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Synthesis And Characterization Of Fluoro And Chloro Bimetallic Alkoxides: As Precursor For Luminescence Metal Oxide Materials Via Sol-Gel Technique

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ABSTRACT

Heterometallic alkoxides are broadly recognized as versatile precursor for luminescence materials, efforts are being made to develop novel routes by applying the concept of geometrical molecular design, for their synthesis and to design single source precursors suited to photoluminescence materials. Novel and new series of bimetallic alkoxides has been prepared by metathesis route. They exhibit a lower sensitivity towards hydrolysis and so they are easier to handle as compared to other alkoxides. All compounds were characterized by elemental analysis, FT-IR and multinuclear NMR spectroscopies. FT-IR revealed that the molecular structure of metal alkoxides was retained to a large extent in 4:1 halogenated alcohol-benzene solution. The heteronuclear NMR spectroscopy provides useful information about chemical shifts for better understanding the likely structure based on interactions with their coordinating metals. The mass spectra show similar types of fragmentation pattern. SEM-EDS analyses showed consistent with the formulation. XRD patterns show an enhanced homogeneity at high temperature. TGA measurements show that thermal decomposition occurs in steps that depend entirely on the chemical compositions and the synthesis routes. SEM observation reveals that the morphology and particle size strongly depends on synthesis routes for their precursor.

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KEYWORDS

Precursor chemistry; Fluoro and chloro bimetallic alkoxides; Geometric design; Luminescence materials.

INTRODUCTION

In recent years, the elucidation of the structural features and reactivity patterns of polymetallic alkoxides of lanthanide metals have attracted the attention of

many researchers because of their unique 4f shell electronic structures. This attention was driven by the search for single source molecular precursors for the synthesis of ultra fine materials with targeted stoichiometric ratio at low cost for a broad spectrum of in-

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dustrial thin film applications such as ceramic oxide, superconductors, ferroelectric, dielectric and biocompatible oxide materials^[1-5].

Metal alkoxides are very good single source molecular precursor to monocrystalline metal oxides nanoparticles with high technology applications, because they have attractive properties such as the solubility, ease of sublimation and good thermal stability even though they are expensive and moisture sensitive^[6-10]. The synthesis of metal alkoxides generally depends on the electronegativity and the electronic configuration of the central metal. The M-O-C bond polarities, size and shape of the alkyl group, atomic radius, coordination number of the metal and degree of polarization govern the solubility and volatility for molecular precursors. Alkoxides that display the highest nuclearity are often non-volatile and non-soluble^[11-12]. These properties make the alkoxides most appropriate for the oxide film preparation via chemical routes such as hydrolysis and chemical deposition^[8,13]. 'Single source' precursors can afford high tech materials at low temperature by using chemical routes based on soluble metal alkoxides. Simple and cost-efficient routes for single source precursors can be developed by applying the concept of geometrical molecular structure design which is based on the choice of a proper type of molecular structure and its completion with ligands, providing the necessary number of donor atoms for the chosen core as well as sterical protection^[14].

We believe that a chemistry of lanthanide heterometallic alkoxides is now within reach.

In the present investigation, we synthesized for the first time covalent and novel heterometallic halogenated alkoxides with a high yields and purity at a favorable low temperature using metathesis route.

EXPERIMENTAL

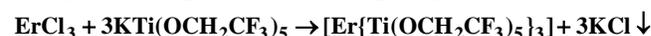
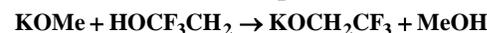
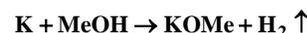
Sample preparation

All experimental operations were carried out in an inert atmosphere using standard vacuum line and taking stringent precautions to avoid hydrolysis from atmospheric humidity. The solvents were distilled from Na/K alloy or LiAlH₄, or CaH₂ prior to use. 2,2,2-trifluoroethanol, 2,2,2-trichloroethanol,

1,1,1,3,3,3-hexafluoro-2-propanol, arsenic(III) chloride, antimony(III) chloride, phosphorus(III) chloride, zirconium(IV) chloride, titanium(IV) chloride, ytterbium(III) chloride, silicon(IV) chloride and erbium(III) chloride (anhydrous,) were purchased from Aldrich and used as received.

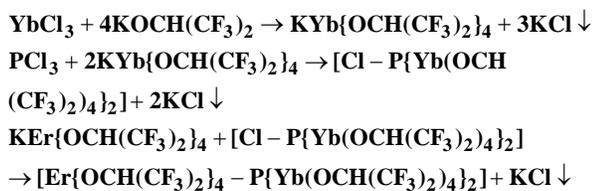
(a) Preparation of bimetallic alkoxides: [Er{Ti(OCH₂CF₃)₃}₃]

