Synthesis of nano particle of inorganic oxides by polymer matrix

P PRAMANIK

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India

Abstract. Ultrafine ($\leqslant 150$ nm) powders of spinels [MFe_2O_4 where M = Ni(II), Co(II) and Zn(II)]; rare-earth orthoferrites [$RFeO_3$ where R = Sm, Nd and Gd], and rare-earth garnets [$R_3Fe_3O_{12}$ where R = Sm, Nd and Gd] with good purity and chemical homogeneity were prepared through two new versatile chemical routes. The first route involved the coprecipitation of the desired metal nitrates from their aqueous solution, in presence of a water soluble polymer- polyvinyl alcohol (PVA), by triethyl ammonium carbonate solution. The other process involved complete evaporation of a mixture of optimum amounts of PVA and the desired aqueous metal nitrate solutions, with and without the addition of optimum amounts of urea when the mixture was evaporated to a pasty mass. In addition, detailed study on the reported potassium ferricyanide route was also carried out for the production of the rare-earth orthoferrite powders. The various precursor as well as the heat-treated mixed-oxide powders, prepared through each of the routes, were compared by the physical characterization studies involving thermal gravimetry and differential scanning calorimetry, infrared spectroscopy, X-ray powder diffraction, transmission electron microscopy, and room temperature magnetic measurements.

Keywords. Spinel; rare-earth orthoferrites; rare-earth garnets; ultrafine powders; chemical route; PVA; triethylammonium carbonate; potassium ferricyanide.

1. Introduction

The chemical synthesis route plays a crucial role in designing the final products and is also better and less cumbersome method for the production of fine-grained mixed-oxide powders. The benefit that can be obtained from the use of a controlled chemical processing route is well recognized (Uhlmann *et al* 1984), especially for multicomponent system. The use of chemistry in the preparation of materials can avoid three major problems—diffusion, impurities and agglomeration. The reason being that the fine chemically prepared powders allow for shorter diffusion distance and improved homogeneity, the chemical precursors used can be easily refined to increase the purity and careful control of solvent removal from the precursors will lead to the production of crushable agglomerate. However the chemical preparative routes generally involve more complex methods compared to the conventional ceramic routes and an improved level of skill is required for realizing the benefits. A variety of chemical synthesis routes exist for the preparation of fine grained mixed-oxide powders such as the precursor compound methods, the coprecipitation methods, the sol-gel methods, the solvent evaporation methods and the hydrothermal methods.

2. Experimental

In the present investigation, the author has developed the following versatile chemical synthesis routes for the preparation of fine-grained mixed-oxide powders. However, the author reports the synthesis of only the ferrite (spinel ferrites, iron garnets and orthoferrites) systems using these routes. The routes are: (i) Chemical coprecipitation using triethylammonium-carbonate (or, TEAC) solution, (ii) evaporation of the PVA

added mixed-metal-nitrate solution, in the presence and in the absence of optimum amounts of urea (i.e. (PVA + urea) and (PVA, nurea) methods respectively.

In addition, the following route has also been used by the author for the preparation of fine orthoferrite powders: (iii) ferricyanide precursor route.

2.1 TEAC coprecipitation method

The origin of TEAC method is from an attempt to modify the existing chemical coprecipitation routes. In the present method, an organic carbonate solution has been used as the precipitant in lieu of the traditionally used inorganic salt solutions where a proper pH control is essential for obtaining unsegregated product. Moreover, the use of inorganic salts (such as ammonium-hydroxides, -carbonates, -oxalates etc), are unsuitable as precipitants for mixed-oxide systems containing Cu(II), Zn(II), Cd(II), and Ni(II) ions. This is because these mentioned metal ions tend to form soluble complexes with ammonia and pass into the filtrate, subsequently changing the stoichiometry of the precursors. On the other hand, use of other inorganic salt solutions such as NaOH/KOH, $Na_2(C_2O_4)$/$K_2(C_2O_4)$ etc may result in contaminated precursor materials. Since the Na^+/K^+ ions tend to get occluded into the precursor matrix, their removal required extensive washings of the precursor material which enhances the possibility of loss of certain desirable cations from the system and consequently, the stoichiometry of the final product may get affected.

