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Preparation of fine particles through aqueous processing route

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Abstract   . Aqueous processing routes for preparation of oxides in micron, sub micron and nano size have gained enormous importance due to their ability to alter shapes and sizes of the end product by varying preparation parameters. The most studied oxides are the ones used as magnetic and ceramic materials This paper briefly reviews the preparation of ferrites, aluminum oxides/hydroxides, aluminates and non oxides following aqueous routes as one of the process steps The aqueous processing routes include precipitation by sol-gel method, co precipitation at ambient temperature and hydrothermal precipitation The work done by the authors and their co-workers for preparing the above mentioned oxides has been briefly discussed Fine particles of zinc oxide, barium aluminates and Mn-doped barium aluminates were prepared following precipitation-calcination route

Keywords   Fine particles, aqueous processing, ferrites, aluminium oxides/hydroxides, aluminates, iron oxides

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1. Introduction

The most widely accepted, commercially used technique for preparation of ceramic metal oxides in general and ferrites in particular is the classical ceramic method. By altering the preparation parameters oxide particles of different shapes and sizes can be obtained. Depending on the end-use requirement, the preparation conditions can be optimised. Literature on preparation of ferrites, hematite, oxides/hydroxides of aluminum, barium aluminates and pure iron oxides/aluminum substituted iron oxides through aqueous processing route has been briefly reviewed and the work done by the authors and their co-workers has been included.

2. Ferrites

Ferrites can be prepared by almost all existing methods used for the preparation of oxides. With the increase in their applications in modern electronic devices considerable amount of R and D efforts have gone in preparation of nano particles especially through aqueous processing techniques which includes organometallic precursor, co-precipitation, sol-gel and hydrothermal routes.

2.1. Organometallic precursor method for ferrites :

The organometallic precursor method involves the synthesis of a compound, the metal-organic precursor in which the reactants

are present in the required stoichiometry [1]. Preparation of $Ni_{1-x}Zn_xFe_2O_4$ ferrites for example involves the preparation of a hydrazinium metal hydrazine-carboxylate precursor, (N_2H_5) $Ni_{1-x}Zn_xFe_2(N_2H_3COO)_6.3H_2O$ with $0 \le x \le 1$ [2]. Upon heating, the precursor decomposes, yielding the ferrites. Spinel ferrites have also been prepared by thermal decomposition of another precursor, crystallized pyridinates, $Me_3Fe_6(CH_3COO)_{17}$ $O_3OH.12C_5H_5N$, with Me = Mg, Mn, Ni, Co [3]. In the classical ceramic method, reactions are generally slow because of large diffusion distance [4]. The high reactivity and fast diffusion makes the precursor method ideal for the preparation of nanosize spinel ferrites [5-7].

2.2   Ferrites by co-precipitation method :

The co-precipitation method for ferrite formation is based on the formation of aqueous solutions of chlorides, nitrates, sulphates, oxalates, carbonates of Fe^{3+}, and of divalent Ni, Co, Mg, Mn, Zn, Ba, Sr etc [8-13]. Required concentration of the aqueous solutions are mixed together and precipitated simultaneously using an alkali as the precipitating agent. The precipitates are then filtered, washed and dried resulting into the ferrite particles. The ferrite particles so obtained are calcined at 180-300°C in air. A large number of ferrites have been prepared using this technique [14-24]. Several parameters such as solubility product of various metal ion compounds (e.g. hydoxides, carbonates, oxalates etc.), pH, concentration, rate of mixing, temperature of precipitation, mode of washing,

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temperature of drying and calcination have to be controlled to produce satisfactory results through the co-precipitation route. This technique is most widely used for the synthesis of fine grained oxide powders because of simple processing route and the chemistry involved is relatively straightforward.

2.3. Ferrites through sol-gel method :

Sol-gel technique is another important aqueous processing route for preparation of fine-sized oxides. This process involves the preparation of a sol (an aqueous colloidal suspension of the desired oxides in hydrated form) from the nitrates or other salts by controlled precipitation. The sol is converted to gel by partial dehydration. The gel is completely dried and fired to obtain the product. Metal oxide powder with particle size in the range of 3–100 nm are obtained. This technique has received much attention because of its application to an extremely wide variety of materials. They offer the possibility of controlling not only the size, distribution of particles but also their shapes. A variety of ferrites have been prepared from colloidal suspensions [25, 26]. Ultrafine Mn-Zn ferrites with low loss and high permeability have been prepared from amorphous citrate gel [27,28].