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



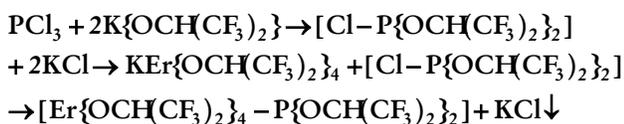
One equivalent of potassium was reacted with dry methyl alcohol. The excess methanol was removed completely. The freshly prepared potassium methoxide was taken in dry benzene, followed by addition of two-equivalent of 2,2,2-trifluoroethanol at room temperature and the whole content was stirred and refluxed for 3h. In the same content one-fifth equivalent of titanium(IV) chloride was added and the content was stirred and refluxed under nitrogen atmosphere for 4h. Finally in the same content one-third equivalent of anhydrous erbium(III) chloride was added at room temperature and the content was stirred and refluxed under nitrogen atmosphere overnight. The compound was separated out by filtration. Finally the mother liquor was concentrated under vacuum. The pink solid product was obtained in quantitative yield. The yield of potassium chloride was quantitative. SEM-EDS analyses showed that the Er/Ti ratio was correct and consistent with structural formulae and no K or Cl was present within the expected error. The compound was soluble in parent alcohols and stable for long time in alcohols. (Yields=99%). Anal. Calcd. For [Er{Ti(OCH₂CF₃)₃}₃]: C, 20.04; H, 1.67. Found: C, 19.87; H, 1.43. IR (cm⁻¹): IR (cm⁻¹): $\gamma_{\text{C-O}}$ 1634(s), $\gamma_{\text{C-C}}$ 1413(br), $\gamma_{\text{C-O}}$ 1045(br), γ_{OCH} 1087(m), $\gamma_{\text{C-F}}$ 1238(s), $\gamma_{\text{C-C}}$ 822(m), $\gamma_{\text{M-O-M}}$ 597(w).

(b) Preparation of [Er{OCH(CF₃)₂}₄-P{Yb(OCH(CF₃)₂)₄}₂]



Four equivalent of $\text{KOCH}(\text{CF}_3)_2$ was added with one-fourth equivalent of anhydrous ytterbium(III) chloride, the content was stirred and refluxed under nitrogen atmosphere for 4 h. In the same content the one-half equivalent of phosphorus(III) chloride was added, stirred and refluxed under nitrogen atmosphere for 4 h. Finally in the same content one equivalent of $[\text{KEr}\{\text{OCH}(\text{CF}_3)_2\}_4]$ was added and the content was again stirred and refluxed under nitrogen atmosphere overnight. The compound was separated out by filtration and concentrated under vacuum. The quantitative yield was obtained for pink gel as final product and as well as for potassium chloride. SEM-EDS analyses showed that the Er:Yb:P ratio was correct and consistent with structural formulae and no K or Cl was present within the expected error. The compound was soluble in parent alcohols and stable for long time in alcohols. (Yields=99%). Anal. Calcd. $[\text{Er}\{\text{OCH}(\text{CF}_3)_2\}_4 - \text{P}\{\text{Yb}(\text{OCH}(\text{CF}_3)_2)_4\}_2]$: For: C, 16.94; H, 0.47. Found: C, 16.58; H, 0.41. IR (cm^{-1}): IR (cm^{-1}): $\gamma_{\text{C-O}}$ 1638(br), $\gamma_{\text{C-C}}$ 1413(m), $\gamma_{\text{C-O}}$ 1056(s), γ_{OCH} 1102(s), $\gamma_{\text{C-F}}$ 1289(w), $\gamma_{\text{C-C}}$ 842 (br), $\gamma_{\text{M-O-M}}$ 686(m).

(c) Preparation of $[\text{Er}\{\text{OCH}(\text{CF}_3)_2\}_4 - \text{P}\{\text{OCH}(\text{CF}_3)_2\}_2]$



Two equivalent of $\text{K}\{\text{OCH}(\text{CF}_3)_2\}$ was reacted with one equivalent of phosphorus(III) chloride (benzene) the content was stirred and refluxed under nitrogen atmosphere for 4 h. In the same content one equivalent of $[\text{KEr}\{\text{OCH}(\text{CF}_3)_2\}_4]$ was added during stirring and refluxed under nitrogen atmosphere overnight. The compound was separated out by filtration and mother liquor was concentrated under vacuum. The quantitative yield was obtained for pink gel as final product and as well as for potassium chlo-

ride. SEM-EDS analyses showed that the Er/P ratio was correct and consistent with structural formulae and no K or Cl was present within the expected error. The compound was soluble in parent alcohols and slightly soluble in non-polar solvents. (Yields=99%). Anal. Calcd. For: C, 17.99; H, 0.50. Found: C, 17.67; H, 0.37. IR (cm^{-1}): IR (cm^{-1}): $\gamma_{\text{C-O}}$ 1637 (br), $\gamma_{\text{C-C}}$ 1377(s), $\gamma_{\text{C-O}}$ 1018(w), γ_{OCH} 1088(s), $\gamma_{\text{C-F}}$ 1257(m), $\gamma_{\text{C-C}}$ 848(w), $\gamma_{\text{M-O-M}}$ 634(m).