The use of organic salt solutions as precipitant overcomes the problems of contaminations of the precursor materials and hence also the tedious washings. The organic component, being volatile gets easily removed from the precursor material during calcination. Their removal during the calcination of the precursor material, adds to the amount of gases evolved during the process and thus facilitates the generation of powders with finer particles. Literature reports the use of triethylammonium-oxalate (Pramanik *et al* 1988) as a precipitant for a variety of mixed-oxide systems. However, this coprecipitation process requires a delicate control of exact oxalate ion concentration. Even a slight excess of oxalate ions in the mixture gives rise to soluble complexes of the metal oxalates, due to the formation of stable anionic complexes. And, even the multidented network structure of the organic oxalate fails to anchor all the metal ions, resulting in a possibility of leaching of the ions of the transition metals (such as: Cu(II), Zn(II), Ni(II), Cd(II), etc) from the precipitate. The TEAC solution is a mixture of distilled triethylamine, ethyl alcohol, water, and CO_2. Apart from having all the advantages of an organic based precipitant, the TEAC coprecipitating reagent has several other advantages. These are as follows:

(I) In the TEAC coprecipitation process, the solutions are mixed rapidly and the desired pH is reached more or less instantaneously. Thus, the highest level of supersaturation for each of the elements is achieved simultaneously and their segregation in the product is largely circumvented, provided the constituent cations do not have widely differing solubilities.

(II) A precise control of carbonate ion concentration is not required in the system i.e. an excess of the triethylammonium-carbonate in the mixture does not affect the final stoichiometry of the product.

(III) The triethylamine used in the preparation of TEAC solution, is less costly and commercially more viable than other higher order amines, such as tributyl- or tripropyl-amine, and this adds to the viability of the TEAC solution for large scale preparation of the mixed-oxide precursors.

(IV) The recovery process of triethylamine from the filtrate is relatively simple and this adds to the process economics.

In this process, the desired cationic salts are taken into aqueous solution in accordance with the required stoichiometry and thoroughly mixed in the presence of polyvinyl alcohol (PVA) (about 5% with respect to the predicted theoretical yield of the desired mixed oxide).

The precipitation is carried out by pouring the cationic mixture (heated at 70°C) into the required amounts of TEAC solution (heated at 70°C) with vigorous stirring. For complete precipitation, theoretically one mole of triethylammonium-carbonate is required for every gram-ion of metal present of valency two and every 2/3 gram-ion metal of valency three. However, in practice the TEAC solution is always kept in excess (1·5 to 2 times), to compensate for any dilution of the precipitating reagent as a consequence of volatilization of CO_2 gases from the system during heating. The resulting mixture is then put to heat to just before boiling with thorough stirring for 1 h and then the precipitate allowed to settle. After settling of the precipitate, it is separated through filtration. The mixed metal carbonate precipitate is dried in an air-oven at about 150°C and ground to fine powders. This resulting precursor yields the fine powders of the desired oxide-system on thermal decomposition.

The chemical reaction involved can be represented as follows:

$$M^{n+} + [(C_2H_5)_3NH]_2CO_3 \longrightarrow M_2(CO_3)_n + [(C_2H_5)_3NH]^+, \qquad (1)$$
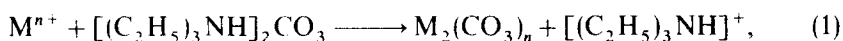
where M^{n+} represent the metal ion present in the system.

2.1a   *Role of PVA:*   The presence of the water soluble polymer, PVA, in the system during the precipitation process, using triethylammonium-carbonate, is expected to offer a three-dimensional polymeric network environment for the precursor nuclei. The precursor nuclei get embedded in this structure and consequently the formation of a three-dimensional network of the mixed-metal-carbonate complex is expected. This is supported by the observed colloidal nature of the precipitate.

2.1b   *Role of ethyl alcohol in TEAC solution:*   The presence of ethyl alcohol in the TEAC solution plays a dual role. It helps to keep the triethylammonium-carbonate (which is a mixture of distilled triethylamine, water, ethyl alcohol and CO_2 gas) in a homogeneous solution form. Additionally it also helps the colloidal form of the mixed metal carbonate precipitate and also prevents their loss from the system during the filtering process.

