

Novel Heteroleptic Heterobimetallic Alkoxide Complexes as Facile Single-Source Precursors for Ta⁵⁺ Doped TiO₂–SnO₂ Nanoparticles

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The nanometric mixed tin–titanium oxide doped with a M⁵⁺ cation was recently shown as a promising thermoelectric material. We report here synthesis of novel molecular precursors for above material using a convenient approach of reacting a metal chloride with a metal alkoxide. Heterometallic complexes with simple addition formula [(EtOH)₂(OEt)₂Ti(μ-OEt)₂SnCl₄] (1 · EtOH) and [(EtOH)(OEt)₃Ta(μ-OEt)₂SnCl₄] (2) were isolated in quantitative yield, which on recrystallization from isopropanol afforded mixed-alkoxide complexes [(PrⁱOH)₂(OPrⁱ)₂Ti(μ-OEt)₂SnCl₄] (3) and [(PrⁱOH)(OPrⁱ)₃Ta(μ-OEt)₂SnCl₄] (4), respectively, thus indicating the robustness of the heterometallic M(μ-OEt)₂Sn core in the solution phase. Facile conversion of these precursors to halide-free spinodal form of Ta⁵⁺-doped TiO₂–SnO₂ as a potential thermoelectric material is reported.

Introduction

Thermoelectric materials, which convert thermal energy into electric energy, has attracted a renewed interest over the past decade, thanks to the discovery of some new thermoelectric materials with high values of the thermoelectric figure-of-merit (zT).¹ Despite this advancement, which has been possible mainly because of the incorporation of new ideas, such as nanostructuring,² many challenges remain in the way to obtain the ultimate advanced thermoelectric materials displaying better performance, chemical and thermal stability at the appropriate operating temperatures and environmental safety levels. At present, the best thermoelectric materials for medium range temperatures are narrow band gap semiconductors made of weakly bonded heavy elements, such as Bi₂Te₃ (zT = 0.9) and PbTe (zT = 0.8).³ The future of such materials is strongly restricted because of the toxicity, rarity, or price

of the constituent elements. These materials also show low resistance toward high temperature oxidative environment. Since the discovery of good thermoelectric properties in the layered Na_xCoO₂,⁴ a number of new oxides have been investigated as possible candidates for oxide thermoelectric materials.⁵ In this regards, the TiO₂–SnO₂ system is very attractive because not only a variety of stable nanostructures with low thermal conductivity can be reproduced in this system, but it is also free from toxic or precious elements.⁶ However, the densification property and electrical conductivity of this system need to be improved. The Sn-rich compounds are difficult to sinter to high density because of the predominance of nondensifying transport mechanisms. On the other hand, the band gaps of rutile TiO₂ (~3.0 eV) and SnO₂ (~3.6 eV) are too large to meet the requirements for good thermoelectrics. An improved densification can be achieved by intimate mixing of constituent elements at atomic level, whereas the electrical conductivity can be improved by doping this system with cations such as Nb⁵⁺/Ta⁵⁺ or by heat treatment in reducing atmosphere.⁶

The Chemical Solution Deposition (CSD) routes to solid-state materials such as Sol–Gel (SG) processing or Metal–Organic Decomposition (MOD) are quite attractive because of their inherent advantages.⁷ These chemical routes have rarely been exploited for the synthesis of mixed (Ti,Sn)O₂

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nanoparticles, particularly, the use of aqueous medium is seldom addressed in the literature. Even though many homo-metal halo-alkoxides have been successfully used to get halide-free metal oxide nanomaterials,⁸ the reactions between a metal halide and a metal alkoxide to get heterometal halo-alkoxides remain very less explored, affording either no heterometallics or forming ionic complexes of the type $[\text{Mo}(\text{OMe})_5(\text{CH}_3\text{CN})]_n$, $[\text{Bi}_2\text{Cl}_7]$ and $[\text{Co}_2\text{Ta}_2(\text{OMe})_{12}(\text{CH}_3\text{CN})_4][\text{CoCl}_3(\text{CH}_3\text{CN})]_2$.⁹ In this paper, we show that such reactions can occur in mild conditions, affording novel complexes with simple addition formula. To our knowledge, the $[\text{Mg}\{\eta^4\text{-Ti}_2(\text{OEt})_8\text{Cl}\}(\mu\text{-Cl})]_2$ ¹⁰ remains the only structurally characterized molecular addition complex reported under this category, though an oxo complex $[\text{Bi}_2\text{V}_2\text{Cl}_6(\mu\text{-O})_2(\mu\text{-OC}_2\text{H}_4\text{OCH}_3)_4(\text{OC}_2\text{H}_4\text{OCH}_3)_2]$, obtained from the reaction of $\text{VO}(\text{OPr}^f)_3$ and BiCl_3 in the presence of 2-methoxy ethanol, is also known.¹¹ Moreover, only a handful of halo-alkoxo heterometallic tin(IV) derivatives are known so far, all prepared by the metathesis reaction of metal halide and alkali metal alkoxometallates.¹²

