Max Planck Institute of Colloids and Interfaces

Nonaqueous Routes to Metal Oxide Nanoparticles

or

Is Organic Chemistry the Key to the Synthesis of Metal Oxide Nanoparticles?

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Outline of the Lecture

- Short summary of aqueous sol-gel chemistry
- Why should we use nonaqueous systems?
- Basics of nonaqueous sol-gel chemistry:

  Hydroxylation: Reaction of alcohols with metal halides

  Condensation: Ether, ester, and alkyl halide elimination
- Literature examples: Nonaqueous synthesis of oxide gels and nanoparticles
- Own work: Nonaqueous synthesis of binary and ternary metal oxides
- Discussion of new formation mechanisms
- Summary

Aqueous Sol-Gel Chemistry

Molecular Precursor —Inorganic Polymerization Reactions→ **Metal Oxide Network**

Molecular Precursors: Inorganic salts

Metal organic compounds (metal alkoxides)

Inorganic Polymerization Reactions: Hydrolysis

Condensation

Example: **Transformation of Metal Alkoxides to Metal Oxides**

Hydrolysis: $M\text{-}OR + H_2O \longrightarrow M\text{-}OH + ROH$

Condensation: $M\text{-}OH + HO\text{-}M \longrightarrow M\text{-}O\text{-}M + H_2O$

Prog. Solid State Chem. **1988**, *18*, 259-341; Chem. Rev. **1990**, *90*, 33-72

Nonaqueous Sol-Gel Routes to Oxides

Why are nonaqueous reaction systems advantageous?

Aqueous sol-gel procedures have some general drawbacks:

- Fast hydrolysis rate of metal alkoxides
- In the most cases, the as-synthesized precipitates are amorphous
- Many experimental parameters have to be controlled carefully:

  pH, method of mixing, temperature, rate of oxidation, nature and concentration of anions….
- Surface adsorbed water has a significant effect on the properties

Nonaqueous sol-gel procedures are able to overcome many of these specific problems!

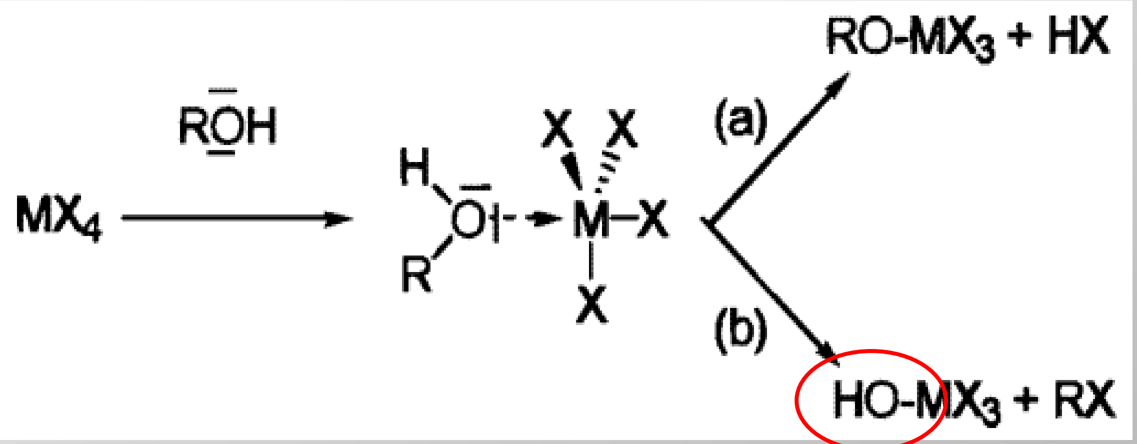
Corriu and Leclercq: Angew. Chem. Int. Ed. **1996**, *35*, 1420-1436

Nonaqueous Sol-Gel Routes to Oxides

1. Nonhydrolytic Hydroxylation Reactions

(Formation of M-OH bonds)

1.1 Reaction of alcohols with metal halides:



1) Coordination of the alcohol to the metal centre

2) a) Formation of metal alkoxide under elimination of HX

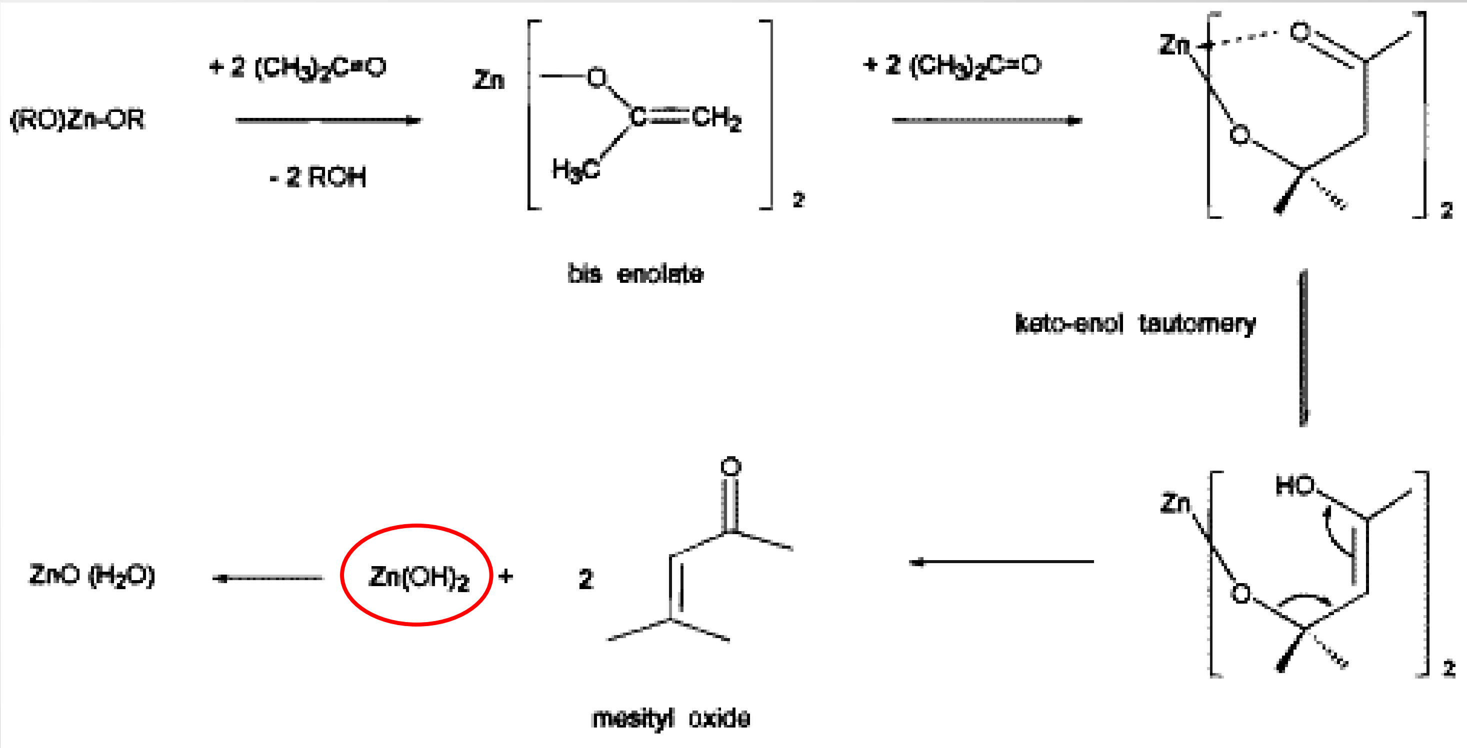
b) Formation of hydroxyl group and elimination of alkyl halide RX (if R is an electron-donor substituent, the nucleophilic attack of the chloride on the carbon group is favored)

A. Vioux: Chem. Mater. **1997**, *9*, 2292-2299

Nonaqueous Sol-Gel Routes to Oxides

1. Nonhydrolytic Hydroxylation Reactions

1.2 Reaction of carbonyl compounds with basic alkoxides:



Goel et al.: Mater. Res. Soc. Symp. Proc. **1992**, *271*, 3

Nonaqueous Sol-Gel Routes to Oxides

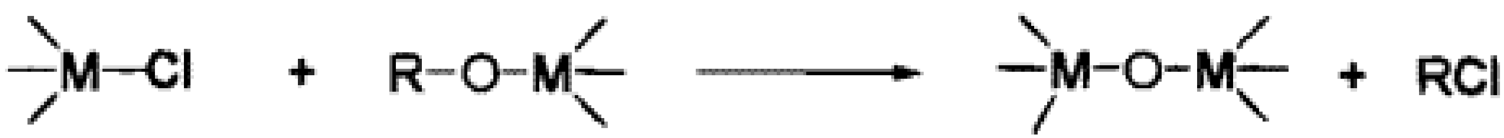
2. Aprotic Condensation Reactions

(M-O-M Bond Formation)

Reaction between two metal alkoxides under ether elimination

Reaction between metal acetates and metal alkoxides under ester elimination

Reaction between metal alkoxides and metal halides under alkyl halide elimination



A. Vioux: Chem. Mater. **1997**, *9*, 2292-2299

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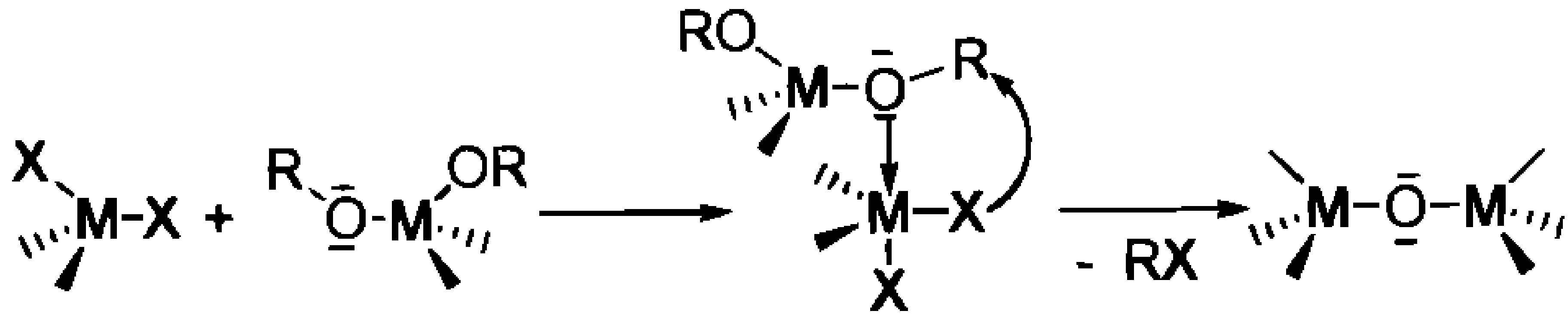
Nonaqueous Sol-Gel Routes to Oxides

2. Aprotic Condensation Reactions

Alkyl Halide Elimination:

Condensation between alkoxide and halide functions

Proposed reaction scheme:



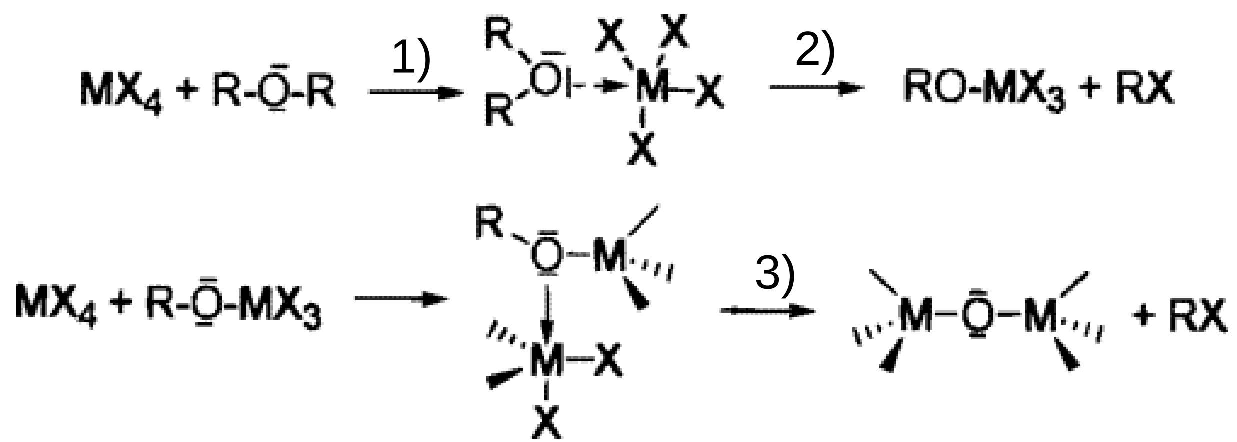
1) Alkoxy group coordinates to the metal centre of a second molecule
2) Release of an alkyl halide molecule leading to the M-O-M bond (nucleophilic cleaviage of the OR bond: Electronice effects on the carbon centre are critical.