2.4. Ferrites by hydrothermal precipitation route .

Hydrothermal precipitation of ferrite directly from the solution is achieved by this process. In this method, alkaline solution is added to a stoichiometric solution of metallic salts with metal ions in the divalent/trivalent state. This results in a suspension of the mixture of hydroxides by adding precipitating agents like NaOH/KOH/urea/NH₄OH etc. The slurry is treated in an autoclave at high temperature and pressure which promotes the reaction converting the precipitate into bimetallic or tri-metallic oxides [29,30]. Mn-Zn ferrites have been prepared by this method and spherical particles of the order of 10 nm diameter have been obtained [31,32].

2.4.1. Hematite :

Ferrite grade hematite samples were prepared through hydrothermal precipitation route. The preparation parameters investigated were : pH of precipitation, synthesis temperature and initial iron concentration [33]. Depending on the preparation conditions hematite particles with widely varying microstructures and magnetic properties were obtained. The procedure for preparation of hematite was tested with different source materials like the electrolytic iron powder, abundantly available waste materials such as iron scrap and blue dust [34]. Purification of solution was done by solvent extraction when hematite was prepared from waste materials. It was observed that magnetic properties and microstructural features were largely governed by the preparation parameters [33,34]. Table 1 compares the average particle size of hematite samples obtained from TEM and XRD [104] peak at different pH of preparation. Polycrystalline pseudo-cubic hematite particles were formed at a pH of 3. It is observed that the number of sub particles decreased

Table 1. pH dependence of particle size, mean crystalline diameter (MCD) and degree of polycrystallinity [33].

Condition →	pH 3	pH 4.5	pH 7	pH 11
Average particle size (TEM) in nm	650	250	120	60
MCD values from XRD for [104] peak in nm	43.0	53 2	53 7	52 5
No of subparticle	~3400	~100	~10	~1

with the increase in pH. At a pH of 3 the number of subparticles was 3400 and gradually reduced to 1 when the pH of precipitation was 10. The polycrystalline nature had a bearing on the magnetic properties giving unusually high value of coercivity for the sample prepared at pH 3 [33]. Microstructure dependent coercivity in monodispersed hematite particles was also studied [35]. A typical micrograph obtained at a pH of 3 is shown in Figure 1. The grain growth mechanism was put forward using barium carbonate as the spacer [36].
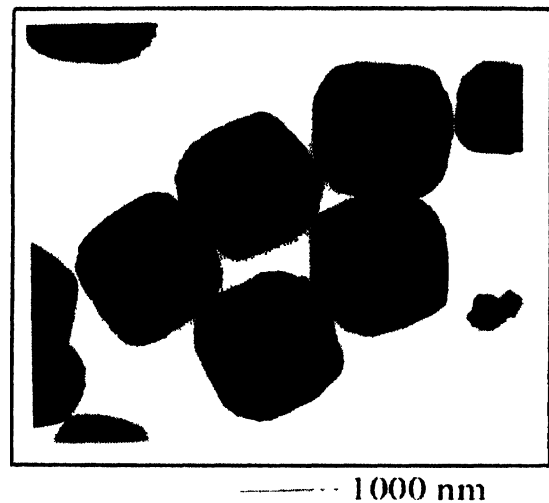

——··· 1000 nm

Figure 1. A typical TEM of mono-dispersed pseudo-cubic hematite particles [34]

2 4.2. Mn-Zn/Ni-Zn ferrites :

A novel method was developed for the preparation of Mn₀.₆₅Zn₀.₃₅Fe₂O₄ wherein pH of ferric chloride solution was first adjusted with ammonia and chloride ions were removed by repeated washing to lower the concentration of ammonium chloride in the hydroxide slurry (presence of excess ammonium chloride helps in the stablising zinc and manganese ammines which stay in the solution resulting in non-stoichiometric ferrite formation). Both manganese and zinc chlorides were mixed in required proportions and desired pH was adjusted with ammonia. Iron hydroxide and Mn-Zn hydroxide slurries were mixed and treated hydrothermally at 180°C for preparing different samples to study the effect of pH on microstructural and magnetic properties of Mn₀.₃₅Zn₀.₆₅Fe₂O₄ [37]. Series of nano-sized Mnₓ-Zn₁₋ₓFe₂O₄ ferrite samples were prepared with x varying between 0 to 1 from metal chloride solutions with ammonia as a precipitating agent following the procedure mentioned above

and their microstructural and magnetic properties were studied in detail [38]. Appearance of super paramagnetism was observed on annealing $Mn_{0.65}$-$Zn_{0.35}$ Fe_2O_4[39]. Mössbauer studies were carried out on nano-size Mn_x-Zn_{1-x} Fe_2O_4 [40] prepared at a pH of 9

Effect of preparation parameters on nano-sized Ni_x-Zn_{1-x} Fe_2O_4 ferrites using hydrothermal precipitation route has shown that the presence of small amounts of alkali can obstruct the formation of Ni-Zn or Zn ferrite whereas such an effect was not observed for nickel ferrite [41].

