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THERMAL SYNTHESIS OF INORGANIC MATERIALS

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ABSTRACT

Solid-state and hydrothermal procedures for the synthesis of some inorganic materials (mostly metal oxides) are comparatively described and discussed in relation to the characteristics of the precursor (starting) and (final) synthetic materials as well as to the synthesis steps. Besides the method employed, factors such as temperature, molar ratio of reactants, time, atmosphere, texture, morphology and especially structural defects, crystallinity, reactivity, solid solution and nature of the synthetic materials are discussed. Mechanical treatments, oxygen and CO_2 losses and non stoichiometry in some of these materials are also commented on. Instrumental methods for the characterization of these materials are briefly mentioned.

INTRODUCTION

Both the amount and kind of inorganic materials produced by thermal methods are rapidly increasing due to the useful applications of some of them and to variable routes for their preparation. Such inorganic compounds are mostly (although not exclusively) metal oxides or mixed oxides and include materials with superconducting and/or magnetic properties. The expanding field of the superconductors will not be examined here, since it is actually the subject of many specialized publications. Furthermore, inorganic materials such as metals and alloys are beyond the scope of this study.

Most of the elements of the periodic table may constitute the inorganic oxides, where the transition and rare earth elements due to their special electronic configuration give rise to materials with interesting properties.

Besides the thermal procedures employed for the synthesis of inorganic materials, many other factors (sometimes inter-related) can determine the properties of these solids. These are: kind of precursors (or starting materials), particle size and morphology,

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reactivity and degree of crystallinity. Moreover, often neglected factors such as mechanical treatments or pretreatments e.g. grinding and pressure may lead to a mechanochemical reaction, influencing the course of the thermal synthesis. Finally, solid solutions of one or more metallic elements and non stoichiometry may also be present in such syntheses. These factors also have implications for the properties of the synthetic materials. Therefore, a careful control of the above mentioned factors must be considered together with the thermal method used for the synthesis of inorganic materials.

METHODOLOGY AND CHARACTERIZATION OF SYNTHETIC PRODUCTS

The thermal methods described here for the synthesis of some inorganic materials such as metal oxides (which also include oxyhydroxides) and hydroxides are of two kinds: a) those taking place in the solid-state, and b) hydrothermal, the latter occuring in the presence of water.

a) Heating of solids at high temperatures (around 1000°C) can cause several changes in the structure and/or properties of the powder, with the formation of new products as a result of transformation or decomposition reactions. This classical method is also widely employed for the formation of mixtures, by sintering two or more oxides, with the formation of new phases during the solid-solid reaction. Detailed examples will be given in the following sections of this work.

b) Hydrothermal methods here will cover all reactions occuring in the presence of water, such as hydrolysis, precipitation and coprecipitation, and including crystal growth, displacements and other effects observed in aqueous solutions. Traditional hydrothermal procedures have been extensively used for the synthesis of iron oxides and related metallic oxides. In these methods metallic iron salts are used as precursors and are precipitated or coprecipitated in an aqueous medium at alkaline pH, and aged at temperatures up to 80°C during determined periods of time. At atmospheric pressure, the temperature in hydrothermal synthesis can not be higher than 100°C. When hydrothermal syntheses are carried out in autoclave, higher temperatures are reached at the saturating water pressure. Also higher temperatures may be needed, when intermediate reaction steps are taking place between the precursor and the final synthetic product (the oxide material). This can be typified i.e. in the synthesis of metal spinel oxides, where the starting material (precursor) is reacted with water-free glycerol at reflux temperatures (246°C) forming metallic alkoxide or mixed metal alkoxide [1]. Then the hydrothermal synthesis follows (second reaction step) when these alkoxides are hydrolyzed by boiling water, resulting in the spinel oxide formation [1,2].

Taking into account the above classification this study will comment on and discuss mainly the 12 papers of the section of Thermal synthesis of inorganic materials, which were published in the first volume of the 9th ICTA Proceedings and discussed in Jerusalem during this Congress. These articles are listed in Table 1. Some of these investigations employ both synthesis methods, the solid state and the hydrothermal.