Experimental Section

General Procedures. All manipulations were carried out under argon using Schlenk tubes and vacuum line techniques. SnCl_4 , $\text{Ti}(\text{OEt})_4$, and $\text{Ta}(\text{OEt})_5$ (all Aldrich) were used as received. Solvents were purified on an MB SPS-800 instrument. FT-IR spectra were recorded as Nujol mulls on a Bruker Vector 22 spectrometer. ¹H and ¹¹⁹Sn NMR spectra were recorded on a Bruker AC-300 spectrometer using CDCl_3 and toluene-*d*₈ as a solvent, respectively. ¹¹⁹Sn NMR chemical shifts were referenced externally to SnEt_4 . Analytical data were obtained from the Service Central d'Analyses du CNRS. Raman experiments were carried out with LabRam HR equipment (Jobin Yvon). TG-DTA data were collected in air using a Setaram TGA92-12 thermal analyzer (thermal ramp 5 °C/min, temperature range 20–600 °C). X-ray powder patterns were obtained with a Bruker (Siemens) D 500 diffractometer using the $\text{CuK}\alpha$ radiation. The Transmission Electron Microscopy was performed on a 200 kV FEG TEM-STEM, FEI Tecnai F20-ST equipped with an EDAX spectrometer. The nanopowders were deposited on a carbon film supported by a copper grid.

Synthesis of 1–4. $[(\text{EtOH})_2\text{Ti}(\text{OEt})_4\text{TiSnCl}_4] \cdot (\text{EtOH})$. SnCl_4 (4.3 mL, 36.2 mmol) was added dropwise to a *n*-pentane solution (70 mL) of $\text{Ti}(\text{OEt})_4$ (8.22 g, 36.1 mmol) at 0 °C. The reaction mixture was stirred for 2 h at room temperature, followed by decantation of the *n*-pentane. The colorless slightly viscous material obtained was then dissolved in 30 mL of EtOH and stirred further for 1 h. Removal of ethanol under vacuum afforded the title complex in almost quantitative yield (22.0 g, 98%). Colorless crystals suitable for X-ray analysis were obtained from a concentrated ethanol solution. Yield, 18 g (80%). Anal. Found: C, 26.73; H, 5.97; Cl, 22.63; Sn, 18.90; Ti, 7.57%. Calcd for $\text{C}_{12}\text{H}_{32}\text{Cl}_4\text{O}_6\text{SnTi} \cdot \text{C}_2\text{H}_6\text{O}$ (626.85): C, 26.80; H, 6.02; Cl, 22.65; Sn, 18.94; Ti, 7.64%. FT-IR (Nujol, Cm^{-1}): 3200 $\nu(\text{OH})$, 1650w $\delta(\text{OH})$, 1169 m, 1130s $\nu(\text{OR})$; 1095s, 1029s $\nu(\text{C-O})_{\text{terminal}}$,

973s $\nu(\text{C-O})_{\text{bridging}}$, 917s, 860s, 813s, 727 m; 582s, 462s, 410 m $\nu(\text{M-O})$. ¹H NMR (CDCl_3 , ppm, 20 °C): 0.97 (br, 18H, CH_3), 4.02 (br, 12H, CH_2). ¹H NMR (CDCl_3 , ppm, –40 °C): 1.19, 1.24 (t, $J = 6.8$ Hz, 12H, terminal CH_3), 1.31 (t, $J = 6.8$ Hz, 6H, bridging CH_3), 3.67 (br, 2H, OH), 4.03 (br, 4H, CH_2), 4.18 (q, $J = 6.8$ Hz, 4H, CH_2), 4.48 (q, $J = 6.8$ Hz, 4H, CH_2). ¹¹⁹Sn NMR (tol-*d*₈, ppm): $\delta -554.6$ ppm.

