



HAL
open science

Asymmetry-Induced Redistribution in Sn(IV)–Ti(IV) Hetero-Bimetallic Alkoxide Precursors and Its Impact on Thin-Film Deposition by Metal–Organic Chemical Vapor Deposition

Shashank Mishra, Erwann Jeanneau, Liang Tian, Ioana Nuta, Elisabeth Blanquet, Deobrat Singh, Rajeev Ahuja, Catherine Marichy, Stéphane Daniele

► **To cite this version:**

Shashank Mishra, Erwann Jeanneau, Liang Tian, Ioana Nuta, Elisabeth Blanquet, et al.. Asymmetry-Induced Redistribution in Sn(IV)–Ti(IV) Hetero-Bimetallic Alkoxide Precursors and Its Impact on Thin-Film Deposition by Metal–Organic Chemical Vapor Deposition. *Crystal Growth & Design*, 2021, 10.1021/acs.cgd.1c01136 . hal-03510420

HAL Id: hal-03510420

<https://hal.science/hal-03510420v1>

Submitted on 4 Jan 2022

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

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Asymmetry-Induced Redistribution in Sn(IV)- Ti(IV) Hetero-Bimetallic Alkoxide Precursors and its Impact on Thin Films Deposition by Metal-Organic Chemical Vapor Deposition

Shashank Mishra,^{a} Erwann Jeanneau,^b Liang Tian,^c Ioana Nuta,^c Elisabeth Blanquet,^c Deobrat Singh,^d Rajeev Ahuja,^{d,e} Catherine Marichy,^f Stéphane Daniele^g*

^a *Université Lyon 1, IRCELYON-UMR 5256, 69626 Villeurbanne Cedex, France.*

^b *Université Lyon 1, ISA-UMR 5280, Centre de Diffractométrie Henri Longchambon, 69100
Villeurbanne, France.*

^c *Université Grenoble Alpes, SIMaP, 38402 St Martin d'Hères Cedex, France.*

^d *Condensed Matter Theory Group, Department of Physics and Astronomy, Uppsala University,
Box 516, 75120 Uppsala, Sweden.*

^e *Department of Physics, Indian Institute of Technology Ropar, Rupnagar 140001, Punjab, India.*

^f *Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, Univ Lyon, Université Claude
Bernard Lyon 1, F-69622 Villeurbanne, France.*

^s Université Lyon 1 - CPE Lyon, CP2M - CNRS, UMR 5128, 43 Bvd du 11 Novembre 1918,
69616 Villeurbanne, France.

E-mail: shashank.mishra@ircelyon.univ-lyon1.fr

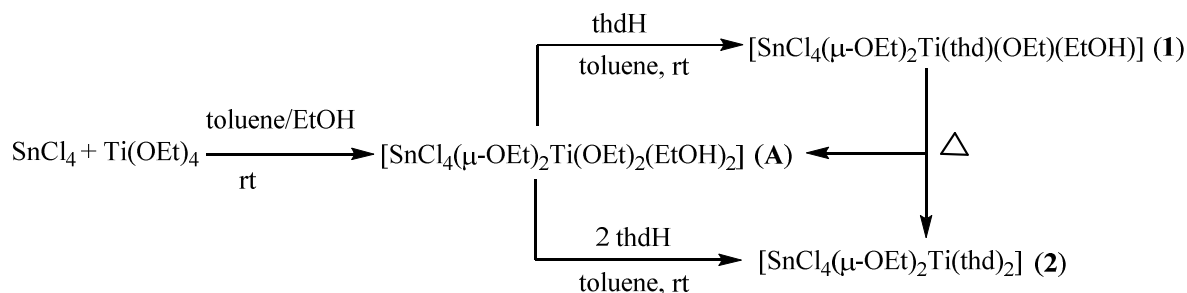
ABSTRACT. With an aim to enhance the stability and volatility of the heterometallic derivative $[\text{SnCl}_4(\mu\text{-OEt})_2\text{Ti}(\text{OEt})_2(\text{HOEt})_2]$ (**A**), obtained conveniently and quantitatively as a simple adduct formula from the equivalent reaction of commercially available SnCl_4 and $\text{Ti}(\text{OEt})_4$ in toluene/ethanol, its modification with 2,2,6,6-heptane-3,5-dione (thdH) is reported. The modified precursor $[\text{SnCl}_4(\mu\text{-OEt})_2\text{Ti}(\text{thd})(\text{OEt})(\text{HOEt})]$ (**1**), obtained from equimolar reaction of **A** and *thdH*, is stable at room temperature but rearranges on heating into **A** and $[\text{SnCl}_4(\mu\text{-OEt})_2\text{Ti}(\text{thd})_2]$ (**2**), as confirmed by the vapor pressure measurements and DFT calculations. The heterometallic **2** can be obtained in excellent yield from the reaction of **A** and *thdH* in 1:2 molar ratio and is stable in solid and solution phase up to 200 °C. However, the asymmetric nature of its structure consisting of fragments of titanium β -diketonate and tin chloride connected by bridging ethoxo groups, leads to breakdown into two homometallic components in gas phase, leading to deposition of tin-rich metal oxide films on the substrate.

The development of materials by soft chemical methods like sol-gel, Metal Organic Chemical Vapour Deposition (MOCVD), Atomic Layer Deposition (ALD), Metal-Organic Decomposition (MOD), etc. has always been closely associated with the chemistry of molecular precursors.¹⁻⁶ The molecular engineering to optimize the required properties in the precursors is usually achieved through judicious choice of ligands. Metal derivatives of the alkoxide and β -diketonate ligands