Touboul and Vachon [3] sintered mixtures of Bi_2O_3 and V_2O_5 in the concentration range 12.5-100 mol % V_2O_5 at temperatures up to 700°C. From the phase diagram, seven compounds were found: $Bi_2V_8O_{23}$ between 450 and 514°C; $BiVO_4$ and Bi_5VO_{10} wich melt congruently;

TABLE 1

Methods for the thermal synthesis of some inorganic materials*

Heating in the solid state	Hydrothermal
The Bi_2O_3-V_5O_5 system [3]	
Reactivity of MoO_3 towards $Cr_2V_{14}O_{13}$ [4]	
New Cu-Sb oxides [5]	
Transformation of $Y(OH)_3$ to Y_2O_3 [6]	Preparation of $Y(OH)_3$ [6]
	Mixed Al-Me hydroxides (Me = Ca, Mg, Li) [7]
	Mn_3O_4 via Mn alkoxide [8]
α-Fe_2O_3 via $Fe(OH)_3$ containing foreign metallic ions [9]	
Evolution and transformation of γ-Fe_2O_3 [10]	
CeO_2-ZrO_2 system [11]	
	Mg-Al double hydroxides [12]
Displacement reactions in the formation of $CaWO_4$ and $CaMoO_4$ [13]	
	$Mg(OH)_2$ [14]

*Other examples for the synthesis of metal oxides are not listed here

$Bi_{14}V_4O_{31}$, $Bi_{14}V_2O_{26}$, $Bi_6V_4O_{19}$ and $Bi_7V_3O_{18}$, all melting incongruently. The crystal data of the latter two compounds were established pointing to a perovskite structure with vacant octahedral sites which determine the ionic conductivities. X-ray crystallography and DTA were used to characterize the powdered mixtures.

Walczak and Filipek [4] studied the reactivity of MoO_3 towards $Cr_2V_4O_{13}$ starting with a mixture of oxides whose composition was 90 mole % $Cr_2V_4O_{13}$ and 10% MoO_3. This mixture was ground, disked and heated between 400 and 635°C for different periods. They also claimed the formation of a solid solution in the synthesis, where V^{5+} substituted Mo^{6+} in the $Cr_2V_4O_{13}$ lattice. Additionally, the latter compound decomposed to V_2O_5 but a MoO_3 phase was not detected. Mixtures containing up to 15.30 mole % MoO_3 were monophasic, but with 17.65 mole % MoO_3 content in addition to the solid solution, the final product contained $CrVMoO_7$. The mechanism of these syntheses is not well understood. The interpretation was based on X-ray powder diffraction and DTA results.

Shimada et al [5] prepared $CuSb_2O_6$ from an equimolar mixture of cupric oxide (<325 mesh) and antimony trioxide (preheated at 450°C), which was gradually heated in air to 1000°C. Then, powder mixtures of $CuSb_2O_6$ and CuO with mole ratios ranging from 2 to 9 were heated at 950-1150°C in air to produce the new compound $Cu_4SbO_{4.5}$. As well, mixtures of $CuSb_2O_6$ and CuO in mole ratios of 2 to 7 were pelletized and the pellets heated at 900-1250°C for 2-24 h in a piston cylinder type apparatus at 10 Kbar. The reaction was also carried out in an oxygen atmosphere at 10 bar in sealed quartz tubes. Then, the thermal decomposition of $CuSb_2O_6$ resulted in a different $Cu_4SbO_{4.5}$ form. The high pressure reactions of $CuSb_2O_6$ with CuO are clearly dependent on the mole ratio (n) and then on the temperature and pressure. Thus, the appearance of the new oxide $Cu_9Sb_4O_{19}$ was restricted to the following conditions: n=5; T=1000-1100°C and P=10 Kbar.

Several characterization procedures were employed in order to determine the structure, composition and stability of these oxides. The new phases were identified by X-ray diffraction (XRD) and then the crystallographic parameters of the new oxide $Cu_9Sb_4O_{19}$ were calculated. The composition of the formed oxides was determined by X-ray fluorescence analysis. The valence states of Cu and Sb were assessed by X-ray photoelectron spectroscopy (XPS) techniques. The stability of $Cu_9Sb_4O_{19}$ in air was investigated using a simultaneous DTA-TG apparatus. TG indicated also that the various mixtures of

$CuSb_2O_6$ and CuO lose oxygen at 900-950°C.

