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Synthesis and physico-chemical studies of double alkoxides and their allied compounds

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Alkoxide-based molecular routes used as single-source precursors for the synthesis of ultrafine materials with correct stoichiometry ratios have become an area of intense scientific interest due to the technological relevance in terms of simple equipment, low-temperature processing and low cost. The crystallization behavior of allied compounds can be controlled with the help of tuning the properties of different chelating agents in the reaction conditions to increase the solubility of metal alkoxides. Physico-chemical studies of alkoxides and their derivatives were carried out using FTIR, NMR, mass spectrometry, thermogravimetric analysis (TGA)–differential thermal analysis (DTA) and scanning electron microscopy (SEM). The mass spectra show the same types of fragmentation pattern in the compounds. The X-ray diffraction patterns show enhanced homogeneity. TGA–DTA measurements show that thermal decomposition occurs in steps and depends entirely on the chemical composition and the synthesis route. The SEM observations reveal a high microstructural uniformity of polycrystalline nature. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: preparation; heterometallic alkoxides; nanocrystalline bimetallic oxides; nonhydrolytic sol–gel process

INTRODUCTION

The synthesis and the reactivity studies of metal alkoxides continue to be an area of research interest on account of their relevance to areas such as biology, organic synthesis, materials science and catalysts.[1–3] The use of metal alkoxides as molecular precursors for preparing high-purity ceramic oxide superconductors, ferroelectrics, dielectrics and biocompatible oxide materials and thin films has been a growing field for the last decade, at the expense of the more traditional routes.[4–9]

Metal alkoxides are useful for preparing heterometallic oxides directly from solution via the sol–gel method (thus avoiding the use of calcination), if the products obtained are amorphous and can be converted into crystalline solids by hydrothermal techniques.[10] The purity and stoichiometry ratios of the final products depend strongly on the chemical ratio of the double alkoxides.[11,12] Bimetallic alkoxides are derived from two different electronegative elements. As the strength of the Lewis acid increases with the reduction of donor ligands, leads the formation of heterometallic species with high chemical homogeneity at the molecular level.[13] The metal alkoxides are used as molecular precursors because they have attractive properties, such as solubility, sublimation facility and thermal stability.[14–18] The M–O–C bond polarities, the size and shape of the alkyl group, the atomic radius, the coordination number of the metal and the polarization degree mainly govern the solubility and volatility of the molecular precursors.[19,20] Alkoxides that display the highest nuclearity are often non-volatile and non-soluble, when compared with other metal alkoxides. These properties make the alkoxides most appropriate to oxide film preparation via chemical routes such as hydrolysis and chemical deposition.[16,21]

In our investigations we have prepared covalent heterometallic alkoxides and their allied derivatives with a high purity at a favorable low temperature. As we know, the chemical reactivity of metal alkoxides towards nucleophilic reactions depends largely on the electrophilic character of the metal and its ability to increase its coordination number. The coordination unsaturation is the main driving force behind the reactivity of metal alkoxides.

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EXPERIMENTAL

All experimental operations were carried out in an inert atmosphere using standard vacuum line techniques and taking stringent precautions to avoid hydrolysis from atmospheric humidity. All solvents were distilled from Na–K alloy or $LiAlH_4$, or CaH_2 prior to use. Zirconium tetrachloride (Aldrich), erbium trichloride (anhydrous, Aldrich), silicon tetrachloride (Aldrich) and ferric chloride (anhydrous, Aldrich) were used as received. Titanium tetrachloride (Aldrich) was distilled before use to remove oxide impurities. The bimetallic alkoxides and their corresponding derivatives were characterized by physico-chemical techniques. The IR spectra were recorded as KBr pellets on a BioRad FTIR-165 spectrometer. The carbon and hydrogen analyses of the alkoxides were obtained using an EA 1110 (CE instrument) elemental analyzer. ^1H NMR spectra were recorded for $CDCl_3$ or C_6D_6 solution on a Bruker DRX–300 MHz spectrometer. The Mass was recorded on a JMS-DX 303 Spectrometer. Powder X-ray diffraction measurements were performed at room temperature on D8-Discover (with GADDS) Bruker operating with Cu $K\alpha_1$ radiation. The powder morphology of the compounds before and after heat treatment was investigated using a scanning electron microscope (SEM) Philips XL30S FEG XL V.5.50 The thermogravimetric and differential thermal analysis (DTA–TGA) measurement were performed on a TA Instruments SDT960 in nitrogen atmosphere. The compounds were heated in nitrogen at a rate of $5\,^{\circ}C\ min^{-1}$. The experiments were performed in quartz crucibles, which also served as the reference.