Pathak and Pramanik (1992) prepared a series of ceramic mixed-oxide systems through this route which include ceramic superconductors ($YBa_2Cu_3O_x$ and $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$), spinels, orthoferrites, and garnets. However, only the studies on the spinels [MFe_2O_4 where M = Ni(II), Co(II), and Zn(II)], the orthoferrites [$RFeO_3$ where R = Nd(III), Sm(III), and Gd(III)] and the garnets [$R_3Fe_5O_{12}$, where R = Y(III), Sm(III), and Gd(III)], are included in this paper.

2.2   *Polyvinyl alcohol added mixed-metal solution evaporation method:* (*in the presence of urea (PVA + urea) and in the absence of urea (PVA. nurea)*)
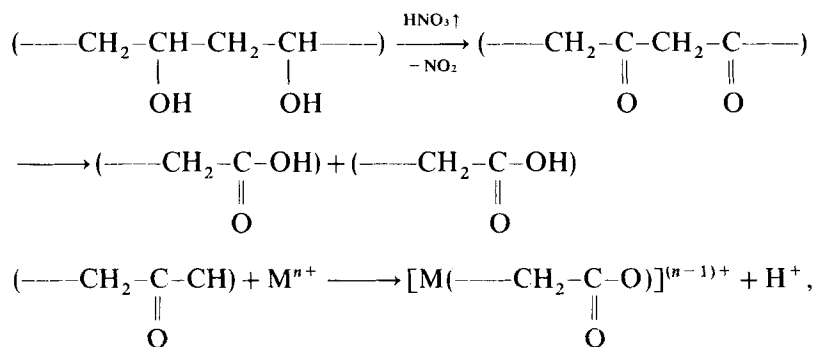
Polyvinyl alcohols (PVA) are widely used as binders for pelletization and moulding of various mixed-oxide powders. The PVA easily decomposes exothermally at low ignition

temperature (500°C), leaving behind very little carbon residue. The thermal gravimetry and differential scanning calorimetry (TG/DSC) curves have confirmed it. This characteristic of PVA along with its water soluble nature has motivated the initiation of this route. The route involves evaporation of a viscous PVA added mixed-metal-nitrate solution (between 130°C to 150°C) followed by calcination of the evaporated mass.

In case of the urea added process, the urea (by weight) is introduced into the system with thorough stirring, when the PVA-added mixed metal-nitrate solution evaporates to a pasty mass. The optimum urea to cation ratio is 1:1. Excess of urea in the system is observed to have a detrimental effect on the grain-size due to larger heat of calcination of the product. In this process, appropriate amounts of the desired metal-nitrates are taken into aqueous solution. They are thoroughly mixed and 10% (w/v) aqueous solution of PVA is then added to it, maintaining the desired metal ion to vinyl alcohol monomer unit of PVA mole ratio. The molecular weight of the polyvinyl alcohols (PVA) used for the present study is 1,25,000 Dalton. The PVA helps the homogeneous distribution of the metal ions in its polymeric network structure (by coordination through the secondary alcoholic groups), and inhibits their segregation/precipitation from the solution. The resulting viscous liquid mixture of PVA-metal-nitrate solution is gradually evaporated by heating between 130°C to 150°C, over a hot plate or spray dryer.

The PVA, in presence of nitric acid in the solution medium, gets oxidized to the corresponding ketone, and at elevated temperatures it is ultimately converted to the carboxylic acid with simultaneous C–C bond breaking. As evaporation proceeds, the nitrate salts also decompose with simultaneous liberation of brown fumes of NO_2. On complete evaporation of the PVA-added mixed-metal-nitrate solution (in presence/absence of urea), a voluminous, carbonaceous fluffy mass results, which is presumed to be constituted of metal carboxylates (which is expected to be formed *in situ*, from the reaction of the metal ions with the residue of the decomposed PVA), metal-oxides, undecomposed metal nitrates, and carbon. This composition is changeable depending on various experimental conditions such as: sample bed-temperature during the complete evaporation process, nature of metal ions present in the system, amount of PVA in the starting solution etc.