Sato et al [6] hydrothermally synthesized yttrium hydroxides by the reaction of aqueous solutions of yttrium salts (chloride and nitrate) at alkaline pH. Careful control of the alkaline concentration, OH/Y molar ratios, time and aging temperatures determined the characteristics of $Y(OH)_3$. Accordingly, amorphous $Y(OH)_3.H_2O$ was formed in the presence of excess alkali, presumably after 1 hour aging at 50°C. Then, this amorphous material was crystallized into hexagonal $Y(OH)_3$ by aging for 9 days at 80°C in sodium hydroxide solution, at variable OH/Y molar ratios.

By heating in the solid state, amorphous yttrium hydroxide decomposed thermally to amorphous yttrium oxide at about 500°C and then crystallized to cubic Y_2O_3 at higher temperature. Crystalline, hexagonal $Y(OH)_3$ was also thermally transformed to cubic Y_2O_3 but at lower temperatures than the amorphous hydroxide. No explanation was given for this interesting behavior. On the other hand the following sequences were given for the thermal transformation of monoclinic $\alpha\text{-}Y(OH)_3$: $\alpha\text{-}Y(OH)_3 \xrightarrow[450°C]{} YOOH \xrightarrow[700°C]{} Y_2O_3$ (cubic)

The hydrothermal and solid state synthesis (products) and the transformations of the yttrium compounds were monitored and characterized by DTA, TG, IR spectrosocpy and X-ray diffraction.

Pernice et al [7] prepared mixed metallic hydroxides (Mg + Al; Li + Al; Ca + Al) by the earlier methods of Mascolo and Marino [15], who employed aqueous suspensions of Mg-Al hydroxides at controlled Mg/Mg+Al molar ratios. These suspensions were kept in sealed teflon containers and rotated for one week at 80°C in air thermostated oven (lower temperatures were also employed for the preparation of other mixed metal hydroxides). Then the resulting products were filtered, washed and dried, taking precautions to avoid carbonation during the whole hydrothermal process. The uptake of (atmospheric) CO_2 by mixed metallic hydroxides was also studied by Mortland and Gastuche [16] who prepared Mg-Al double hydroxides by alkaline precipitation from $MgCl_2$ and $AlCl_3$ solutions. Carbonation should be avoided since it reduces the electrical conductivity of the mixed metal hydroxides. The metallic composition of these compounds, their crystal size, intercalation of water molecules and anionic species in their interlayer sites also affected the conductivity. DTA was used in order to follow the loss of intercalated water at increasing carbonation degrees.

Mendelovici and Sagarzazu [8] transformed $MnCO_3$ or manganese oxides (starting material) into a Mn_3O_4 (hausmanite) lattice structure containing OH groups. The synthesis of hausmanite by this new process took place in two steps: first, the starting material was refluxed with glycerol at 246°C for 16 h, yielding a light brownish solid identified as Mn alkoxide or glycerate. In the second step the Mn glycerate complex was hydrolyzed with boiling water, resulting in a dark brownish powder with the lattice structure of $MnO.Mn_2O_3$. The latter showed differences in composition, crystallinity, reactivity and surface area in comparison to Mn_3O_4 obtained by classical solid-state heating (at 950°C) of the same starting materials. Moreover, the hydrous hausmanite compound showed additional thermal events due to loss of OH groups and to Mn^{2+} oxidation when heated in air until 1300°C. X-ray powder diffraction, DTA, sorptometry (BET) and IR spectroscopy techniques were used to follow this synthesis and to characterize the reaction products.