Nonaqueous Sol-Gel Routes to Oxides

2. Aprotic Condensation Reactions

Alkyl Halide Elimination:

Condensation between alkoxide and halide functions, where the alkoxy group is produced *in-situ* by alcoholysis or etherolysis:



1) Coordination of the organic oxo compound, ether (R=alkyl) or alcohol (R=H and alkyl), to the metal centre
2) Release of hydrogen halide in the case of alcoholysis (R=H) or alkyl halide in the case of etherolysis (R=alkyl)
3) Condensation of metal alkoxide and halide under alkyl halide elimination

Nonaqueous Sol-Gel Routes to Oxides

Alkyl Halide Elimination:

1. Silica gels:

First report (?):

Synthesis of silica by heating tetrachlorosilane with phenylethanol $C_6H_5C(OH)HCH_3$:

$$SiCl_4 + (+)\text{-1-phenylethanol} \xrightarrow{-10°C} SiO_2 \cdot x\,H_2O + \text{rac. 1-chloro-1-phenylethane}$$

Gerrard and Woodhead: J. Chem. Soc. **1951**, 519-522

1992:

Synthesis of silica gels by reacting silicon tetrahalides with various oxygen donors such as tert-butanol, benzyl alcohol, dibenzyl ether and benzylaldehyde.

$$\equiv SiOR + XSi\equiv \xrightarrow{T = RT – 110°C,\ 15\ min – 1\ month} \equiv Si\text{-}O\text{-}Si\equiv + RX$$

Corriu et al.: J. Non-Cryst. Solids **1992**, *146*, 301-303

Nonaqueous Sol-Gel Routes to Oxides

Alkyl Halide Elimination:

2. Titania and alumina gels

$$AlX_3 + Al(OR)_3 \xrightarrow{\text{Reflux, 3-32h}} Al_2O_3 + RX$$

$$TiX_4 + Ti(OR)_4 \xrightarrow{\text{110°C, 8-10d}} TiO_2 + RX$$

Amorphous, monolithic gels

Calcination at 800°C (Al) or 400°C (Ti) leads to the formation of the crystalline oxide phases

Corriu et al.: J. Mater. Chem. **1992**, *2*, 673-674

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Nonaqueous Sol-Gel Routes to Oxides

Alkyl Halide Elimination:

3. Titania gels via *in-situ* produced alkoxides

$$TiCl_4 + iPr\text{-}O\text{-}iPr \xrightarrow{110^\circ C,\ 7d} TiO_2 + iPrCl + \text{hydrocarbons}$$

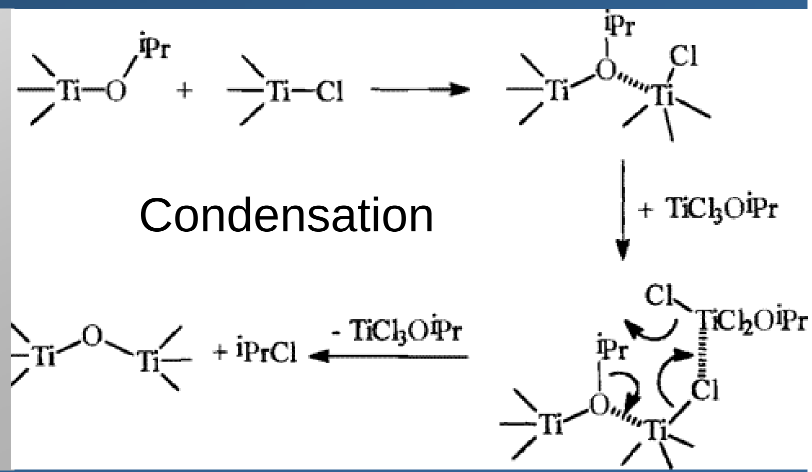
Proposed 2-Step Mechanism:

1) Formation of the alkoxide at RT (Alkoxylation):

≡Ti-Cl + *i*PrO-*i*Pr ⟶ ≡Ti-O*i*Pr + *i*Pr-Cl

2) Condensation (at 100°C):

≡Ti-O*i*Pr + ≡Ti-Cl ⟶ ≡Ti-O-Ti≡ + *i*Pr-Cl



Arnal et al.: J. Mater. Chem. **1996**, *6*, 1925-1932; Chem. Mater. **1997**, *9*, 694-698

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Nonaqueous Sol-Gel Routes to Oxides

Alkyl Halide Elimination:

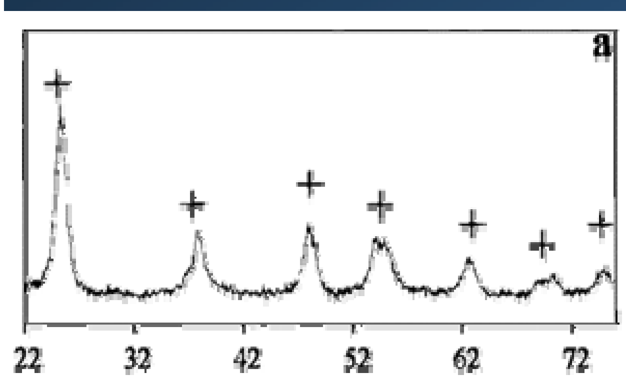
4. Crystalline titania nanoparticles

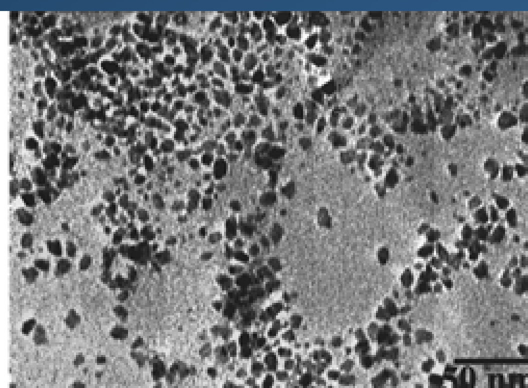
Synthesis procedure:

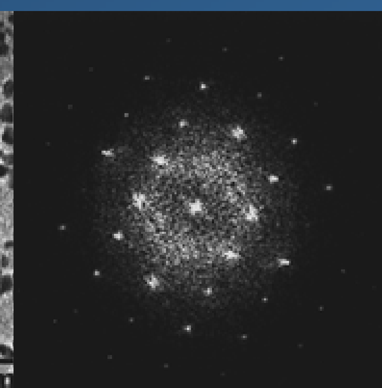
1) $TiCl_4$ + trioctylphosphine oxide (TOPO) + heptadecane: Heat to 300°C under N_2
2) Injection of $Ti(O\textit{i}Pr)_4$ to the hot mixture

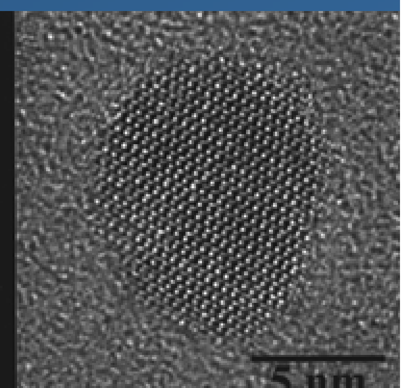
White precipitate, yield less than 50%, crystalline (anatase), particle size 3-9 nm

Reaction scheme: $TiCl_4 + Ti(O\textit{i}Pr)_4 \longrightarrow 2\ TiO_2 + 4\ \textit{i}PrCl$









Trentler et al.: J. Am. Chem. Soc. **1999**, *121*, 1613-1614

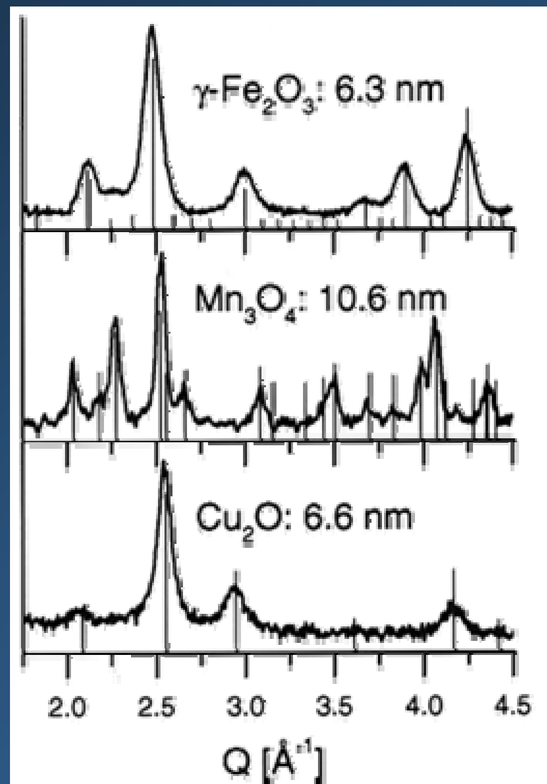
Nonaqueous Sol-Gel Routes to Oxides

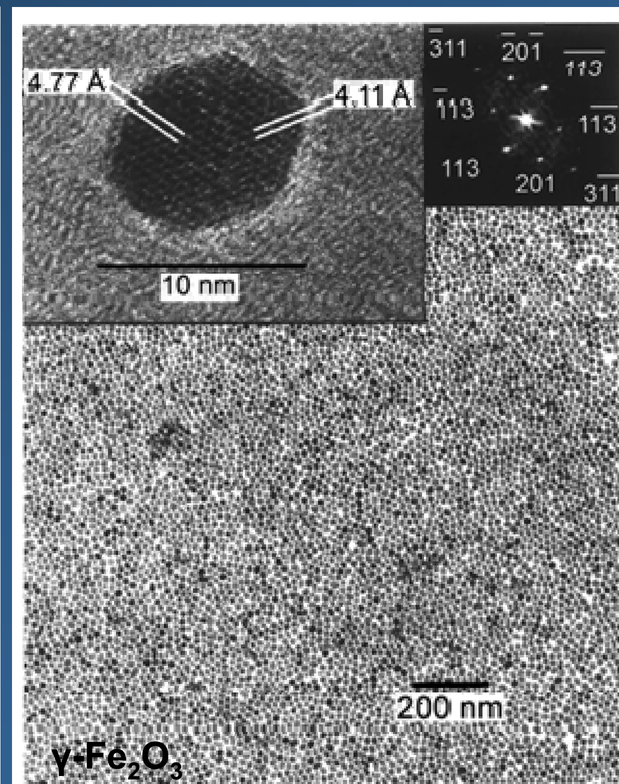
5. Crystalline γ-Fe_2O_3 and MnO nanoparticles

Synthesis procedure:

1) Metal Cupferron complexes M^xCup_x [M=Fe^{3+}, Cu^{2+}, Mn^{2+}; Cup=$C_6H_5N(NO)O^-$] are injected into octylamine at 250°C-300°C under inert atmosphere
2) Cooling to RT results in the precipitation of nanocrystals

Thermal decomposition of metal cupferronates, resulting in the formation of crystalline, redispersible nanoparticles





Rockenberger et al.: J. Am. Chem. Soc. **1999**, *121*, 11596-11597

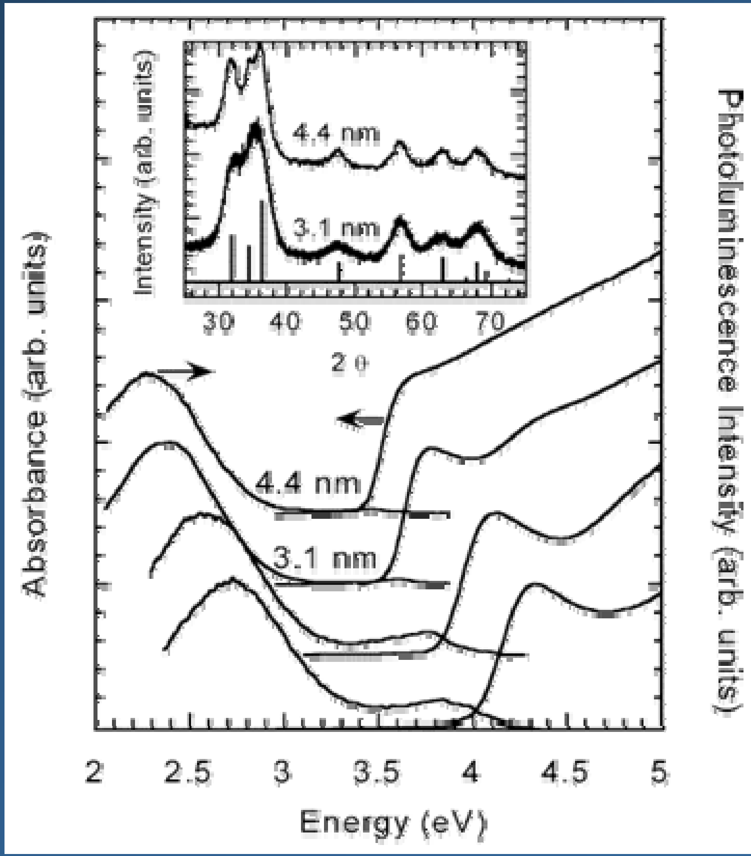
Nonaqueous Sol-Gel Routes to Oxides

6. ZnO nanoparticles

Synthesis procedure:

1) Addition of diethylzinc in decane to octylamine
2) Inject this reaction mixture to TOPO at 200°C
3) Keep T at around 150°C-180°C
4) Addition of methanol to precipitate the ZnO nanoparticles

Crystalline (wurtzite structure), redispersible in hexane, 3.1 nm ± 10%



Shim et al.: J. Am. Chem. Soc. **2001**, *123*, 11651-11654

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Nonaqueous Sol-Gel Routes to Oxides

Alkyl Halide Elimination:

7. Zirconia nanoparticles

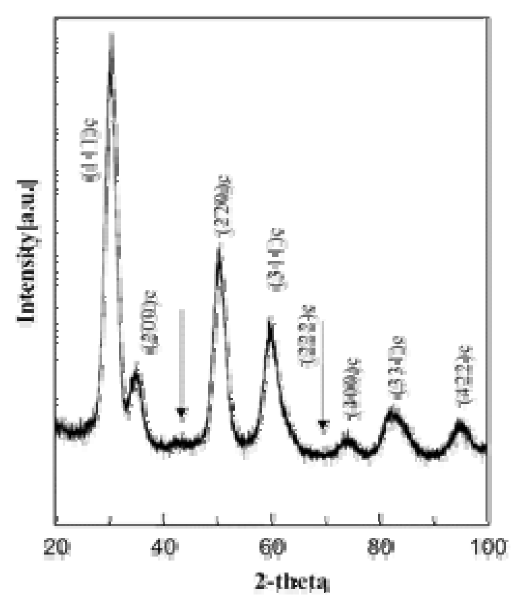
Synthesis procedure:

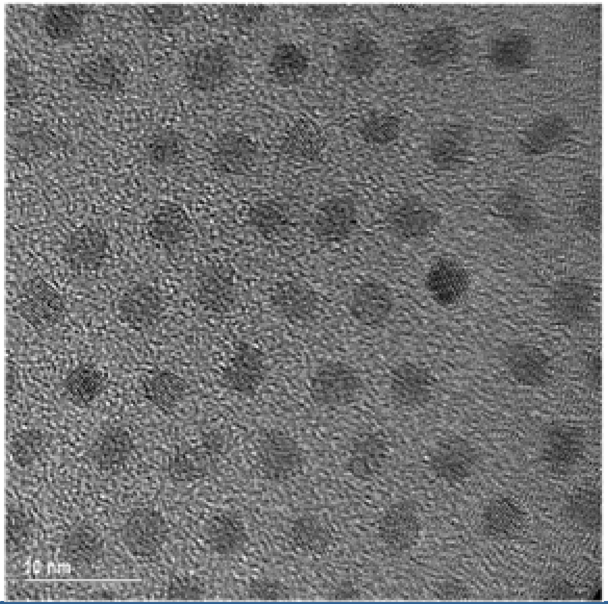
1) $Zr(O\textit{i}Pr)_4 \cdot HO\textit{i}Pr$ + $ZrCl_4$ in trioctylphosphine oxide (TOPO) at 60°C under Ar

2) Heat to 340°C, keep temperature for 2h

3) Cool to 60°C and add acetone to precipitate the zirconia nanoparticles

Crystalline nanoparticles (high-T tetragonal phase), uniform in shape and size (4 nm), multigram synthesis





Joo et al.: J. Am. Chem. Soc. **2003**, *125*, 6553-6557

Nonaqueous Sol-Gel Routes to Oxides

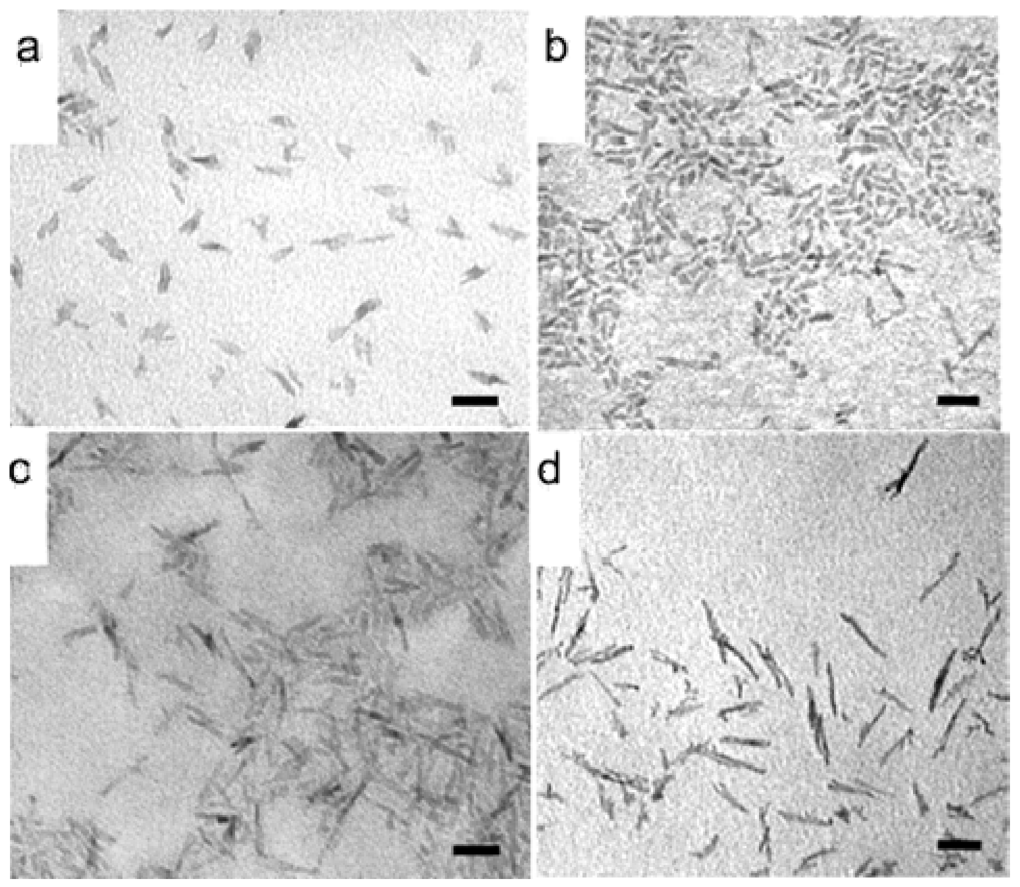
Alkyl Halide Elimination:

8. Titania nanoparticles

Synthesis procedure:

1) $Ti(OiPr)_4$ + $TiCl_4$ in dioctyl ether, trioctylphosphine oxide (TOPO), and lauric acid at 300°C under Ar
2) Quenching with cold toluene
3) Addition of acetone to precipitate the titania nanoparticles

Crystalline nanoparticles (anatase phase), bullet- to rod-like shape



Jun et al.: J. Am. Chem. Soc. **2003**, *125*, 15981-15985

Nonaqueous Sol-Gel Routes to Oxides

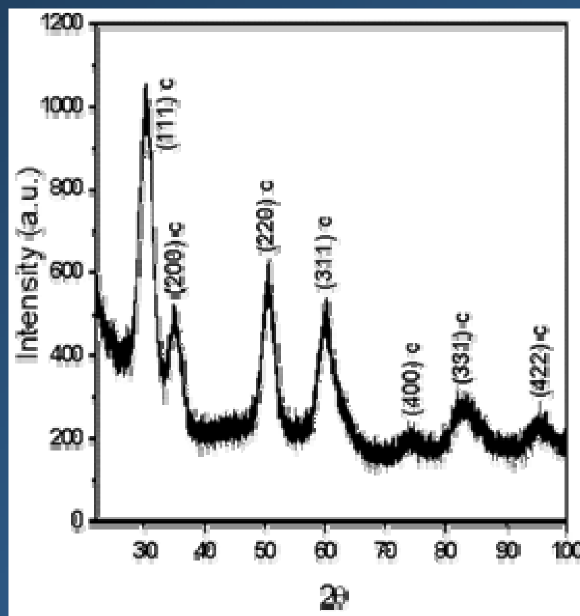
Alkyl Halide Elimination:

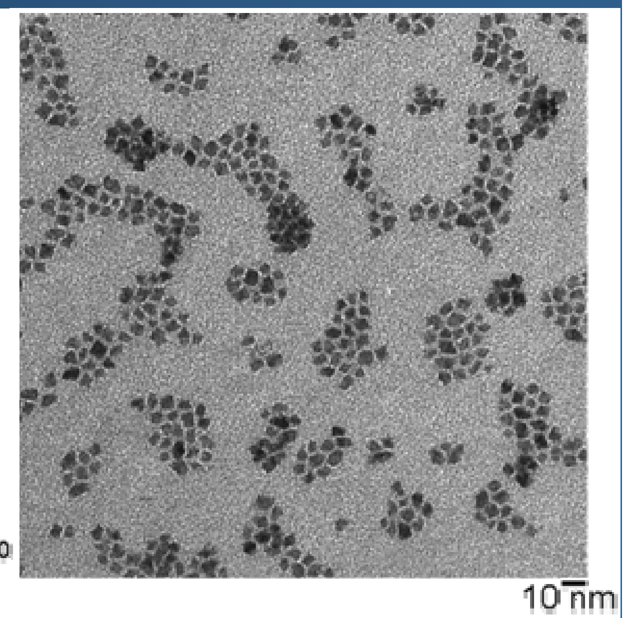
9. Hafnia nanoparticles

Synthesis procedure:

1) $Hf(O\textit{i}Pr)_4 \cdot HO\textit{i}Pr$ + $HfCl_4$ in trioctylphosphine oxide (TOPO) at 60°C under Ar
2) Heat to 360°C, keep temperature for 2h
3) Cool to 60°C and add acetone to precipitate the hafnia nanoparticles

Crystalline nanoparticles (cubic structure), uniform in shape and size (5.5 nm), redispersible in hexane





Tang et al.: Chem. Mater. **2004**, *16*, 1336-1342

Nonaqueous Sol-Gel Routes to Oxides

Alkyl Halide Elimination:

10. Functionalized titania nanoparticles

Synthesis procedure:

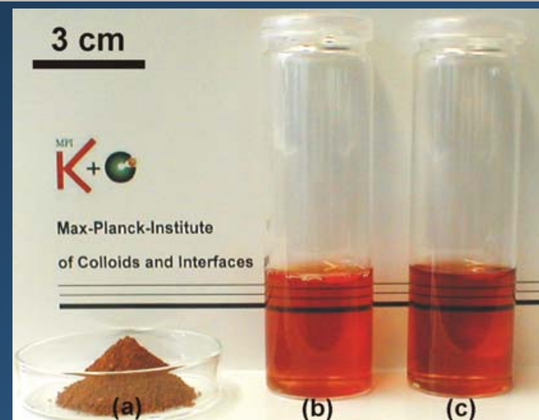
1) $TiCl_4$ + Benzyl alcohol + enediol ligands

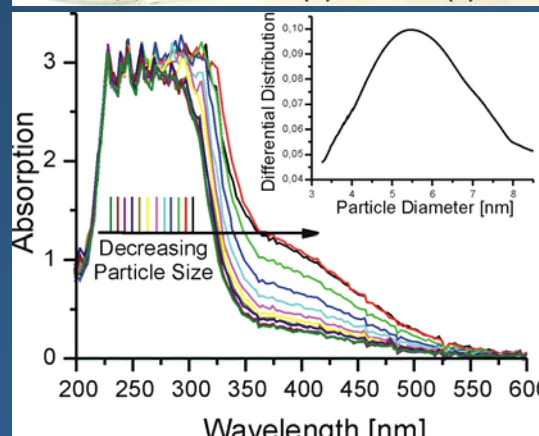
   [dopamine $(HO)_2C_6H_3CH_2CH_2NH_2{\cdot}HCl$; 4-*tert*-butylcatechol $(CH_3)_3CC_6H_3(OH)_2$]

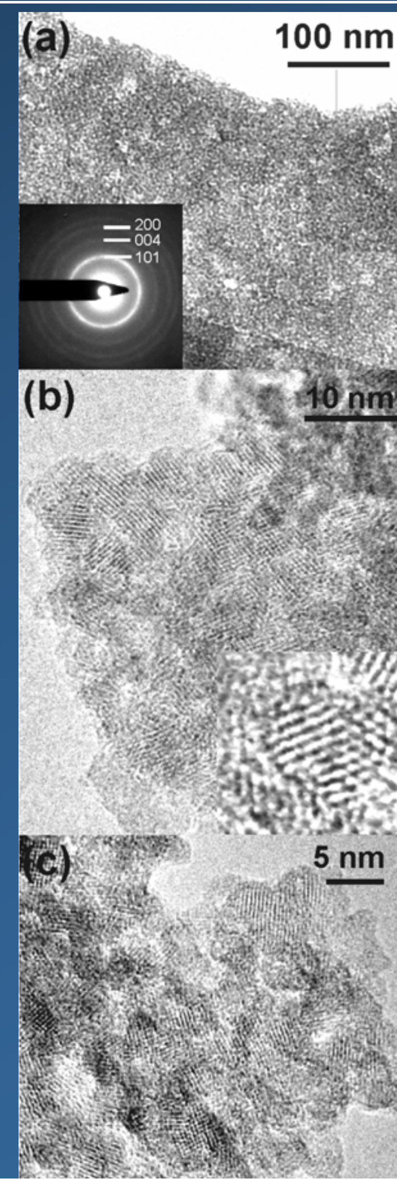
2) Heat to 70-80°C for 2-5d

3) Centrifuge precipitate, wash and dry at 60°C

   Crystalline nanoparticles in form of powders, uniform in shape and size (5.5 nm), soluble in either water or organic solvents (depending on functionalization)







Niederberger et al.: Chem. Mater. **2004**, *16*, 1202-1208

Nonaqueous Sol-Gel Routes to Oxides

Summary:

All these presented literature examples are based either on the ***thermal decomposition*** of organo-metal precursors or on the ***alkyl halide elimination*** process.

