

# Preparation of multicomponent oxides via non-hydrolytic sol–gel routes from novel bimetallic alkoxides

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## Abstract

New series of double alkoxides of erbium and its oxides have been prepared by non-hydrolytic sol–gel reactions for the first time. These compounds were characterized with the help of FT-IR, NMR, Mass, DTA-TGA and SEM. The mass spectra show similar types of fragmentation pattern in all compounds. The XRD diffraction pattern shows an enhanced homogeneity at high temperature. TGA/DTA measurements show that thermal decomposition occurs in steps and entirely depends on the chemical compositions and the synthesis routes. The SEM observation reveals a high dense and smooth microstructural uniformity of polycrystalline nature. The physico-chemical properties show that crystallization behaviors can be controlled with the help of fine-tuning the chemical properties of chelating agents in order to increase the solubility of metal alkoxides.

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**Keywords:** Bimetallic alkoxides; Bicomponent oxides; Non-hydrolytic sol–gel

## 1. Introduction

In recent years, much research activity has been oriented towards the development of “soft chemistry” approaches for the synthesis of inorganic oxides. The investigation and the use of heterometallic alkoxides as single-source molecules precursors for synthesis of oxides have seen a rapid growth during the last one decade. The control of particle size and the morphology of the oxide is of crucial importance nowadays both from the fundamental and industrial point of view [1].

Non-hydrolytic sol–gel process is considered the best chemical route for the preparation of oxides from metal alkoxides because it is easy to control particle size, homogeneity can be achieved at the molecular level with good crystalline [2,3]. Ultrafine materials with right stoichiometry using single-source precursors have become an area of immense scientific interest due to its technological relevance in terms of simple equipments,

low temperature processing and low cost for preparing the high-purity ceramic oxide superconductors, ferroelectric materials, and luminescence materials for optical amplifiers as well as the thin films [4–6].

The metal alkoxides are very good molecular precursors because they have attractive properties such as the solubility, sublimation and thermal stability [7–14]. Formation of amorphous products can be converted into crystalline solids by hydrothermal techniques [15]. The purity and stoichiometry of the final products can be controlled depending on the chemical ratio of the double alkoxides [16–18]. In the present investigation, we synthesized for the first time covalent novel heterometallic alkoxides and their allied derivatives with the highest purity via non-hydrolytic sol–gel reactions at a favorable low temperature.

## 2. Experimental

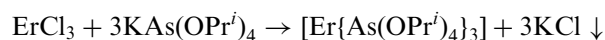
All experimental operations were carried out in inert atmosphere using a standard vacuum line and taking

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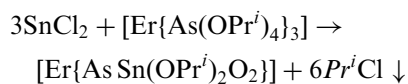
stringent precautions to avoid hydrolysis from atmospheric humidity. The solvents were distilled from Na/K alloy or LiAlH<sub>4</sub> or CaH<sub>2</sub> prior to use. Arsenic (III) chloride, antimony (III) chloride, tin (II) chloride, zinc (II) chloride, erbium trichloride (anhydrous), silicon tetrachloride and ferric chloride (anhydrous) were purchased from Aldrich and used as received. The bimetallic alkoxides and its corresponding oxides were characterized by physico-chemical techniques. The infrared spectra of the compounds were recorded as KBr pellets on a BioRad FT-IR 165 spectrometer. The C, H and O analyses of the alkoxides were carried out using an EA 1110(CE instrument) elemental analyzer. <sup>1</sup>H NMR spectra were recorded for CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> solution on a Bruker DRX–300 MHz spectrometer. The mass spectra were recorded on a JMS-DX 303 Spectrometer. Powder X-ray diffraction measurements were examined at room temperature on D8-Discover (with GADDS) Bruker operating with CuKα<sub>1</sub> radiation. The powder morphology of the compounds was performed at room temperature using a scanning electron microscope (SEM) Philips XL30S FEG XL V.5.50. The thermogravimetric and differential thermal analysis (TGA/DTA) measurements were performed on TA Instruments SDT 960 in nitrogen atmosphere. The compounds were heated in the nitrogen atmosphere at a rate of 5 °C/min. The experiments were performed in quartz crucibles, which also served as the reference.