$[(\text{HOEt})(\text{OEt})_5\text{TaSnCl}_4] \cdot (\text{EtOH})$ (2). Using the above procedure, derivative 2 was obtained from $\text{Ta}(\text{OEt})_5$ (1.04 g, 2.55 mmol) and SnCl_4 (0.30 mL, 2.56 mmol) in a mixture of toluene (5 mL) and EtOH (1 mL) and crystallized from concentrated solution at –20 °C. Yield: 1.70 g (93%). Anal. Found: C, 20.14; H, 4.32; Cl, 19.93; Sn, 16.63; Ta, 25.27%. Calcd for $\text{C}_{12}\text{H}_{31}\text{Cl}_4\text{O}_6\text{SnTa}$ (714.75): C, 20.15; H, 4.34; Cl, 19.87; Sn, 16.60; Ta, 25.32%. FT-IR (Nujol, Cm^{-1}): 3192br $\nu(\text{OH})$, 1657w $\delta(\text{OH})$, 1341w, 1273w; 1170s, 1107s $\nu(\text{OR})$; 1076s, 1016s $\nu(\text{C-O})_{\text{terminal}}$, 934s $\nu(\text{C-O})_{\text{bridging}}$, 902w, 869s, 727w; 524s, 471 m $\nu(\text{M-O})$. ¹H NMR (CDCl_3 , ppm, 20 °C): 1.39 (t, $J = 6.8$ Hz, 18H, CH_3), 4.10 (br, 1H, OH), 4.63, 4.82 (m, $J = 6.8$ Hz, 12H, CH_2). ¹¹⁹Sn NMR (tol-*d*₈, ppm): $\delta -548$ ppm.

$[(\text{Pr}^f\text{OH})_2(\text{OPr}^f)_2\text{Ti}(\text{OEt})_2\text{SnCl}_4] \cdot (\text{EtOH})$ (3). The title complex as colorless crystalline material was obtained by stirring the complex 1 (2.18 g, 3.47 mmol) in toluene (10 mL) and isopropanol (10 mL) for 30 min, followed by crystallization from a concentrated solution (7 mL) at –20 °C. Yield: 1.97 g (89%). Anal. Found: C, 30.0; H, 6.23; Cl, 22.15; Sn, 18.55; Ti, 7.50. Calcd for $\text{C}_{16}\text{H}_{40}\text{Cl}_4\text{O}_6\text{SnTi}$ (636.86): C, 30.15; H, 6.28; Cl, 22.30; Sn, 18.64; Ti, 7.52%. FT-IR (Nujol, Cm^{-1}): 3210br $\nu(\text{OH})$, 1613 $\delta(\text{OH})$, 1358 m, 1323w; 1166s, 1136s, 1129s $\nu(\text{OR})$; 1026s, 1009s $\nu(\text{C-O})_{\text{terminal}}$, 932s $\nu(\text{C-O})_{\text{bridging}}$, 883s, 876s, 825s, 730w, 623s; 550 m, 516s, 488s, 440 m $\nu(\text{M-O})$. ¹H NMR (CDCl_3 , ppm, 20 °C): 1.20 (d, $J = 6.2$ Hz, 24 H, Me_2CH), 1.60 (t, $J = 6.2$ Hz, 6H, MeCH_2), 4.10 (br, 2H, OH), 4.60 (sept, 4H, Me_2CH), 4.95 (q, 4H, CH_2). ¹¹⁹Sn NMR (tol-*d*₈, ppm): $\delta -566$ ppm.

$[(\text{Pr}^f\text{OH})(\text{OPr}^f)_3\text{Ta}(\text{OEt})_2\text{SnCl}_4] \cdot (\text{EtOH})$ (4). Using the above-described procedure, recrystallization of the complex 2 (1.45 g, 2.03 mmol) from isopropanol (2 mL) and toluene (5 mL) at –20 °C gave title derivative as colorless crystals. Yield: 1.43 g (92%). Anal. Found: C, 25.07; H, 5.10; Cl, 18.44; Sn, 15.40; Ta, 23.42. Calc. for $\text{C}_{16}\text{H}_{39}\text{Cl}_4\text{O}_6\text{SnTa}$ (768.93): C, 24.97; H, 5.07; Cl, 18.47; Sn, 15.44; Ta, 23.53%. FT-IR (Nujol, Cm^{-1}): 3179br $\nu(\text{OH})$, 1631w $\delta(\text{OH})$, 1342w, 1305w; 1150s, 1107s $\nu(\text{OR})$, 1010s $\nu(\text{C-O})_{\text{terminal}}$, 924 m $\nu(\text{C-O})_{\text{bridging}}$, 900w, 873s, 819 m, 722w; 576 m, 516s, 469 m $\nu(\text{M-O})$. ¹H NMR (CDCl_3 , ppm, 20 °C): 1.25 (d, $J = 6.2$ Hz, 24 H, Me_2CH), 1.63 (t, $J = 6.2$ Hz, 6H, MeCH_2), 4.10 (br, 1H, OH), 4.52 (sept, 4H, Me_2CH), 4.96 (q, 4H, CH_2). ¹¹⁹Sn NMR (tol-*d*₈, ppm): $\delta -580$ ppm.