However:

Halides often remain in the final oxide material and are not easy to remove!

Are there other elimination processes available to extend the available nonaqueous reaction processes?

Nonaqueous Sol-Gel Routes to Oxides

Synthesis of Perovskites and Related Materials

Why Perovskites?

Ferroelectric properties, high dielectric constant

Applications: Electroceramics ($BaTiO_3$-based multilayer capacitors are a multibillion dollar industry)

Why nano?

- Advantageous sintering behavior:

Nanophase powders densify at faster rates and reach the same density at much lower temperatures.

- Miniaturization of electroceramic devices

Perovskites: Bhalla et al.: Mat. Res. Innovat. **2000**, *4*, 3-26; *Nanoceramics:* Arora: Adv. Eng. Mater. **2004**, *6*, 244-247

Nonaqueous Sol-Gel Routes to Oxides

Synthesis of Perovskites and Related Materials

General Synthesis Protocol:

All procedures were carried out in the glovebox.

1) Dissolve Alkali Metal (Li) or Alkaline Earth Metals (Sr,Ba) in Benzyl Alcohol ($C_6H_5CH_2OH$)
2) Addition of Metal Alkoxides: $Ti(O\textit{i}Pr)_4$, $Zr(O\textit{i}Pr)_4$ or $Nb(OEt)_5$
3) Heat Treatment in Autoclave at 200°C-220°C

No water, no halide precursors, no surfactants!

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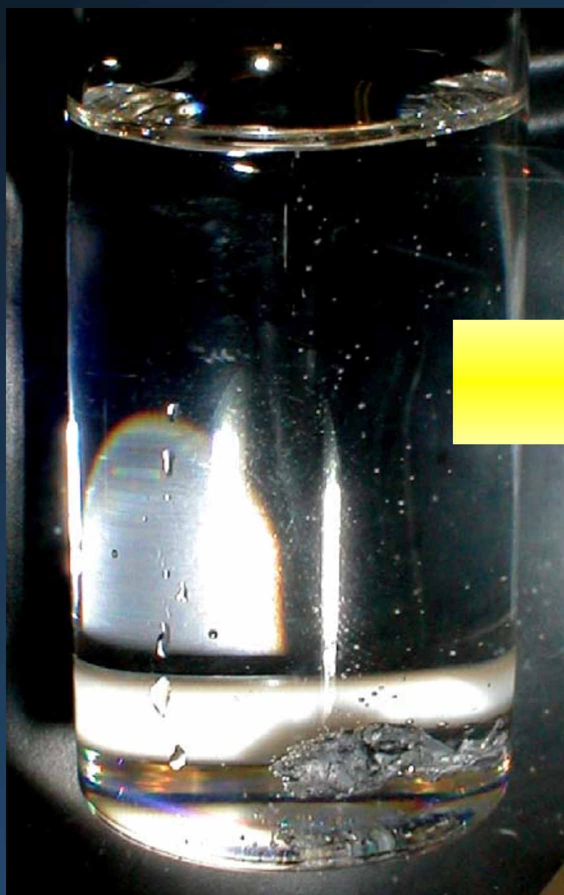
Nonaqueous Sol-Gel Routes to Oxides

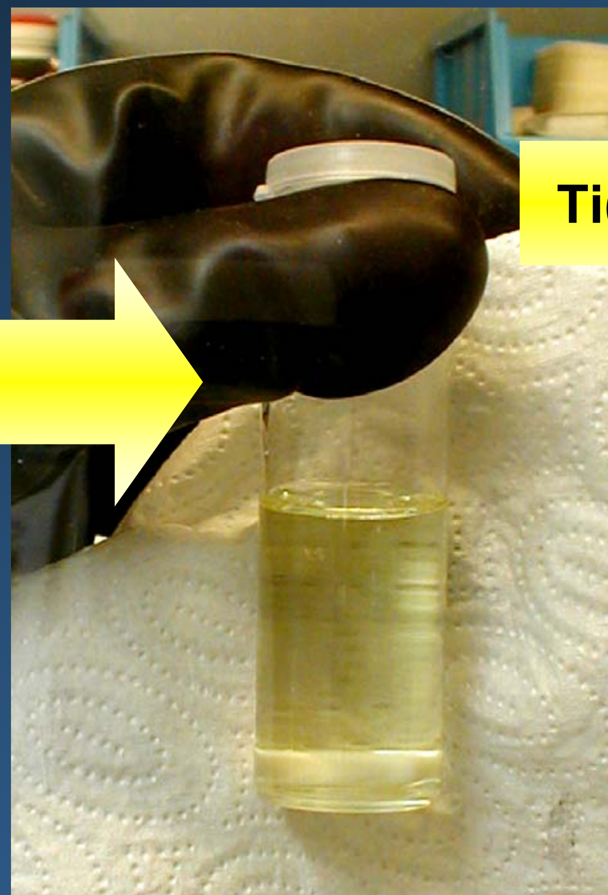
Typical Procedure: Synthesis of $BaTiO_3$

Nonaqueous Sol-Gel Routes to Oxides

Dissolution of metallic Ba in Benzyl alcohol



Clear, transparent solution



$Ti(O\textit{i}Pr)_4$

Heat treatment in the autoclave

White precipitation – Centrifugation and Washing: White powder

Nonaqueous Sol-Gel Routes to Oxides

Which materials can be obtained by this approach?

Ba + Benzyl Alcohol + $Ti(O\textit{i}Pr)_4$ $\xrightarrow{200°C}$ $BaTiO_3$

Sr + Benzyl Alcohol + $Ti(O\textit{i}Pr)_4$ $\xrightarrow{200°C}$ $SrTiO_3$

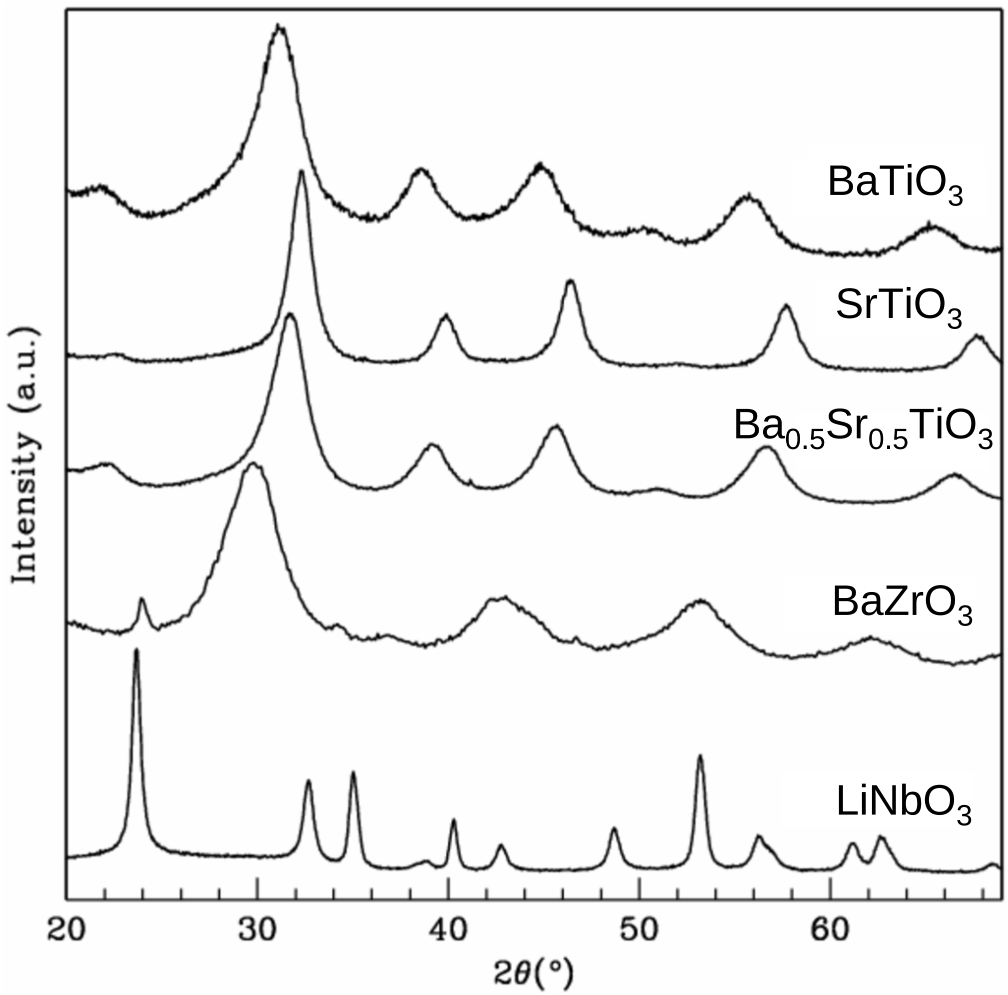
Ba,Sr + Benzyl Alcohol + $Ti(O\textit{i}Pr)_4$ $\xrightarrow{200°C}$ $(Ba,Sr)TiO_3$

Ba + Benzyl Alcohol + $Zr(O\textit{i}Pr)_4$ $\xrightarrow{220°C}$ $BaZrO_3$

Li + Benzyl Alcohol + $Nb(OEt)_5$ $\xrightarrow{220°C}$ $LiNbO_3$

Niederberger et al.: Angew. Chem. Int. Ed. **2004**, *43*, 2270-2273

Nonaqueous Sol-Gel Routes to Oxides



XRD Analysis:

Titanates:

- Phase-pure
- Broad peaks
- Discrimination cubic-tetragonal impossible

Bariumzirconate:

- $BaZrO_3$ + $BaCO_3$

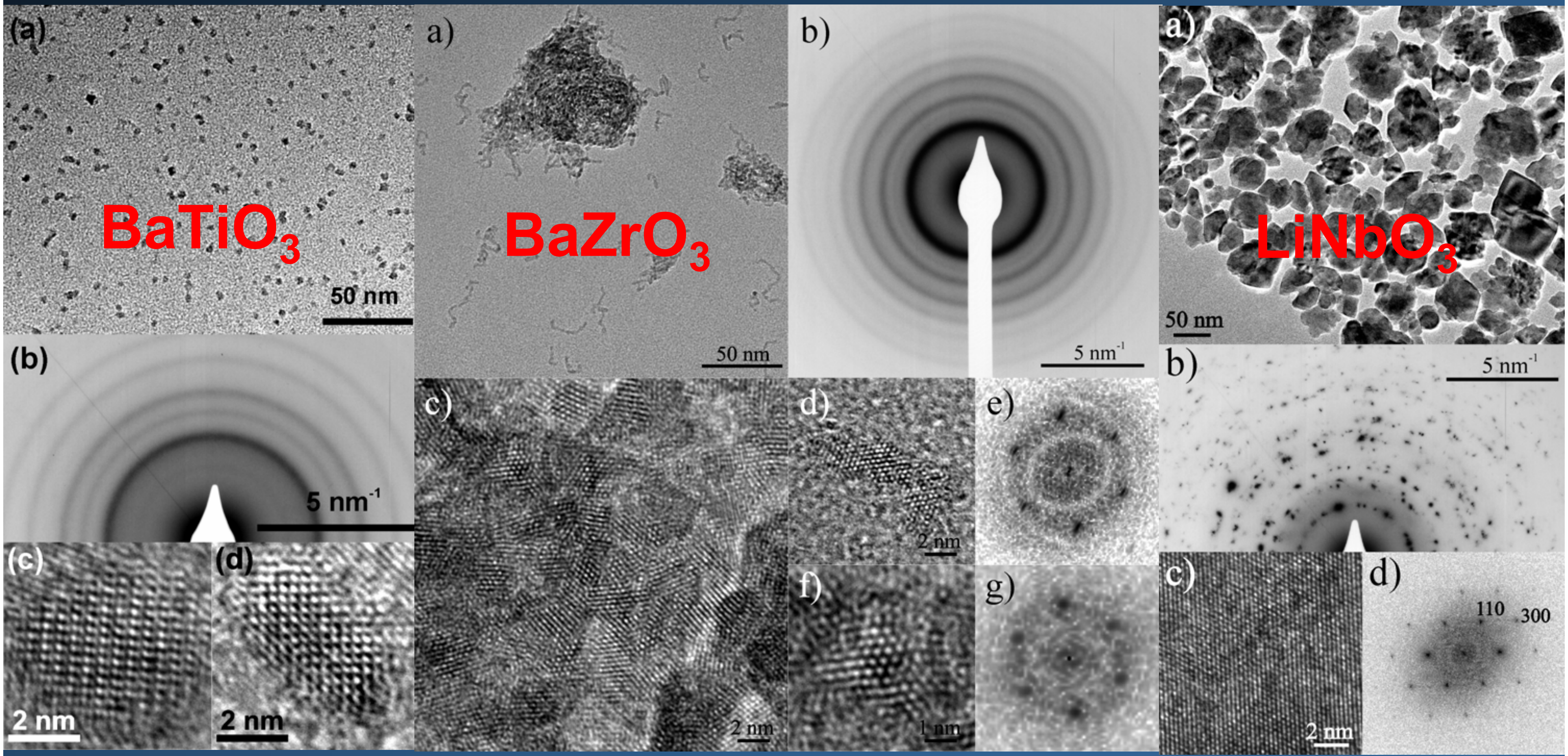
Lithiumniobate:

- Sharper reflections
- Phase-pure

Niederberger et al.: Angew. Chem. Int. Ed. **2004**, *43*, 2270-2273

Nonaqueous Sol-Gel Routes to Oxides

TEM Characterization



Niederberger et al.: Angew. Chem. Int. Ed. **2004**, *43*, 2270-2273

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Nonaqueous Sol-Gel Routes to Oxides

Formation Mechanism

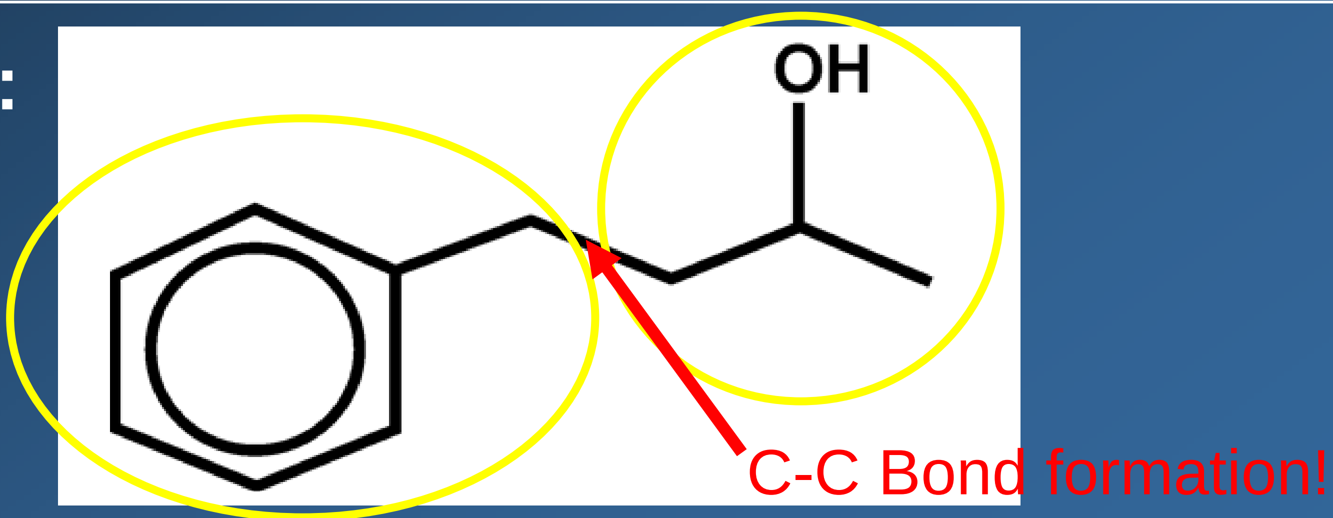
Expected: Ether Elimination Process:

≡M-O-R + R-O-M≡ ⟶ ≡M-O-M≡ + R-O-R

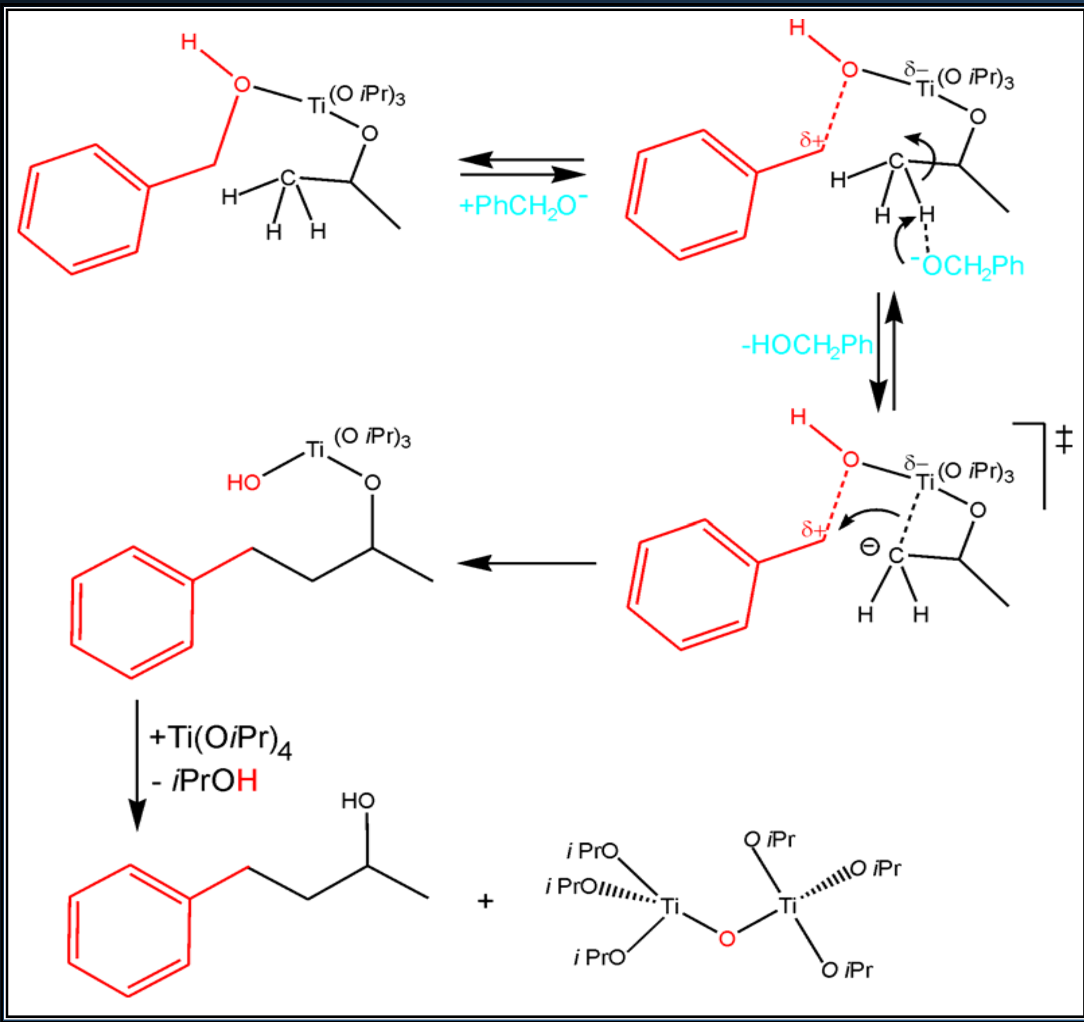
$Ba(OR)_2 + Ti(OR)_4 \longrightarrow BaTiO_3 + 3\ R\text{-}O\text{-}R$

R = *iso*-Propyl, Benzyl

However:



Nonaqueous Sol-Gel Routes to Oxides



1) Coordination of benzyl alcohol: Activation of benzylic carbon atom via weakening of C-O bond
2) Deprotonation of β-carbon atom of isopropoxy ligand
3) Nucleophilic attack leading to 4-phenly-2-butoxide formation and OH
4) Condensation and elimination of 4-phenly-2-butanol

Niederberger et al.: J. Am. Chem. Soc. **2004**, in print

Nonaqueous Sol-Gel Routes to Oxides

Perovskites: Summary

- General soft-chemistry route to nanocrystalline perovskites and related compounds
- No surfactants/stabilizers: Benzyl alcohol as solvent, reactant and stabilizer
- No additional inorganics: High purity
- Simple, low temperature process
- Yields in gram quantities (Yield > 90%)
- Novel formation mechanism involving a C-C bond formation

Nonaqueous Sol-Gel Routes to Oxides

Synthesis of Binary Metal Oxide Nanoparticles

General Synthesis Protocol:

All procedures were carried out in the glovebox.

1) Metal Alkoxide + Benzyl Alcohol ($C_6H_5CH_2OH$)

Metal Alkoxides:

$VO(O\textit{i}Pr)_3$, $Nb(OEt)_5$, $Hf(OEt)_4$, $Ta(OEt)_5$, $Sn(O\textit{t}Bu)_4$, $In(O\textit{i}Pr)_3$

2) Heat Treatment in Autoclave at 200°C-250°C

No water, no halide precursors, no surfactants!

Nonaqueous Sol-Gel Routes to Oxides

Which materials can be obtained by this approach?