have become the predominant single-source precursors for oxide-based ceramic materials, mainly through sol-gel processing and MOCVD, respectively, because of their commercial availability, high solubility in routinely used organic solvents, and easy tunability of their hydrolytic characteristics and mass-transport properties.⁷⁻¹⁰ Another important axis of the molecular engineering is the synthesis of bi- and higher metallic derivatives with appropriate properties.¹¹⁻¹⁸ These single-source precursors simultaneously provide two or more metals in an accurate stoichiometry, allowing complex ceramic materials to be generated in one step by eliminating the prerequisite of matching the reaction rates in a multicomponent precursor mixture.¹⁹⁻²³ Among the various properties desired in MOCVD precursors, the most important ones are the high volatility and good thermal stability for efficient transport, as well as high reactivity to easily obtain the desired material.²⁴⁻²⁶ One of the important tactics to enhance volatility is to introduce heterolepticity in the molecules, which usually makes them loosely packed in the lattice and hence more volatile. However, the impact of the asymmetric structure of a bi-metallic precursor on its volatility as well as the composition and the quality of the deposited material is poorly studied. Previously, we have reported synthesis of a heterometallic derivative $[\text{SnCl}_4(\mu\text{-OEt})_2\text{Ti}(\text{OEt})_2(\text{HOEt})_2]$ (**A**) in quantitative yield by a convenient reaction between commercially available reagents SnCl_4 and $\text{Ti}(\text{OEt})_4$.^{27,28} This work was motivated by the potential usefulness of the $\text{TiO}_2\text{-SnO}_2$ system as eco-friendly oxide-based thermoelectric materials.^{29,30} Besides, the mixed tin-titanium oxides are also promising materials for the photovoltaic and photocatalytic applications.³¹⁻³³ While the use of above single-source single molecular precursors in sol-gel process ensured the synthesis of mixed nanoparticles of rutile $\text{Ti}_{0.5}\text{Sn}_{0.5}\text{O}_2$ without the generation of pure SnO_2 grains (which are hard to be sintered to high density) and thus allowing complete densification at low temperature by the spark plasma sintering (SPS) process, the spinodal

decomposition in the TiO₂-SnO₂ system produced nanoscale TiO₂/SnO₂-rich lamellae, where the high density of the well-organized interfaces reduced the thermal conductivity of the ceramic. To make above Sn-Ti heterometallic complexes more suitable for deposition by MOCVD method, we have now modified it with a sterically hindered β -diketonate (2,2,6,6-heptane-3,5-dione, abbreviated as thdH) to obtain a couple of novel molecular precursors and studied their thermal and vapor pressure behavior to assess the suitability of these complexes as precursors for the vapor phase production of TiO₂-SnO₂, Ti-doped SnO₂ or Sn-doped TiO₂ thin films.

The reaction of SnCl₄ with Ti(OEt)₄ provides a practical and quantitative approach to a heterobimetallic Sn(IV)-Ti(IV) derivative with the simple addition formula [SnCl₄(μ -OEt)₂Ti(OEt)₂(HOEt)₂] (**A**),²⁷ which in subsequent reactions in toluene with 2,2,6,6-heptane-3,5-dione (thdH) in 1:1 and 1:2, stoichiometry gives access to heteroleptic mixed species of alkoxo- β -diketonato, [SnCl₄(μ -OEt)₂Ti(thd)(OEt)(HOEt)] (**1**) and [SnCl₄(μ -OEt)₂Ti(thd)₂] (**2**), respectively (Scheme 1). Both compounds are highly soluble in chloroform, dichloromethane and ethanol, but show slightly less or poor solubility in toluene and *n*-pentane, respectively. Given the simple addition nature of the obtained products and excellent yield (typically above 90%), these reactions are easily scalable to the multigram scale. It assumes importance in view of large amounts (typically 5–10 g) of precursors needed for optimizing vapor pressure measurements and film deposition processes. These compounds are also more stable to moisture than the precursor compound **A**. At higher temperatures, however, compound **1** rearranges to produce a mixture of **A** and **2**, as shown by the isolation and structural characterization of the solvated dichloromethane species [SnCl₄(μ -OEt)₂Ti(thd)₂] \cdot CH₂Cl₂ (**2a**) from the products obtained after **1** was maintained at 80°C for a few hours, followed by crystallization from dichloromethane.



Scheme 1. Synthesis of heteroleptic alkoxo- β -diketonato bimetallic Sn-Ti species and redistribution of **1** into **A** and **2**.

The new compounds were thoroughly characterized by elemental analysis, spectroscopic (FT-IR, ^1H and ^{119}Sn NMR) and single crystal X-ray diffraction (XRD) studies. While solvated species **1** showed broad absorption and weak shoulder in the region $3200\text{-}3400\text{ cm}^{-1}$ and 1660 cm^{-1} for ν O-H and δ O-H, respectively, the absence of such absorption bands in the FT-IR spectra of **2** and **2a** confirmed the formation of non-solvated species. The FT-IR spectra of **1**, **2** and **2a** exhibited characteristic bands of the alkoxy and β -diketonate groups attached to the metal in the $1200\text{-}400\text{ cm}^{-1}$ region (Figure S1). Although the room temperature ^1H NMR spectra of these complexes were deceptively simple due to their fluxional behaviour, they confirmed the integration ratio between the ethoxide and heptanedionate ligands. The ^{119}Sn NMR of **1**, **2** and **2a** showed only a sharp peak at δ -548 to -600 ppm, which was consistent with values in the literature for the 6-coordinate Sn(IV) centre.^{34,35} The molecular structures of $[\text{SnCl}_4(\mu\text{-OEt})_2\text{Ti}(\text{thd})(\text{OEt})(\text{HOEt})]$ (**1**) and $[\text{SnCl}_4(\mu\text{-OEt})_2\text{Ti}(\text{thd})_2]$ (**2**) consist of Sn(IV) and Ti(IV) six-coordinated centres bridged by two ethoxo groups (Figure 1). Except for the fact that the complex **2a** crystallizes with a solvated dichloromethane molecule, the molecular structure of the **2** and **2a** are quite similar. Therefore, structure of **2a** is presented in Supporting Information only (Figure S2). The overall molecular geometry of all these structures can be described as a fusion of two octahedra built about Sn(IV)