X-ray Crystallography. Crystals of 1, 3, and 4 were mounted on an Oxford-Diffraction Gemini diffractometer equipped with an Atlas CCD detector and using Mo radiation. Intensities were collected at 150 K by means of the CrysAlisPro software.¹³ Reflection indexing, unit-cell parameters refinement, Lorentz-polarization correction, peak integration, and background determination were carried out with the CrysAlisPro software.¹³ A numerical absorption correction was applied by modeling the crystal faces.¹⁴ The structures were solved by direct methods with SIR97,¹⁵ and the refinement was achieved using the CRYSTALS software.¹⁶ Crystallographic and refinement data of (1) (CCDC no. 759075): $\text{C}_{12}\text{H}_{32}\text{Cl}_4\text{O}_6\text{SnTi} \cdot \text{C}_2\text{H}_6\text{O}$, monoclinic, $P2_1/n$, mol wt. = 626.85, $a = 9.6432(7)$ Å, $b = 17.175(1)$ Å, $c = 16.276(1)$ Å, $\beta = 97.526(7)^\circ$, $V = 2672.4(3)$ Å³, $Z = 4$, $\mu = 1.66$ mm^{–1}, $T = 150$ K,

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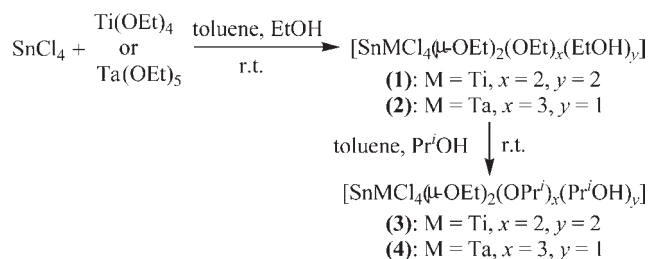
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Scheme 1. Synthesis of 1–4



measured reflections = 16663, independent reflections = 6468, $R_{\text{int}} = 0.031$, data = 6468, restraints = 2, parameters = 245, $S = 0.94$, $R[F^2 > 2\sigma(F^2)] = 0.046$, $wR(F^2) = 0.123$. (3) (CCDC no. 780822): Formula $\text{C}_{16}\text{H}_{40}\text{Cl}_4\text{O}_6\text{SnTi}$, monoclinic, $P2_1/m$, mol wt. = 636.86, $a = 9.6599(8)$ Å, $b = 14.9929(10)$ Å, $c = 10.1380(9)$ Å, $\beta = 106.034(9)^\circ$, $V = 1411.2(2)$ Å³, $Z = 2$, $\mu = 1.57$ mm⁻¹, $T = 100$ K, measured reflections = 15378, independent reflections = 3682, $R_{\text{int}} = 0.033$, data = 3682, restraints = 40, parameters = 181, $S = 0.96$, $R[F^2 > 2\sigma(F^2)] = 0.040$, $wR(F^2) = 0.071$, residual electron density = -1.80 to 0.97 e.Å⁻³. (4) (CCDC no. 759072): $\text{C}_{16}\text{H}_{39}\text{Cl}_4\text{O}_6\text{SnTa}$, monoclinic, $P2_1/n$, mol wt. = 768.93, $a = 9.9743(9)$ Å, $b = 14.803(2)$ Å, $c = 19.005(3)$ Å, $\beta = 100.05(1)^\circ$, $V = 2763.0(6)$ Å³, $Z = 4$, $\mu = 5.27$ mm⁻¹, $T = 150$ K, measured reflections = 10962, independent reflections = 4793, $R_{\text{int}} = 0.060$, data = 4793, restraints = 74, parameters = 253, $S = 0.96$, $R[F^2 > 2\sigma(F^2)] = 0.061$, $wR(F^2) = 0.161$.

Sintering of the Nanopowder to Prepare Bulk Ceramic. The as-prepared powder obtained from the hydrolysis of above complexes were pressed into pellets (10 mm in diameter and 2 mm in thickness) by uniaxial pressing (60 MPa) in a steel die. The pellets were sintered at 1500 °C using a heating rate of 1.6 °C/min and kept at this temperature and ambient pressure for 4 h before let it cool down to room temperature at a rate of 1.6 °C/min. A thin foil for TEM observation was obtained from a sintered pellet by mechanical thinning of a 2 × 2.5 rectangle down to a thickness of 30 μm followed by an ion milling of Ar⁺ at 5 kV.