Furuichi et al [9] studied the formation of crystalline α-Fe_2O_3 from poorly crystalline Fe(III) hydroxides containing a variety of foreign metallic ions (Me) in different oxidation states (Me^{2+}=Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}; Me^{3+}= Al^{3+} and Cr^{3+}). The mixing of Me was carried out by the combination of hydrothermal and solid state procedures, as follows: a) coprecipitation, where a 6M NaOH solution was added to 0.1 M $Fe(NO_3)_3$ solution containing the Me-salt at a fixed Me/Fe+Me mole ratio. The pH was adjusted to 12 (at 30°C) for the precipitation process; b) gel mixing, where slurries of a Fe gel (Fe(III) hydroxide) and Cu(II) hydroxide gel were mixed at pH 12 and stirred for 15 min. The Cu and Fe gels (So=285 m^2g^{-1}) were previously prepared from the respective 0.1 M nitrate solutions adjusted with 6M NaOH to pH 12; c) mortar mixing: 500 mgs of $Fe(OH)_3$ and desired amounts of $Cu(OH)_2$ or CuO (derived from the heating of the $Cu(OH)_2$ at 110 and 400°C) were mixed (and ground) in agate mortar for 30 min.

The resulting products in each of these procedures were heated in air up to 600°C and the iron oxides produced by heating were examined with DTA, TG and X-ray powder diffraction. DTA of pure, amorphous Fe-gel (So=285 m^2g^{-1}) showed a sharp exothermic peak at 414°C marking the crystallization of the gel into α-Fe_2O_3. When the Fe-gels contained 10 mole% Me (as prepared by the coprecipitation procedure), the exothermic peak corresponding to the α-Fe_2O_3 transformation was observed at higher temperatures than that of the pure Fe-gels, namely 550° and 475°C for the samples containing Me^{2+} and Me^{3+} respectively.

This was interpreted as a retardation effect of Me on the α-Fe_2O_3 crystallization. The retardation effect of Cu^{2+} mixed by coprecipitation was similar to that observed in the gel mixing procedure. This (retardation) effect was weaker in samples prepared by mortar mixing.

In the case of the samples prepared by coprecipitation and containing Me^{3+}(Al or Cr ions), the formation of Al_2O_3 and Cr_2O_3 was not detected upon heating. XRD results also indicated a shift in the α-Fe_2O_3 lines to higher angles, which was interpreted as a solid solution formation of Fe^{3+} with Me^{3+}. The authors conclude that Me^{2+} which form some $MeFe_2O_4$ (ferrite) during the heating process retard the α-Fe_2O_3 formation more than Me^{3+} ions which substitute for Fe^{3+} in the oxide structure.

Macias et al [10] employed known procedures in order to obtain γ-Fe_2O_3 (maghemite) by the respective solid state decomposition of γ-FeOOH, α-FeOOH, $N_2H_5Fe(N_2H_3COO)_3.H_2O$, and the layered compound $FeOOCH_3$ [17]. Another Fe_2O_3 sample in colloidal state was prepared from the mixture of Fe^{2+} + $2Fe^{3+}$ treated with 3M $HClO_4$ in ammoniacal medium at pH 9 [18]. The evolution of γ-Fe_2O_3 to α-Fe_2O_3 (hematite) in each case was studied by X-ray powder diffraction, DTA, sorptometry (BET) and electron microscopy. From this study it was inferred that the thermal transformation of maghemite to hematite was favored by platelike particles and by lattice distortions in the crystal. This particular morphology permits closer contact between maghemite particles which in turn enables a thorough sintering of the resulting hematite. The compaction between particles (in the DTA container) also affected the DTA exothermic peak, characteristic of the γ-Fe_2O_3 to α-Fe_2O_3 transition. Others factors affecting the stabilization of γ-Fe_2O_3 are further discussed.

Magistris et al [11] mixed and milled ceria and zirconia powders in mortar with agate balls for 24 h. This treatment produced a slurry, which was dried, pressed as flat disks and submitted to a heating-cooling cycle (from 1600 to 1000°C and to room temperatures). The cooling rate allowed the sample to rearrange to tetragonal symmetry. The redox behaviour of the resulting mixed oxide material was examined by thermoanalytical methods under controlled atmospheres (air, oxygen and argon with 5% hydrogen). The reduced material has a cubic unit cell in contrast with the tetragonal structure of the oxidized sample. Weight and oxygen losses were performed by TG and EGA (evolved gas analysis), equipped in line with a QMS (quadrupole mass spectrometer). Thermodilatometry (TDM), XRD and electron microscopy were also used to characterize the materials. It is interesting to point out that such material kept its mechanical properties after several TDM cycles, in spite of the large dimensional variation exhibited during the redox treatment.