2.5 Ferrite grade zinc oxide through aqueous processing-calcination route :

Zinc oxide is prepared commercially by two methods, the American (or direct) process [42-48] which uses zinc ore and concentrate, and the French (or indirect) process [49-51] which uses zinc metal. Zinc oxide is also produced industrially using wet process from purified solutions of zinc sulfate or chloride by precipitating the basic carbonate, which is then washed, filtered, and finally calcined. Due to the increased specificity with respect to surface area and purity for ferrite industry, wet chemical methods have gained importance for preparation of zinc oxide. Zinc ash is an important secondary source of zinc. Preparation of zinc metal/zinc powder from zinc ash following aqueous processing route has been reported [52-55]. Ferrite grade zinc oxide was prepared through aqueous processing of zinc ash followed by calcination [56]. Zinc was quantitatively dissolved in sulphuric acid medium. The ferrous iron impurity present in the leach solution was oxidised with hydrogen peroxide followed by precipitation of total iron impurity by pH adjustment to 4.5 with dilute sodium hydroxide solution. Copper impurity was removed by cementation using zinc dust. Zinc hydroxide was precipitated from the purified zinc sulphate solution with precipitating agents such as ammonia, ammonium carbonate, sodium carbonate and urea. The zinc hydroxide was calcined at 940°C for obtaining ZnO. Table 2 shows that the particle size of ZnO depended on the nature of precipitating agent indicating that difference in the formation precursor zinc hydroxide.

Table 2. Effect of precipitating agent on particle size ZnO [56]

Sl. No	Nature of precipitating agent	Average Particle size Micron
1	Ammonia	16 97
2	Sodium carbonate	78.04
4	Ammonium carbonate	4.70
5.	Urea	16 26

3. Aluminum oxides/hydroxides/aluminates

Aluminium oxides/hydroxides form an extremely important class of oxides which finds wide ranging applications such as abrasives, adhesives, gels, cement, glass, ceramics, refractory materials, catalysts, cosmetics, dyes, detergents, fire retardants, fillers, paints, pigments, pharmaceutical [57-61], and many others. Similar to the ferrites, both physical and chemical properties of oxides/hydroxides of aluminum can be tailor-made for particular use and this has resulted in enormous research activity in this field [62,63].

3.1. Aluminum oxides/hydroxides by sol-gel synthesis route :

Roy and co-workers [64-67] recognized the potential for achieving very high levels of chemical homogeneity in colloidal gels and used the sol-gel method in 1950s and 1960s to prepare a large number of novel ceramic oxide compositions of Al, Si, Ti and Zr etc which could not otherwise be made following the traditional ceramic route. In line with ferrite preparation, a majority of the sol-gel work on alumina involves organic precursors, the aqueous sol-gel process being very limited. Kobayashi and Lin [68] prepared alumina films from aqueous sols derived by hydrolyzing $AlCl_3$. Matijevic and his colleague [69] prepared monodispersed spherical aluminium hydroxides from $Al_2(SO_4)_3$ by a sol-gel route. Transparent alumina sols were prepared by peptizing hydrous aluminium oxides by acetic acid [70]; these sols showed excellent colors when doped with transition metal ions. Transparent alumina gels were also recently prepared from a controlled hydrolysis of $AlCl_3.6H_2O$ [71]. Pierre and Ulhmann have studied extensively [72] the structure of alumina gels obtained from aqueous aluminium salt solutions by hydrolysis and ageing. Boehmite sols, suitable for the preparation of nano-sized α-Al_2O_3 powders, were obtained from aqueous Al-nitrate solutions [73]. Morgado et al [74] studied the effect of preparation conditions on the peptizability of boehmite sols from base hydrolysis and ageing of aluminium nitrate solutions.