Results and Discussion

Synthesis and Spectroscopic Characterization. Reactions of $\text{Ti}(\text{OEt})_4$ or $\text{Ta}(\text{OEt})_5$ with SnCl_4 in a hydrocarbon solvent, followed by a treatment with ethanol, proceed in a smooth manner to afford quantitative yield of novel heterometallic molecular complexes, which are simple addition products of the initial reactants, that is, $[(\text{EtOH})_x(\text{OEt})_y\text{M}(\mu\text{-OEt})_2\text{SnCl}_4] \cdot z\text{EtOH}$ (1: M = Ti, x = y = 2, z = 1; 2: M = Ta, x = 1, y = 3, z = 0). These heterometallics are quite stable and can be kept unchanged for several months under inert atmosphere. Their robustness in solution phase is reflected by the fact that these can be recrystallized from a variety of alcohols (other than the parent ones). Thus, room temperature interactions of 1 and 2 from isopropanol, followed by recrystallization at -20 °C, afforded the mixed-ligand complexes $[(\text{Pr}^i\text{OH})_x(\text{OPr}^i)_y\text{M}(\mu\text{-OEt})_2\text{SnCl}_4]$ (3: M = Ti, x = y = 2; 4: M = Ta, x = 1, y = 3), where the more bulky isopropoxo groups replaced only terminal ethoxo groups (Scheme 1). The impossibility to replace all the methoxo or ethoxo groups with isopropoxo groups by alcohol exchange reactions in

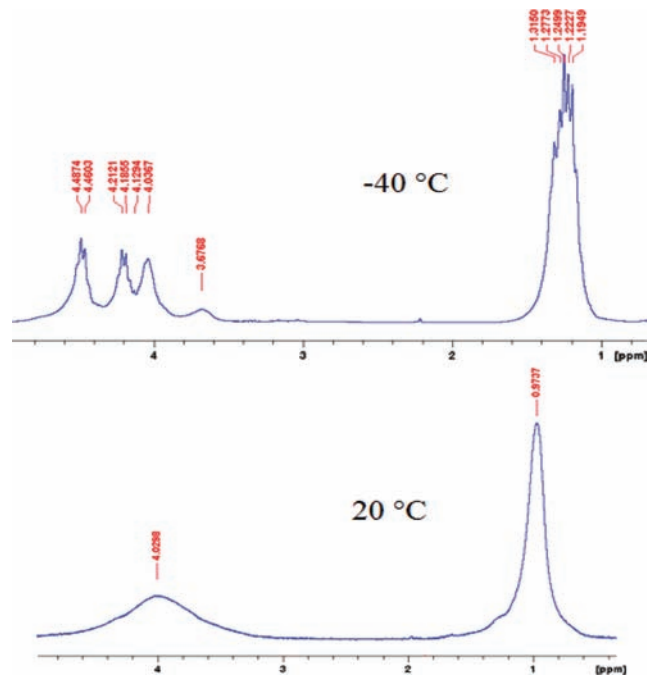


Figure 1. Variable-temperature ¹H NMR spectra of 1.

$\text{M}(\text{OR})_5$ (M = Nb, Ta; R = Me, Et) has been confirmed previously by the structural characterization of the resulting mixed-alkoxo complexes by Kessler et al.¹⁷

The FT-IR spectra of 1–4 account for the solvated species by showing a broad absorption in the region 3200–3400 cm⁻¹ (Figure S1). The room-temperature ¹H NMR spectra of 1–4 are simple because of the fluxional behavior of these derivatives. The fluxionality can, however, be checked by lowering the temperature of measurements. For example, the two broad peaks observed in the room temperature ¹H NMR spectrum of 1 at δ 0.97 and 4.02 ppm because of methyl and methylene protons, respectively, split at -40 °C in to two well-defined triplets or quartets each for terminal and bridging ethoxy groups (Figure 1). The ¹¹⁹Sn NMR of 1–4 show a sharp peak at δ -548 – 580 ppm, which is consistent with the literature values on 6-coordinated Sn(IV) center.¹⁸ The presence of well-defined multiplets in expected integral ratios for the terminal and bridging alkoxy groups in the low temp ¹H and only one signal in the ¹¹⁹Sn NMR spectra of 1–4, as well as isolation of the mixed-ligand complexes 3 and 4 all indicate that the heterometallic $\text{M}(\mu\text{-OEt})_2\text{Sn}$ core is quite robust, which is retained in the solution phase. It assumes significance as many heteroleptic heterometallics such as $[\text{NiAl}_2(\text{OPr}^i)_4(\text{acac})_4]$ and $[\text{Co}_2\text{Ti}_2(\text{acac})_2(\text{OPr}^i)_{10}]$ have been reported previously to be destroyed when redissolved in alcohols.¹⁹ Moreover, the above approach of simply mixing the commercially available metal halide and metal alkoxide to get molecular heterometallic complexes is far simpler and more convenient than the commonly used metathesis reactions,²⁰ which do not always proceed with the expected alkoxy-metallate anion transfer to the nucleophilic metal center,