(a) *Preparation of bimetallic alkoxides*: The preparation of bimetallic alkoxides was carried out under dry atmosphere in oven-dried glasswares.



One equivalent of potassium was reacted with isopropyl alcohol followed by the addition of one-fourth equivalent of arsenic chloride and the whole content was refluxed under stirring for 3 h. In the same content one-third equivalent of anhydrous erbium trichloride was added and the content was stirred and refluxed under nitrogen atmosphere for 24 h. The compound was separated by filtration. Finally, the mother liquor was concentrated and the compound was obtained in quantitative yield. By following the same procedure the other bimetallic alkoxides of antimony (III) and silicon (IV) were synthesized as shown in Table 1.

(b) *Preparation of derivatives*: 3-equivalents of anhydrous stannous chloride was taken with one equivalent of heterometallic alkoxide in anhydrous dichloromethane in nitrogen atmosphere. The mixture was refluxed under stirring for 36 h in the presence of 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 in the nitrogen atmosphere.



By following the same procedure the other derivatives were prepared (Table 2).

### 3. Result and discussions

As we know the reactivity of metal alkoxides is based on functional alcohols and the π-donor ability of ligands, which leads to stabilization of central metal in higher coordination states [1]. The present studies

Table 1

Millimoles ratio and nature for the alkoxides: (weight of compound & KCl was obtained in quantitative yield)

K in gm (mmole)	M = Si/As/SbMCl <sub>3</sub> /MCl <sub>4</sub> gm (mmole)	ErCl <sub>3</sub>	Nature	Compounds
8.15 (208.43)	7.08 (41.68)	3.80 (13.88)	Pink viscous	[Er{Si(OPr <sup>i</sup> ) <sub>3</sub> } <sub>3</sub> ]
6.69 (171.09)	7.75 (42.75)	3.90 (4.24)	Pink solid	[Er{As(OPr <sup>i</sup> ) <sub>4</sub> } <sub>3</sub> ]
8.00 (204.60)	11.67 (51.15)	4.66 (17.03)	Pink solid	[Er{Sb(OPr <sup>i</sup> ) <sub>4</sub> } <sub>3</sub> ]

Table 2

Millimoles ratios and nature for derivatives (yield was obtained in quantitative yield)

Metal halides gm (mmole)	Double alkoxides gm (mmole)	Nature of the derivatives	Derivatives
1.12(6.17)	2.34(2.05)	Light Pink solid	[Er{Si·As(OPr <sup>i</sup> ) <sub>2</sub> O <sub>3</sub> } <sub>3</sub> ]
2.26(9.89)	3.75(3.29)	Light Pink solid	[Er{Si·Sb(OPr <sup>i</sup> ) <sub>2</sub> O <sub>3</sub> } <sub>3</sub> ]
1.00(5.27)	2.04(1.70)	Light Pink solid	[Er{As·Sn(OPr <sup>i</sup> ) <sub>2</sub> O <sub>2</sub> } <sub>3</sub> ]
0.74(5.42)	2.00(1.81)	Light Pink solid	[Er{As·Zn(OPr <sup>i</sup> ) <sub>2</sub> O <sub>2</sub> } <sub>3</sub> ]
1.19(6.28)	2.62(2.11)	Light Pink solid	[Er{Sb·Sn(OPr <sup>i</sup> ) <sub>2</sub> O <sub>2</sub> } <sub>3</sub> ]
0.71(5.19)	2.15(1.73)	Light Pink solid	[Er{Sb·Zn(OPr <sup>i</sup> ) <sub>2</sub> O <sub>4</sub> } <sub>3</sub> ]