A series of other bimetallic alkoxides such as $[\text{Er}\{\text{Si}(\text{OR})_5\}_3]$, $[\text{Er}\{\text{Si}(\text{OR}')_5\}_3]$, $[\text{Er}\{\text{As}(\text{OR})_5\}_3]$, $[\text{Er}\{\text{As}(\text{OR}')_5\}_3]$, $[\text{Er}\{\text{Sb}(\text{OR})_4\}_3]$, $[\text{Er}\{\text{Sb}(\text{OR}')_4\}_3]$, $[\text{Er}\{\text{Zr}(\text{OR})_5\}_3]$, and $[\text{Er}\{\text{Yb}(\text{OR}'')_4\}_3]$ was synthesized as shown in TABLE 1. Here, $\text{R} = \text{CH}_2\text{CF}_3$, $\text{R}' = \text{CH}_2\text{CCl}_3$, $\text{R}'' = \text{CH}(\text{CF}_3)_2$. All compounds were soluble in mother solvents, but partially soluble in non-polar solvents.

2. Characterization techniques

Bimetallic alkoxides were characterized by physico-chemical techniques. FT-IR spectra of these compounds were recorded as KBr pellets on a BioRad FT-IR 165 spectrometer with a spectral resolution of 4 cm^{-1} using transparent KBr pellets. The samples were thoroughly crushed and mixed with KBr at an approximate ratio by weight of sample:KBr of 1 : 20. The C and H analyses carried out using EA 1110 (CE instrument) elemental analyzer. ^1H and ^{19}F NMR spectra were recorded in CDCl_3 or C_6D_6 solvents and using TMS and CCl_3F as standard reference for chemical shift measurement and ^{31}P nuclei were recorded at 161.9 MHz in ppm from external H_3PO_4 at room temperature on Bruker DRX-300 MHz spectrometer. The mass spectra were recorded using JMS-DX 303 mass spectrometer under standard electron beam ionization conditions ($E_1 = 70 \text{ eV}$) with direct probe introduction. Powder X-ray diffraction measurements were examined at room temperature on D8-Discover (with GADDS) Bruker operating with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$) with an operating voltage of 40 kV. The powder morphology and X-ray microanalysis metal ratio in the compounds was performed at room temperature using a scanning electron microscope with an energy-dispersive X-ray spectrum analyzer equipped with EDS system (SEM) Philips XL30S FEG XL V 5.50. The thermogravimetric

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TABLE 1: Millimolar ratio and nature for the alkoxides (Weight of compound & KCl was obtained in quantitative yield)

No.	K in g(mmol)	Alcohol g(mmol)	Halides g(mmol)	ErCl ₃ g(mmol)	Nature	Compounds
1	1.08(27.62)	3.83(38.28)	0.87(5.10)	0.47(1.70)	Pink solid	[Er{Si(OR) ₅ } ₃]
2	1.12(28.64)	5.72(38.29)	0.87(5.10)	0.47(1.70)	Pink solid	[Er{Si(OR') ₅ } ₃]
3	1.49(38.36)	5.75(57.53)	1.74(9.58)	0.87(3.19)	Pink viscous	[Er{As(OR) ₄ } ₃]
4	1.49(38.36)	8.59(57.53)	1.74(9.58)	0.87(3.19)	Colorless liquid	[Er{As(OR') ₄ } ₃]
5	2.03(51.91)	7.78(77.84)	2.96(12.97)	1.18(4.32)	Brown solid	[Er{Sb(OR) ₄ } ₃]
6	2.07(52.94)	11.85(79.36)	3.02(13.22)	1.21(4.40)	Pink viscous	[Er{Sb(OR') ₄ } ₃]
7	2.12(56.26)	8.43(84.29)	2.13(11.23)	1.02(3.73)	Pink solid	[Er{Ti(OR) ₅ } ₃]
8	1.29(33.25)	4.98(49.78)	1.54(6.61)	0.60(2.19)	Pink solid	[Er{Zr(OR) ₅ } ₃]
9	1.65(42.19)	10.60(63.08)	2.93(10.48)	0.95(3.47)	Pink solid	[Er{Yb(OR'') ₄ } ₃]
10	2.93(74.94)	18.87(112.29)	5.13(37.35)	10.21(37.31)	Pink gel	[Er(OR'') ₄ P(OR'') ₂]
11	1.95(49.87)	10.26(61.05)	1.70(12.42)	1.79(6.54)	Pink gel	[Er(OR'') ₄ P{Yb(OR'') ₄ } ₂]

R = CH₂CF₃, R' = CH₂CCl₃, R'' = CH(CF₃)₂

analysis measurement was performed on TA Instruments SDT960 under nitrogen atmosphere with a thermal ramp of over 25-110°C temperature ranges. The compounds were heated in the nitrogen atmosphere at a rate of 5°C/min from temperature to 690°C. The experiments were performed in quartz crucibles, which also served as the reference.

RESULTS AND DISCUSSION

The best method for preparing metal oxide with right control over particle size and shape via soft-chemistry routes^[15]. With the help of soft-chemistry routes good control in properties can be obtained from the molecular precursor to the final product with high purity and homogeneity and at low processing temperatures. Metal alkoxides reactivity is based on functional alcohols and π donor ability of the alkoxy ligands, which leads to stabilization of the central metal in higher oxidation states^[1]. The alkoxides of f-block elements, the methoxide tends to adopt polymeric structures, while tert-butoxides due to their steric bulk are mostly monomeric. Isopropoxides are in between the two cases both in terms of their steric demand as well as their structural properties, resulting in various modes of aggregations in solution and solid state^[3-5].