and Ti(IV) via a common edge (O1 and O2). The six-coordination sphere around the titanium atom consists of all oxygen atoms, whereas the tin atom has a O₂Cl₄ environment. The Ti–O distances in **1**, **2** and **2a** vary from 1.742 (4) to 2.075(4) Å, the bond involving terminal OEt groups in **1** [1.742 (4) Å] being expectedly shorter than those involving terminal EtOH [2.075 (4) Å], bridging OEt [1.931(5)–2.047(4) Å] and bidentate thd [1.921(4)–1.974(4) Å]. The Sn–O bond distances, 2.086 (3)– 2.155(5) Å, are consistent with the literature values on Sn–μ-O bond distances.^{27,28} The axial Sn–Cl bonds [2.386(1)–2.465(1) Å] are slightly longer than those present in equatorial positions i.e., *trans* to the bridging Sn–O [2.366(2)–2.378(1) Å]. The equatorial O–Ti–O bond angles involving either terminal alkoxides (92.8° in **1**) or between two β-diketonato ligands (84.0–86.4° in **2** and **2a**) are significantly larger than the angle subtended by the bridging O1–Ti–O2 groups [73.43(1)–77.5(2)°]. The axial O–Ti–O bond angles, 166.8, 161.5 and 163.2 for **1**, **2** and **2a**, respectively, suggest a distorted octahedral geometry around Ti center. The tin center too has a distorted octahedral geometry because of the presence of a varying range of angles [68.65 (17)° to 100.88(8)°] involving O1–Sn–O2, O–Sn–Cl and Cl–Sn–Cl.

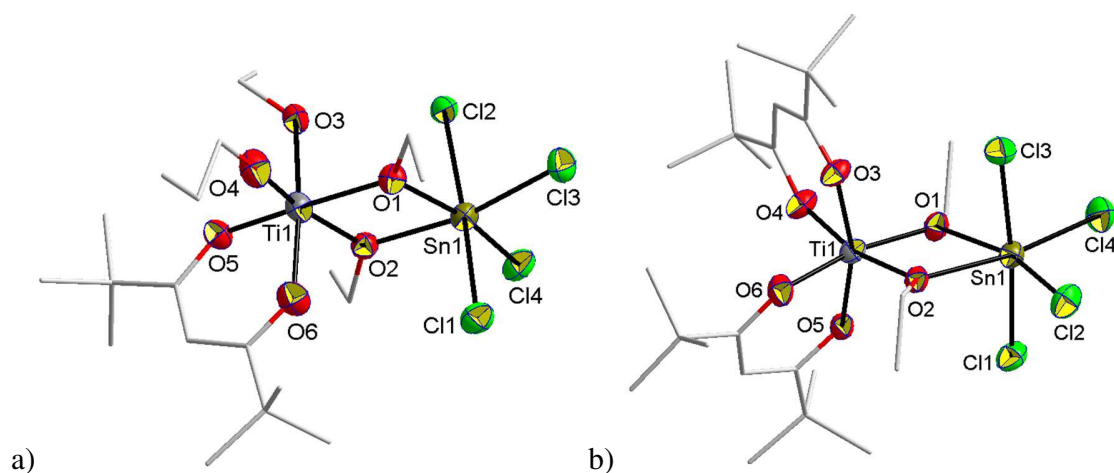


Figure 1. Perspective views of (a) [SnCl₄(μ-OEt)₂Ti(thd)(OEt)(HOEt)] (**1**) and (b) [SnCl₄(μ-OEt)₂Ti(thd)₂] (**2**) with displacement ellipsoids drawn at the 30% probability level. H atoms are

omitted for clarity. Selected bond lengths (Å) and angles (°) for (**1**): Ti1—O1 1.970 (4), Ti1—O2 2.047 (4), Ti1—O3 2.075 (4), Ti1—O4 1.742 (4), Ti1—O5 1.974 (4), Ti1—O6 1.921 (4), Sn1—O1 2.122 (3), Sn1—O2 2.086 (3), Sn1—Cl3 2.369(1), Sn1—Cl2 2.378(1), Sn1—Cl1 2.465(1), Sn1—Cl4 2.386(1), O1—Ti1—O2 73.43(1), O2—Ti1—O6 87.32(16), O2—Ti1—O4 170.57(17), O4—Ti1—O5 97.86(17), O1—Sn1—O2 69.63(13), O1—Sn1—Cl1 86.75(10), Cl3—Sn1—Cl4 93.84(5), Cl2—Sn1—O2 164.36(10), Cl2—Sn1—Cl3 99.29(6). (**2**): O1—Ti1 1.931(5), O2—Ti1 1.944(5), O3—Ti1 1.939(5), O4—Ti1 1.953(5), O5—Ti1 1.943(5), O6—Ti1 1.930(5), O1—Sn1 2.155(5), O2—Sn1 2.150(5), Cl1—Sn1 2.390(2), Cl2—Sn1 2.368(2), Cl3—Sn1 2.389(2), Cl4—Sn1 2.366(2), O1—Sn1—O2 68.65(17), O2—Sn1—Cl1 87.17(15), O1—Sn1—Cl2 95.41(13), O2—Sn1—Cl2 164.02(14), Cl1—Sn1—Cl2 91.51(8), Cl2—Sn1—Cl4 100.88(8), O4—Ti1—O2 91.7(2), O2—Ti1—O3 97.0(2), O4—Ti1—O1 169.3(2), O2—Ti1—O1 77.5(2), O2—Ti1—O6 171.2(2), O3—Ti1—O6 84.1(2).