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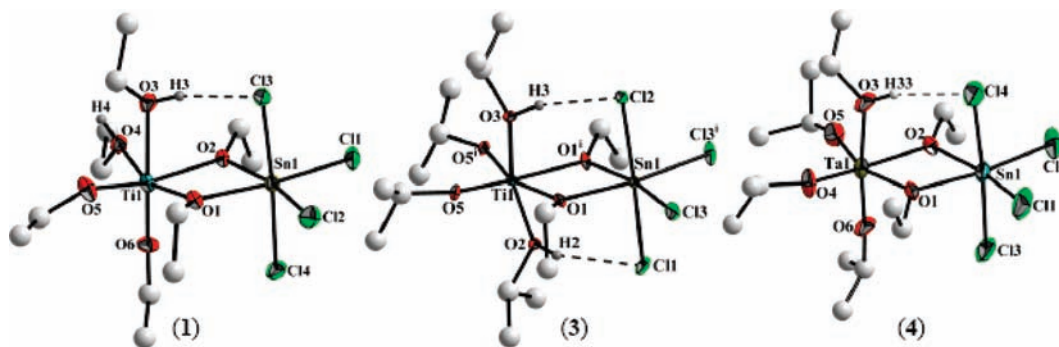


Figure 2. Molecular structures of **1**, **3**, and **4** with displacement ellipsoids drawn at the 30% probability level. C-atoms are drawn as ball and stick and H-atoms of alkyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): (**1**) O3–Ti1 = 2.177(3), O5–Ti1 = 1.768(4), O1–Sn1 = 2.093(3), Sn1–Cl1 = 2.370(1), Cl3···H3 = 2.385(1), O2–Ti1–O1 = 73.2(1), O1–Sn1–O2 = 71.4(1), Cl2–Sn1–Cl1 = 96.89(6), Cl3–Sn1–Cl4 = 176.0(4); (**3**) O3–Ti1 = 2.068(4), O5–Ti1 = 1.800(9), O1–Sn1 = 2.080(2), Sn1–Cl1 = 2.439(1), Cl2···H3 = 2.315(1), O1¹–Ti1–O1 = 71.6(1), O1–Sn1–O1¹ = 71.3(1), Cl3–Sn1–Cl3¹ = 97.56(5), Cl1–Sn1–Cl2 = 177.50(5); (**4**) Ta1–O3 = 2.117(8), Ta1–O5 = 1.797(9), Sn1–O1 = 2.107(7), Sn1–Cl1 = 2.349(5), Cl4···H33 = 2.282(5), Ta1···Sn1 = 3.432(1), O2–Ta1–O1 = 70.6(3), O2–Sn1–O1 = 69.9(3), Cl2–Sn1–Cl1 = 97.8(2), Cl3–Sn1–Cl4 = 175.7(1). Symmetry code (i): $x, 1/2 - y, z$.

and sometimes no heterometallic species are formed.²¹ In many cases, these metathesis reactions also proceed with the retention of the salt to form “ate” derivatives or clustered species with trapped halide or alkali-metal ion.²²

X-ray Structures. The identity of the complexes **1**, **3**, and **4** was further confirmed by the single-crystal X-ray diffraction analysis (Figure 2). The three complexes are formed by the bridging chelating ligation of the metal alkoxide moiety to the SnCl₄ molecule, the Ti or Ta metal centers in the former moiety being also attached to additional adducting alcohol molecules to complete the octahedron around it. The overall molecular geometry can be seen as combination of MO₆ (M = Ti or Ta) and SnCl₄O₂ octahedra via a common edge comprising of two oxygen atoms O1 and O2 (O1¹). The M–O (M = Ti, Ta) distances in **1**, **3**, and **4** vary from 1.720(9) to 2.177(3) Å, the bonds involving terminal ROH [2.053(3)–2.177(3) Å] and bridging OEt [1.995(3)–2.095(8) Å] being unsurprisingly longer than those involving terminal OR groups [1.762(4)–1.813(8) Å]. The Sn–O bond distances, 2.075(3)–2.110(9) Å, compare well with the literature values on Sn–μ-O bond distances.¹² The equatorial Sn–Cl bonds (trans to the bridging Sn–O) are slightly shorter [2.349(5)–2.377(1) Å] than those present in axial positions [2.385(4)–2.451(1) Å]. In contrast to cis position of the EtOH molecules in **1** [O3–Ti–O4 = 79.7(1)°], the two PrⁱOH molecules in **3** happen to be in trans position [O2–Ti–O3 = 153.8(2)°]. The adducting EtOH or PrⁱOH molecule in **1**, **3**, and **4** are involved in inter- or intramolecular H-bonding with chloride anions present on tin center present [H···Cl = 2.282(1)–2.385(5) Å], leading to a slight increase in the Sn–Cl bond length for these chlorides [av. 2.432 Å for H-bonded chlorides as against 2.371 Å for non-H-bonded ones] (Figures 1 and S2). The equatorial O–M–O bond angles involving terminal alkoxides [97.8(2)–102.4(4)°]