Bar-On and Nadiv [12] synthetized Mg-Al double hydroxides by the similar hydrothermal method of Mascolo and Marino [15]. The former authors also used different starting materials, namely mixtures of magnesia with Al hydroxide gel and magnesia with γ-Al_2O_3, at an Al/Mg molar ratio 2:1. When the latter mixture was refluxed with water for 236 h a unique double hydroxide was formed, exhibiting a layer structure with a calculated c'spacing 7.36 Å, shorter than any value reported in the literature for similar layered compounds. It was found that the c'spacing increased its value as the refluxing time was gradually decreased; at 4 h reflux time it gave 7.60 Å, which is the normal value shown by the other mixtures. However, the a unit cell parameter was not visibly affected by the refluxing periods, giving an almost constant value, at 3.05 Å. The c'spacing at 7.36 Å was attributed to the content of AlO_2^- anions in the interlayer space of this peculiar double hydroxide, which caused concomitantly the expulsion of CO_2 from this site. Thus, the content of CO_2 decreased about 30% from the initial content, remaining at only ~1% CO_2 in the refluxed mixture. X-ray powder diffraction, DTA and IR spectroscopy were employed for the examination and characterization of the Mg-Al double hydroxides.

Bayer and Wiedemann [13] studied the displacement reactions between Ca-sulfate or Ca-carbonate minerals with Na-tungstate or Na-molybdate reagents respectively. The starting Ca-minerals were used in the form of single crystals or powders. The sodium reagents were used as solids, melts or as solutions. In the latter case, the Ca solids (starting minerals) were hydrothermally reacted at different temperatures (20-100°C) with an excess of the aqueous Na-molybdate solutions for different times.

The corresponding displacement reactions given by the authors are:

$$CaSO_4 + Na_2WO_4 \text{ (or } Na_2MoO_4\text{)} + H_2O \rightarrow CaWO_4 \text{ (or } CaMoO_4\text{)} + Na_2SO_4$$

$$CaCO_3 + Na_2WO_4 \text{ (or } Na_2MoO_4\text{)} + H_2O \rightarrow CaWO_4 \text{ (or } CaMoO_4\text{)} + Na_2CO_3$$

The same products resulted when the reactions were carried out by heating in the solid state, at high temperatures. The different solubilities of the Ca-minerals and their structure influence the reaction (calcite reacted faster than aragonite). Moreover, if the coordination number of the Ca ions in the mineral is close to scheelite ($CaWO_4$) or powellite ($CaMoO_4$) the reaction may proceed faster. A pronounced effect of time and temperature is only apparent when the starting minerals are in form of powders; thus particle size and morphology of the starting solids also play a role.

The displacement reactions were also examined when both initial reactants were present as solids (solid-solid reaction) and heated to high temperatures. Then, it was found (by DSC) that the reaction proceeds already (in the solid state) at 680°C at 1°C/min. With faster heating rates (8°/min) the formation of scheelite and Na_2SO_4 was not completed even at 750°C. Thermomicroscopic/DSC measurements, TG, DTG, electron microscopy with EDAX analysis and XRD were employed to follow these reactions.

Broadbent et al [14] prepared magnesium hydroxide, by leaving magnesium oxide in contact with a large excess of water for a long time and then drying below 100°C. The dried material was then compacted in the form of disks at 10000 lbs. for 3 minutes. The resulting disks were submitted to heating treatments up to 800°C under different degassing conditions and subsequently tested for moduli of rupture. It was found that sintering taking place at 800°C, resulted in the strongest material. The breaking loads of the treated materials were also correlated to the corresponding surface area. The thermal decomposition stages of $Mg(OH)_2$ into MgO and the fluids evolved during this process were monitored by TG, infrared CO_2 analysis and sorptometry (BET).

GENERAL DISCUSSION

This discussion will refer to the papers examined in this study and to related works, in order to find common points in the synthesis of oxides and to correlate the properties of the synthetic products.