Preparation of bimetallic alkoxides

The preparation of bimetallic alkoxides was carried out under dry atmosphere in oven-dried glassware.

$$K + {}^{i}Pr \longrightarrow KO^{i}Pr + H_2 \uparrow$$

$$6KO^{i}Pr + MCl_5 + 5KCl \downarrow$$

$$ErCl_3 + 3KM(O^{i}Pr)_6 \longrightarrow [Er\{M(O^{i}Pr)_6\}_3] + 3KCl \downarrow$$

$$M = Ta, Nb$$

One equivalent of potassium was reacted with isopropyl alcohol followed by addition of one-sixth of an equivalent of metal chloride and the whole contents stirred for 3 h. To this was added one-third of an equivalent of anhydrous erbium trichloride and the contents stirred and refluxed under nitrogen atmosphere for 24 h. The compound formed was separated by filtration. The mother liquor was concentrated and the compound was obtained in quantitative yield. Other bimetallic alkoxides were synthesized using the same procedure. The results are given in Table 1.

Preparation of derivatives

Three equivalents of anhydrous metal chloride were taken along with one equivalent of heterometallic alkoxide in anhydrous dichloromethane. The reaction was refluxed and stirred for 36 h in the presence of a catalytic amount of ferric chloride (anhydrous) in some reactions. The heterogeneous solution was filtered and washed several times with dry benzene. The powder was dried under vacuum.

$$3M^{*}Cl_4 + [Er\{M(O^{i}Pr)_6\}_3] \longrightarrow [Er\{M \cdot M^{*}(O^{i}Pr)_2(O)_4\}_3]$$

$$+ 12^{i}PrCl \uparrow$$

$$M^{*} = Si, Ti, Zr$$

Other derivatives were synthesized using the same procedure and the results are given in Table 2.

RESULTS AND DISCUSSION

Metal alkoxide reactivity is based on functional alcohols and the π-donor ability of the alkoxy ligands, which leads to stabilization of the central metal in higher oxidation states.[4] The present studies describe the non-hydrolytic sol–gel process for the synthesis of allied derivatives via bimetallic alkoxides. In non-hydrolytic sol–gel techniques, the metal alkoxides considered to be good molecular precursors are carefully hydrolyzed to produce an inorganic polymerization network through M–O–M linkages at the molecular level with the highest purity and with the right stoichiometry.[22–27] In homogenous reaction conditions, traces of impurities are removed completely at the molecular level.[1–3] These compounds were characterized using elemental analysis, the results of which are given in Table 3.

The metal alkoxides and their corresponding derivatives were characterized using FTIR spectroscopy to observe the characteristic absorption peaks. Striking similarities were observed in the solid and solution states, dominated by ligand vibrations between the alkoxides and their derivatives.[28–32] Selected FTIR data for the important absorption peaks are

Table 1. Millimolar ratio, yield and nature of bimetallic alkoxides, g = gms

$KM(O^{i}Pr)_6$ (M = Ta, Nb)	$ErCl_3$	Compound wt (g)	Product	KCl wt (g)	Nature of compound
26.46	8.81	15.26 (15.61)	$[Er\{Ta(O^{i}Pr)_6\}_3]$	11.78 (11.83)	Pink solid
31.65	10.51	15.46 (15.71)	$[Er\{Nb(O^{i}Pr)_6\}_3]$	13.98 (14.13)	Pink viscous liquid

