

Precursors for ceramics synthesis

Decrease diffusion lengths by using intimately mixing of cations. Solid precursors containing the desired cations.

Coprecipitation: salts of different metals are precipitated together (as low solubility solids). Either a solid solution or an intimate mixture of two salts.

Precursor: Cations are incorporated in the same (stoichiometric) solid.

Thermal decomposition at relatively low temperature → poorly cryst. Solid.

Either with oxidation state preservation or by changing oxidation state.

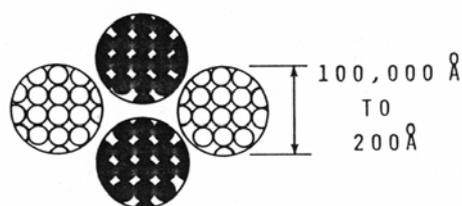


Figure 1. Conventional solid state reaction techniques give slow reaction kinetics.

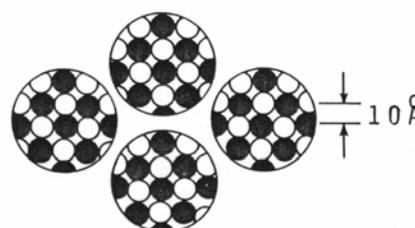


Figure 2. Solid solution precursor techniques give fast reaction kinetics

1

Coprecipitation

Soluble salts of the desired cations are dissolved (usually in water)

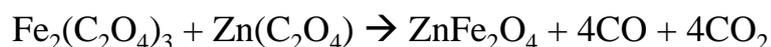
Coprecipitation by heating or by addition of a precipitating agent (forming insoluble salts)

Hydroxides, carbonates, oxalates, formates, citrates... (how about nitrates?)

ZnFe₂O₄: zinc and iron oxalate are dissolved in water (?)

Heated to evaporate water. → precipitate as fine powder, solid solution?

Heat to decompose:



2

Carbonate precursors

Formation of mixed oxides: $M_{1-x}M'_xO$, ($M, M' = Ca, Mg, Mn, Fe, Co, Zn, Cd$)

Calcite type solid solutions used as precursors.

Ideal for formation of mixed oxides with rock salt structure due to structural similarity.

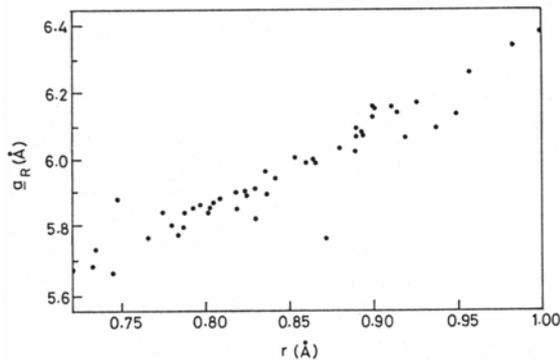
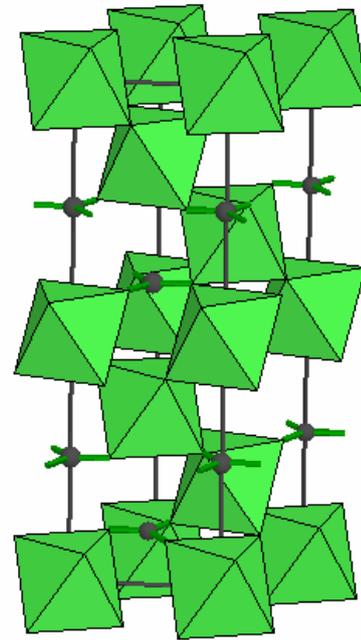
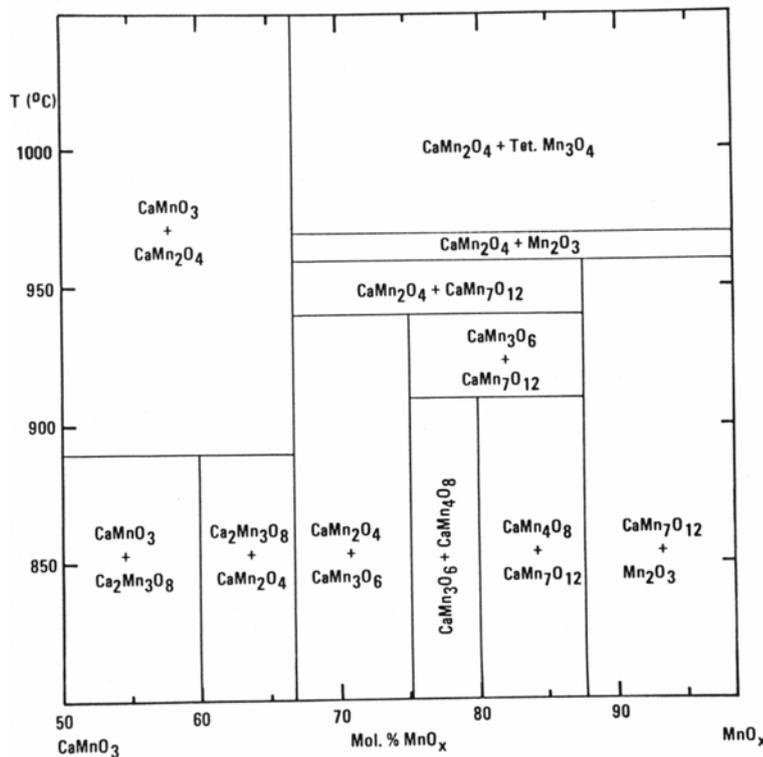