The interactions of co-existing anions with the hydroxide gels were extensively studied by Serna et al [75]. Gels precipitated in the presence of NO_3^-, $SO4^-$ and CO_3^{2-} ions behaved as a positively charged polymeric material [76-78], containing variable amounts of these co-existing anions on their surface. The interaction of nitrate appeared to be predominantly electrostatic, while sulphate and carbonate seemed to co-ordinate with aluminium ions.

3.2. Aluminium oxides/hydroxides by homogeneous precipitation :

The homogenous precipitation involves hydrolysis of aluminium salts in the presence or absence (thermally forced hydrolysis) of a hydrolyzing agent, addition of a base to acidic salt solution (like NH_4OH, $NaOH$, Na_2CO_3 etc), or precipitation by using seeds/modifiers in a supersaturated aluminate liquor; aluminium hydroxides, oxide-hydroxides and/or basic aluminium salts are the usual products. The formation of a particular phase is generally seen to depend on the chemical and physical environment prevailing during precipitation [79].

Numerous methods are available on precipitation of different grades of aluminium hydroxides from aqueous salt solutions of
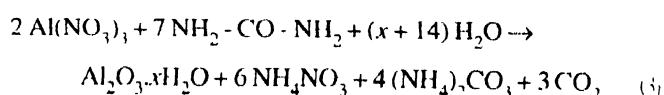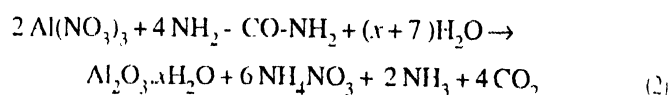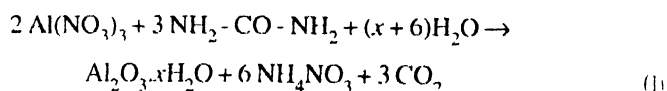
aluminium by using alkali hydroxides, bicarbonates and aqueous ammonia [80–88]. Sato and his co-worker studied the effect of pH on the composition and crystallinity of the precipitates obtained from aqueous solutions of aluminium sulphate and ammonia [82]. With increasing pH, formation of bayerite was seen to take place in preference to pseudo-boehmite. It was observed that during the neutralization of aqueous $Al_2(SO_4)_3.12H_2O$ with either NaOH or NH_3, basic aluminium sulphate was formed when NaOH or NH_3/Al^{3+} mole ratio was less than 3 while crystalline $Al(OH)_3$ was seen to form when the molar ratio exceeded 3 [82]. Shein *et al* studied in detail the effect of flow rate, reaction temperature, reactant concentration and dimensions of the reactor on the morphology of $Al(OH)_3$ [88]. Aluminium hydroxide precipitation from the basic sulphate and chloride solutions was found to yield a range of particles of variable sizes and shapes [89]. Sub-micron mono-sized particles were seen to be formed by heating perchlorate or chloride solutions [90], the particles so obtained were intersecting flat plates with overall ellipsoidal shape and surface areas as high as 200 m^2/g. Self-hydrolysis of aluminium sulphate solutions [91,92] was observed to yield mono-sized spherical particles under restricted conditions.

Sub-micron sized, reactive aluminas were prepared by calcination of hydroxides obtained by hydrolysis of Al-salts using urea [93–95]; this route was said to have advantage as the particle size of the precursors was retained during calcination. The effect of various co-existing ions on the morphology of basic aluminium sulphate prepared from aluminium sulphate and urea was studied by Nagai *et al* [96]. Aluminium salts like NO_3^-, F^-, $HCOO^-$ and CH_3COO^- gave non-crystalline products; the presence of SO_4^{2-}, $C_2O_4^{2-}$ or citric acid led to the formation of aggregated particles consisting of plate-like micro-crystals. Similarly Fujita *et al*, Sacks *et al* and Blendel *et al* [97–100] observed that ultra-fine spherical aluminium hydroxides/basic sulphates could be prepared from aluminium sulphate and urea. Recently, preparation and characterization of light, ultra-fine basic aluminium sulphate has been reported by Pradhan *et al* [101]. The role of co-existing ions on the morphology and particle size could be explained on the basis of their complexation with Al, resulting in nucleation at different pH values. However, the role of SO_4^{2-} ion on the spherical morphology has not been clearly understood.