Table 2. Millimolar ratios for the synthesis of oxo-derivatives, g = gms

MCl_4[a]	Double alkoxides	Yield	Product	Nature of derivative
3.78	1.25	1.87 (1.91)	$[Er\{Ta \cdot Zr(O^iPr)_2(O)_4\}_3]$	Brown, viscous
3.83	1.27	1.72 (1.77)	$[Er\{Ta \cdot Ti(O^iPr)_2(O)_4\}_3]$	Brown, viscous
4.15	1.38	1.80 (1.85)	$[Er\{Ta \cdot Si(O^iPr)_2(O)_4\}_3]$	Liquid pink, viscous
5.02	1.67	1.97 (2.12)	$[Er\{Nb \cdot Si(O^iPr)_2(O)_4\}_3]$	Light pink, solid
4.92	1.64	1.81 (1.86)	$[Er\{Nb \cdot Ti(O^iPr)_2(O)_4\}_3]$	White, solid
4.68	1.56	1.63 (1.68)	$[Er\{Nb \cdot Zr(O^iPr)_2(O)_4\}_3]$	Yellow, solid

[a] M = Si, Ti, Zr.

Table 3. Elemental analysis of the heterometallic alkoxides and their oxo-derivatives

Compound	Analysis, found (calc.) (%) C	H	O
$[Er\{Ta(O^iPr)_6\}_3]$	35.97 (36.56)	6.79 (7.12)	15.73 (16.24)
$[Er\{Ta \cdot Zr(O^iPr)_2O_4\}_3]$	13.68 (14.12)	2.17 (2.74)	18.09 (18.83)
$[Er\{Ta \cdot Ti(O^iPr)_2O_4\}_3]$	14.97 (15.43)	2.79 (3.00)	20.02 (20.57)
$[Er\{Ta \cdot Si(O^iPr)_2O_4\}_3]$	15.84 (16.11)	2.79 (3.13)	20.87 (21.49)
$[Er\{Nb(O^iPr)_6\}_3]$	42.94 (43.41)	7.89 (8.44)	18.87 (19.29)
$[Er\{Nb \cdot Zr(O^iPr)_2O_4\}_3]$	16.86 (17.06)	2.79 (3.32)	22.13 (22.75)
$[Er\{Nb \cdot Ti(O^iPr)_2O_4\}_3]$	18.73 (19.02)	3.23 (3.69)	24.97 (25.36)
$[Er\{Nb \cdot Si(O^iPr)_2O_4\}_3]$	19.69 (20.07)	3.14 (3.90)	26.07 (26.76)

given in Table 4. In general, weak- to medium-intensity bands appear in most of the spectra in the 3400 cm^{-1} region; these may be due to unavoidable slight hydrolysis of the compounds during mulling and recording.

The room-temperature ^1H NMR ($CDCl_3$ or C_6D_6) spectrum exhibits two resonances for isopropyl protons in the proper integration ratio. Although sharp peaks were not observed, due to the paramagnetic behavior of the compounds, the methine septet and methyl doublet merge together and appear as broad peaks, satisfies the full integration ratio. When the terminal alkyls of the alkoxy groups are replaced with metal halides, significant downfield chemical shifts were observed for the methyl and methine protons of the bridging alkoxy group in the derivatives, compared with those of the corresponding parent alkoxides. This is probably due to the delocalization of electrons in empty orbitals of the coordination sphere. The results are given in Table 5.