Generally speaking, well crystallized materials are formed by thermal syntheses taking place in the solid state, especially in the high temperature range (700°C) where crystallizations or recrystallizations do occur. On the other hand, less crystalline and amorphous materials are generated by some hydrothermal synthesis methods, i.e. in the Mn_3O_4 product resulting from hydrolysis of manganese alkoxide [8] and in iron spinel oxide obtained from the hydrolysis (forced hydrolysis) of iron alkoxides. Classical hydrothermal methods for the synthesis of metal oxides or hydroxides, employing alkaline precipitation from metallic salts and controlled aging, also yield amorphous material [5,9]. In some experiments the amorphous product crystallizes during the aging process, which depends on the nature of the product, aging conditions and molar ratio, as shown by Sato et al [6] for the transformation of amorphous $Y(OH)_3$ into hexagonal $Y(OH)_3$. Molar ratio of the reactants (n) is also an important variable in determining the composition (and stoichiometry) of the resulting phases, as formed by solid state heating. Thus, the complete formation of the new oxide $Cu_4SbO_{4.5}$ from the reaction of $CuSb_2O_6$ + CuO (at fixed pressure and temperature conditions) occurs only at $n = 3.5$ [5].

In the hydrothermal preparation of double Al-Mg hydroxides Mascolo and Marino [15] found that the Mg/Mg+Al molar ratio also determined the crystallographic parameters and ordering of the formed phase. In the preparation of such double hydroxides [7,12] the uptake of CO_2 should be avoided, since it is one of the factors affecting conductive properties. The CO_2 expulsion has also been checked in the preparation of $Mg(OH)_2$ [14].

The Tc values of α-Fe_2O_3 prepared from Fe hydroxides containing foreign metallic ions [9] increased with an increase in the amount of a foreign metal admixed from 0 to 10 mole %. In hydrothermal synthesis, when the final product is a monometallic oxide (not a mixed oxide), the molar ratio Metal/OH of the precursor also influences the crystallographic composition of the synthetic product, under determined aging conditions [6].

The influence of experimental factors such as temperature and time are quite common in the synthesis of materials, especially when the kinetics of such reaction is investigated. In the syntheses herein described, both of these factors are present in almost all the methods. Thus, the temperature range and time of treatment are important in hydrothermal syntheses as well as in the solid-state and determine, selectively, not only the completion of the reaction but also the kind of resulting inorganic material. This is also valid for displacement reactions [13], which show a pronounced effect of temperature, time (and sample configuration) on the formation and crystallinity of $CaWO_4$ and $CaMoO_4$. Thermal treatments can also induce oxygen losses in some inorganic materials, as shown hereabove in the formation of Cu-Sb oxides [5] and in the ceria-zirconia system [11]. This also affects the stoichiometry of the materials.

The effect of pressure (and atmosphere) on the synthesis products is stressed in the paper of Shimada et al [5], describing the solid-state preparation of new Cu-Sb oxides. Mechanical effects can also be important in the formation and (polymorphic) transformation of other types of inorganic materials submitted to pressure or other mechanical treatments. Atmosphere, on the other hand, plays an important role, together with other factors, in the (controlled) thermal decomposition of metallic oxalates, another method employed for the synthesis of metallic oxides [19].

The formation of solid solutions is common in inorganic materials, especially when more than one metallic ion is involved in the final oxide structure and when the substituting ions have similar Pauling radii and coordination numbers. Thus, solid solutions are mentioned here in the V_2O_5 - Bi_2O_3 system [3], and in the reaction of MoO_3 + $Cr_2V_4O_{13}$ (Mo^{6+} replacing V^{5+}) [4]. The above mentioned syntheses were performed in the solid state, but isomorphic substitution can also take place in hydrothermal syntheses, i.e. when trivalent metallic ions substitute for Fe^{3+} in α-Fe_2O_3 [9].

Important factors such as crystallinity and reactivity of inorganic materials will be related in this discussion mostly to the synthesis of iron oxides, which have been extensively investigated. The effect of crystallinity which is associated with crystallite size and structural defects is relvant for the precursor or parent material which produces, by thermal decomposition or transformation, the desired iron oxide. Also mechanochemical transformation of iron oxyhydroxides yields oxides of variable composition, texture and crystallinity [20-22].