Metal alkoxides are thermodynamically and kinetically more stable and terminal alkoxy groups are more reactive as compared to their bridging alkoxy groups^[3-5]. The alkoxides were prepared by metathe-

sis reactions and these compounds do not reveal any hygroscopic characteristic when isolated in the Schlenk line under Argon/Nitrogen atmosphere at room temperature. However these alkoxides was thermally unstable and tend to decompose when subjected to heat even under reduced pressure 220°C /10⁻³mm of Hg. We have carried out a study of structure and stability of the product of modification with chelating ligands. They exhibits excellent photoluminescence with life lifetime 4.5 μ s with potential application for optical amplifier^[16].

The metal alkoxides were characterized by FT-IR and the characteristic absorption peaks are shown in TABLE 2. IR spectra of solid and dissolved state for these compounds are quite similar indicating that the molecular entities remains almost unchanged in solution, which suggest that the molecular structure is retained in solution dominated by the ligands vibrations between the alkoxides. The peak maxima in the fingerprint region 1649-569cm⁻¹ are assigned as follows^[17-21]. 1649-1615cm⁻¹ C-O stretching, 1461-1377cm⁻¹ C-C stretching, 1056-958cm⁻¹ C-O bending, 848-799cm⁻¹ C-C bending, 569-686cm⁻¹ M-O-M stretching, 1058-1102cm⁻¹ and 1238-1289cm⁻¹ stretching frequencies for OCH and C-F respectively. In general, weak to medium intensity bands appears in most of the spectra at about 3,400cm⁻¹ due to unavoidable hydrolysis of the compounds during interpretations and analysis.

The NMR technique has proved to be very useful tool in studying these compounds at room tem-

TABLE 2: Important FT-IR spectral bands (cm⁻¹) of alkoxides

	ν_{C-O}	ν_{C-C}	ν_{C-O}	ν_{OCH}	ν_{C-F}	ν_{C-C}	$\nu_{M-O-M'}$
1	1632(br)	1461(m)	966(s)	1093(br)	1264(m)	842(br)	570(m)
2	1635(br)	1447(s)	1019(vs)	1093(vs)	1245(s)	817(vs)	569(vs)
3	1615(br)	1461(s)	966(s)	1095(br)	1264(s)	806(s)	569(m)
4	1635(br)	1447(m)	1020(m)	1095(s)	1238(m)	815(s)	569(s)
5	1624(br)	1447(m)	1018(m)	1094(s)	1241(m)	816(s)	569(s)
6	1638(br)	1461(m)	1021(s)	1096(s)	1261(vs)	799(vs)	632(br)
7	1634(s)	1413(br)	1045(br)	1087(m)	1238(br)	807(br)	607(m)
8	1639(m)	1459(br)	959(m)	1058(m)	1280(s)	822(m)	597(w)
9	1649(br)	1457(m)	958(s)	1092(m)	1283(s)	845(s)	583(w)
10	1637(br)	1377(s)	1018(w)	1088(s)	1257(m)	848(m)	634(m)
11	1638(br)	1460(m)	1056(s)	1102(s)	1289(w)	842(w)	686(m)

M=Er, M'=As, Sb, Si, Ti, Zr, Yb, P, br=broad, vs=very strong, s=strong, m=medium, w=weak

TABLE 3: ¹H, ¹⁹F and ³¹P-NMR spectral data (δ /ppm) for the complexes

Compounds	OCH ₂	OCH	¹⁹ F	³¹ P	Solvent
1. [Er{Si(OR) ₅ } ₃]	3.74	-	-76.83	-	C ₆ D ₆
2. [Er{Si(OR) ₅ } ₃]	3.70	-	-	-	CDCl ₃
3. [Er{As(OR) ₄ } ₃]	3.48	-	-76.84	-	CDCl ₃
4. [Er{As(OR') ₄ } ₃]	4.14	-	-	-	CDCl ₃
5. [Er{Sb(OR) ₄ } ₃]	3.94	-	-77.63	-	CDCl ₃
6. [Er{Sb(OR') ₄ } ₃]	3.93	-	-	-	CDCl ₃
7. [Er{Ti(OR) ₅ } ₃]	-	-	-77.67	-	CDCl ₃
8. [Er{Zr(OR) ₅ } ₃]	-	3.92	-75.22	-	C ₆ D ₆
9. [Er{Yb(OR'') ₄ } ₃]	-	4.03	-76.28	-	CDCl ₃
10. [Er(OR'') ₄ P(OR'') ₂]	-	4.05	-76.16	26.83(s)	CDCl ₃
11. [Er(OR'') ₄ P{Yb(OR'') ₄ } ₂]	-	4.11	-76.13	27.57(s)	C ₆ D ₆

R = CH₂CF₃, R' = CH₂CCl₃, R'' = CH(CF₃)₂

perature to elucidate molecular structures. ¹H, ¹⁹F and ³¹P NMR data are given in TABLE 3. At room-temperature ¹H NMR (CDCl₃ or C₆D₆) spectra exhibits -CH₂/₋CH peaks with correct integration ratios. Although the peaks are not sharp due to the para magnetic behavior of the compounds and also probably due to the merging of terminal and bridging alkoxy groups or due to presence of fluxional process which rapidly exchange in between bridging and terminal ligands on the NMR time scale. The ¹⁹F signals was observed at -76.13 and -77.67ppm and ³¹P NMR signal at 26.83 and 27.57ppm exhibits a single broad resonance probably due to merging of terminal and bridging alkoxy groups on the NMR time scale due to fast exchange process. The up field chemical shift was observed for ¹H and ¹⁹F nuclei due to their π bonding coordination with metals, when compared

with their corresponding chemical shifts in parent alcohols. The extreme downfield chemical shift for ³¹P was observed probably due to higher coordination state for phosphorus with the central metal.