describe the non-hydrolytic sol–gel process for the synthesis of allied oxides derivatives using bimetallic alkoxides as single-source molecular precursor. In non-hydrolytic sol–gel techniques, the metal alkoxides are considered to be good molecular precursors and they can be carefully hydrolyzed to produce inorganic network through  $M-O-M$  linkages maintaining the highest purity and correct stoichiometry at molecular level [19–24]. Alkoxides are thermodynamically and kinetically stable and the terminal alkoxy groups are more reactive as compared to bridging alkoxy group. It is known that the metal alkoxides and metal chlorides react together through non-hydrolytic reactions, allowing a greater structural homogeneity at the molecular level and the traces of impurities are minimized [25–27].

The solubility of these alkoxides is rather high in their mother alcohol with fresh samples, but the solubility goes on decreasing on aging due to loss of solvating molecules.

The compounds were characterized by FT-IR and the characteristic absorption peaks are shown in Table 3. Striking similarities have been observed in solid and solution states dominated by the ligand vibrations between the alkoxides and its derivatives [28–32]. A significant peak was observed in between 1052 and 1022  $\text{cm}^{-1}$  that supports the formation of  $M'-O-M''$  bridging, which support the formation of oxide derivatives. In general a major down field shift in frequencies was observed in oxides derivatives when compared with parent bimetallic alkoxides.

In general, weak to medium intensity bands appear in most of the spectra at about 3400  $\text{cm}^{-1}$  region due to unavoidable slight hydrolysis of the compounds during the mulling and recording (Table 3).

$^1\text{H}$  NMR has proved to be very useful in studying these compounds at room temperatures for better understanding for elucidating molecular structures. At room-temperature  $^1\text{H}$  NMR ( $\text{CDCl}_3$  or  $\text{C}_6\text{D}_6$ ) spectrum exhibits two resonance peaks for isopropyl protons with

correct integration ratio, but the peaks are not sharp due to the paramagnetic behavior of the compounds. The merging of two doublets for the gem-dimethyl protons and two heptets for the methine protons supports the presence of the isopropoxy groups in terminal and bridging positions. When the terminal alkyl of alkoxy groups are replaced with metal halide as alkyl halide, significant downfield chemical shifts are observed for methyl and methine protons of bridging alkoxy group probably due to the delocalization of electrons in the empty orbital of coordination sphere support the formation of oxides derivatives. The  $^1\text{H}$  NMR data are given in Table 4.

The mass spectra do not give any conclusive evidence of the formation of heterometallic oxides in gas phase probably due to the breakdown of the heterometallic alkoxides under the high vacuum pressure used in mass spectrometer. The terminal alkoxy groups are first removed followed by bridging alkoxy group from heterometallic alkoxides. The ion peaks observed correspond to the liberated alkoxy group and simple metal alkoxides followed by their decomposition into corresponding metal oxides. The important fragmentation peaks are given in Table 5.

Table 4  
 $^1\text{H}$ -NMR spectral data ( $\delta/\text{ppm}$ ) for the complexes