It has been found by Macias et al [10] that γ-Fe_2O_3 samples prepared from thermal decomposition of different iron oxyhydroxides and other compounds have quite different XRD parameters, surface area and microstrains. This influences the $\gamma\text{-}Fe_2O_3 \rightarrow \alpha\text{-}Fe_2O_3$ transformation temperature, which according to the authors, is inversely related to the level of structural defects of the solid (γ-Fe_2O_3); this means that lattice distortions in maghemite induce an easier conversion into hematite.

On the other hand, the transformation of hematite and goethite into spinel oxides like magnetite and maghemite was investigated by an adequate thermomechanical treatment in alkali-iodide disks [23-25].

These works have shown that the transformation into magnetic spinel oxides is favored by defective structures of the starting materials.

As well as by the above mentioned solid-state treatments, iron oxide can also be synthesized by hydrothermal methods or by a combination of precipitation and calcination of the formed powders. These methods are quite interesting, since they may determine properties like reactivity and homogeneity of the resulting solids. Thus, for example Matijević [26] has employed several hydrothermal techniques in order to prepare metal oxide (mostly iron oxides) particles of uniform size and shape. On the other hand Gallagher et al [27] prepared iron oxides (by suitable spray and freeze drying techniques), using aqueous solutions made from a wide variety of starting iron salts. They concluded that the particular choice of iron salt (precursor) had a marked effect on the reactivity of the resulting Fe_2O_3. A test used for the reactivity was by solubility of the powder in hot 2.5 M HCl for 10 min and subsequent determination of dissolved Fe. The unequal solubilities of materials of similar surface area indicated that structural defects and degree of crystallinity ruled their reactivity. Fe_2O_3 samples ($So=10\ m^2g^{-1}$) prepared by solid state decompositions at low temperatures had a significantly greater HCl solubility than those having the same surface area but prepared at higher temperatures. The explanation is that the former are less crystalline and fewer defects have been removed by annealing.

Enhanced reactivities were also observed in the finely divided spinel oxides synthesized in our laboratory via metal glycerate (alkoxide) in comparison to the reactivities of well crystallized spinels prepared by conventional methods (solid state calcination of starting oxides) [8]. Such reactivities were determined by a dissolution test in cold HCl. The comparative formation of ferrimagnetic spinels was also investigated in iron oxides synthesized by the glyceration method. Thus, when metal substituted iron oxides, such as Al-goethite (containing 9.6 mole % Al), were used as starting materials (precursors), Al-Fe glycerate* was produced after the 1st step (glyceration) [1]. Hydrolysis (2nd step) of such **alkoxide** resulted in a limited formation of spinel solid solution in comparison to the high amounts of ferrimagnetic spinel produced by hydrolysis of pure iron alkoxide. The formation of such Fe-Al solid solution was also ascertained from the calcination of the mixed alkoxide at

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*Registered in JCPDS

1000°C, resulting in Al-substituted hematite powder, whose XRD patterns indicated the corresponding shift of the α-Fe_2O_3 lines to lower values [1].

Alternative routes for a low temperatures synthesis of complex metal oxides can be also achieved by the use of so called solid-solution precursors [28]. The precursors may be adequate mixtures of multimetallic isomorphous carbonates [28,29] , coprecipitated at alkaline pH which yield single phase, solid solution carbonates. The latter are decomposed to mixed metal oxides under controlled heating conditions. This method, which has also been extended to oxalate solid-solution precursors [30] offers some advantages: it allows the controlled, homogeneous mixing of different metallic ions on an atomic scale thus reducing the diffusion distance. Faster solid-state reactions at lower temperatures are therefore achieved in comparison with the traditional ceramic methods used for the synthesis of mixed metal oxides.

To conclude, it is not possible in this contribution to cover all the existing literature and ongoing works made on the thermal synthesis of inorganic materials. Our study is limited to some synthesis methods for metal oxides, referring to the papers appearing in the 9th ICTA Proceedings (1988) and related works. Although some emphasis has been given to iron oxides, especially on the preparation of magnetic spinels, this study does not include applications of metal oxides in areas such as catalysis or superconductivity.

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