Mass spectrometric results were obtained but no conclusive evidence for heterometallic species was observed in the gas phase. These compounds breakdown into heterometallic ensemble finally decomposes into simple metal oxides under the high vacuum pressure used in mass spectrometer. The important fragmentation data is given in TABLE 4. The terminal alkoxy groups are first removed followed by bridging alkoxy group followed by their decomposition into corresponding metal oxides.

The purity for these compounds was established with the help of quantitative yield of the products, potassium chloride and the microelemental analysis.

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TABLE 4: Mass spectrum with important fragmentation peaks

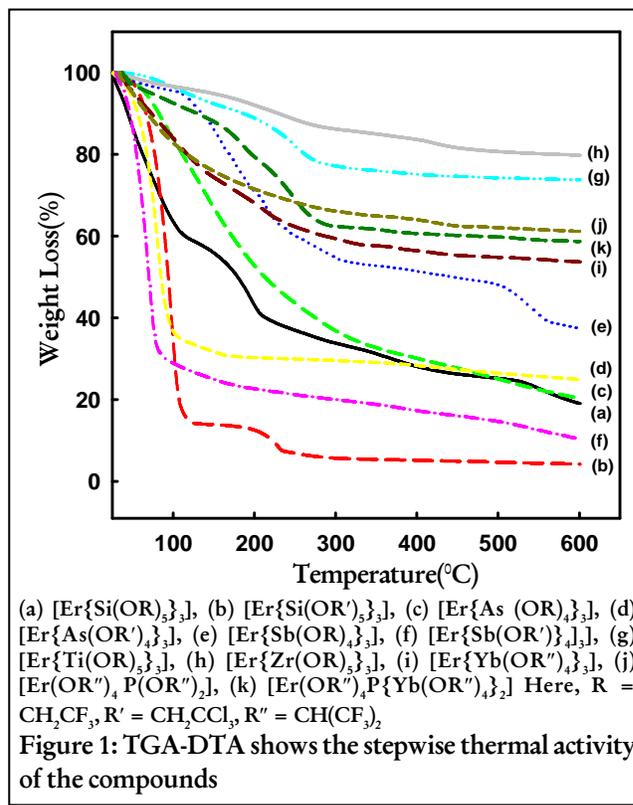
Compounds	m/z + I	Interpretation
1 [Er{Si(OR) ₅ } ₃]	325 5	Si(OCH ₂ CF ₃) ₄
	383 20	Er ₂ O ₃
2 [Er{Si(OR') ₅ } ₃]	382 15	Er ₂ O ₃
	473 10	Si(OCH ₂ CCl ₃) ₄
	612 5	Er(OCH ₂ CCl ₃) ₃
3 [Er{As(OR') ₄ } ₃]	198 25	As ₂ O ₃
	383 7	Er ₂ O ₃
4 [Er{Sb(OR) ₄ } ₃]	292 17	Sb ₂ O ₃
	464 12	Er(OCH ₂ CF ₃) ₃
5 [Er{Sb(OR') ₄ } ₃]	292 15	Sb ₂ O ₃
6 [Er{Ti(OR) ₅ } ₃]	99 100	Alcohol
	262 20	O=Ti(O-CH ₂ CF ₃)
	464 40	Er(OCH ₂ CF ₃) ₃
	282 15	O=Er(OCH ₂ CF ₃) ₃
	444 10	Ti(OCH ₂ CF ₃) ₄
7 [Er{Zr(OR) ₅ } ₃]	99 35	Alcohol
	123 20	ZrO ₂
	282 20	O=Er(-OCH ₂ CF ₃) ₃
8 [Er{Yb(OR') ₄ } ₃]	394 40	Yb ₂ O ₃
	383 55	Er ₂ O ₃
	167 90	Alcohol
9 [Er(OR'') ₄ P(OR'') ₂]	167 85	Alcohol
	220 90	P ₄ O ₆
	383 60	Er ₂ O ₃
	532 30	P(OR) ₃
	669 15	Er(OR) ₃
10 [Er(OR'') ₄ P{Yb(OR'') ₄ } ₂]	167 100	Alcohol
	350 20	O=Er(OR)
	284 20	P ₄ O ₁₀
	394 15	Yb ₂ O ₃
	382 10	Er ₂ O ₃
	356 15	O=Yb(OR)
	532 20	P(OR) ₃
	668 60	Er(OR) ₃
	674 55	Yb(OR) ₃

R = CH₂CF₃, R' = CH₂CCl₃, R'' = CH(CF₃)₂

TABLE 5: Elemental analysis of heterometallic alkoxides [found/(calcd)]