Benzyl Alcohol + $VO(O\textit{i}Pr)_3 \xrightarrow{200°C/4d} V_2O_3$

Benzyl Alcohol + $Nb(OEt)_5 \xrightarrow{220°C/4d} Nb_2O_5$

Benzyl Alcohol + $Hf(OEt)_4 \xrightarrow{250°C/2d} HfO_2$

Benzyl Alcohol + $Ta(OEt)_5 \xrightarrow{250°C/1d} Ta_2O_5$

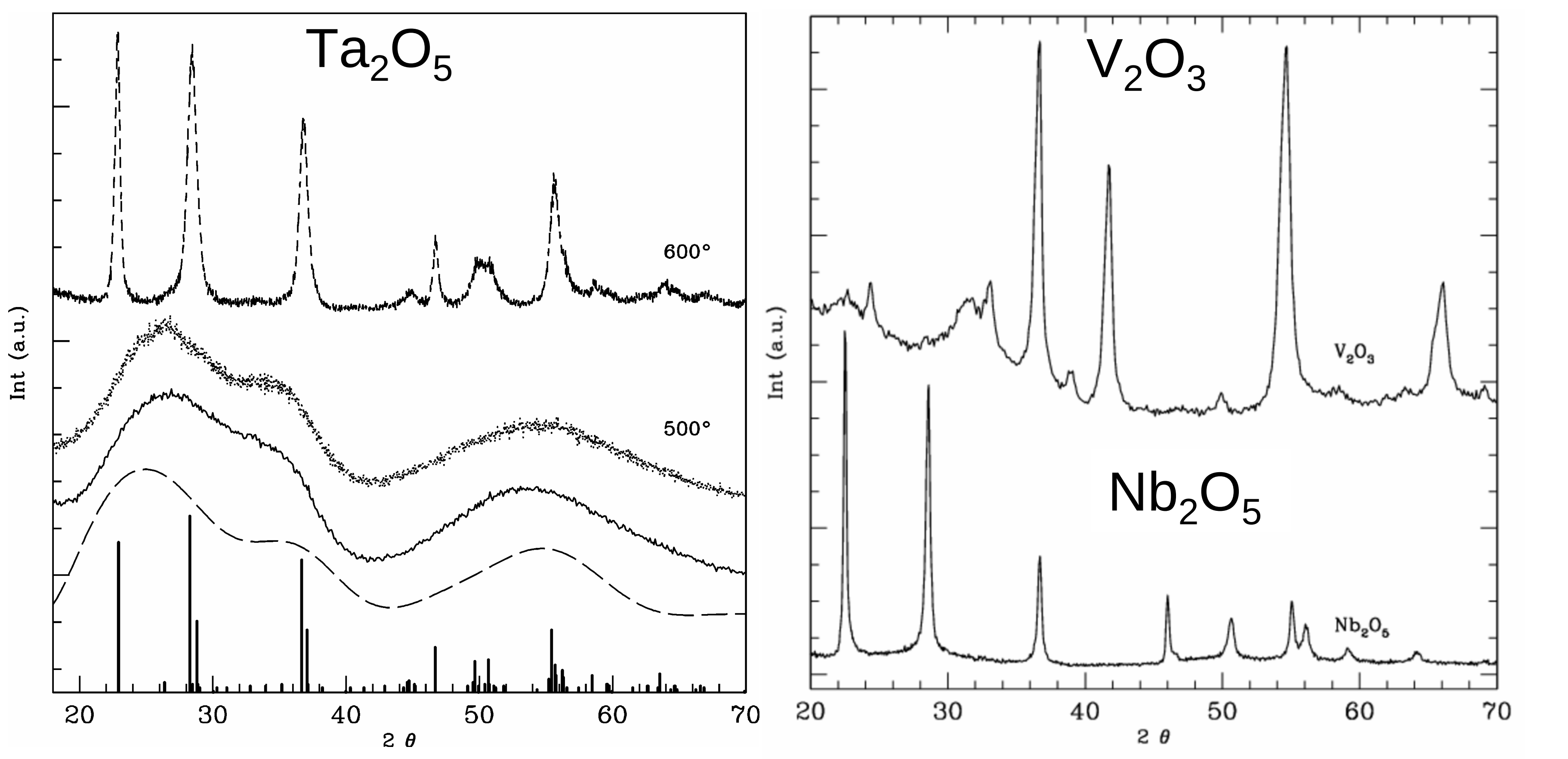
Benzyl Alcohol + $Sn(O\textit{t}Bu)_4 \xrightarrow{220°C/2d} SnO_2$

Benzyl Alcohol + $In(O\textit{i}Pr)_3 \xrightarrow{220°C/2d} In_2O_3$

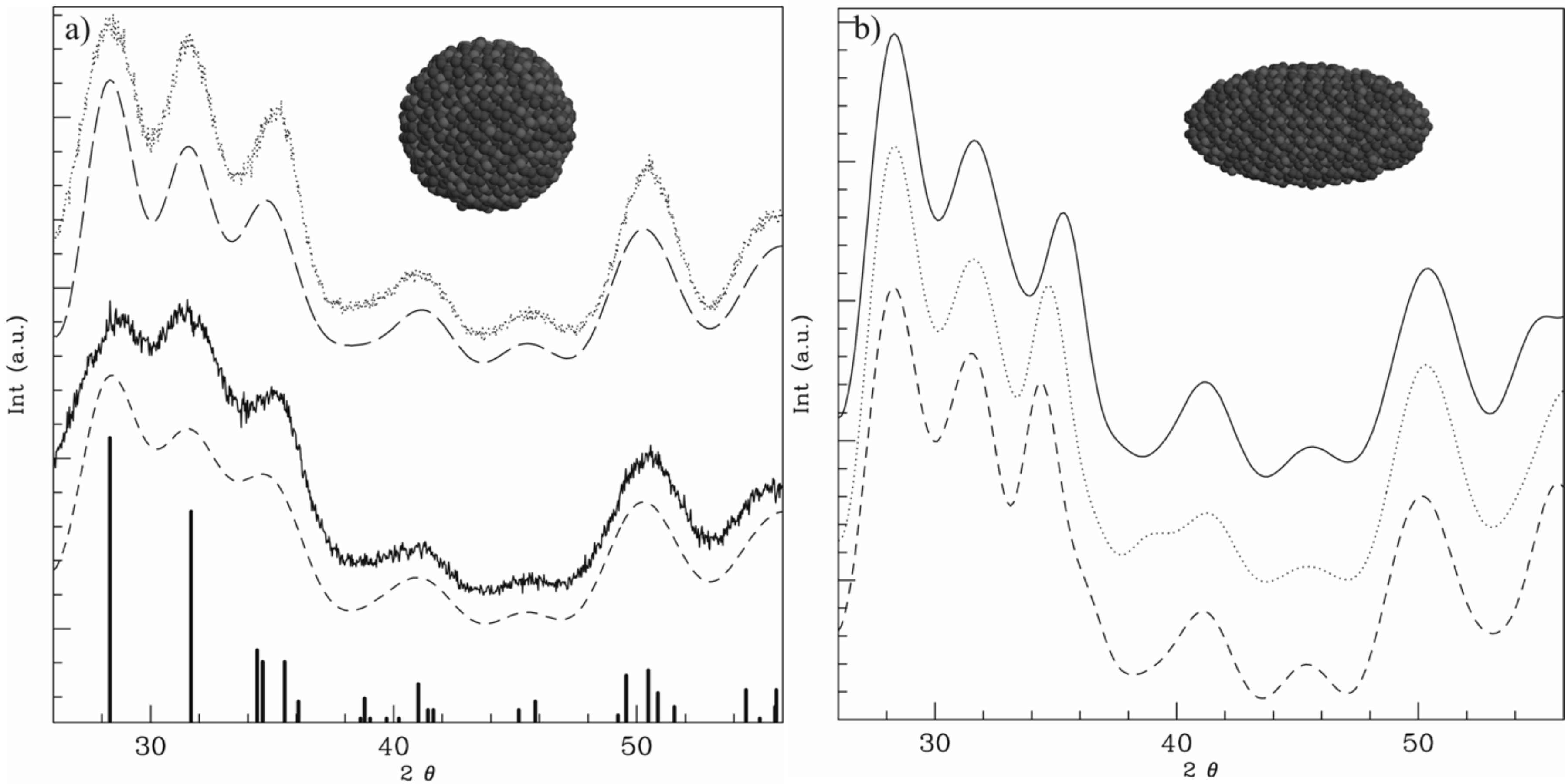
Pinna et al.: Colloids Surf. A **2004**, in print; German Patent Application No. 10 2004 016 131.3

Nonaqueous Sol-Gel Routes to Oxides

XRD Characterization



Nonaqueous Sol-Gel Routes to Oxides



HfO_2

German Patent Application No. 10 2004 016 131.3

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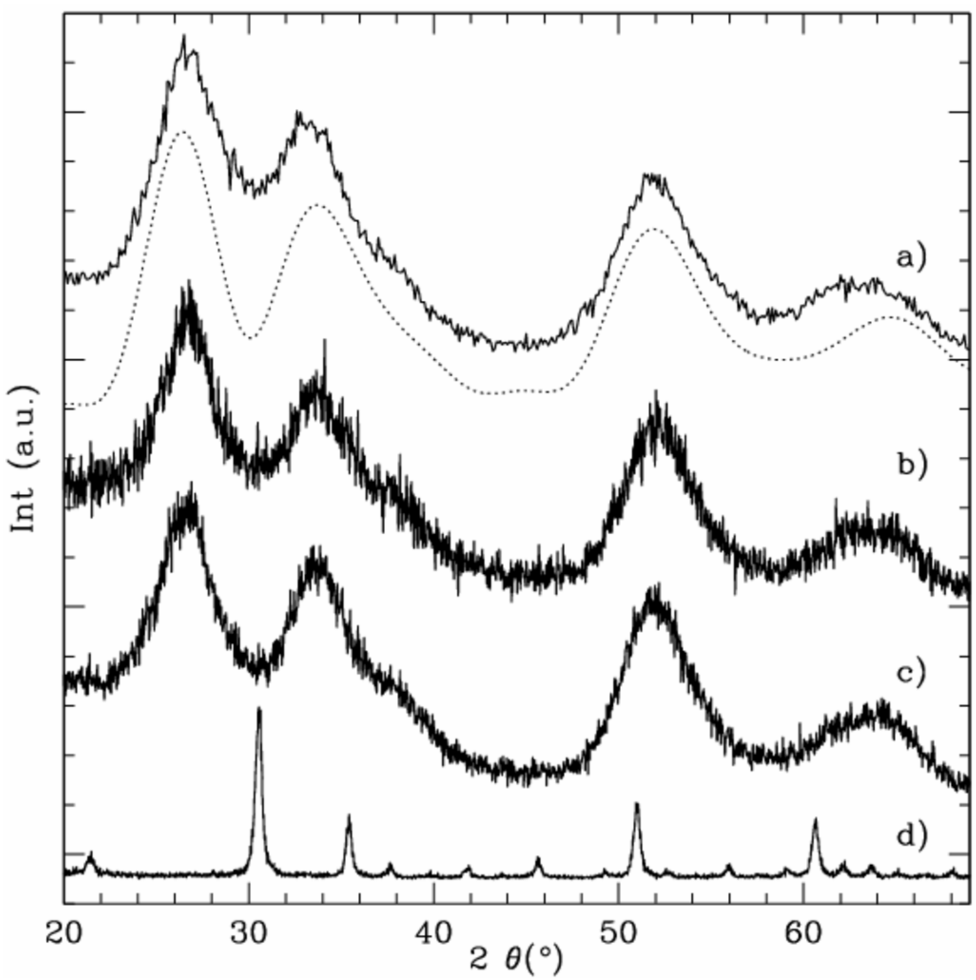