Fig. 1. Plot of the rhombohedral lattice parameters a_R of a variety of binary and ternary carbonates of calcite structure (e.g. Ca-M, Ca-M-M, Mg-M, M-M where M, M = Mn, Fe, Co, Cd, etc.) against the mean cation radius.



3



The low decomposition temperature may allow formation of oxides preserving a high oxidation state. Formation of $CaMnO_3$ by standard methods requires $1300^\circ C$, days of heating and repeated crushing/heating. Using a carbonate precursor $CaMnO_3$ may be prepared at $900^\circ C$ for 30 minutes.

May also be used for preparation of low temperature phases

Note changes in oxidation state

Figure 3. Isobaric ($P_{O_2} = 1.0 \text{ atm}$) subsolidus phase relations in the manganese-rich portion of the Ca-Mn-O system

4

Oxides prepared from carbonate precursors

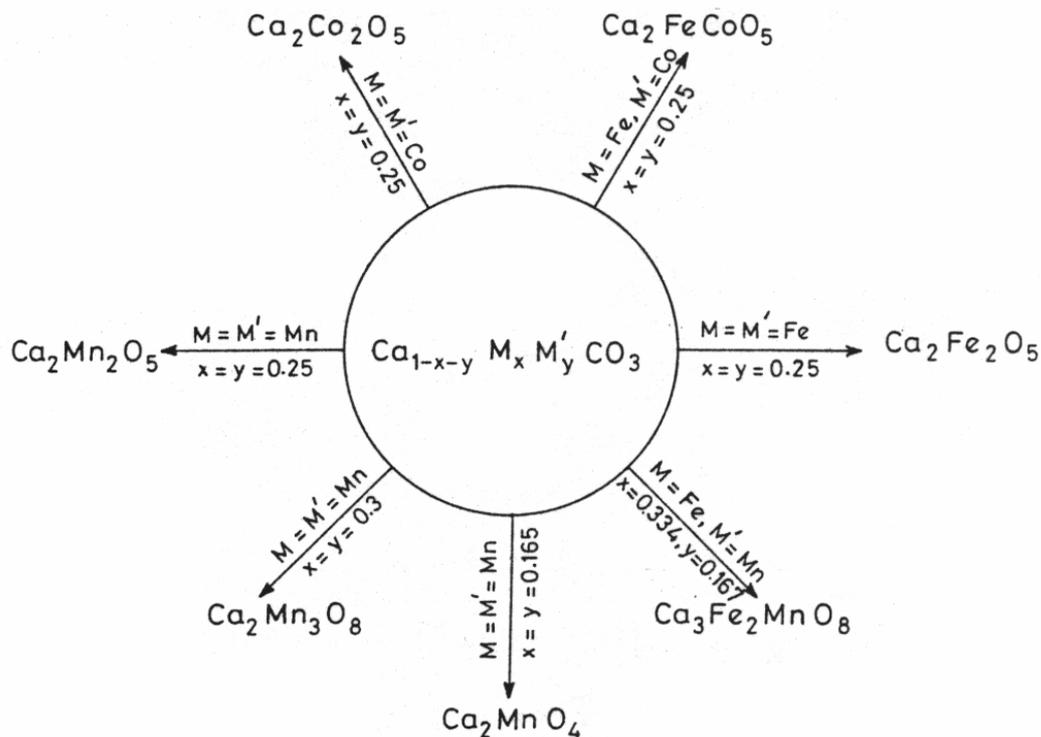


Fig. 4. Some of the complex oxides prepared by the decomposition of carbonate precursors.