Table 5. Room-temperature ^1H data (δ/ppm) for the heterometallic alkoxides and their derivatives

Compound	CH_3	CH	Solvent
$[Er\{Ta(O^iPr)_6\}_3]$	0.98	3.70	$CDCl_3$
$[Er\{Ta \cdot Zr(O^iPr)_2O_4\}_3]$	1.16	4.07	$CDCl_3$
$[Er\{Ta \cdot Ti(O^iPr)_2O_4\}_3]$	1.16	3.96	C_6D_6
$[Er\{Ta \cdot Si(O^iPr)_2O_4\}_3]$	1.16	3.82	C_6D_6
$[Er\{Nb(O^iPr)_6\}_3]$	0.95	3.66	C_6D_6
$[Er\{Nb \cdot Zr(O^iPr)_2O_4\}_3]$	1.06	4.04	$CDCl_3$
$[Er\{Nb \cdot Ti(O^iPr)_2O_4\}_3]$	1.04	3.79	C_6D_6
$[Er\{Nb \cdot Si(O^iPr)_2O_4\}_3]$	1.11	3.89	C_6D_6

Table 4. Selected FTIR data for the heterometallic alkoxides and their derivatives (cm^{-1})[a]

Compound	ν_{C-O}	ν_{C-H}	ν_{M-O-C}	$\nu_{M'-O-M''}$	n_{C-C}	$n_{M-O-M'}$
$[Er\{Ta(O^iPr)_6\}_3]$	1636.21	1467	1168.01	—	875	588.22
$[Er\{Ta \cdot Zr(O^iPr)_2O_4\}_3]$	1630.07	1464.84	1168.16	1021.04	860	485.00
$[Er\{Ta \cdot Ti(O^iPr)_2O_4\}_3]$	1621.93	1464.99	1188.67	1020.18	870	484.00
$[Er\{Ta \cdot Si(O^iPr)_2O_4\}_3]$	1636.76	1465.05	1263.26	1019.68	806	468.35
$[Er\{Nb(O^iPr)_6\}_3]$	1626.24	1464.64	1261.80	—	802.46	584.99
$[Er\{Nb \cdot Zr(O^iPr)_2O_4\}_3]$	1635.13	1463.71	1262.23	1020.68	885.0	484.25
$[Er\{Nb \cdot Ti(O^iPr)_2O_4\}_3]$	1634.70	1462.03	1261.78	1020.74	895.0	484.73
$[Er\{Nb \cdot Si(O^iPr)_2O_4\}_3]$	1637.29	1464.51	1265.92	932	809.73	483.68

[a] M = Er; M′ = Ta, Nb; M″ = Si, Ti, Zr.

The mass spectra do not give any conclusive evidence of heterometallic molecules in the gas phase, probably due to breakdown of the heterometallic compounds under the high vacuum. The ions observed correspond to simple metal alkoxides, followed by decomposition into simple oxides. The important fragmentation peaks are given in Table 6.

Thermogravimetric and differential thermal analyses

The thermal behavior was investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) under a nitrogen atmosphere. This provided evidence for the onset of decomposition of compounds at low temperature and support for the formation of their corresponding derivatives due to the nonexistence of terminal alkoxy group.

Table 6. Mass spectroscopy data of the alkoxides and their oxo-derivatives

Compound	m/ζ	I	Interpretation
$[Er\{Ta(O^iPr)_6\}_3]$	345	20	$Er(O^iPr)_3$
	476	15	$Ta(O^iPr)_5$
$[Er\{Ta \cdot Zr(O^iPr)_2O_4\}_3]$	123	43	ZrO_2
	213	50	TaO_2
	345	54	$Er(O^iPr)_3$
	382	72	Er_2O_3
	442	75	Ta_2O_5
	476	65	$Ta(O^iPr)_5$
$[Er\{Ta \cdot Ti(O^iPr)_2O_4\}_3]$	284	58	$Ti(O^iPr)_5$
	345	35	$Er(O^iPr)_3$
	442	60	Ta_2O_5
	476	20	$Ta(O^iPr)_5$
$[Er\{Ta \cdot Si(O^iPr)_2O_4\}_3]$	213	30	TiO_2
	345	17	$Er(O^iPr)_3$
	382	15	Er_2O_3
$[Er\{Nb(O^iPr)_6\}_3]$	266	25	Nb_2O_5
	345	38	$Er(O^iPr)_3$
	383	20	Er_2O_3
	387	28	$Nb(O^iPr)_5$
$[Er\{Nb \cdot Zr(O^iPr)_2O_4\}_3]$	109	25	NbO
	123	80	ZrO_2
	125	80	NbO_2
	266	25	Nb_2O_5
	345	25	$Er(O^iPr)_3$
$[Er\{Nb \cdot Ti(O^iPr)_2O_4\}_3]$	144	70	Ti_2O_3
	204	40	Ti_3O_5
	284	40	$Ti(O^iPr)_5$
	345	25	$Er(O^iPr)_3$
	388	15	$Nb(O^iPr)_5$
	266	20	Nb_2O_3
$[Er\{Nb \cdot Si(O^iPr)_2O_4\}_3]$	109	75	NbO
	125	50	NbO_2
	345	38	$Er(O^iPr)_3$
	388	20	$Nb(O^iPr)_5$