Thermogravimetric analysis was used to estimate the thermal stability and volatility of the new precursors and to provide a first validation of the potential use of these metal-organic precursors for MOCVD (Figure 2a). The curves for compounds **A** and **1** had common characteristics with an onset of weight loss at low temperature (around 100°C) and residues of 40% and 25%, respectively (as compared to theoretical residues of 40 and 34% for SnTiO₄). These data demonstrated very low thermal stability and non-volatility of these two compounds. Compound **2** exhibited higher thermal stability (up to 200 °C), which is usually the case when β-diketonate ligand is added in the metal coordination sphere. Nevertheless, with a 40% final residue, it did not appear that the volatility of the modified precursor improved a lot. These studies indicated that the thermal characteristics of the new precursors at atmospheric pressure are not very favorable for their use in the conventional MOCVD. In order to more accurately assess the volatility of the compounds,

vapor pressure studies were conducted on compounds **A**, **1** and **2**. The vapor pressure values are given in the Supporting Information. Their temperature dependence (Figure 2b) is obtained by linear least-squares treatment of the data and fitted using the equation $\log(p/\text{Pa}) = A/(T/\text{K}) + B$ (Table 1). The results obtained show that the progressive addition of the *thd* ligand makes it possible to obtain increasingly volatile compounds **1** and **2**. For $[\text{SnCl}_4(\mu\text{-OEt})_2\text{Ti}(\text{thd})(\text{OEt})(\text{HOEt})]$ (**1**), the change of the slope trend at about 373 K shows that it must be thermally unstable. Indeed, the difference in slope in Figure 2b for the temperature range 357-370 K suggested that it underwent a redistribution of ligands to transform into compound $[\text{SnCl}_4(\mu\text{-OEt})_2\text{Ti}(\text{thd})_2]$ (**2**). Subsequent crystallization of the products from dichloromethane obtained after **1** was maintained at 80°C for a few hours and structural determination by single crystal X-ray studies, which showed the isolated species as the solvated dichloromethane species $[\text{SnCl}_4(\mu\text{-OEt})_2\text{Ti}(\text{thd})_2]\cdot\text{CH}_2\text{Cl}_2$ (**2a**), further confirmed the above redistribution of **1** into **A** and **2** (Figure S3). Using van't Hoff equation, it was obtained the enthalpy of sublimation and the entropy of the studied precursors (Tables S2 and S3). The DFT calculations on the precursors provided further confirmation on above redistribution of **1** into **A** and **2**. The optimized structures of these compounds showed geometrical parameters which were largely consistent with their single crystal X-ray data (see supplementary information, Table S1). The cohesive energy of reactant **1**, calculated from the ab initio molecular dynamics (AIMD) simulations at 353 K, was found to be -4.33 eV/atom, which is slightly less than the cohesive energy of the products of above redistribution (-4.37 eV/atom), indicating that the products were more stable than the reactant at 353 K.

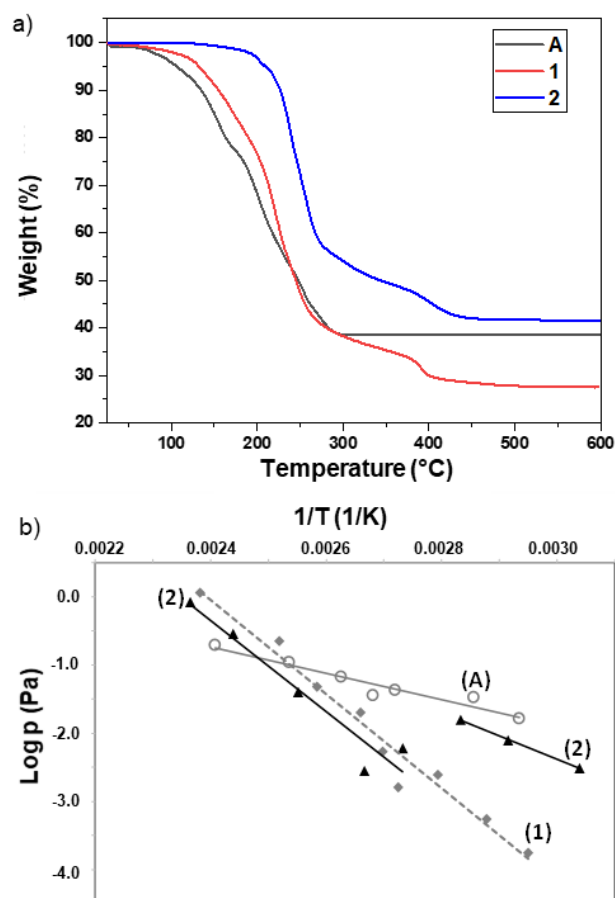


Figure 2. (a) TGA curves and (b) temperature variation of vapor pressure of $[\text{SnCl}_4(\mu\text{-OEt})_2\text{Ti}(\text{OEt})_2(\text{HOEt})_2]$ (**A**) (\circ), $[\text{SnCl}_4(\mu\text{-OEt})_2\text{Ti}(\text{thd})(\text{OEt})(\text{HOEt})]$ (**1**) (\diamond) and $[\text{SnCl}_4(\mu\text{-OEt})_2\text{Ti}(\text{thd})_2]$ (**2**) (\blacktriangle). The fit parameters of the linear trends are given in the Table 1. **Erreur ! Source du renvoi introuvable.**

Table 1. Sublimation parameters from the vaporization of **A**, **1** and **2**.

Precursor	T range /K	Log (p/Pa) = A/(T/K) + B	
		A	B
(A)	340 to 420	-1919 ± 232	3.869 ± 0.623

(1)	320 to 360	-3414 ± 118	7.861 ± 0.346
	360 to 420	-6684 ± 1035	15.693 ± 2.643
(2)	340 to 420	-6895 ± 472	16.499 ± 1.27

Although the vapour pressures obtained (around 0.1 Pa at 323 K) were slightly lower than the typical values used in MOCVD or ALD processes,³⁶ the most volatile and stable compound **2** was tested in mixed TiO₂-SnO₂ thin-film deposition by CVD. Film deposition was performed at 330 °C on Si wafer or Si/SiO₂ substrates under low pressure conditions with the precursor container maintained at 150 °C. The Scanning Electron Microscopy (SEM) images of the deposited films exhibited a nano-structured granular layer that was not dense but uniformly covered and continuous (Figure 3). Depending upon substrate's position in the reactor and deposition time, the film thickness varied in the range 10-170 nm, as indicated by the ellipsometry measurements (please see Supporting Information for more details). However, XRD and Energy-Dispersive X-ray spectroscopy (EDX) studies at different points in the film showed varying Ti and Sn ratio with the compositions changing in the range Ti_{0.33}Sn_{0.66}O₂ to SnO₂ (one particular XRD is displayed as Fig. 3c). For gaining a deeper knowledge of the composition and chemical state of the elements present, X-ray photoelectron spectroscopy (XPS) studies were conducted on a representative sample (Fig. 3d-f). The survey spectra revealed that besides containing tin, titanium and oxygen, these films also had a high carbon content upto 28% because of incomplete decomposition of the precursor. Quantitative analysis of the sample revealed an Sn/Ti stoichiometry close to 2. In the core level spectra, the presence of Ti⁴⁺ is indicated by the binding energies at 458.4 eV and 464.2 eV, due to Ti 2p_{3/2} and Ti 2p_{1/2}, respectively,^{37,38} whereas the electron binding energy (BE) value

for Sn 3d_{5/2} appears at 486.6 eV, indicating the presence of an oxygen-deficient SnO_x (with 2 ≥ x ≥ 1).