Precipitation of aluminium hydroxides are also widely practised by using seeds/modifiers from the alkaline aluminate liquor [102–105]. Baksa *et al* had studied in detail [102,103] the effect of seed size, seed quantity and sulphate modifiers on the particle size of $Al(OH)_3$. The effect of each of precipitation temperature, impurity, retention time and seeding on the rate of crystal growth, nucleation and quality of $Al(OH)_3$ has been reported by Satpathy and Vidyasagar [104]. The role of various organic impurities during the precipitation using seed has been studied by Alamdari and co-workers [105]; it was observed that oxalate ion decreased the activation energy for nucleation on a seed surface while manitol had a poisoning effect.

3.3. Aluminum oxides/hydroxides by hydrothermal precipitation route :

Boehmite was prepared following a hydrothermal precipitation route from aluminum salt solutions [106–109]. Crystalline boehmite samples ($Al_2O_3.xH_2O$, $1 < x > 1.5$) were prepared by a moderately high temperature neutralization of aluminium nitrate in the temperature range of 160–220°C. Urea was used as the neutralising agent. Depending on the aluminium to urea ratio the following chemical reactions would take place :

$$2\,Al(NO_3)_3 + 3\,NH_2 - CO - NH_2 + (x+6)H_2O \rightarrow$$
$$Al_2O_3.xH_2O + 6\,NH_4NO_3 + 3\,CO_2 \qquad (1)$$

$$2\,Al(NO_3)_3 + 4\,NH_2 - CO-NH_2 + (x+7)H_2O \rightarrow$$
$$Al_2O_3.xH_2O + 6\,NH_4NO_3 + 2\,NH_3 + 4\,CO_2 \qquad (2)$$

$$2\,Al(NO_3)_3 + 7\,NH_2 - CO - NH_2 + (x+14)\,H_2O \rightarrow$$
$$Al_2O_3.xH_2O + 6\,NH_4NO_3 + 4\,(NH_4)_2CO_3 + 3\,CO_2 \qquad (3)$$

Detailed studies were carried out for characterization of boehmites samples employing techniques such as XRD, FTIR, TG-DTA and the morphology of the samples was studied by TEM. It was observed that during hydrothermal precipitation first a partly amorphous gel (pseudo-boehmite) was formed which got transformed into crystalline boehmite. TEM of the crystalline boehmite showed a fibrillar morphology. The larger particle size values were obtained from TEM as compared to the MCD (5 to 8 nm) values obtained from XRD. This indicated polycrystalline nature of boehmite.

It was observed that when boehmite was precipitated from different inorganic salt solutions under similar conditions [107], hydrolysis of $Al_2(SO_4)_3$ started at a lower temperature as compared to other salts *e.g.*, $AlCl_3$ or $Al(NO_3)_3$. The physical properties such as surface area, water of hydration, tap density *etc* also varied with the nature of the salt as given in Table 3. Boehmite prepared from aluminium sulphate exhibited minimum weight loss at two hours and highest surface area with lowest tap density.
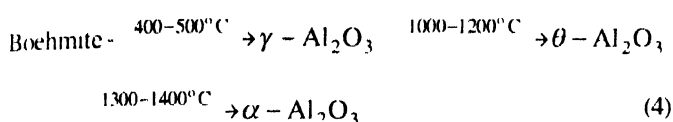
Table 3. The weight loss, surface area and tap density of boehmites precipitated from different inorganic aluminium salts [107]

Type of Al-salt	%weight loss of samples calcined for 1 h at 725°C obtained at different precipitation time			Surface area m^2/g	Tap density g/cm^3
	0 h	1 h	2 h		
$Al_2(SO_4)_3$	18.98	17.96	17.28	98.6	0.165
$AlCl_3$	21.15	19.94	19.62	87.5	0.224
$Al(NO_3)_3$	22.56	19.82	19.51	86.0	0.290

A study of the interaction of various precipitation parameters such as precipitation temperature, aluminium concentration (using aluminium sulphate salt) and urea to aluminium molar ratio by 2^3 full factorial matrix [108] showed a response surface

for the formation of stoichiometric boehmite. The design matrix under the studied range of variables showed the best conditions of precipitation as : temperature 160–200°C, aluminium concentration 0.1 to 0.2 M, time 2 hours and urea to aluminium ratio as 4.