(a) SnO_2

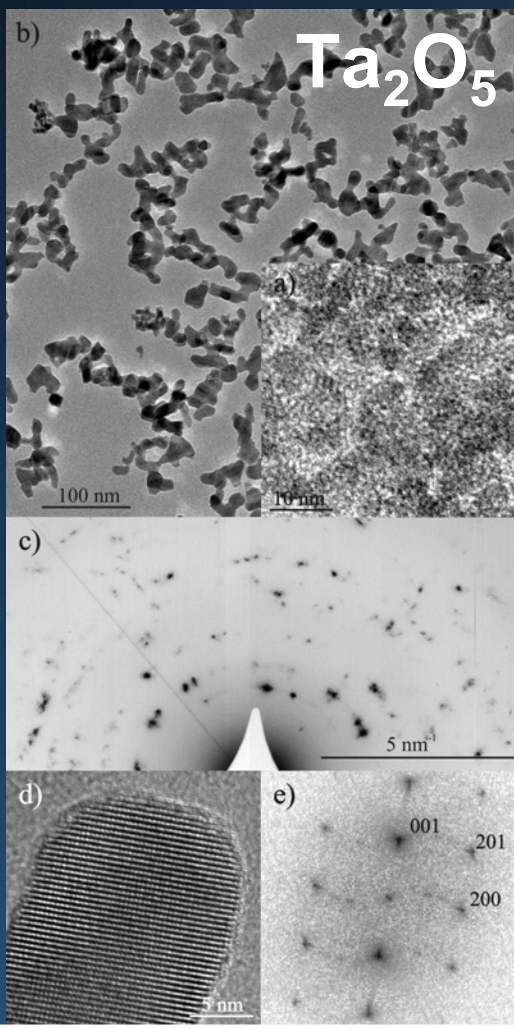
(b) $Sn_{0.95}In_{0.05}O_x$

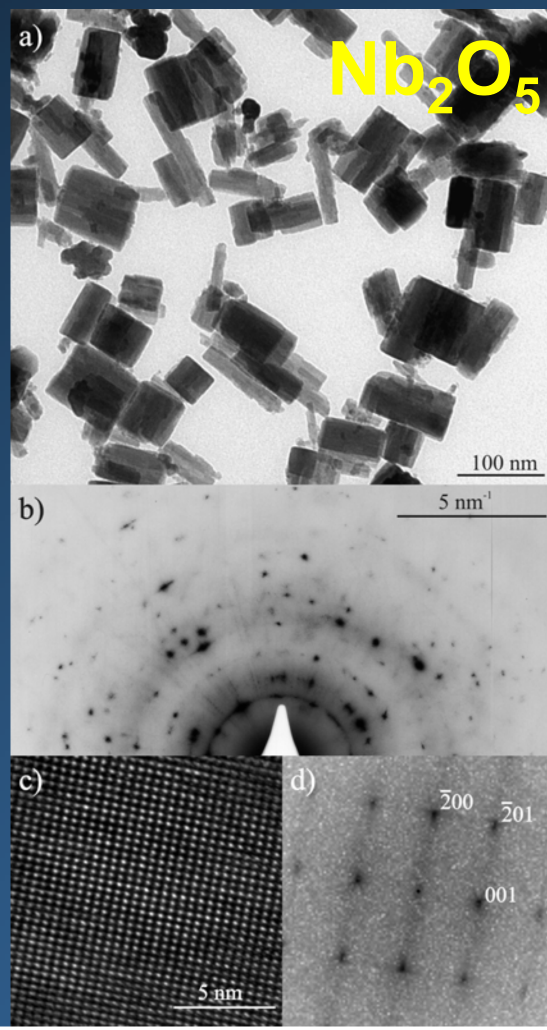
(c) $Sn_{0.9}In_{0.1}O_x$

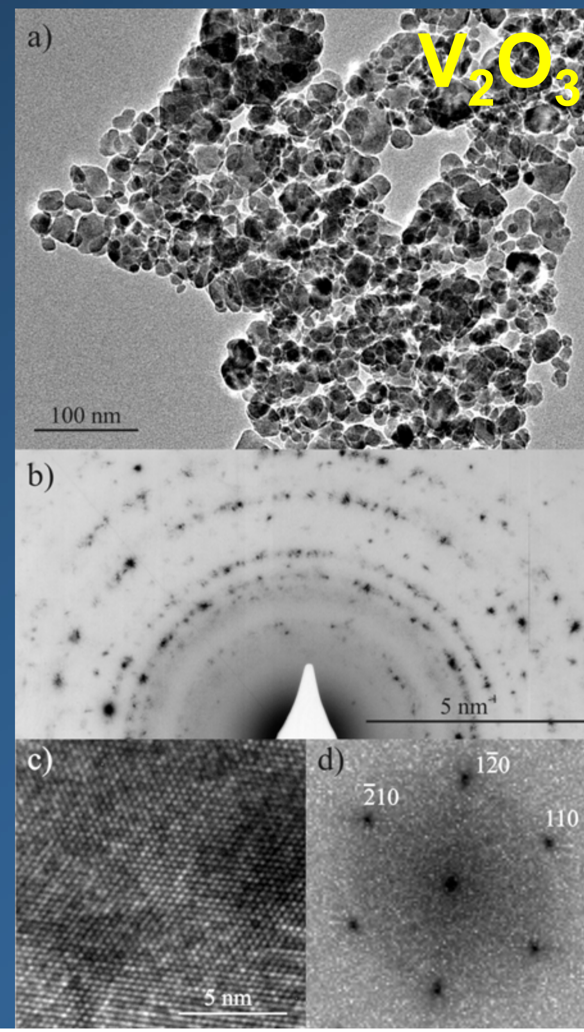
(d) In_2O_3

Nonaqueous Sol-Gel Routes to Oxides

TEM Characterization



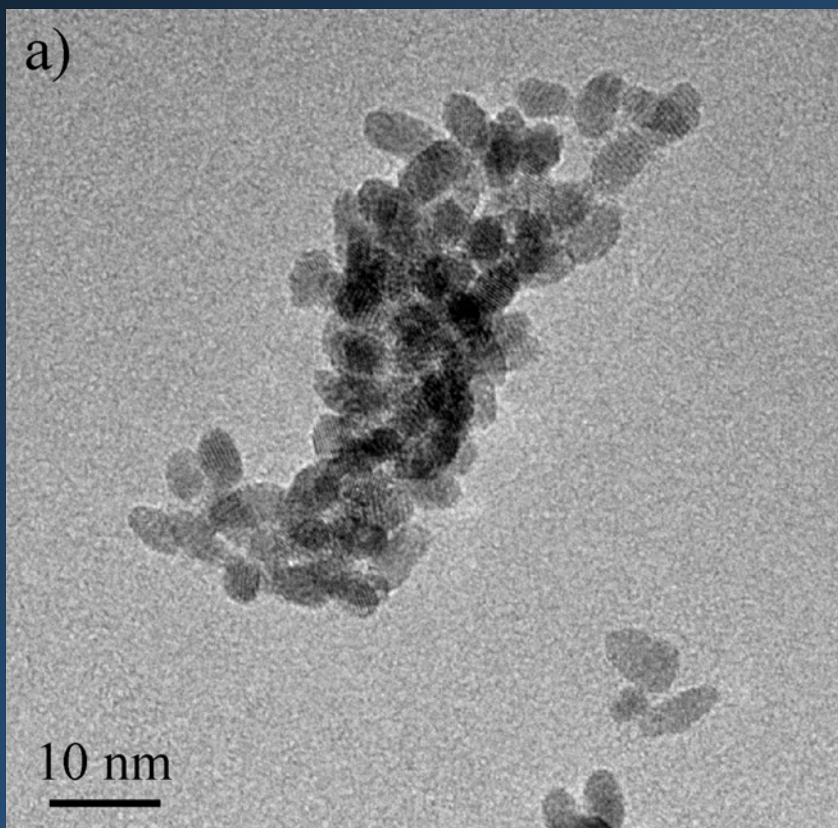


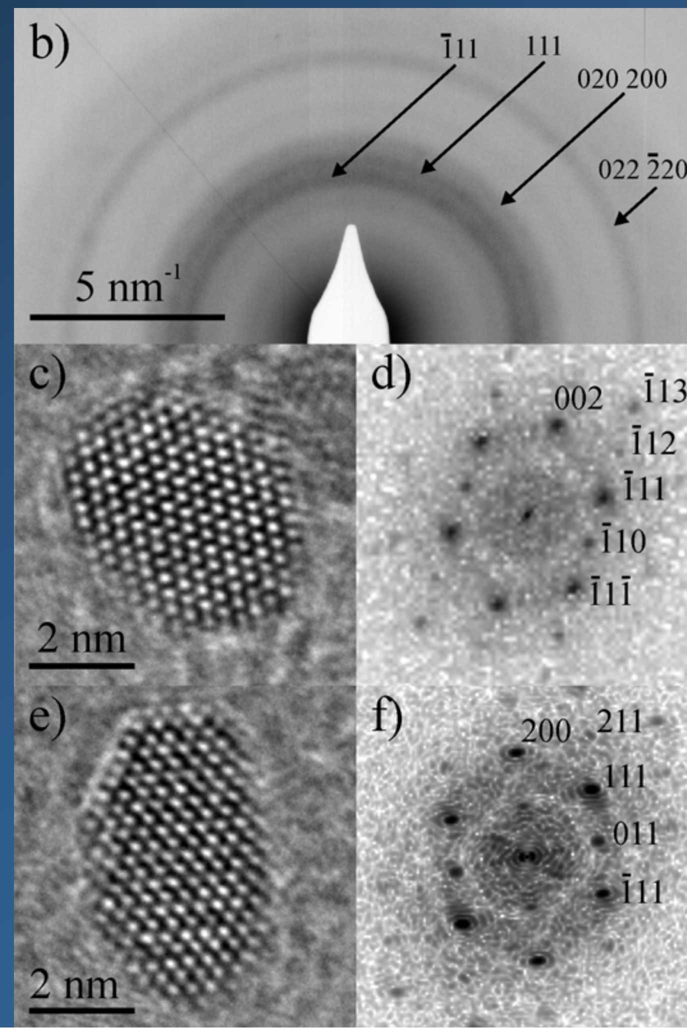


Nonaqueous Sol-Gel Routes to Oxides

TEM Characterization

HfO_2





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Nonaqueous Sol-Gel Routes to Oxides

Formation Mechanism of HfO_2

NMR analysis of the final reaction mixture:

Diethyl ether, ethyl benzyl ether and dibenzyl ether (main species!)

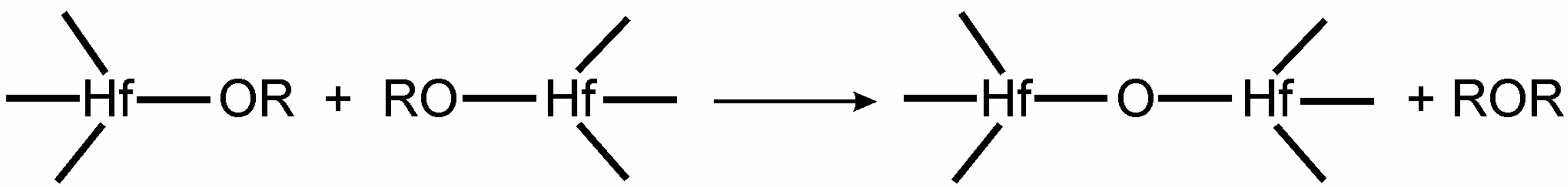
(1) $Hf(OEt)_4 + x\,BA \longrightarrow Hf(OEt)_{4-x}(BA)_x + x\,EtOH$

$x = 0 - 4$

BA = benzyl alcohol $C_6H_5CH_2OH$

EtOH = ethanol

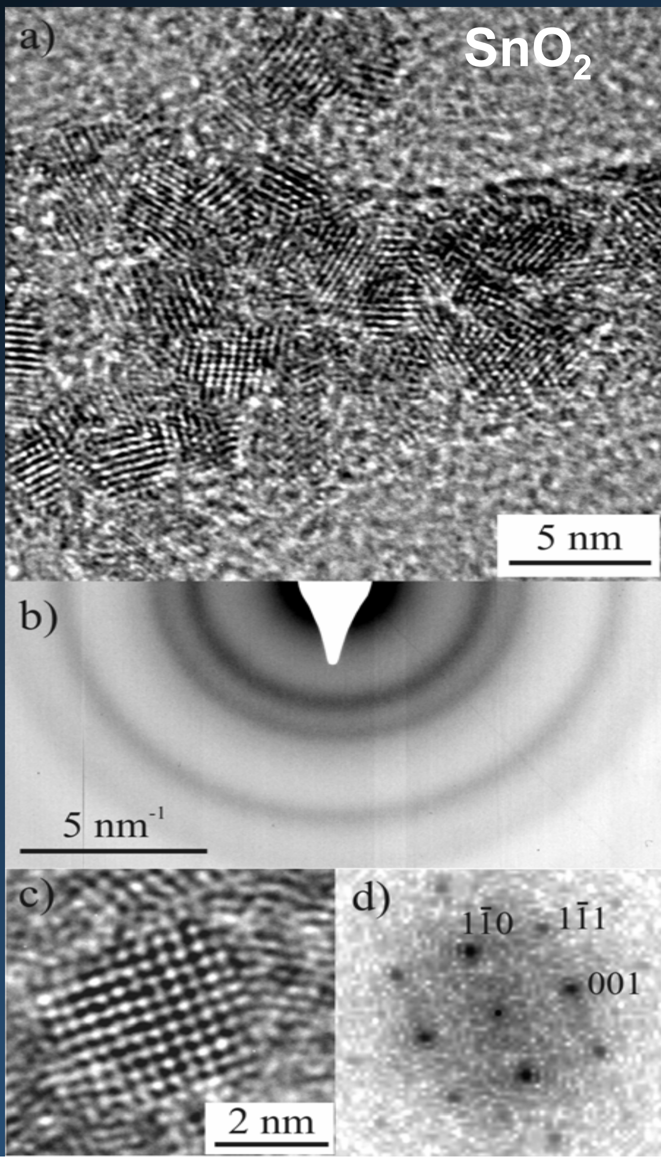
(2)