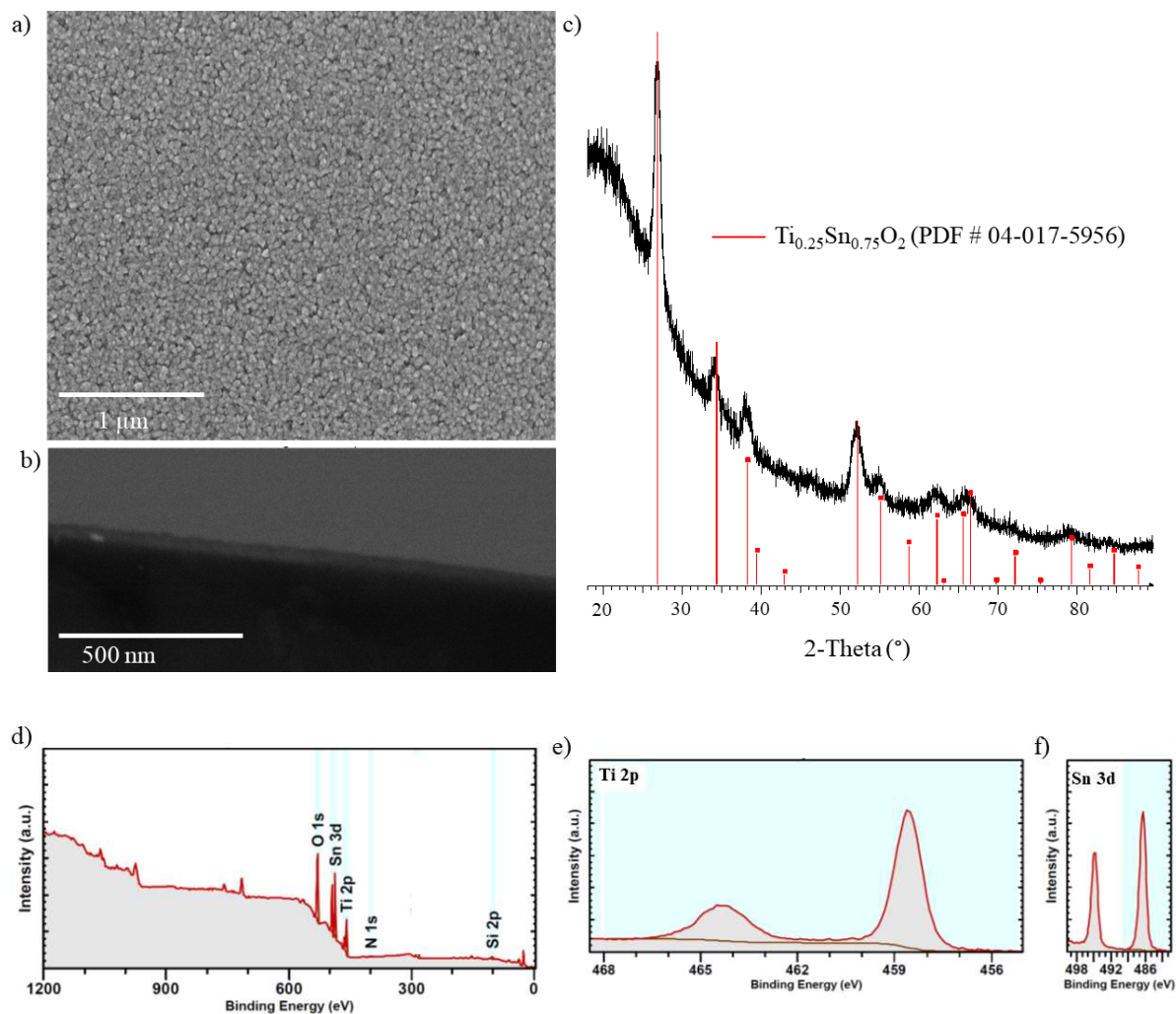
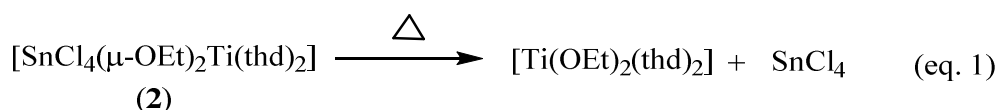


Figure 3. Characterization of thin films deposited on Si wafers using the precursor **2**: (a and b) Representative surface and cross-sectional SEM images, (c) XRD, and (d-f) XPS spectra.

These results suggest that the asymmetric structure of the bi-metallic compound led to a fragmentation of the molecule under CVD conditions (eq. 1), thus resulting in an asymmetry of reactivity with a multi-halogenated fragment being much more reactive than the fragment

containing the β -diketonate ligands. Indeed, both Ti and Sn fragments have been employed separately in CVD experiments for the deposition of TiO_2 and SnO_2 , respectively. While the closely related compound $[\text{Ti}(\text{OPr}^i)_2(\text{thd})_2]$ is commercially available and bench-mark precursor for the CVD deposition of TiO_2 ,³⁹ the tin fragment SnCl_4 has also been employed frequently for the deposition of SnO_2 .⁴⁰ As the above Ti precursor requires higher temperature (~ 500 °C) than SnCl_4 , it is no surprise that under our CVD conditions (substrate temperature 330 °C) a majority of Ti-species is pumped off leaving behind Sn-rich films.