The studies on transformation of hydrothermally prepared boehmite to α-Al$_2$O$_3$ showed that boehmite obtained in the present hydrothermal route transformed into γ-Al$_2$O$_3$ at 400–500°C and the γ-alumina obtained was stable up to 1000°C. In order to study the thermal transformation sequence of boehmite into α-Al$_2$O$_3$, the boehmite derived from aluminium sulphate was calcined at 1200, 1300 and 1400°C for 2 h and the calcined products were characterized by XRD. The sequence of transformation is given below :

$$\text{Boehmite} - \xrightarrow{400-500^\circ C} \gamma - Al_2O_3 \xrightarrow{1000-1200^\circ C} \theta - Al_2O_3$$

$$\xrightarrow{1300-1400^\circ C} \alpha - Al_2O_3 \tag{4}$$

It was interesting to note that κ-, η-, or δ-Al$_2$O$_3$ were not formed as a major intermediate oxide during the transformation of γ-Al$_2$O$_3$ to either θ- or α-Al$_2$O$_3$ [109].

3.4. Barium aluminates through aqueous processing-calcination route :

Almost all metals can form aluminates or corresponding aluminium metalates (e.g. aluminium titanates) with aluminium [110]. Except the alkali metal aluminates which are stable only in solutions, all other aluminates are solids at room temperature. These aluminates find diversified applications starting from industrial catalysts to structural ceramics in high temperature regions due to their superior physical properties, such as : higher thermal shock resistance, higher melting point, lower thermal expansion coefficients and much better properties, than those displayed by conventionally used metal oxide ceramics [111]. Among these aluminates, the most widely used group of aluminates are barium aluminates. Barium is known to form several types of stoichiometric as well as non-stoichiometric aluminates with aluminium. The most studied and also used aluminates of barium are the stoichiometric aluminates, such as : BaO.Al$_2$O$_3$ (barium mono-aluminate), 3BaO.Al$_2$O$_3$ (tribarium mono-aluminate), BaO.4Al$_2$O$_3$ (barium tetra-aluminate) and BaO.6Al$_2$O$_3$ (barium hexa-aluminate).

3.4.1. Barium mono-aluminate :

Conventionally barium mono-aluminate is prepared through ceramic route involving high temperature heat treatment of component oxides or salts. Many processes have been reported for preparation of barium mono-aluminate from precursors obtained by sol-gel or aqueous route from the salt solutions of aluminium and barium [112–115]. Kurihara *et al* [112] prepared several ternary metal oxides of the composition MAl$_2$O$_4$ (M = Mg, Ca, Ba, Ni and Co) from the aqueous salt solutions of the

respective metal ions; very fine particles of size ranging from 20 to 200 μm were obtained by calcining these gels. Multi-component oxides having perovskite or spinel structures were prepared from gels under refluxing conditions in the temperature range 100–700°C [113]; the products were nanometric in size and this method had an advantage in terms of operational cost and procedural simplicity. The oxides prepared by this method can be used in the preparation of ceramic shapes or in grounding mixes. Various other non-conventional methods for preparing BaAl$_2$O$_4$ were also reported [116–119]. These methods include hydrothermal synthesis from respective hydroxide gels followed by calcination [119].

Barium mono-aluminate (BaAl$_2$O$_4$) was synthesized by calcination of hydrothermally prepared precursors. The precursors were obtained through the hydrolysis of a mixture of nitrate solutions of barium and aluminum at 180°C using urea as the precipitating agent [120]. The XRD and FTIR of the sample precipitated at 180°C, showed it to be a mixture of orthorhombic BaCO$_3$ (α-BaCO$_3$) and boehmite (γ-AlOOH). The XRD patterns of compounds obtained on calcination at 500 and 800°C showed the presence of only crystalline BaCO$_3$, the reflections corresponding to any transitional alumina/boehmite being distinctly absent. The presence of barium carbonate and barium carbonate interlaced with alumina was observed in the SEM/EDS of the sample calcined at 800°C. XRD and FTIR confirmed the formation of BaAl$_2$O$_4$ $\geq$ 1000°C. The most probable sequence of reactions leading to the formation of barium monoaluminate was proposed on the basis of the XRD, SEM/EDS, TG-DTA and FTIR observations as : (i) conversion of aqueous aluminium and barium nitrates to BaCO$_3$-AlOOH by hydrothermal precipitation in the presence of urea, (ii) formation of orthorhombic BaCO$_3$-BaCO$_3$ interlaced amorphous alumina at 500–800°C and, (iii) finally resulting in the formation of the crystalline BaAl$_2$O$_4$ at about 1000–1200°C.