Compounds	$\text{CH}_3$	CH	Solvent
$[\text{Er}\{\text{Si}(\text{OPr}^i)_5\}_3]$	1.07(br)	4.12(br)	$\text{C}_6\text{D}_6$
$[\text{Er}\{\text{As}(\text{OPr}^i)_4\}_3]$	1.20(d)	3.93(h)	$\text{CDCl}_3$
$[\text{Er}\{\text{Sb}(\text{OPr}^i)_4\}_3]$	1.00(br)	3.74(br)	$\text{C}_6\text{D}_6$
$[\text{Er}\{\text{Si} \cdot \text{As}(\text{OPr}^i)_2\text{O}_3\}_3]$	1.16(d)	4.17(h)	$\text{CDCl}_3$
$[\text{Er}\{\text{Si} \cdot \text{Sb}(\text{OPr}^i)_2\text{O}_3\}_3]$	1.16(d)	4.15(h)	$\text{CDCl}_3$
$[\text{Er}\{\text{As} \cdot \text{Sn}(\text{OPr}^i)_2\text{O}_2\}_3]$	1.18(d)	4.01(br)	$\text{CDCl}_3$
$[\text{Er}\{\text{As} \cdot \text{Zn}(\text{OPr}^i)_2\text{O}_2\}_3]$	1.26(br)	4.16(br)	$\text{CDCl}_3$
$[\text{Er}\{\text{Sb} \cdot \text{Sn}(\text{OPr}^i)_2\text{O}_2\}_3]$	1.19(br)	4.00(br)	$\text{CDCl}_3$
$[\text{Er}\{\text{Sb} \cdot \text{Zn}(\text{OPr}^i)_2\text{O}_4\}_3]$	1.18(d)	3.99(h)	$\text{CDCl}_3$

br = broad, h = heptet.

Table 3  
Important FT-IR spectral bands ( $\text{cm}^{-1}$ ) of the compounds

$\nu_{\text{C-O}}$	$\nu_{\text{C-H}}$	$\nu_{\text{C-O}}$	$\nu(\text{OPri})$	$\nu_{\text{M-O-C}}$	$\nu_{\text{M'-O-M''}}$	$\nu_{\text{C-C}}$	$\nu_{\text{M-O-M'}}$
1653br	1469s	1054vs	1124vs	1174s	—	772vs	503s
1630vs	1461m	1025w	1102m	1162w	—	804m	620br
1615vbr	1460w	1021w	1106m	1161vw	—	854br	600br
1635w	1468m	1050vs	1123vs	1174m	1050vs	805m	503m
1610m	1427m	1024vs	1098vs	1263m	1024vs	802m	647m
1615s	1459w	1022m	1098m	1161w	1022m	802w	544br
1610vs	1427w	1024vs	1098vs	1263s	1024s	802s	647br
1620vs	1459w	1022m	1160m	1161w	1098m	805br	544br
1617vs	1468w	1024m	1098m	1262br	1098	802s	517br

$M = \text{Er}$ ,  $M' = \text{Si}$ ,  $\text{As}$ ,  $\text{Sb}$ ,  $M'' = \text{As}$ ,  $\text{Sb}$ ,  $\text{Sn}$ ,  $\text{Zn}$ .

br = broad, vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

The purity of compound was established with the help of quantitative yield of Potassium chloride, yield of the compound, elemental analysis and as well as EDS. Elemental analysis of the compounds is shown in Table 6. Attempt was made to purify by crystallization