The AIMD calculations on **2** at 623 K further confirmed its dissociation into two homometallic components i.e. $\text{Ti}(\text{thd})_2(\text{OEt})_2$ and SnCl_4 , as indicated by high energy fluctuation for **2** below 4 ps in the Figure 4, which smoothens gradually after the dissociation (the dissociated SnCl_4 shown in dotted red circle in Fig. 4). The associated negative dissociation energy (-0.83 eV) indicates exothermic nature of the reaction and, therefore, an energetically favorable transformation.⁴¹

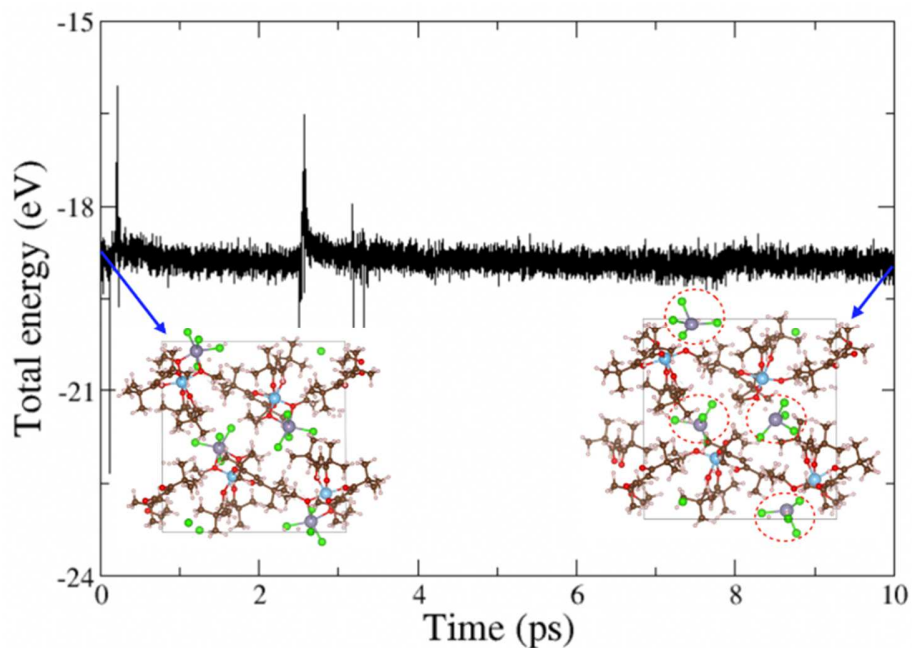


Figure 4. The ab initio molecular dynamics (AIMD) simulations of **2** at 623 K.

In conclusion, the thermal behavior of a series of bi-metallic Ti-Sn precursors was evaluated in terms of their molecular structure resulting from the progressive addition of the thd ligand. The thd ligand improved the volatility of the precursors but also generated a strong asymmetry in the structure, which is consisted of SnCl_4 and $\text{Ti}(\text{thd})(\text{OEt})(\text{EtOH})$ or $\text{Ti}(\text{thd})_2$ fragments bridged through two ethoxo groups. During gas phase deposition, this structural asymmetry led to different reactivities of the two metallic fragments and the deposition of a tin-rich layer. These results show that having a volatile bimetallic precursor is not a guarantee of film homogeneity by MOCVD, as it is equally important to ensure that the reactivity of each metal center is not too different.

ASSOCIATED CONTENT

Supporting Information Available. Experimental details of synthesis of new precursors, their characterization, vapor pressure measurements, MOCVD deposition and DFT calculations, FT-IR

spectra of new precursors, single crystal structure of **2a**, digital images of precursor **1** before and after heating as well as ellipsometry parameters on selected samples. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

Accession Codes

CCDC1558712, 1558713 and 1558714 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

The following files are available free of charge.

Cif files of **1**, **2** and **2a** (file type, i.e., cif)

Supplementary information (file type, i.e., PDF)

AUTHOR INFORMATION

Corresponding Author

* Shashank Mishra, E-mail: shashank.mishra@ircelyon.univ-lyon1.fr; Fax : (+33) 472445399.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

S.M. is grateful to (the late) Prof. R. C. Mehrotra, (the late) Prof. L. G. Hubert-Pfalzgraf and Prof. A. Singh for introducing him to the fascinating world of metal alkoxides. Authors thank Ms.

Laurence Burel (IRCELYON) for SEM images. D.S. and R.A. thanks the Swedish Research Council (VR-2016-06014 & VR-2020-04410) and J. Gust. Richert stiftelse, Sweden (2021-00665) for financial support. SNIC and HPC2N are acknowledged for providing the computing facilities.

REFERENCES

1. Brune, V.; Grosch, M.; Weißing, R.; Hartl, F.; Frank, M.; Mishra, S.; Mathur, S. Influence of the Choice of Precursors in the Synthesis of Two Dimensional Transition Metal Dichalcogenides. *Dalton Trans.* **2021**, *50*, 12365-12385.
2. Mishra, S.; Daniele, S. Molecular engineering of metal alkoxides for solution phase synthesis of high-tech metal oxide nanomaterials. *Chem. Eur. J.* **2020**, *26*, 9292–9303.
3. Mishra, S.; Daniele, S. Metal-Organic Derivatives with Fluorinated Ligands as Precursors for Inorganic Nanomaterials. *Chem. Rev.* **2015**, *115*, 8379-8448.
4. Seisenbaeva, G. A.; Kessler, V. G. Precursor directed synthesis – “molecular” mechanisms in the Soft Chemistry approaches and their use for template-free synthesis of metal, metal oxide and metal chalcogenide nanoparticles and nanostructures. *Nanoscale* **2014**, *6*, 6229-6244.
5. Bloor, L. G.; Carmalt, C. J.; Pugh, D. Single-source precursors to gallium and indium oxide thin films. *Coord. Chem. Rev.* **2011**, *255*, 1293-1318.
6. Mishra, S.; Daniele, S.; Hubert-Pfalzgraf, L. G. Metal 2-ethylhexanoates and related compounds as useful precursors in materials science. *Chem. Soc. Rev.* **2007**, *36*, 1770-1787.
7. Bradley, D. C.; Mehrotra, R. C.; Rothwell, I. P.; Singh, A. *Alkoxo and Aryloxo derivatives of Metals*, Academic Press, New York, 2001.