5

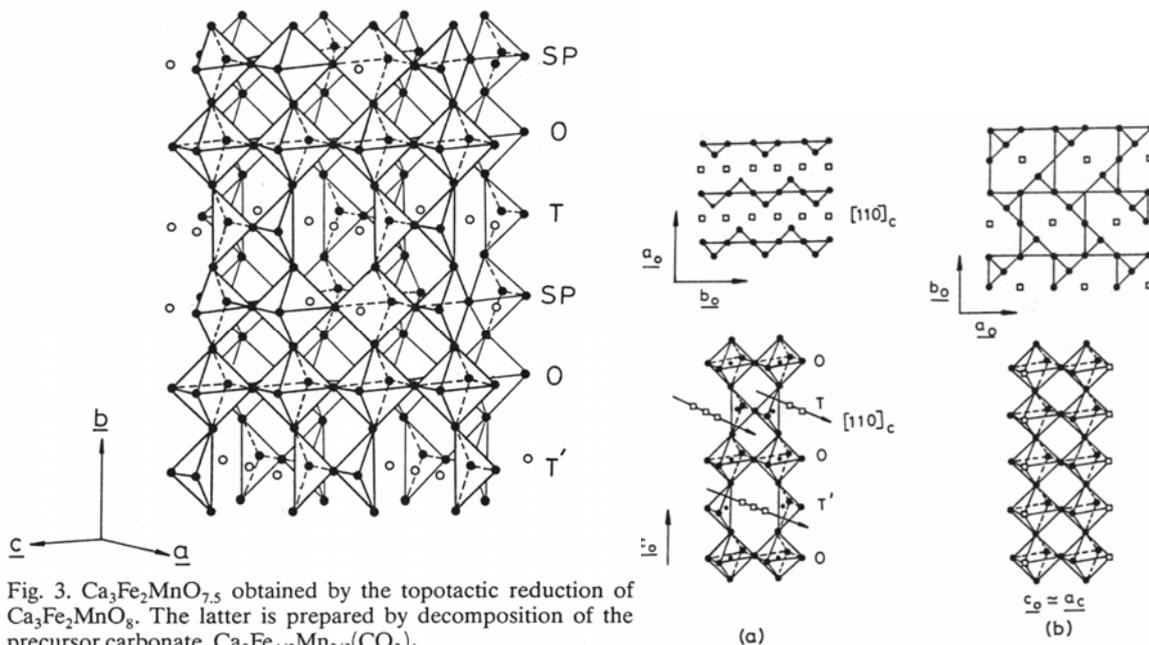


Fig.2. Structures of (a) $\text{Ca}_2\text{Fe}_2\text{O}_5$ (brown-millerite) and (b) $\text{Ca}_2\text{Mn}_2\text{O}_5$. Oxygen vacancy ordering in the a - b plane is also shown.

6

Preparation method

Prepare a slightly acidic solution of the cations (e.g. nitrates) with the wanted proportions.



Add ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$ to precipitate



Filter and wash the precipitate



Calcine under appropriate atmosphere for 0.5 – 150 hours at 800-1000°C

Also used with hydroxide, nitrate, and cyanide solid solutions.

E.g. $\text{Ln}_{1-x}\text{M}_x(\text{OH})_3$

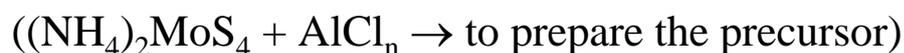
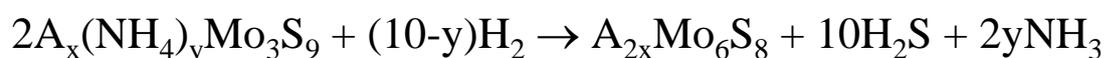
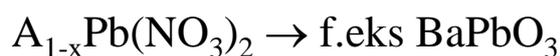
Coprecipitation depends on:

- Similar solubility of the metal salts
- Similar precipitation rate
- Formation of solid solution

Successful preparation by calcination may depend on:

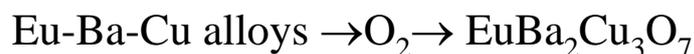
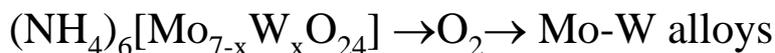
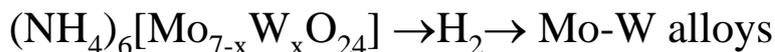
- Similar decomposition temperatures for the metal precursors
- Structural similarity and compatibility of the oxides

7



8

Redox



Organometallic precursors are used in a range of syntheses, e.g. organoaluminium silicate for aluminosilicates.