Compounds	C(calcd)	H(calcd)
1. [Er{Si(OR) ₅ } ₃]	19.87(20.72)	1.68(1.73)
2. [Er{Si(OR') ₅ } ₃]	14.07(14.53)	1.09(1.2)
3. [Er{As(OR) ₄ } ₃]	17.87(18.22)	1.34(1.52)
4. [Er{As(OR') ₄ } ₃]	12.88(13.22)	0.97(1.10)
5. [Er{Sb(OR) ₄ } ₃]	12.07(12.45)	0.97(1.04)
6. [Er{Sb(OR') ₄ } ₃]	16.46(16.73)	1.18(1.39)
7. [Er{Ti(OR) ₅ } ₃]	19.87 (20.04)	1.43(1.67)
8. [Er{Zr(OR) ₅ } ₃]	18.3 4(18.67)	1.28(1.56)
9. [Er{Yb(OR') ₄ } ₃]	15.89(16.05)	0.27(0.44)
10. [Er(OR'') ₄ P(OR'') ₂]	17.67(17.99)	0.37(0.50)
11. [Er(OR'') ₄ P{Yb(OR'') ₄ } ₂]	16.58(16.94)	0.41(0.47)

R = CH₂CF₃, R' = CH₂CCl₃, R'' = CH(CF₃)₂

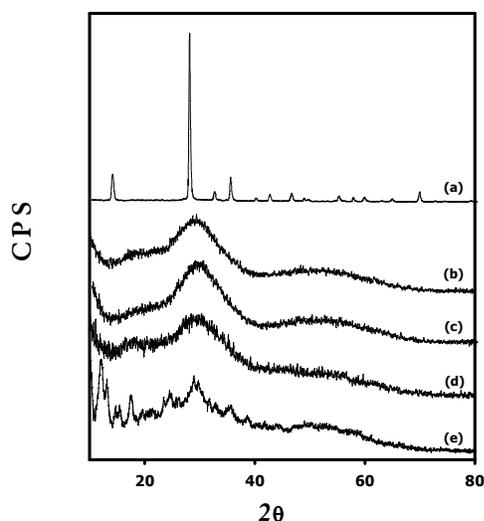


Elemental analyses are consistent with the products. Elemental analyses of these compounds are given in TABLE 5. Attempt was made to purify these compounds by crystallization. Although no suitable crystals for X-ray studies were obtained. In few cases we get the crystal for compounds (1-2) and (6-7), but they were highly unstable for X-ray studies. SEM-EDS analyses support the correct metal ratio according to the formulation.

Thermogravimetry analysis

The thermal behavior was investigated by TGA under nitrogen atmosphere for allowing identification of major thermal process taking place during evaporation, decomposition and phase crystallization. The decomposition profiles are shown in figure 1.

The thermal decomposition of alkoxides may be described as a smooth stepwise process from 20°C to around 600°C. The weight loss related to the release of organic substances in the samples. The TGA data clearly indicate that the chemical geometry of alkoxides is very much similar. A initial weight loss is observed at 50-80°C correspond to the removal of solvent. The maximum weight loss takes place



(a) $[\text{Er}\{\text{Si}(\text{OR}')_3\}_3]$, (b) $[\text{Er}\{\text{Si}(\text{OR})_3\}_3]$, (c) $[\text{Er}\{\text{Sb}(\text{OR})_4\}_3]$, (d) $[\text{Er}\{\text{Sb}(\text{OR}')_4\}_3]$, (e) $[\text{Er}(\text{OR}'')_4\text{P}\{\text{Yb}(\text{OR}')_3\}_2]$

Figure 2: XRD diffraction patterns describe the amorphous nature of the compounds at R.T.

around 110°C-319°C. The TGA results can be summarized as follows: At 110-319°C the removal of organic solvent takes place from the alkoxides. At 320-500°C correspond to the pyrolysis of organic moieties, which are present in alkoxides and finally, above 500°C onwards-crystalline phases for simple oxides takes place^[22].

XRD and SEM

The XRD patterns showed no diffraction peaks suggesting that the compounds are amorphous at room temperature except compound (a) and on heating initiation for crystallization takes places, the peaks becomes more sharp thereby supporting high homogeneity at the near atomic level. Compound (a) shows good crystallinity at room temperature probably due to the presence of chlorine. The XRD diffraction patterns are shown in figure 2. (file JCPDS no.00-