Table 5  
Mass spectrum with important fragmentation peaks

Compounds	$m/z+$	I	Interpretation
[Er{Si(OPr <sup>t</sup> ) <sub>5</sub> } <sub>3</sub> ]	264	15	Si(OPr <sup>t</sup> ) <sub>4</sub>
	344	30	Er(OPr <sup>t</sup> ) <sub>3</sub>
	383	15	Er <sub>2</sub> O <sub>3</sub>
[Er{As(OPr <sup>t</sup> ) <sub>4</sub> } <sub>3</sub> ]	198	15	As <sub>2</sub> O <sub>3</sub>
	252	15	As(OPr <sup>t</sup> ) <sub>3</sub>
	344	45	Er(OPr <sup>t</sup> ) <sub>3</sub>
	382	15	Er <sub>2</sub> O <sub>3</sub>
[Er{Sb(OPr <sup>t</sup> ) <sub>4</sub> } <sub>3</sub> ]	290	15	Sb <sub>2</sub> O <sub>3</sub>
	299	35	Sb(OPr <sup>t</sup> ) <sub>3</sub>
	344	10	Er(OPr <sup>t</sup> ) <sub>3</sub>
	383	15	Er <sub>2</sub> O <sub>3</sub>
[Er{Si · Sb(OPr <sup>t</sup> ) <sub>2</sub> O <sub>3</sub> } <sub>3</sub> ]	264	8	Si(OPr <sup>t</sup> ) <sub>4</sub>
	292	5	Sb <sub>2</sub> O <sub>3</sub>
	344	10	Er(OPr <sup>t</sup> ) <sub>3</sub>
	383	5	Er <sub>2</sub> O <sub>3</sub>
[Er{As · Sn(OPr <sup>t</sup> ) <sub>2</sub> O <sub>2</sub> } <sub>3</sub> ]	135	24	SnO
	198	22	As <sub>2</sub> O <sub>3</sub>
	252	10	As(OPr <sup>t</sup> ) <sub>3</sub>
	264	12	Sn(OPr <sup>t</sup> ) <sub>4</sub>
	344	5	Er(OPr <sup>t</sup> ) <sub>3</sub>
	383	8	Er <sub>2</sub> O <sub>3</sub>
[Er{Sb · Sn(OPr <sup>t</sup> ) <sub>2</sub> O <sub>2</sub> } <sub>3</sub> ]	135	32	SnO
	237	6	Sn(OPr <sup>t</sup> ) <sub>2</sub>
	292	2	Sb <sub>2</sub> O <sub>3</sub>
	299	3	Sb(OPr <sup>t</sup> ) <sub>3</sub>
	344	3	Er(OPr <sup>t</sup> ) <sub>3</sub>
	383	10	Er <sub>2</sub> O <sub>3</sub>
[Er{Sb · Zn(OPr <sup>t</sup> ) <sub>2</sub> O <sub>4</sub> } <sub>3</sub> ]	184	47	Zn(OPr <sup>t</sup> ) <sub>2</sub>
	292	12	Sb <sub>2</sub> O <sub>3</sub>
	299	12	Sb(OPr <sup>t</sup> ) <sub>3</sub>
	344	6	Er(OPr <sup>t</sup> ) <sub>3</sub>
	383	30	Er <sub>2</sub> O <sub>3</sub>

in mother solvent. In few cases we get the crystal but highly unstable for X-ray studies.

**TGA-DTA:** The thermal behaviors investigated by thermogravimetry (TG) and differential thermal analyses (DTA) under a nitrogen atmosphere at the heating rate of 5 °C per minute, gave evidence for the major steps taking place for evaporation, decomposition and phase crystallization.

The thermal decomposition of alkoxides and its derivatives may be described as a smooth stepwise process from 20 °C to around 1200 °C. The TGA-DTA data for all compounds are very similar and clearly indicate the maximum weight loss around 700 °C. The TGA-DTA results can be summarized as follows. At 200 °C the removal of organic solvent takes place from the alkoxides. At 500 °C the organic moieties are removed which are connected to alkoxides and their derivatives. At 1000 °C crystalline phase is observed.