On the basis of the experimental findings, the following tentative reaction mechanism has been proposed for the decomposition of PVA and the subsequent *in situ* metal carboxylate formation:

$$
(\text{---}CH_2\text{-}CH\text{-}CH_2\text{-}CH\text{---}) \xrightarrow[-NO_2]{HNO_3\uparrow} (\text{---}CH_2\text{-}C\text{-}CH_2\text{-}C\text{---})
$$
$$
\quad\quad\quad\quad\underset{OH}{|}\quad\quad\quad\underset{OH}{|} \quad\quad\quad\quad\quad\quad\quad \underset{O}{\|}\quad\quad\quad\underset{O}{\|}
$$

$$
\longrightarrow (\text{---}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH) + (\text{---}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH)
$$

$$
(\text{---}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH) + M^{n+} \longrightarrow [M(\text{---}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}O)]^{(n-1)+} + H^+,
$$

where M^{n+} represents the metal ion present in the system.

In presence of urea in the system, the urea, which is added when the PVA added metal-nitrate solution evaporates to a pasty mass, is expected to decompose completely

during the complete evaporation process. The decomposition of urea can be given by the following equation:

$$H_2N - CO - NH_2 \xrightarrow{\Delta} NH_3 + CO_2 + HNCO.$$
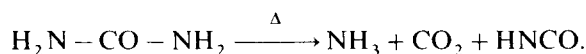
The liberation of ammonia, during the urea decomposition process, shifts the pH of the mixture (of the residual PVA and metal-nitrates) towards higher side (pH > 7). This altered, slightly alkaline environment, suppresses the *in situ* decomposition of the metal-nitrates as well as the reaction between the residual PVA and the nitrate ions during the complete evaporation process (at temperatures less than 150°C). The qualitative composition of the completely evaporated carbonaceous fluffy mass obtained through the PVA-mixed-metal-nitrate evaporation process in the presence of urea, does not differ much from that obtained in the absence of urea, except for the incorporation of some additional nitrate salts.

The voluminous carbonaceous fluffy mass obtained from the complete evaporation of the PVA-added mixed-metal-nitrate solution, in the presence/absence of urea, when ground to fine powders, produces the precursor powders. These precursor powders yield the fine powders of the desired oxide system on thermal decomposition. The high *in situ* temperature, attained during the exothermic decomposition of the precursor powder, facilitates the solid-phase reaction between the constituent metal ions. As a result the desired oxide-phase formation occurs at relatively low external temperatures. The exothermic decomposition of the precursor powder material is accompanied by the evolution of various gases. The evolution of gases not only helps the particles to disintegrate but also helps to dissipate the heat of combustion, thus inhibiting sintering of the fine particles.

A series of mixed-oxide systems including calcia, yttria-, magnesia-stabilized zirconia, lead zirconate titante, lanthanum modified lead zirconate titante, spinels, orthoferrites, and garnets, have been prepared through this route (Pramanik and Pathak 1994; Pramanik *et al* 1995).

2.3 *Ferricyanide precursor method*

This method is not new. It was first reported by Gallagher (1968), but detailed studies on particle size were not carried out. In the present investigation, an attempt has been made to make a detailed study on this route. The results obtained were from the characterization of the fine powders of orthoferrites obtained from the TEAC co-precipitation and PVA-mixed-metal-nitrate solution evaporation route.

In this process, the required amount of rare-earth-metal-nitrate aqueous solution (heated at 70°C) is added to the appropriate amount of potassium ferricyanide solution (heated at 70°C) with vigorous stirring. Fine crystalline precipitate of $R[Fe(CN)_6]$ XH_2O is obtained. The precipitate is gently washed with deionized water, to remove the KNO_3 solution that may be occluded in the precipitate. The precipitate is finally washed with acetone. The precursor compound is thermally decomposed during calcination to yield the fine powders of the respective orthoferrites system.

The chemical reaction involved in the formation of the metal-ferricyanide-precursor material is as follows:

$$R(NO_3)_3 + K_3[Fe(CN)_6] \longrightarrow R[Fe(CN)_6] + 3KNO_3. \tag{2}$$

3. Results and discussion

Characterization of the ultrafine mixed-oxide precursor materials, which were obtained through each of the mentioned chemical routes, has been done by the simultaneously recorded thermal gravimetry and differential scanning calorimetry (TG/DSC) studies. The various mixed-oxide precursors, as well as the subsequently heat treated mixed-oxide powders were further characterized by infrared (IR) spectroscopy studies between 400 and 4000 cm^{-1} region, by X-ray powder diffraction (XRD) studies, by transmission electron microscopy (TEM) studies and by room temperature magnetic studies using a vibrating sample magnetometer (VSM). The particle size of the various mixed-oxide powders, at various heat-treatment temperatures, were determined by X-ray line broadening and TEM studies.