The thermal decomposition of alkoxides and their derivatives may be described as a smooth stepwise process. The TGA–DTA data (Fig. 1) for all compounds were similar and clearly indicate that the chemical geometry of the parent compounds are very much similar to their derivatives and the maximum total weight loss is at round 700 °C was observed in both compounds. The TGA–DTA results can be summarized as follows: (1) removal of the organic solvent from the alkoxides takes places at 200 °C; (2) organic moieties connected with the alkoxides and their derivatives are removed at 500 °C; (3) a crystalline phase is observed at 1000 °C. Several exothermic processes appear, probably either due to combustion or crystallization phenomena. The loss process observed beyond 700 °C occurring without any significant weight loss was attributed to crystallization.

X-ray diffraction and scanning electron microscopy

The X-ray diffraction (XRD) patterns show that the compounds are amorphous (Fig. 2). The XRD peaks became sharper (supporting high homogeneity at the near atomic level) at high temperature, supporting that the crystalline phase can be achieved. Further thermal treatment does not lead to any appreciable change in the diffraction pattern.

The scanning electron micrographs show that the powder consists of very fine particles with or without any pronounced tendency to agglomeration with unfaceted surface, the grain particles sized, being built up of several tiny particles with a poly dispersed nature, with the particles size lying in the range 150–350 nm without any observable defects (Fig. 3). Tantalum derivatives are more crystalline than their corresponding niobium analogues, due to the large size of tantalum. Therefore, it is concluded that the morphological changes in the microstructure of the particles depend strongly on the nature and synthesis route of the molecular precursor.

Based on the physico-chemical studies, the structures shown in Fig. 4 have been elucidated for the double metal alkoxides and their corresponding derivatives.

CONCLUSIONS

Molecular routes to metal oxides have become an important area of intense interest owing to their technological relevance, because the physical and chemical properties of the final materials can be controlled at the molecular level at low temperature. Homogeneously dispersed bimetallic oxides in nanocrystalline or amorphous form were prepared from