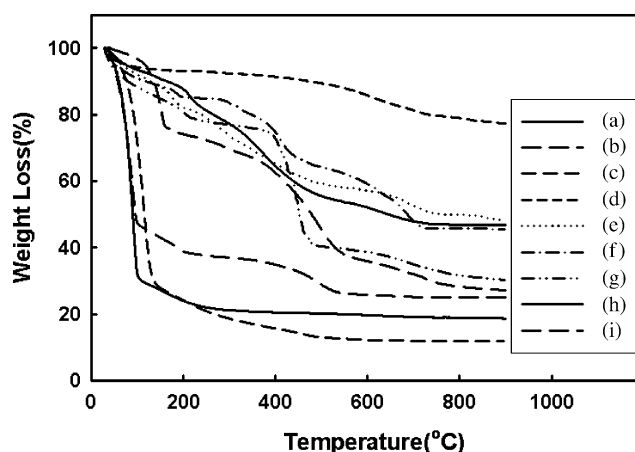


Fig. 1. TGA-DTA shows the stepwise thermal activity of the compounds. (a) [Er{Si(OPr<sup>t</sup>)<sub>5</sub>}<sub>3</sub>], (b) [Er{Si · As(OPr<sup>t</sup>)<sub>2</sub>O<sub>3</sub>}<sub>3</sub>], (c) [Er{Si · Sb(OPr<sup>t</sup>)<sub>2</sub>O<sub>3</sub>}<sub>3</sub>], (d) [Er{As(OPr<sup>t</sup>)<sub>4</sub>}<sub>3</sub>], (e) [Er{As · Sn(OPr<sup>t</sup>)<sub>2</sub>O<sub>2</sub>}<sub>3</sub>], (f) [Er{As · Zn(OPr<sup>t</sup>)<sub>2</sub>O<sub>2</sub>}<sub>3</sub>], (g) [Er{Sb(OPr<sup>t</sup>)<sub>4</sub>}<sub>3</sub>], (h) [Er{Sb · Sn(OPr<sup>t</sup>)<sub>2</sub>O<sub>2</sub>}<sub>3</sub>], (i) [Er{Sb · Zn(OPr<sup>t</sup>)<sub>2</sub>O<sub>4</sub>}<sub>3</sub>].

Table 6  
Elemental analysis of heterometallic alkoxides and its derivatives [found/(calcd)]

Compounds	C	H	O
[Er{Si(OPr <sup>t</sup> ) <sub>5</sub> } <sub>3</sub> ]	47.38(47.50)	8.97(9.23)	20.78(21.11)
[Er{As(OPr <sup>t</sup> ) <sub>4</sub> } <sub>3</sub> ]	38.93 (39.26)	7.47(7.63)	17.27(17.45)
[Er{Sb(OPr <sup>t</sup> ) <sub>4</sub> } <sub>3</sub> ]	34.58(34.82)	6.69(6.77)	14.93(15.47)
[Er{Si · As(OPr <sup>t</sup> ) <sub>2</sub> O <sub>3</sub> } <sub>3</sub> ]	21.76(22.16)	3.94(4.31)	19.07(19.69)
[Er{Si · Sb(OPr <sup>t</sup> ) <sub>2</sub> O <sub>3</sub> } <sub>3</sub> ]	18.87(19.36)	3.24(3.76)	16.87(17.21)
[Er{As · Sn(OPr <sup>t</sup> ) <sub>2</sub> O <sub>2</sub> } <sub>3</sub> ]	17.87(18.02)	3.14(3.50)	15.84(16.02)
[Er{As · Zn(OPr <sup>t</sup> ) <sub>2</sub> O <sub>2</sub> } <sub>3</sub> ]	20.14(20.79)	3.67(4.04)	17.96(18.48)
[Er{Sb · Sn(OPr <sup>t</sup> ) <sub>2</sub> O <sub>2</sub> } <sub>3</sub> ]	15.88(16.13)	2.78(3.14)	13.90(14.33)
[Er{Sb · Zn(OPr <sup>t</sup> ) <sub>2</sub> O <sub>4</sub> } <sub>3</sub> ]	21.76(18.30)	3.94(3.56)	15.82(16.27)

Then several exothermic processes appear probably due to either combustion or crystallization phenomena. The TGA-DTA is summarized in Fig. 1.

**XRD and SEM:** The XRD diffraction patterns show that the compounds are amorphous at room temperature and the XRD peaks are becoming sharper supporting high homogeneity at the near atomic level at high temperature supporting the crystalline phase can be achieved. The XRD diffraction patterns are summarized in Fig. 2.