3.4.2. Barium hexa-aluminates :

Barium hexa-aluminate BaAl$_{12}$O$_{19}$ is the most refractory among all the barium aluminates (m.p. 1900°C) [121]; its thermal behaviour can be improved by doping with other oxides. Due to this reason, BaAl$_{12}$O$_{19}$ finds extensive applications as a combustion catalyst/catalyst support and as a structural ceramic for high temperature applications [122–126]. It is also interesting that barium hexa-aluminate has several structural modifications owing to its inherent non-stoichiometry in the composition. Stevel *et al* [127,128] had showed that BaAl$_{12}$O$_{19}$ has a β-alumina structure with the composition Ba$_{0.7}$Al$_{11}$O$_{17}$. Several authors [129–131] have confirmed this with some new structural suggestions based on either it has Ba poor or Ba rich compositions. Similar to barium monoaluminate, the most conventional method used to prepare barium hexa-aluminate is also the ceramic route. Sol-gel and aqueous precipitation followed by calcination routes are also widely practised to

synthesize $BaAl_{12}O_{19}$ Machida Masato et al [132,133] prepared high surface area $BaAl_{12}O_{19}$ from calcination of precursors obtained from hydrolyzing alkoxides with water. The amount of water added and the ageing period of hydrolyzed precursors strongly influenced the surface area of the products. High specific surface area $BaAl_{12}O_{19}$ powders were prepared by Kajuhiro et al [134] through hydrolysis of Al(OR)$_3$ with acids followed by mixing with an acid peptized sol of $BaCO_3$. The products obtained by this route were said to be suitable as supports for combustion catalyst. Barium hexa-aluminate refractory fibers were obtained by a sol-gel route from $Al_2(OH)_xCl$. $2.5H_2O$ and $BaCl_2$ solutions. Heat treatment of the gels at 100–1200°C produced $BaAl_{12}O_{19}$ [135]. Duhui et al [136] prepared $BaAl_{12}O_{19}$ for catalyst-support uses from respective nitrate solutions using citric acid as the neutralizing agent. It was seen that at 800°C $BaAl_2O_4$ started to form, while the formation of $BaAl_{12}O_{19}$ took place at higher temperatures (1200°C).

Hydrothermal treatment of mixtures of aluminium hydroxides or boehmites and BaO or barium hydroxides and firing the resulting products at 1000–1500°C produces high surface area $BaAl_{12}O_{19}$ suitable as a lubricating material or as a refractory for catalyst support use [137]. Barium aluminates with different compositions were prepared by Djuricic et al [138] from gels obtained by homogeneous precipitation from chloride solutions of Ba and Al using urea as the precipitating agent. The formation kinetics as well as the formation temperature of barium aluminates were found to depend on the secondary gel-treatment procedures prior to calcination. Microwave treatment of the gels before calcination resulted in the formation of β-aluminates at relatively low temperatures.

A high surface area (~22 m^2/g) micro-sized (0.3–2 µ) barium hexa-aluminate powder was prepared by the calcination (at 1400°C for 2 h) of hydrothermally prepared precursors of orthorhombic barium carbonate and boehmite [139]. The precursors were obtained by a hydrothermal treatment (at 180°C, for 1 h) of aqueous solutions of barium and aluminum nitrates of appropriate compositions in the presence of aqueous urea as the neutralizing precipitant. Results of XRD, TG-DTA and SEM measurements suggest the most probable reaction sequence for the preparation of barium hexa-aluminate ceramic powder as : (i) the hydrothermal precipitation of orthorhombic $BaCO_3$ and boehmite (γ-AlOOH) precursors from the aqueous Ba and Al nitrates in the presence of urea, (ii) the formation of an interim mixture of γ-Al_2O_3, $BaCO_3$ and Ba-β_1-alumina in the temperature range of 800–1200°C, and (iii) finally the formation of a ceramic powder of composition $BaO.6Al_2O_3$ having β-alumina type structure at ~1400°C. The final material did not show presence of any other phases like alumina, baria, barium mono-aluminate and tri-barium mono-aluminate phases. The SEM micrograph of barium hexaluminate is shown in Figure 2. Irregular block shaped particles having layered structures can be seen from the micrograph. This type of layered structure is associated with

barium β/hexa-aluminates. The approximate particle diameter value calculated from this micrograph is between 0.3–2 µ

Figure 2. The SEM micrograph of the hexa-aluminate sample obtain, on calcining the hydrothermally prepared precursor at 1400°C [139]