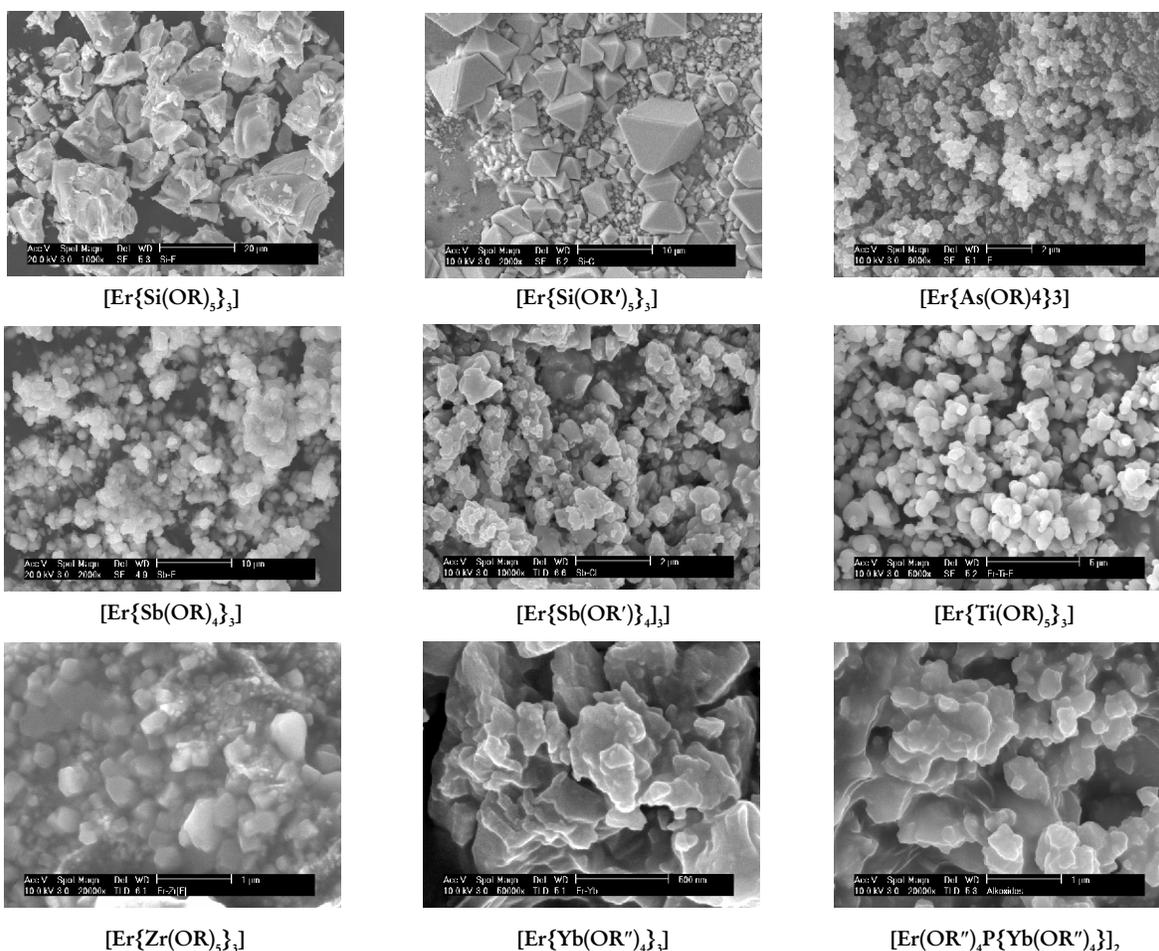


Figure 3: SEM shows surface morphologies at room temperature

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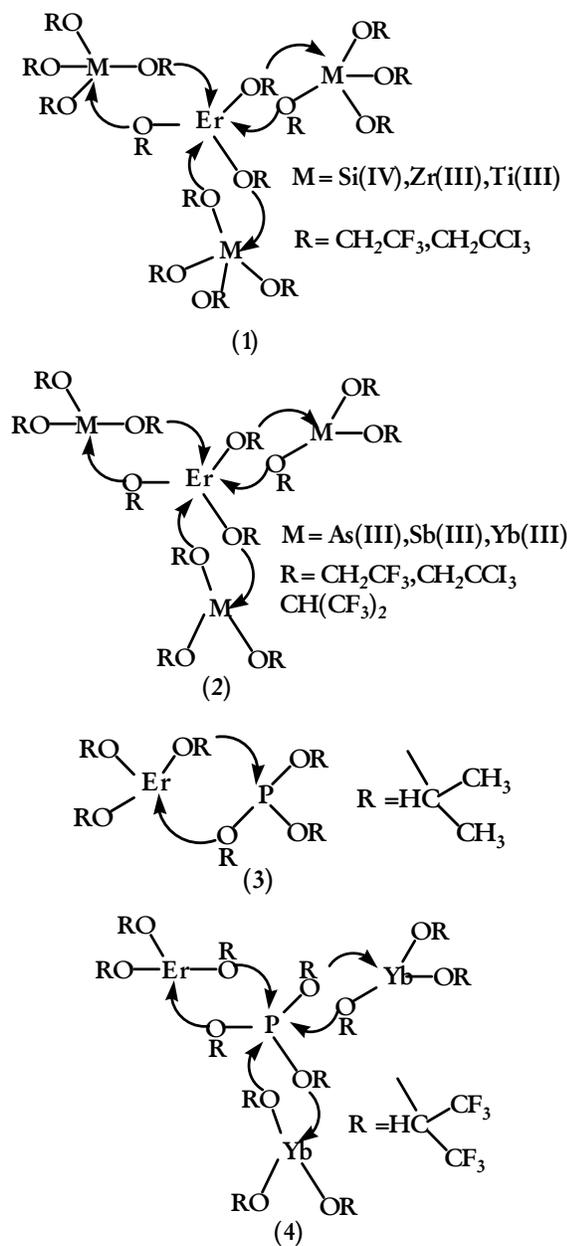


Figure 4: Structures proposed based on the physico-chemical characterizations

005-0602) average crystallite size was estimated to approximate range from 30 to 50nm from line-broadening according to the Debye-Scherrer equation. Further thermal treatment does not lead to any appreciable change in the diffraction pattern^[19].