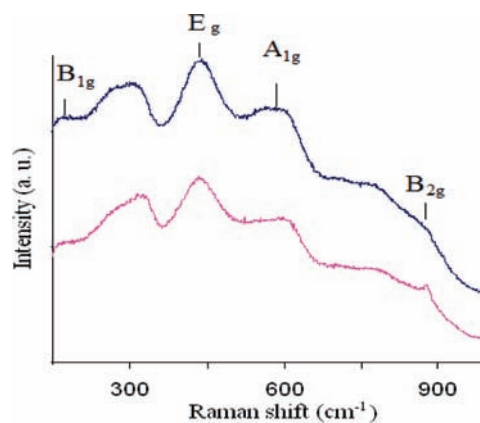


Figure 3. Raman spectra of the as-prepared powder obtained from the hydrolysis of **1** (for undoped material, blue line) or **1** and **2** (for material doped with Ta⁵⁺ ion, red line).

are considerably greater than the angle subtended by the bridging O1–M–O2 groups [70.6(3)–73.2(1)°]. With the axial O–M–O bond angle being 171.2(2)°, 153.8(2)°, and 173.7(4)° for **1**, **3**, and **4**, respectively, the octahedral geometry around Ti or Ta center is significantly distorted. The tin center too has a distorted octahedral geometry due to the presence of different types of bond angles such as O1–Sn–O2, O–Sn–Cl, and Cl–Sn–Cl, which range from 71.3(1)° to 97.8(2)°.

Preparation and Characterization of the Materials.

Hydrolysis of the above complexes was performed in aqueous media without using any organic solvent. To obtain mixed tin–titanium oxide, the neat crystallized powder of **1** or **3** was added to boiling deionized water (100 mL) containing 0.1 equiv of Buⁿ₄NBr salt. Previous work from this laboratory has shown that the use of ammonium bromide salts helps getting highly crystalline TiO₂ nanoparticles (NPs) at low temperature.²³ After refluxing the suspension for 2 h, the NPs were isolated via centrifugation, washed twice each with deionized water and ethanol, and dried at 70 °C for 12 h. To obtain mixed tin–titanium oxide NPs doped with 1% Ta⁵⁺ ion, complexes **1** and **2** (or **3** and **4**) were taken in 100:1 molar

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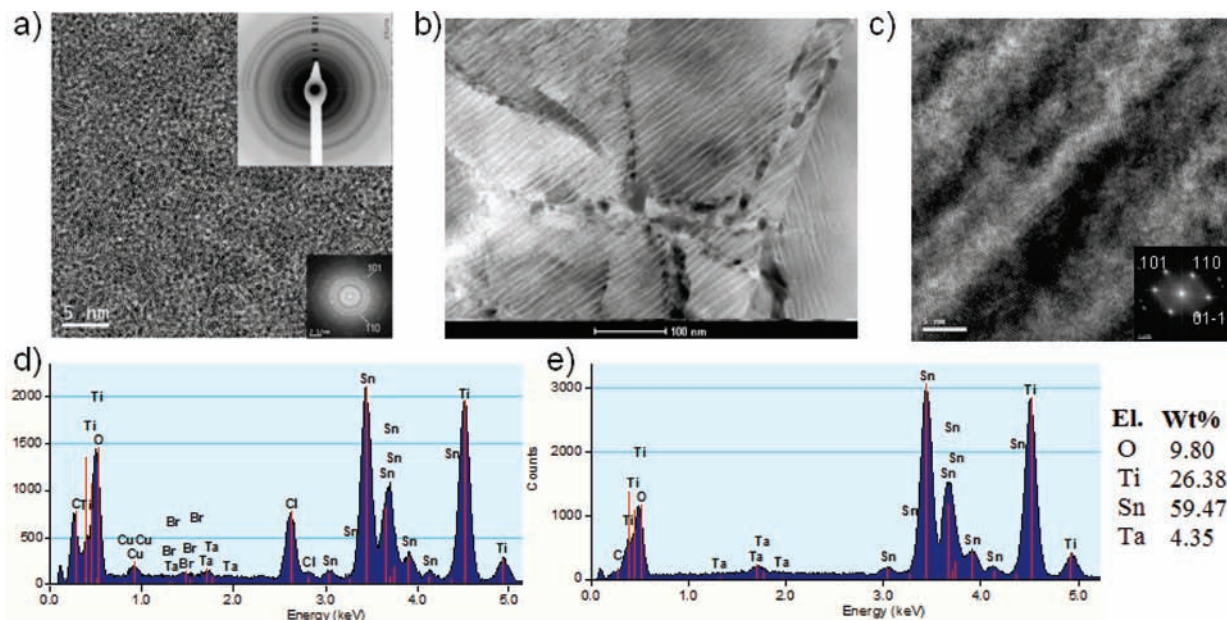