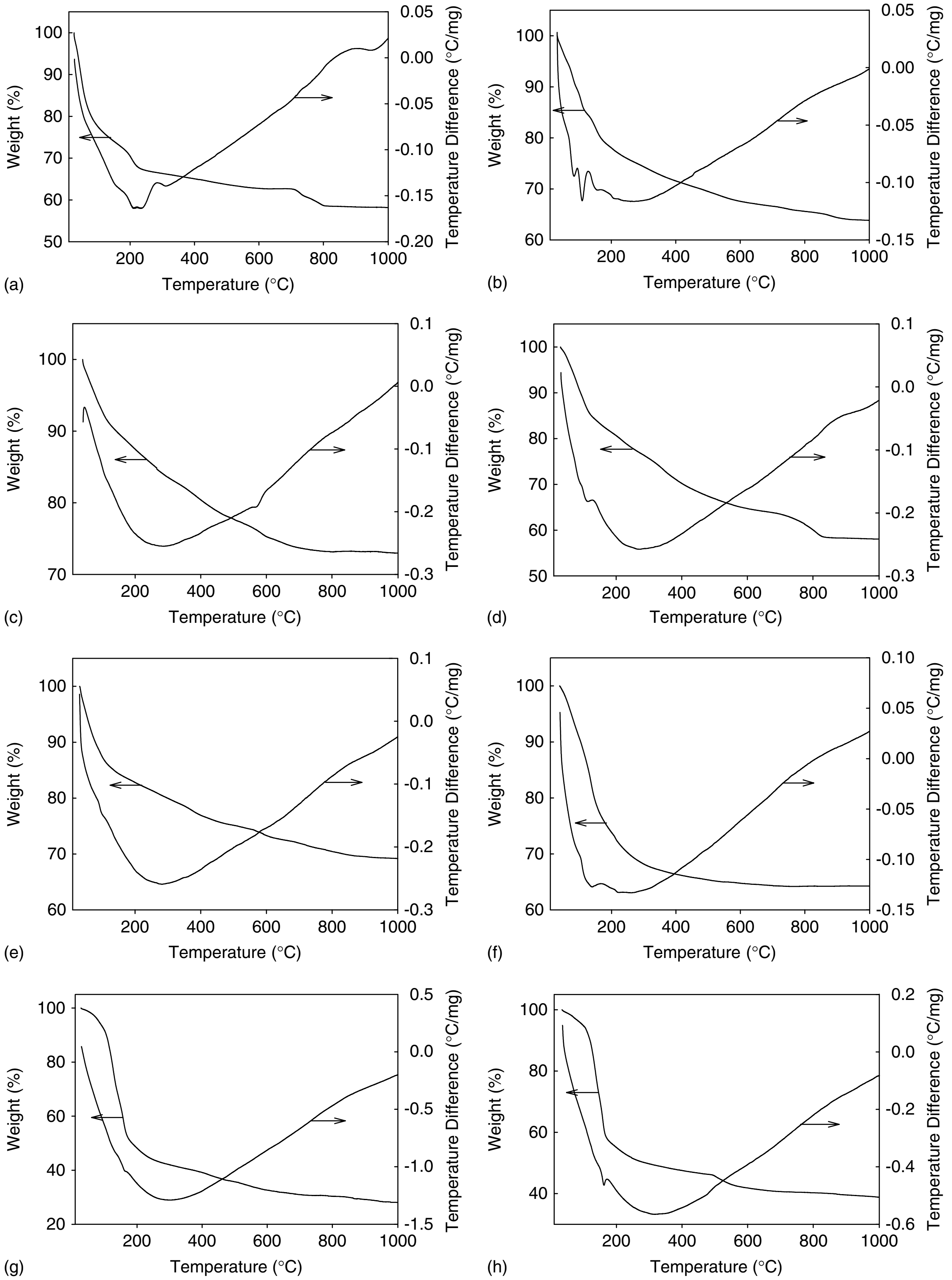

Figure 1. TGA–DTA for the heterometallic alkoxides and its derivatives: (a) [Er{Ta(O^{i}Pr)$_6$}$_3$], (b) [Er{Ta · Si(O^{i}Pr)$_2$O$_4$}$_3$], (c) [Er{Ta · Ti(O^{i}Pr)$_2$O$_4$}$_3$], (d) [Er{Ta · Zr(O^{i}Pr)$_2$O$_4$}$_3$], (e) [Er{Nb(O^{i}Pr)$_6$}$_3$], (f) [Er{Nb · Si(O^{i}Pr)$_2$O$_4$}$_3$], (g) [Er{Nb · Ti(O^{i}Pr)$_2$O$_4$}$_3$], (h) [Er{Nb · Zr(O^{i}Pr)$_2$O$_4$}$_3$].