8. Turova, N. Ya.; Turevskaya, E. P.; Kessler, V. G.; Yanovskaya, M. I. *The Chemistry of Metal Alkoxide*, Kluwer Academic Publishers, Boston, 2002.
9. Condorelli, G. G.; Malandrino, G.; Fragalà, I. L. Engineering of molecular architectures of β -diketonate precursors toward new advanced materials. *Coord. Chem. Rev.* **2007**, *251*, 1931-1950.
10. Tiitta, M.; Niinisto, L. Volatile Metal β -Diketonates: ALE and CVD Precursors for Electroluminescent Device Thin Films. *Chem. Vap. Deposition* **1997**, *3*, 167-182.
11. Gahlot, S.; Jeanneau, E.; Singh, D.; Panda, P. K.; Mishra, Y. K.; Ahuja, R.; Ledoux, G.; Mishra, S. Molecules versus nanoparticles: Identifying a reactive molecular intermediate in the synthesis of ternary coinage metal chalcogenides. *Inorg. Chem.* **2020**, *59*, 7727-7738.
12. John, L.; Sobota, P. Synthesis of Heterometallic Compounds with Uncommon Combinations of Elements for Oxide Nanomaterials Using Organometallics. *Acc. Chem. Res.* **2014**, *47*, 470-481.
13. Chen, Y.; Mishra, S.; Ledoux, G.; Jeanneau, E.; Daniel, M.; Zhang, J.; Daniele, S. Direct synthesis of hexagonal NaGdF₄ nanocrystals from a single-source precursor: Upconverting NaGdF₄:Yb³⁺,Tm³⁺ and its composites with TiO₂ for near-IR-driven photocatalysis. *Chem. Asian J.* **2014**, *9*, 2415-2421.
14. Wei, Z.; Filatov, A. S.; Dikarev, E. V. Volatile Heterometallic Precursors for the Low-Temperature Synthesis of Prospective Sodium Ion Battery Cathode Materials. *J. Am. Chem. Soc.* **2013**, *135*, 12216-12219.

15. Mishra, S.; Mendez, V.; Jeanneau, E.; Caps, V.; Daniele, S. A single source precursor route to group 13 homo- and heterometal oxides as highly active supports for gold catalyzed aerobic epoxidation of *t*-stilbene. *Eur. J. Inorg. Chem.* **2013**, 500-510.
16. Mishra, S.; Ledoux, G.; Jeanneau, E.; Daniele, S.; Joubert, M.-F. Novel heterometal-organic complexes as first single source precursors for up-converting NaYF₄:Yb³⁺, Er³⁺/Tm³⁺ nanomaterials. *Dalton Trans.* **2012**, 41, 1490-1502.
17. Mishra, S.; Jeanneau, E.; Daniele, S.; Mendez, V. Aminoalkoxo-supported heteroleptic hexanuclear gallium(III) wheel as a synthon for group 13 heterometallics: A rare sol-gel precursor for mixed Al-Ga oxide as a support for gold catalysts. *Dalton Trans.* **2010**, 39, 7440-7443.
18. Mishra, S.; Daniele, S.; Ledoux, G.; Jeanneau, E.; Joubert, M. F. Heterometallic Na-Y(Ln) trifluoroacetate diglyme complexes as novel single source precursors for upconverting NaYF₄ nanocrystals co-doped with Yb and Er/Tm ions. *Chem. Commun.* **2010**, 46, 3756-3758.
19. Lu, H.; Wright, D. S.; Pike, S. D. The use of mixed-metal single source precursors for the synthesis of complex metal oxides. *Chem. Commun.* **2020**, 56, 854-871.
20. Schubert, U. Heterobimetallic sol-gel precursors and intermediates. *J. Sol-Gel Sci. Technol.* **2016**, 79, 249-261.
21. John, L.; Sobota, P. Synthesis of Heterometallic Compounds with Uncommon Combinations of Elements for Oxide Nanomaterials Using Organometallics. *Acc. Chem. Res.* **2014**, 47, 470-481.
22. Matthews, P. D.; King, T. C.; Wright, D. S. Structure, photochemistry and applications of metal-doped polyoxotitanium alkoxide cages. *Chem. Commun.* **2014**, 50, 12815-12823.

23. Szafert, S.; John, L.; Sobota, P. Well-defined polynuclear heterobimetallic complexes as precursors for ceramic and magnetic materials. *Dalton Trans.* **2008**, 6509–6520.
24. Hatanpää, T.; Ritala, M.; Leskelä, M. Precursors as enablers of ALD technology: Contributions from University of Helsinki. *Coord. Chem. Rev.* **2013**, *257*, 3297-3322.
25. Emslie, D. J. H.; Chadha, P.; Price, J. S. Metal ALD and pulsed CVD: Fundamental reactions and links with solution chemistry. *Coord. Chem. Rev.* **2013**, *257*, 3282-3296.
26. Potts, S. E.; Carmalt, C. J.; Blackman, C. S.; Abou-Chahine, F.; Leick, N.; Kessels, V. M. M.; Davies, H. O.; Heys, P. N. Bis(cyclopentadienyl) zirconium(IV) amides as possible precursors for low pressure CVD and plasma-enhanced ALD. *Inorg. Chim. Acta* **2010**, *363*, 1077-1083.
27. Mishra, S.; Jeanneau, E.; Mangematin, S.; Chermette, H.; Poor Kalhor, M.; Bonnefont, G.; Fantozzi, G.; Le Floch, S.; Pailhese, S.; Daniele, S. A convenient and quantitative route to Sn(IV)–M [M = Ti(IV), Nb(V), Ta(V)] heterobimetallic precursors for dense mixed-metal oxide ceramics. *Dalton Trans.* **2015**, *44*, 6848–6862.
28. Mishra, S.; Jeanneau, E.; Berger, M.-H.; Hochepped, J.-F.; Daniele, S. Novel heteroleptic heterobimetallic alkoxide complexes as facile single source precursors for Ta⁵⁺-doped TiO₂-SnO₂ nanoparticles. *Inorg. Chem.* **2010**, *49*, 11184-11189.
29. Dynys, F. W.; Berger, M.-H.; Sehirlioglu, A. Thermoelectric Properties of Undoped and Doped (Ti_{0.75}Sn_{0.25})O₂. *J. Am. Ceram. Soc.* **2012**, *95*, 619-626.