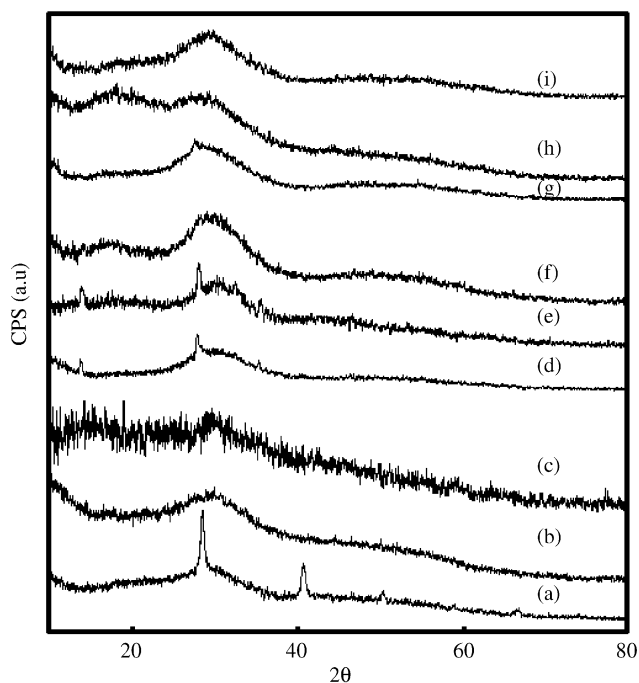


Fig. 2. XRD diffraction patterns describe the amorphous nature of the compounds at R.T. (a)  $[\text{Er}\{\text{Si}(\text{OPr}^i)_5\}_3]$ , (b)  $[\text{Er}\{\text{Si} \cdot \text{As}(\text{OPr}^i)_2\text{O}_3\}_3]$ , (c)  $[\text{Er}\{\text{Si} \cdot \text{Sb}(\text{OPr}^i)_2\text{O}_3\}_3]$ , (d)  $[\text{Er}\{\text{As}(\text{OPr}^i)_4\}_3]$ , (e)  $[\text{Er}\{\text{As} \cdot \text{Sn}(\text{OPr}^i)_2\text{O}_2\}_3]$ , (f)  $[\text{Er}\{\text{As} \cdot \text{Zn}(\text{OPr}^i)_2\text{O}_2\}_3]$ , (g)  $[\text{Er}\{\text{Sb}(\text{OPr}^i)_4\}_3]$ , (h)  $[\text{Er}\{\text{Sb} \cdot \text{Sn}(\text{OPr}^i)_2\text{O}_2\}_3]$ , (i)  $[\text{Er}\{\text{Sb} \cdot \text{Zn}(\text{OPr}^i)_2\text{O}_4\}_3]$ .

The SEM micrograph shows pronounced tendency to agglomeration with unfaceted surface with the grain particles to be micrometer-sized which are built up of several tiny particles with the polydispersed nature without any observable defects. A well-defined structural morphology is observed in the following compounds:  $[\text{Er}\{\text{Si}(\text{OPr}^i)_5\}_3]$ ,  $[\text{Er}\{\text{As}(\text{OPr}^i)_4\}_3]$  and  $[\text{Er}\{\text{Sb} \cdot \text{Sn}(\text{OPr}^i)_2\text{O}_2\}_3]$  with cubical or square shapes, high crystalline perfection and compositional purity, and the particle size lying in the range of 1–5  $\mu\text{m}$ . Therefore it is concluded that the morphological changes in microstructure particles strongly depend on the nature and synthesis routes of the molecular precursor. The SEM is summarized in Fig. 3.

Based on the above physico-chemical studies the following structures have been elucidated for the bimetallic alkoxides and their corresponding derivatives as shown in Fig. 4.

#### 4. Conclusions

In this study, we have investigated and characterized the novel bimetallic alkoxides and its oxide derivatives with a coordinated central erbium atom. These compounds are an attractive potential precursor for mixed metal oxide materials due to its solution stability. The reactions are important, not only for the better understanding of alkoxides chemistry, but also for developing the Er doped wave guide lasing via non-hydrolytic sol-gel processing that will enhance the efficiency of optical amplifiers. These studies show that optical studies depend on the chemical protocol and further work will be necessary to fully understood optical gains. Work is in progress to better control particles size and morphologies in the systems for designing the optical device and improves our knowledge about optical properties.