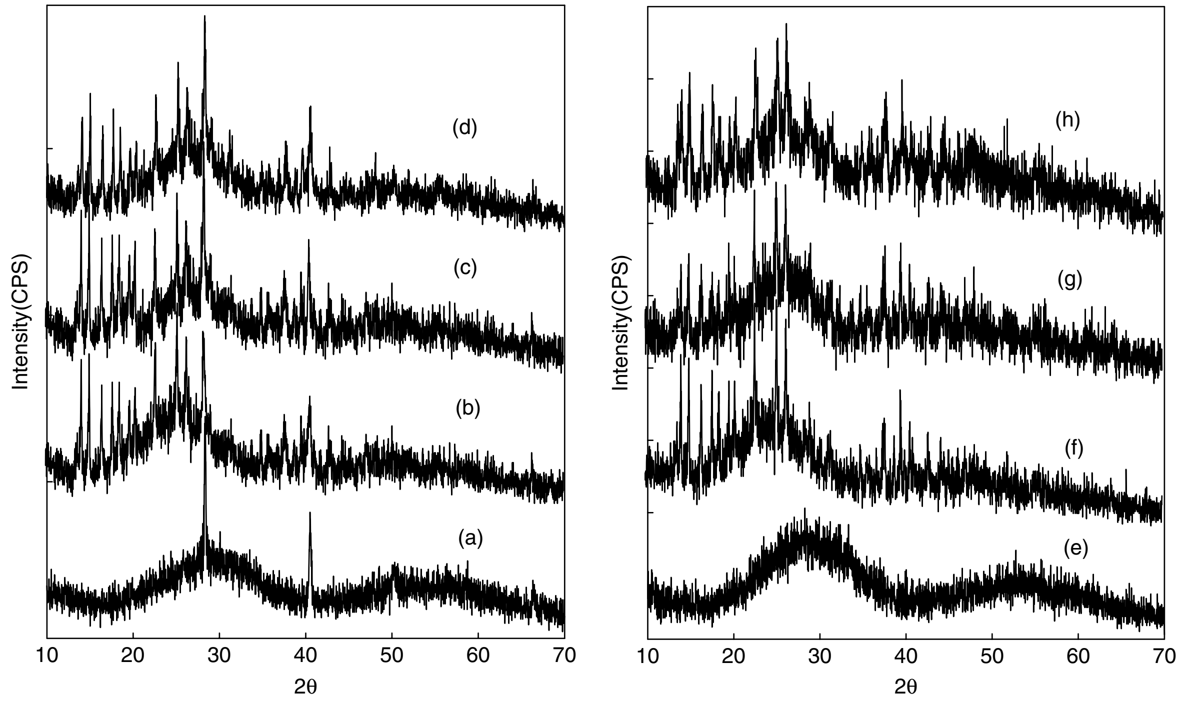

Figure 2. XRD profiles for the heterometallic alkoxides and its derivatives: (a) $[Er\{Ta(O^iPr)_6\}_3]$, (b) $[Er\{Ta \cdot Si(O^iPr)_2O_4\}_3]$, (c) $[Er\{Ta \cdot Ti(O^iPr)_2O_4\}_3]$, (d) $[ErTa \cdot Zr(O^iPr)_2O_4\}_3]$, (e) $[Er\{Nb(O^iPr)_6\}_3]$, (f) $[Er\{Nb \cdot Si(O^iPr)_2O_4\}_3]$, (g) $[Er\{Nb \cdot Ti(O^iPr)_2O_4\}_3]$, (h) $[Er\{Nb \cdot Zr(O^iPr)_2O_4\}_3]$.