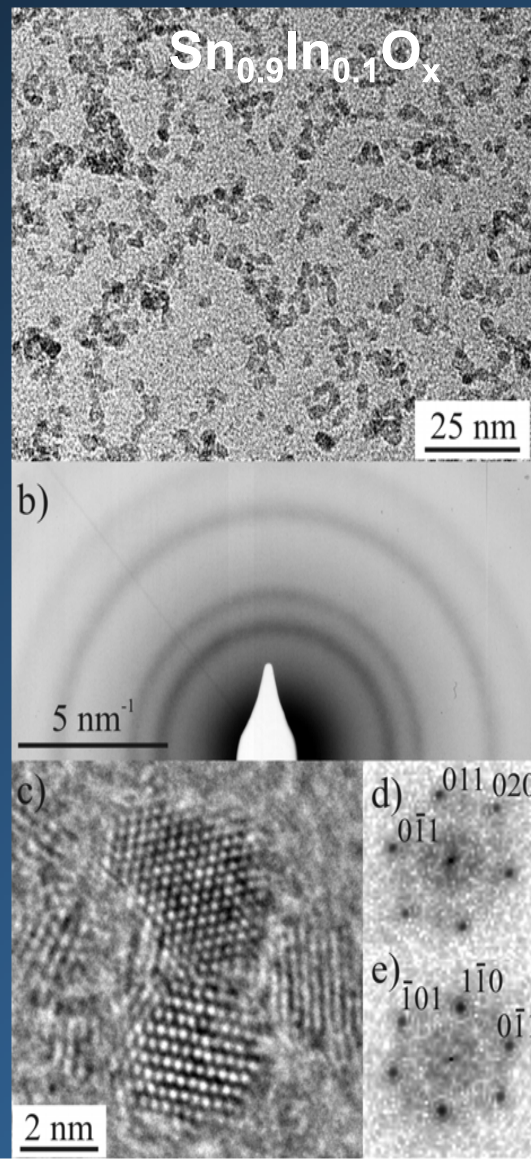


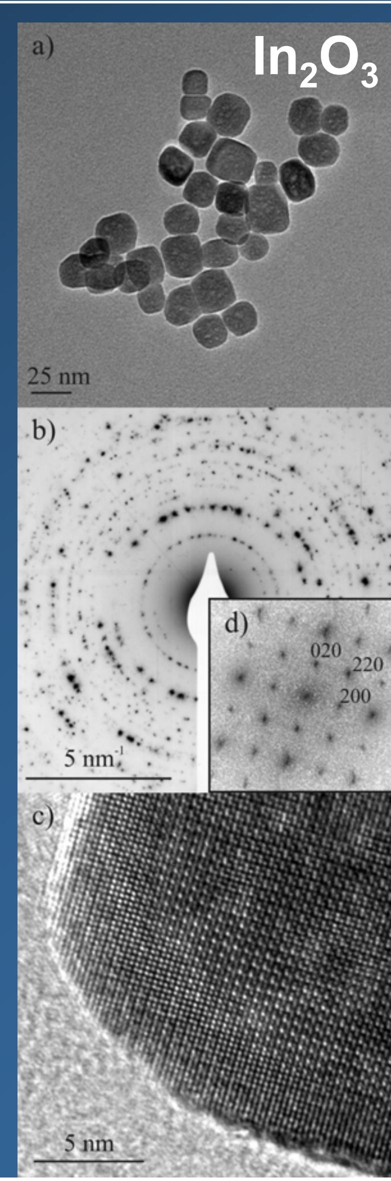
R = $C_6H_5CH_2$ or C_2H_5

Ether elimination process!

Nonaqueous Sol-Gel Routes to Oxides







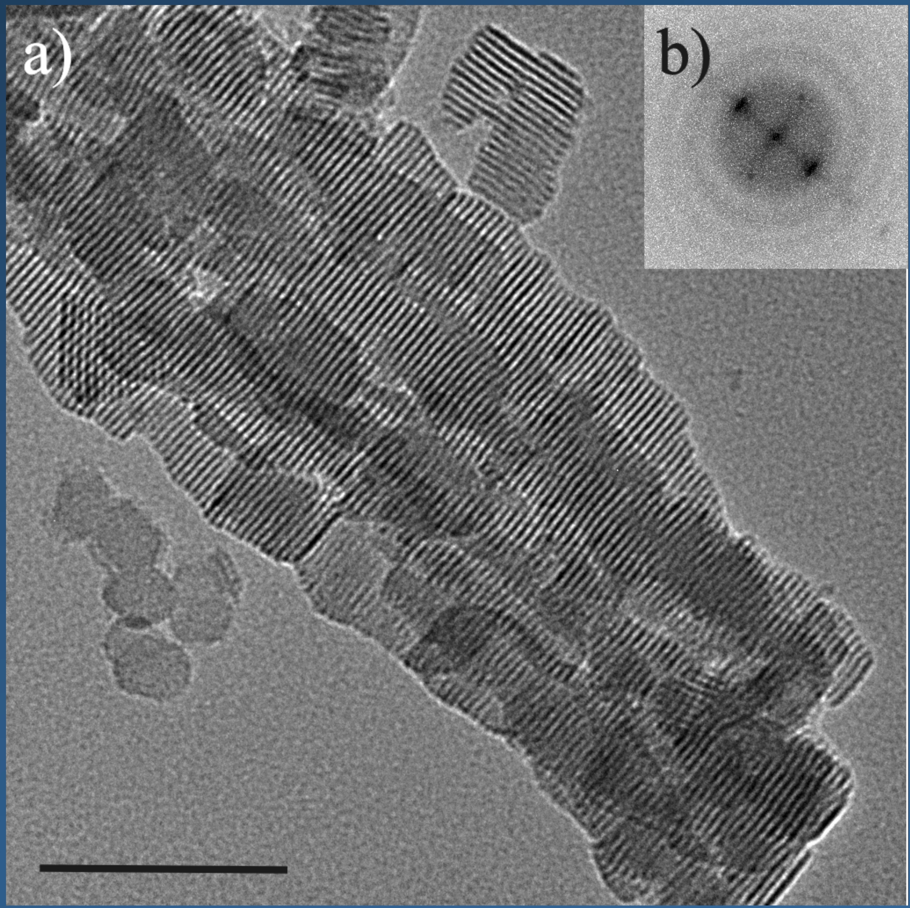
Nonaqueous Sol-Gel Routes to Oxides

Synthesis of Yttria-Based Lamellar Nanohybrids

Synthesis procedure:

1) $Y(O\textit{i}Pr)_3$ + Benzyl alcohol + $Eu(Cl)_3$
2) Heat to 250°C for 2d
3) Centrifuge precipitate, wash and dry at 60°C

Crystalline yttria mesostructure: Lamellar nanocomposite consisting of yttria layers, separated by organic layers of intercalated benzoate molecules



Nonaqueous Sol-Gel Routes to Oxides

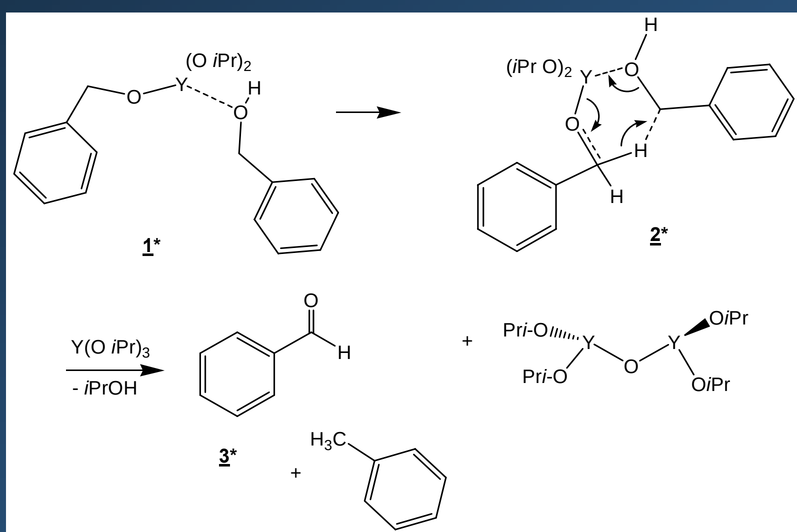
Synthesis of Yttria-Based Lamellar Nanohybrids

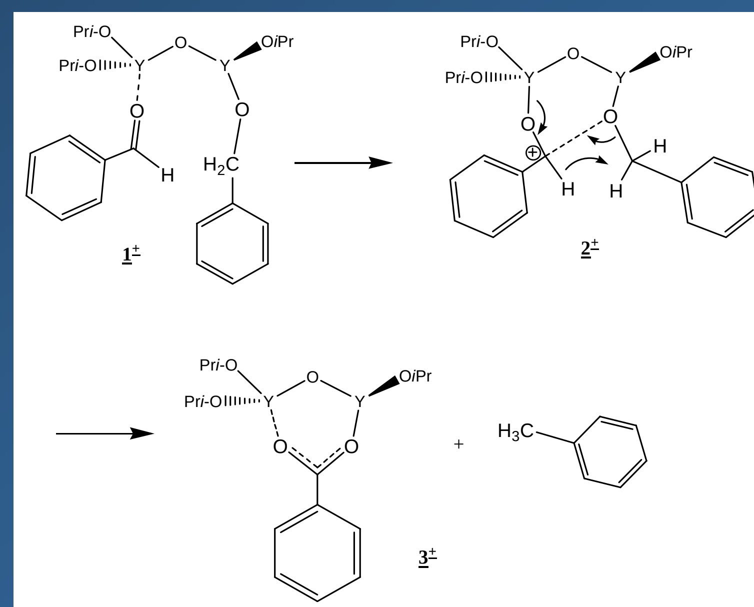
Proposed Formation Mechanism:

1) Condensation similar to $BaTiO_3$: Elimination of 4-phenyl butanol
2) Oxidation of benzyl alcohol to benzoic acid unter formation of toluene in two reactions:

   a) Disproportionation of benzyl alcohol into benzaldehyde and toluene

   b) Reaction of benzaldehyde and benzyl alcohol to the yttria-benzoate composite and toluene





Nonaqueous Sol-Gel Routes to Oxides

Summary Particle Synthesis

- Generally applicable soft-chemistry route to binary, ternary and mixed metal oxide nanoparticles
- No surfactants/stabilizers, no halides, no other additional inorganics
- Simple, low temperature process
- Small particle sizes, small particle size distribution, uniform particle shapes and good crystallinity
- Yields in gram quantities
- Particle sizes (in nm):

$BaTiO_3$	$SrTiO_3$	$Ba_{0.5}Sr_{0.5}TiO_3$	$LiNbO_3$	$BaZrO_3$
4-8	5-10	4-8	20-50	2-3

Ta_2O_5	HfO_2	SnO_2	In_2O_3	$(In,Sn)O_x$	V_2O_3	Nb_2O_5
1-2	4-6	2-3	Ca. 20	2-3	20-50	50-80

Nonaqueous Sol-Gel Routes to Oxides

Summary Formation Mechanisms

Up to now:

Nanoparticle Synthesis based on

Alkyl Halide Elimination

New:

Halide-Free Procedures Based on Other Reactions:

Ether Elimination

C-C-Bond Formation

C-C-Bond Formation and Oxidation/Reduction

Nonaqueous Sol-Gel Routes to Oxides

Outlook

These new systems bear a high potential to synthesize high-purity metal oxide nanoparticles via soft-chemistry routes.

The reactions are simple, easy to scale-up and result in the formation of highly crystalline nanopowders.

Nanoparticles in form of powders are highly desired for many applications and industrial processing steps.

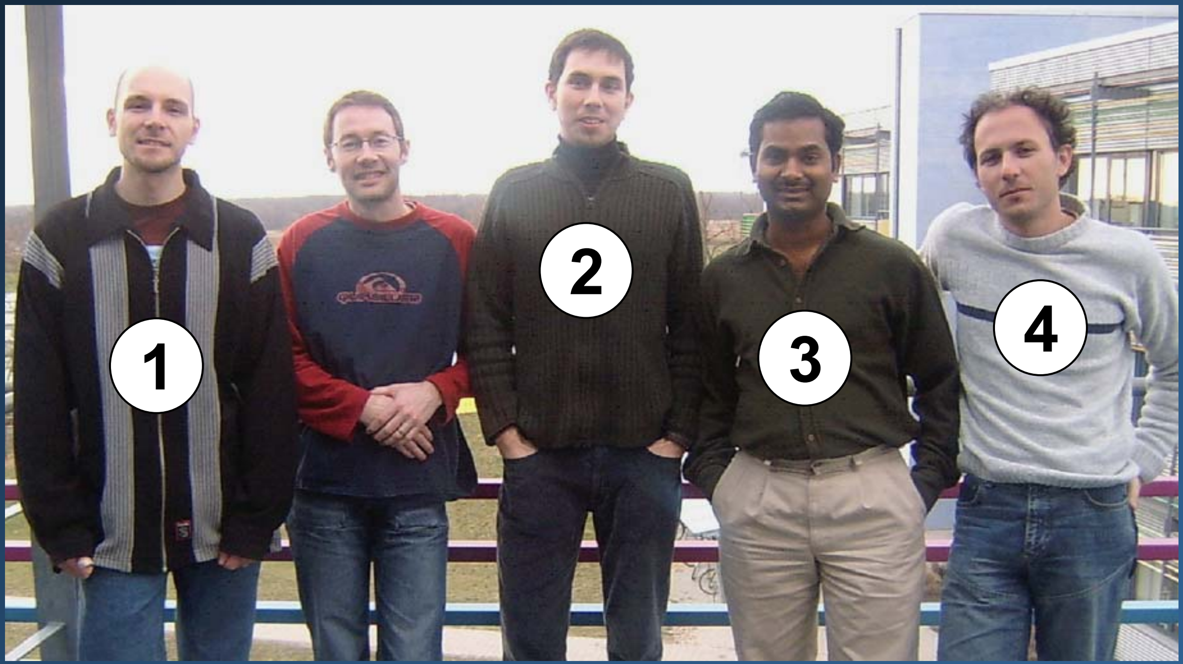
However, for most of the applications, the nanopowders have to be redispersed in aqueous media.

Nonaqueous Sol-Gel Routes to Oxides

Acknowledgement

Prof. Dr. Markus Antonietti

My group:



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