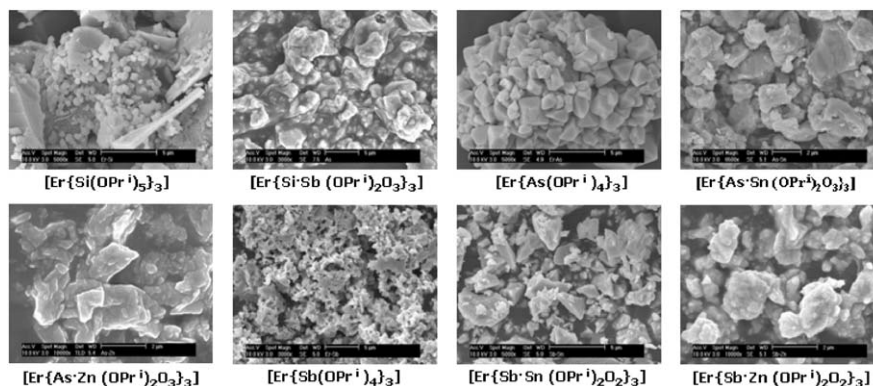


Fig. 3. SEM shows surface morphologies at room temperature.



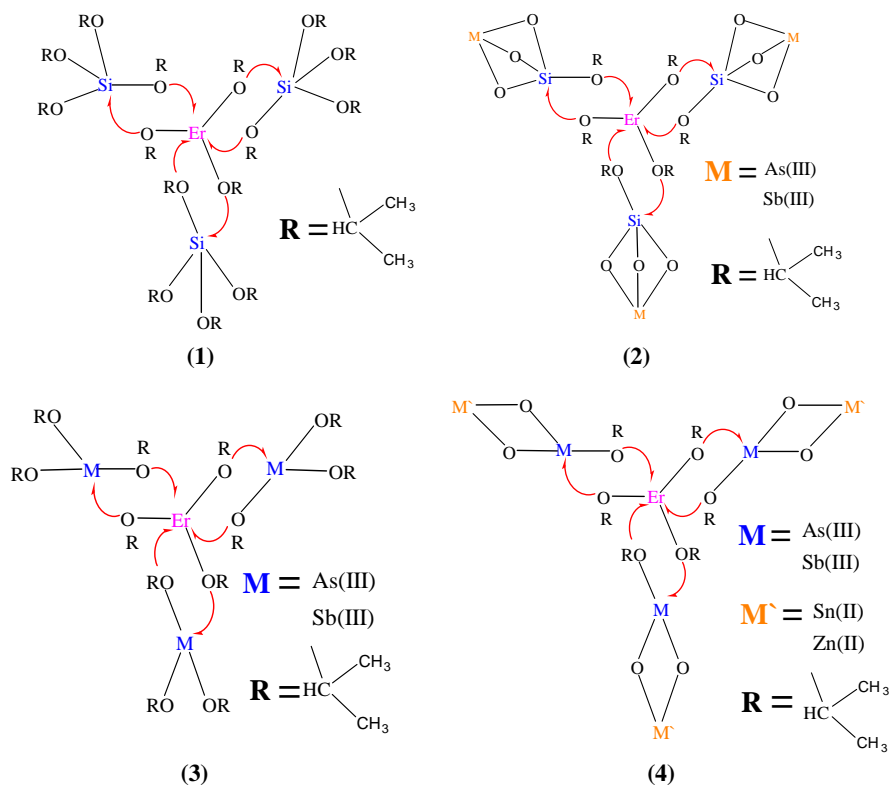


Fig. 4. Structures proposed based on the physico-chemical characterizations.

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