3.5. Manganese-doped barium hexa-aluminate :

Transition/non-transition metal ions are often introduced into the barium hexa-aluminate structure in order to improve its catalytic behavior and develop properties suitable for colored phosphor applications [140–142]. Among various metal ion doped barium hexa-aluminates, the Mn doped materials are most extensively studied as the presence of Mn does not affect the thermal stability, surface areas and phase compositions of the parent barium hexa-aluminates [143–146]. As the properties of the end-products are largely dependent on the synthetic routes followed and on the nature and history of the precursors, a careful choice of reagents and the preparatory route is essential to produce the desired end-materials. Several methods have been reported for the preparation of Mn-doped barium hexa aluminates [147–153]. These methods include (i) by evaporation of a homogeneous solution mixture of Ba, Al and Mn salts followed by calcination (the evaporation-calcination) route [147] impregnation of aqueous Mn^{2+} in Ba and Al hydroxides/oxo-hydroxides followed by calcination (impregnation-calcination route [148,149], and by calcination of precursors obtained through sol-gel routes using inorganic salt solutions of Ba, Al and Mn (sol-gel-calcination route [150–153].

High surface area (~25 m^2/g) Mn-doped barium hexa aluminates with compositions $BaMnAl_{11}O_{19}$ and $BaMn_2Al_{10}O_{19}$ were prepared by a combination of hydrothermal precipitation calcination route [154]. The precursors of the above two compounds were obtained by hydrolyzing a mixture of aqueous solutions of Ba, Al and Mn at 180°C for 1 h in the presence of urea. The XRD and FTIR analysis of the hydrothermally prepared samples showed the presence of carbonate and/or hydroxide phases of Ba and Mn and boehmite. Barium mono-aluminate ($BaAl_2O_4$), Ba-β_{11}-Al_2O_3, γ-Al_2O_3 and a small fraction of MnO, were observed after calcination of these hydrothermally prepared precursors at 1200°C. A mixture of Ba-β_1-Al_2O_3 and Ba-β_{11}-

Al_2O_3 phases were found after calcination at 1400°C for 2 h with no other oxide phases of Ba, Al or Mn.

4. Iron oxides for environment control

Schwertmann, Cornell and co-workers have done pioneering work for preparation of fine particles of iron oxides [155-159]. These includes ferrihydrites, goethite, hematite etc. Depending on the preparation conditions, size and shape of the oxides could be altered. Significant contribution in the field of preparing specific iron oxides has been made by many other researchers [160-172]. Mohapatra et al, have prepared pure crystalline goethite, metal ion doped goethite and studied the conversion of goethite to magnetite [173-175].

Goethite is considered an important material which can control the sorption capacity of soils for toxic metals. The adsorption of heavy metals on the outer surfaces of goethite is strongly influenced by their hydrolytic properties. Metals like Pb, Mn, Ni, Cu, Cd, Co with a high affinity for hydroxyl ions in solution also have a high affinity for the hydroxyl groups of the goethite surfaces. Not only for metal ions, goethite also has a high binding sites for anions like arsenate, phosphate, and molybdate which are tetrahedral oxy-anion and environment pollutant. These anions can adsorb on goethite surfaces competitively. Arsenate adsorbs strongly to iron-oxide surfaces in acidic and near-neutral-pH water [176,177]. Researchers have shown that arsenate is specifically adsorbed onto iron oxides such as goethite through an inner-sphere complex *via* a ligand exchange mechanism. Studies have shown that incorporation of metal ions like Al(III), Mn(II), Cu(II) in goethite matrix can improve its adsorption capacity for As(V) by three times , and remove As(V) from water to the required level of 50 parts per billion [177]. Goethite prepared by micro-emulsion technique showed manifold higher uptake of arsenic when compared to that obtained through co-precipitation method [13]. Studies on adsorption of organic matters, Cu(II), lead, zinc, uranium(VI), Mg(II), Mn(II), calcium, strontium, selenates *etc.* has been reported [178-184] on fine particles of iron and aluminium oxides. From a brief scan of literature it can be seen that preparation of active micron/nano-sized oxides for effluent treatment is an emerging and exciting area of research.

5. Conclusions

Aqueous processing route is versatile for preparation of variety of oxides/oxy-hydroxides and hydroxides. Depending on preparation conditions , morphology, particle size and shape of oxides can be altered. Fine particles in micron, sub micron or nano-size can yield products with altogether different properties. A brief review on preparation of hematite, Mn-Zn/Ni-Zn ferrite, ferrite grade zinc oxide, aluminum oxides/hydroxides/aluminates and Mn-substituted hexa-alumnates following aqueous processing as one of the steps has revealed that tremendous amount of research and development efforts have gone in this

field. Preparation of special oxides through aqueous route for environmental control has also been an active area of research.

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