9

Precursor method

Stoichiometric (mixed metal) compounds

NiFe₂O₄ may be prepared from: Ni₃Fe₆O₃(OH)(OAc)₁₇ • 2py

2-300°C to burn off the organic part

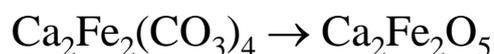
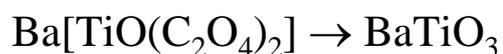
Heating in air at 1000°C for 2-3 days

Table 2-1. Examples of ceramic powders obtained from mixed-metal precursors.

<i>Mixed-metal precursor</i>	<i>Ceramic product</i>
La[Co(CN) ₆] • 5 H ₂ O	LaCoO ₃
Ba[TiO(C ₂ O ₄) ₂]	BaTiO ₃
M ₃ Fe ₆ O ₃ (OH)(OAc) ₁₇ • 12 py	MFe ₂ O ₄ (M = Mg, Mn, Co, Ni) (ferrite spinels)
(NH ₄) ₂ M(CrO ₄) ₂ • 6 H ₂ O	MCr ₂ O ₄ (M = Mg, Ni) (chromites)
(NH ₄) ₂ M(CrO ₄) ₂ • 2 NH ₃	MCr ₂ O ₄ (M = Cu, Zn) (chromites)
MCr ₂ O ₇ • 4 py	MCr ₂ O ₄ (M = Mn, Co) (chromites)
MFe ₂ (C ₂ O ₄) ₃ • x N ₂ H ₄	MFe ₂ O ₄ (M = Mg, Mn, Co, Ni, Zn) (ferrites)

10

Examples:

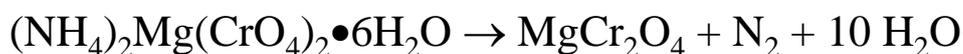


11

Precursor redox reactions



Formation of MCr_2O_4 spinel from $(\text{NH}_4)_2\text{M}(\text{CrO}_4)_2 \cdot 6\text{H}_2\text{O}$



Decomposition of nitrates:

Complex, but involves reduction of N and oxidation of O^{2-} , e.g.:



12

Formation of metastable solids

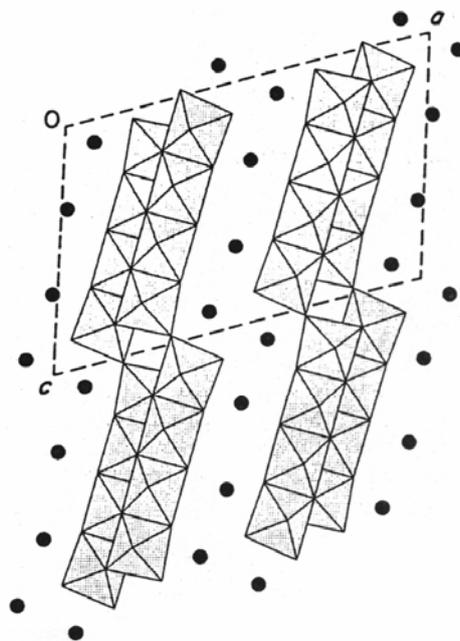
Often the thermodynamically stable material is not the most interesting regarding properties and application

Metastable compounds are difficult to prepare using classical high temperature routes. Soft chemistry (Chimie douce, myk kjemi) methods must be used.

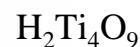
Preparation of metastable phases:

1. Synthesis under conditions where the material is thermodynamically stable followed by quenching to ambient.
2. Preparation of thermodynamically stable compounds, and transformation of these to a metastable compound by a low temperature, soft chemistry, method.
3. Synthesis under non-equilibrium conditions; kinetic control of product formation.

13



$\text{K}_2\text{Ti}_4\text{O}_9$ ion exchange in acid to:



followed by heating
(dehydroxylation, condensation):



Figure 3. Projection of the crystal structure of $\text{K}_2\text{Ti}_4\text{O}_9$ along the $[010]$ direction. The Ti-O substructure is represented with shaded octahedra, and the K atoms are given as black circles. The K atoms lie in $y/b = 0$ (center) and in $y/b = 1/2$ (left and right). The edges of the unit cell are emphasized with broken lines.

14