Figure 4. Characterization of the mixed tin–titanium oxide NPs doped with 1% Ta⁵⁺ ion: (a) HRTEM of the as-prepared powder, with associated FFT (lower inset) and SAED (upper inset) exhibiting diffuse rings corresponding to rutile diffracting planes, (b and c) (S)TEM images of the sample sintered at 1500 °C showing lamellae nanostructure with coherent interfaces, and (d and e) EDX spectra associated with the as-prepared and the sintered samples, respectively, confirming a 1:1 ratio of the titanium and tin metals and absence of the halides in the latter.

ratio and hydrolyzed as described above. The as-prepared samples, both undoped and doped with Ta⁵⁺ ion, show four Raman active modes, that is, A_{1g}, B_{1g}, B_{2g}, and E_g thus indicating a rutile-type structure. The presence of an additional Raman band at ~325 cm⁻¹, which is not predicted by group theory, can be attributed to the microstructure of nanocrystalline metal oxide constituting a new kind of vibration mode (Figure 3).²⁴ The rutile structure is further confirmed by (S)TEM studies revealing the {110} and {101} planes of this phase. The high-resolution TEM image exhibits regular rounded grains of around 3 nm (Figures 4a and S3). The selected area diffraction pattern, shown as upper inset in Figure 4a, exhibits diffuse rings characteristic of nanometric coherent domains of the rutile structure of the nanopowder. The as-prepared NPs are not only strongly hydroxylated and solvated (Figure S4) but also halogenated as evidenced by the EDX spectrum shown in Figure 4d (traces of Br is because of the use of Buⁿ₄NBr during hydrolysis). On heating, these NPs show a constant weight loss of about 14% within the temperature range 50–800 °C (Figure S5). The EDX spectrum of the doped sample sintered at 1500 °C for 4 h, while confirming a 1:1 composition for Ti/Sn and homogeneous doping of the Ta⁵⁺ ion, also reveals a complete absence of the halide ions (Figure 4e). The XRD patterns of the as-prepared and the sintered samples of undoped mixed tin–titanium oxide NPs are shown in Figure 5, the latter indexing well with tetragonal 1:1 solid solution of oxides of tin and titanium (JCPDS 01–070–4407). The preliminary studies exhibit a desired spinodal decomposition for above sintered sample with (S)TEM images showing lamellae nanostructure and coherent interfaces (Figure 4b and c). These results, however, also show a density less than desired (~ 62%), thus underlining a need to improve it

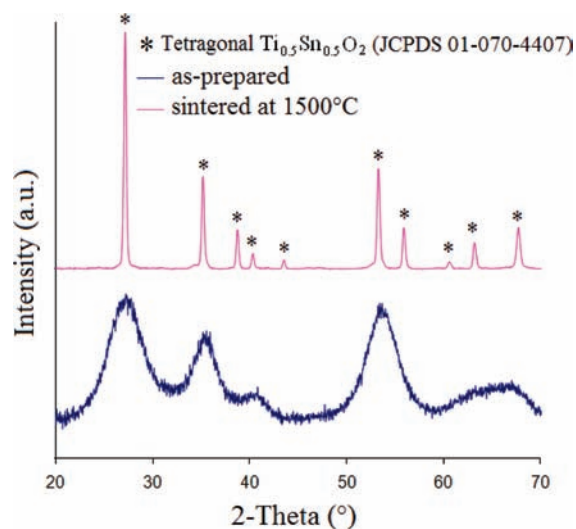


Figure 5. XRD patterns of the as-prepared and the sintered mixed tin–titanium oxide NPs obtained from the hydrolysis of **1**.

further for good thermoelectric properties. Further work involving niobium(V) cation is currently underway to understand the influence of doping on the nanostructuring and density of such materials.

Conclusions

Using commercially available reagents, we reported here a quantitative and easy-to-scale up synthetic pathway for novel heterobimetallic chloro-alkoxo derivatives and demonstrated their utility as precursors for the synthesis of halide-free spinodal type of mixed tin–titanium oxide NPs doped with tantalum(V) ion as a potential thermoelectric material. The derivatives **1–4**, which contain maximum number of terminal chlorides present on tin center, have potential to be used further as attractive synthons for the preparation of heterotri- and even

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higher nuclear metallic alkoxide derivatives by salt elimination reactions.

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Supporting Information Available: FT-IR spectra of **1–4**, extended structure of **1** showing intermolecular H-bonding, HRTEM image, IR spectra, and TG-DTA curve for the as-prepared mixed tin–titanium oxide NPs, and three X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.