As a specimen system, the particle size of nickel-iron ferrite (NIF) produced in different reaction conditions are summarized in table 1.

The TEM particle size measurement studies of the low temperature (450°C) heat-treated NIF powders, prepared through the mentioned methods, indicate that the TEAC method results in relatively finer particles (10–12 nm) than the particles obtained through the PVA solution evaporation route. It is also evident that the addition of optimum amount of urea in the PVA solution evaporation route [i.e. 6 PVA + urea) or (2·5 PVA + urea) methods]. The study also reveals that the 6 PVA method results in relatively coarser particles compared to the particles from the 2·5 PVA method. However at high heat-treatment temperature (900°C), all the powders attain similar values of the particle sizes.

3.1 Spinels

From the studies, it has been observed that the precursors of the spinel ferrites, obtained through the TEAC method and the PVA added solution evaporation route in presence of urea [i.e. (2·5 PVA + urea) and (6 PVA + urea)], are X-ray amorphous. On the other hand, the precursors through the (2·5 PVA, nurea) and the (6 PVA, nurea) methods, result in the respective single-phase ferrite formation in their virgin state. Whereas, the precursors through the (NPVA, nurea) method, are observed to give rise to mixed phases of the spinel ferrite, α-Fe_2O_3, and the oxides of the respective bivalent metal ions in their virgin state.

Table 1. Comparative values of NIF particle sizes obtained from XRD and TEA.

Preparative method	Heat-treatment at 450°C (2 h)			Heat-treatment at 700°C (2 h)			Heat-treatment at 900°C (2 h)		
	D_s	D_v	D_{TEM}	D_s	D_v	D_{TEM}	D_s	D_v	D_{TEM}
TEM	—	—	100–120	143	402	300–350	245	962	1000–1200
(2·5 PVA, NU)	232	373	300–400	232	403	—	298	1827	1000–1200
(2·5 PVA + U)	—	—	150–170	190	478	300–400	309	1092	1000–1200
(6 PVA, NU)	154	125	400–500	155	759	—	290	953	1100–1200
(6 PVA + U)	135	324	300–400	155	560	—	290	1259	900–1000

Note: D_s, D_v and D_{TEM} are diameters of the particles (in Å) obtained through Scherrer formula, variance method and TEM respectively.

Table 2. Comparative studies of the physical properties of the NiF powders.

Preparation route	Metal ion: vinyl alcohol monomer unit (mole ratio)	Particle size from TEM (avg.)	XRD phase	Magnetic studies (σ_m in emu/g)
TEAC method	—	10 12 nm	amorphous	Superpara-magnetic (1·9 emu/g)
(2·5 PVA, nurea) method	1:2·5	30 40 nm	single phase	Ferromagnetic (32·3 emu/g)
(2·5 PVA + urea) method	1:2·5	15 17 nm	amorphous	Superpara-magnetic (12·3 emu/g)
(6 PVA, nurea) method	1:6	40–50 nm	single phase	Ferromagnetic (32·0 emu/g)
(6 PVA + urea) method	1:6	30 40 nm	single phase	Ferromagnetic (26·7 emu/g)
(NPVA, nurea) method	1:0	—	mixed phase	—

The results of the XRD, TEM, and the magnetic studies, for the $NiFe_2O_4$ fine powders, prepared through the various routes and calcined at 450°C for 4 h, are summarized in table 2.

The spinel ferrite particles are observed to be spherical through the TEM studies. The particle sizes, calculated from the XRD line broadening and TEM studies, are observed to increase with increase in the heat-treatment temperature and time, for all the powders prepared through all the routes.

(i)   In the PVA solution evaporation method, the optimum vinyl alcohol monomer unit of PVA to metal ion mole ratio is observed to be 2·5:1 for the production of fine, single-phase, spinel ferrite powders.

(ii) The addition of optimum amount of urea, to the optimum PVA and metal-nitrate mixture, results in finer particles compared to its absence in the system, at low heat-treatment temperatures (< 600°C).

(iii) The EDXS studies show that, within the resolving power of instrument, the point to point homogeneity is observed to be the best for the spinel ferrite powders obtained through the TEAC method.