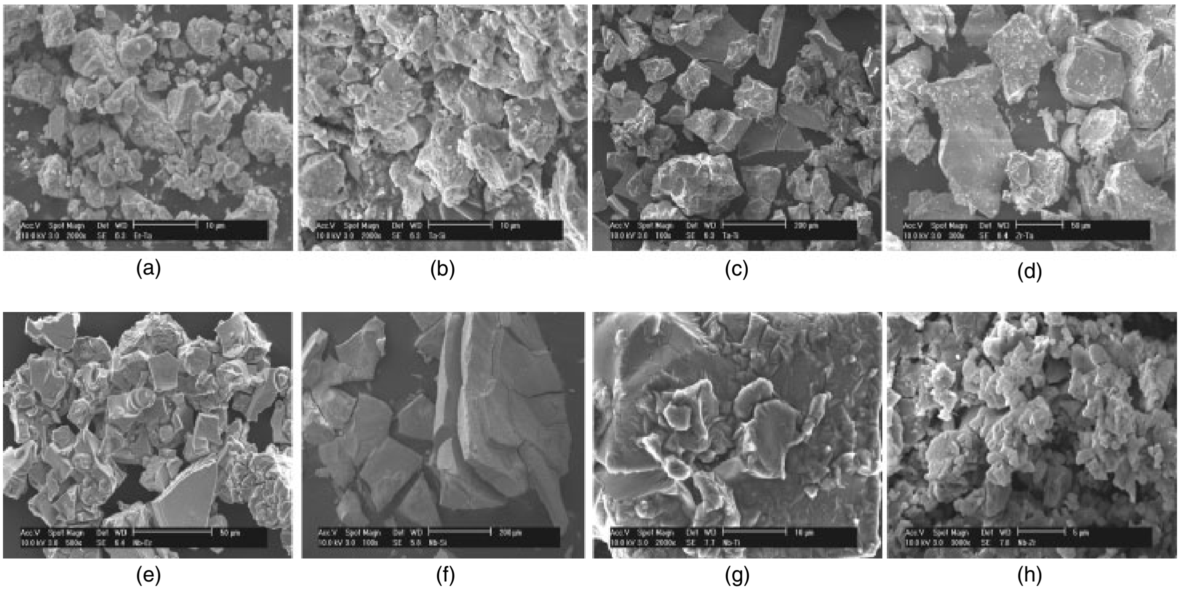

Figure 3. SEM photomicrograph for the heterometallic alkoxides and its derivatives: (a) $[Er\{Ta(O^iPr)_6\}_3]$, (b) $[ErTa \cdot Si(O^iPr)_2O_4\}_3]$, (c) $[ErTa \cdot Ti(O^iPr)_2O_4\}_3]$, (d) $[ErTa \cdot Zr(O^iPr)_2O_4\}_3]$, (e) $[Er\{Nb(O^iPr)_6\}_3]$, (f) $[Er\{Nb \cdot Si(O^iPr)_2O_4\}_3]$, (g) $[Er\{Nb \cdot Ti(O^iPr)_2O_4\}_3]$, (h) $[Er\{Nb \cdot Zr(O^iPr)_2O_4\}_3]$.

double alkoxides via a non-hydrolytic sol–gel process. The physico-chemical properties of the derivatives show that the chemical nature of the starting material plays a key role in controlling the high compositional purity in the final products. Research is still ongoing to find the new chemical routes with unsophisticated procedures to obtain

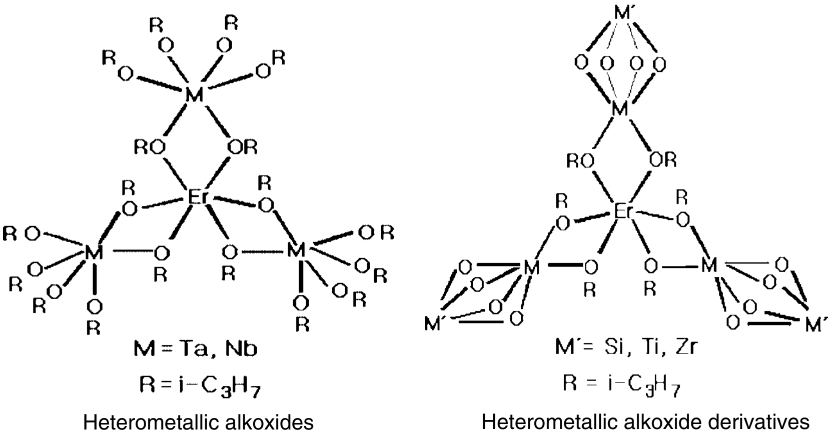

Figure 4. Probable structures for the heterometallic alkoxides and their derivatives.

homogeneous and ultrafine multicomponent materials for optical and other electronic devices.

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