30. Hochepped, J.-F.; Berger, M.-H.; Dynys, F.; Dessombz, A.; Sayir, A. Aqueous Co-precipitated $\text{Ti}_{0.5}\text{Sn}_{0.5}\text{O}_2$ Nanopowders as Precursors for Dense Spinodally Decomposed Ceramics. *J. Am. Ceram. Soc.* **2011**, *94*, 4226-4230.
31. Xu, X.; Yang, G.; Liang, J.; Ding, S.; Tang, C.; Yang, H.; Yan, W.; Yang, G.; Yu, D. Fabrication of one-dimensional heterostructured $\text{TiO}_2@\text{SnO}_2$ with enhanced photocatalytic activity. *J. Mater. Chem. A* **2014**, *2*, 116-122.
32. Ponja, S.; Sathasivam, S.; Chadwick, N.; Kafizas, A.; Bawaked, S. M.; Obaid, A. Y.; Al-Thabaiti, S.; Basahel, S. N.; Parkin, I. P.; Carmalt, C. J. Aerosol assisted chemical vapour deposition of hydrophobic $\text{TiO}_2\text{-SnO}_2$ composite film with novel microstructure and enhanced photocatalytic activity. *J. Mater. Chem. A* **2013**, *1*, 6271-6278.
33. Shinde, D. V.; Mane, R. S.; Oh, I.-H.; Lee, J. K.; Han, S.-H. SnO_2 nanowall-arrays coated with rutile- TiO_2 nanoneedles for high performance dye-sensitized solar cells. *Dalton Trans.* **2012**, *41*, 10161-10163.
34. Verchère, A.; Mishra, S.; Jeanneau, E.; Guillon, H.; Decams, J.-M.; Daniele, S. Heteroleptic Tin(IV) Aminoalkoxides and Aminofluoroalkoxides as MOCVD Precursors for Undoped and F-Doped SnO_2 Thin Films. *Inorg. Chem.* **2020**, *59*, 7167-7180.
35. Mishra, S.; Goyal, M.; Singh, A. Synthesis and spectroscopic (IR, ^1H , ^{13}C , and ^{119}Sn NMR) characterization of mono- and diorganotin(IV) complexes containing sterically hindered N-arylsalicylaldiminate groups. *Main Group Metal Chem.* **2002**, *25*, 437-444.
36. Ritala, M.; Leskela, A. in: H.S. Nalwa (Ed.), Handbook of Thin Film Materials, vol. 1, Academic Press, San Diego, CA, 2001, p.103.

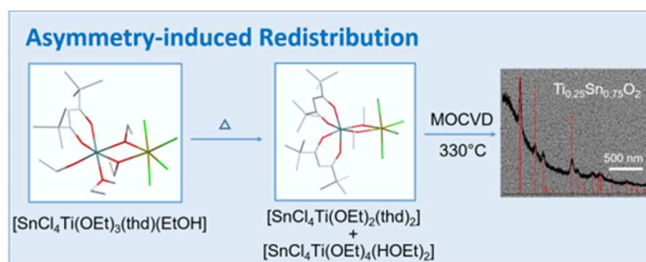
37. Gahlot, S.; Dappozze, F.; Singh, D.; Ahuja, R.; Cardenas, L.; Burel, L.; Amans, D.; Guillard, C.; Mishra, S. Room-temperature conversion of Cu_{2-x}Se to CuAgSe nanoparticles to enhance the photocatalytic performance of their composites with TiO_2 . *Dalton Trans.* **2020**, *49*, 3580–3591.
38. Gahlot, S.; Jeanneau, E.; Dappozze, F.; Guillard, C.; Mishra, S. Precursor-mediated synthesis of Cu_{2-x}Se nanoparticles and their composites with TiO_2 for improved photocatalysis, *Dalton Trans.* **2018**, *47*, 8897–8905.
39. Bhakta, R.; Thomas, R.; Hipler, F.; Bettinger, H. F.; Muller, J.; Ehrhartb, P.; Devi, A. MOCVD of TiO_2 thin films and studies on the nature of molecular mechanisms involved in the decomposition of $[\text{Ti}(\text{OPr}^i)_2(\text{tbaoc})_2]$. *J. Mater. Chem.* **2004**, *14*, 3231-3238.
40. Molloy, K. C. Precursors for the formation of tin(IV) oxide and related materials. *J. Chem. Res.* **2008**, 549-554.
41. Kuntz, P. J.; Nemeth, E. M.; Polanyi, J. C.; Rosner, S. D.; Young, C. E. Energy distribution among products of exothermic reactions. II. Repulsive, mixed, and attractive energy release. *J. Chem. Phy.* **1966**, *44*, 1168-84.

FOR TABLE OF CONTENTS USE ONLY

Asymmetry-Induced Redistribution in Sn(IV)-Ti(IV) Hetero-Bimetallic Alkoxide Precursors and its Impact on Thin Films Deposition by Metal-Organic Chemical Vapor Deposition

Shashank Mishra,* Erwann Jeanneau, Liang Tian, Ioana Nuta, Elisabeth Blanquet, Deobrat Singh, Rajeev Ahuja, Catherine Marichy, Stéphane Daniele

TOC graphic



Synopsis

The introduction of sterically crowded thdH ligand in the Ti-Sn heterometallic precursors improves the volatility of the precursors significantly, but also generates a strong asymmetry in the structure, leading to different reactivities of the two metallic fragments during MOCVD and the deposition of a tin-rich layer.