyo and S. Polarz, *Dalton Trans.*, 2010, 39, 2232–2238.
[14]. L. John, J. Utko, S. Szafert, L. B. Jerzykiewicz, L. Kepinski and P. Sobota, *Chem. Mater.*, 2008, 20, 4231–4239.
[15]. S. Daniele, D. Tcheboukov and L. G. H. Pfalzgraf, *J. Mater. Chem.*, 2002, 12, 2519–2524.
[16]. Z. Wei, H. X. Han, A. S. Filatov and E. V. Dikarev, *Chem. Sci.*, 2014, 5, 813–818.
[17]. A. Navulla, L. Huynh, Z. Wei, A. S. Filatov and E. V. Dikarev, *J. Am. Chem. Soc.*, 2012, 134, 5762–5765.
[18]. G. Mohammadnezhad, M. M. Amini and H. R. Khavasi, *Dalton Trans.*, 2010, 39, 10830–10832.
[19]. S. R. Chen, M. Xue, Y. Q. Li, Y. Pan, L. K. Zhu and S. L. Qiu, *J. Mater. Chem. A*, 2014, 3, 20145–20142.
[20]. J. H. Thurston and K. H. Whit mire, *Inorg. Chem.*, 2002, 41, 4194–4205.
[21]. S. Polarz, A. V. Orlov, M. W. E. van den Berg and M. Driess, *Angew. Chem., Int. Ed.*, 2005, 44, 7892–7896.
[22]. M. Niederberger, N. Pinna, J. Polleux and M. Antonietti, *Angew. Chem., Int. Ed.*, 2004, 43, 2270–2273.
[23]. C. N. R. Rao, *Pure Appl. Chem.*, 1994, 66, 1765–1772.
[24]. C. Y. Chang, H. I. Ho, T. Y. Hsieh, C. Y. Huang and Y. C. Wu, *Ceram. Int.*, 2013, 39, 8245–8251.
[25]. B. C. Gaskins and J. J. Lannutti, *J. Mater. Res.*, 1996, 111, 1953–1959. 35 Y. Hou, D. B. Fast, R. E. Ruther, J. M. Amador, L. B. Fullmer, S. R. Decker