The SEM micrograph shows pronounced tendency to agglomeration with unfacted surface with the grain particles to be micrometer -sized, which are built up to several tiny particles with polydispersed nature without any observable defects in the nanometer

range. A well-defined structural morphology was observed in the following compounds $[\text{Er}\{\text{Si}(\text{OCH}_2\text{CF}_3)_5\}_3]$, $[\text{Er}\{\text{Si}(\text{OCH}_2\text{CCl}_3)_5\}_3]$, $[\text{Er}\{\text{Ti}(\text{OCH}_2\text{CF}_3)_5\}_3]$ and $[\text{Er}\{\text{Zr}(\text{OCH}_2\text{CF}_3)_5\}_3]$ with square shape, high crystalline perfection and compositional purity and the particle size lying in the range of 5-10 μm . Therefore it is concluded that the morphological changes and particles size strongly depend on the nature and synthesis routes of the molecular precursor and the solvents.

Based on the above physico-chemical studies the following structures have been elucidated for the bimetallic alkoxides as shown in figure 4.

CONCLUSIONS

We report here the synthesis of novel heterometallic alkoxides of lanthanide series in quantitative yields for the first time and structurally characterized. These alkoxides are stable under inert atmosphere with good solubility in parent alcohol with wide range of chemical flexibility. Thermal and XRD analysis showed that the chemical structure modifications of the alkoxides altered the physico-chemical behavior of the metal oxides. The heterometallic alkoxy based precursor allows controlled sol-gel chemistry with the nature of ligands for facilitating the synthesis of nanoparticles. The work was carried out as direct continuation of our investigations in the field of alkoxides chemistry and its applications as potential molecular precursors for the future thin film for optical devise and CVD processing for technological applications.

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REFERENCES

- [1] D.C.Bradley, R.C.Mehrotra, D.C.Gaur; Metal Alkoxides, Academic Press, London, (1978).

- [2] L.G.Hubert-Pfalzgraf, H.Guilln; Appl.Organomet. Chem., **12**, 221 (1998).
- [3] N.Y.Turova, E.P.Turevskaya, V.G.Kessler, A.I. Yanovskaya; The Chemistry of metal Alkoxides, Kluwer Academic Publishers, London, (2002).
- [4] D.C.Bradley, R.C.Mehrotra, I.P.Rothwell, A.Singh; Alkoxo, Aryloxo Derivatives of Metals, San Diego, CA: Academic Press, INC., (2001).
- [5] J.Livage; New.J.Chem., **25**, 1 (2001).
- [6] R.C.Mehrotra; J.Non-Cryst.Solids, **100**, 1 (1998).
- [7] L.G.Hubert-Pfalzgraf, S.Daniele, M.J.Decons, J.Vaissermann; J.So-Gel.Sci.Tech., **8**, 49 (1997).
- [8] R.C.Mehrotra, A.Singh, S.Sogani; Chem.Rev., **94**, 1643 (1994).
- [9] J.Livage, M.Henry, C.Sanchez; Prog.Solid State Chem., **18**, 259 (1998).
- [10] L.G.Hubert-Pfalzgraf; New.J.Chem., **11**, 663 (1987), Chem.commun., **6**, 102 (2003).
- [11] J.Livage, C.Sanchez; New.J.Chem., **14**, 513 (1990).
- [12] M.Veith, S.Mathur, C.Mathur; Polyhedron, **17**, 1005 (1998).
- [13] L.G.Hubert-Pfalzgraf; Appl.Organomet.Chem., **6**, 627 (1992).
- [14] V.G.Kessler; Chem.Comm., **11**, 1213 (2003).
- [15] (a)S.V.Pasko, L.G.Hubert-pfalzgraf, A.Abrutis, P.Richard, A.Bartasyte, v.kazlauskienė; J.Mater. chem., **14**, 1245 (2004).
(b)A.Brethon, L.G.Hubert-pfalzgraf, J.C.Daran; Dalton Trans, 250 (2006).
- [16] T.Athar, J.O.Kwon, S.I.Soek; Inorg.Chimica Acta, **358**, 4541 (2005)
- [17] R.M.Silvestein, G.C.Bessler, T.C.Morril; Spectrometric Identification of Organic compounds, John Wiley and sons, New York, (1981).
- [18] M.Ocana, V.Fornes, C.J.Sema; J.Non-Cryst.Solids, **107**, 187 (1989).
- [19] C.J.Brinker, G.Scherer; Sol-gel Science Academic Press, San Diego, (1990).
- [20] J.V.Bell, T.Heisler, H.Goldenson; J.Anal.Chem., **25**, 1720 (1953).
- [21] C.G.Barraclough, D.C.Bradley, J.Lewis, I.M.Thomas; J.Chem.Soc., 2601 (1961).
- [22] M.Veith, S.Mathur; J.Sol-Gel.Sci.Tech., **15**, 145 (2000).