(iv) The superparamagnetic behaviour, observed in all the magnetic spinel powders prepared through the TEAC and the (2·5 PVA + urea) methods, vanishes with increase in the heat-treatment temperatures of the powders [beyond 600°C for the TEAC method and beyond 500°C for the (2·5 PVA + urea) method].

(v)   The values of the saturation magnetization of the fine spinel ferrite particles are observed to be low. The saturation magnetization values tend to approach the bulk values with increase in the particle size through increase in the heat-treatment temperatures of the powders.

(vi) TEAC (triethylammonium carbonate) is observed to be a good coprecipitating agent for the preparation of contamination-free, ultrafine, single-phase, spinel ferrite powders with good homogeneity. Through the TEAC coprecipitation method, control of the particle size can be obtained by an appropriate selection of the heat-treatment temperature and time.

(vii) The PVA solution evaporation route is technically simpler for the preparation of fine spinel ferrite particles at low external temperatures, compared to the other routes.

Through the various studies made and the experiments conducted, it can be concluded that, of the various routes considered, the TEAC and the (2·5 PVA + urea) methods are found to be the best for the production of homogeneous, single-phase, ultrafine powders of the desired spinel ferrite systems.

3.2 *Rare earth orthoferrite systems*

The precursors of RIO materials, prepared through the TEAC and the (2·5 PVA + urea) methods, are observed to be amorphous, while the precursors through the ferricyanide method show crystalline phase corresponding to the $RFe(CN)_6$ system. All the precursors, when calcined at 400°C, result in X-ray amorphous powders. These powders are observed to gradually crystallize into the respective RIO phase with increase in the heat-treatment temperatures.

(i) The powders through the (2·5 PVA + urea) method are observed to give rise to the respective crystalline RIO phase at a relatively low external temperatures (around 500°C) compared to the TEAC (800°C) or the ferricyanide method (above 600°C).

(ii) At low temperature heat-treatment of the powders, the TEAC method is observed to result in finer particles ($\approx$ 15–20 nm) compared to the particles prepared through the ferricyanide method (20–30 nm) or, the (2·5 PVA + urea) method (30–40 nm). This is clearly depicted in tables 3–5.

(iii) At high temperature heat-treatment of the powders, the particle sizes of the powders produced through the ferricyanide and the (2·5 PVA + urea) methods are observed to have similar values (80–100 nm), while powders through the TEAC method still result in comparatively lower particle sizes (60–70 nm).

(iv) The crystallite/particle agglomeration is observed to be higher in the powders which are prepared through the TEAC method and heat-treated at lower temperatures ($\approx$ 600°C) than those which are prepared through the ferricyanide or the (2·5 PVA + urea) method under similar heat-treatment conditions. The observed agglomeration decreases with increase in crystallite/particle sizes through increase in the heat-treatment temperatures. The RIO powders through the (2·5 PVA + urea) and the ferricyanide methods are observed to be porous aggregates.

(v) The magnetic studies show that RIO powders possess high magnetic anisotropy and the magnetic saturation is not attained within the maximum field of 15 KOe. The magnetization values are observed to improve with increase in the heat-treatment temperatures. The powders, through the TEAC method, are observed to produce better magnetization while the magnetic anisotropy appears to be higher for the powders prepared through the ferricyanide route.

(vi) The RIO powders prepared through the ferricyanide route are observed to be the best in terms of the cation homogeneity, since an exact one-to-one cation stoichiometry can be maintained in the precursor material through the $RFe(CN)_6$ compound formation. All the powders are observed to improve and attain similar degree of cation homogeneity with the increase in the heat-treatment temperatures.

Thus it can be concluded that the ferricyanide method is indeed a better method for the production of RIO powder with good homogeneity and moderately good particle

Table 3. Crystallite sizes of the calcined (400°C, 2 h) SmFeO$_3$(SIO) powders.

Heat treatment temperatures	Crystallite size from $d_{[111]}$ line (Å)		
	TEAC method	Ferricyanide method	(2·5 PVA + urea) method
600°C (2 h)	Amorphous	Amorphous	313
800°C (2 h)	290	300	370
900°C (6 h)	372	453	410
1400°C (2 h)	455	508	509

Table 4. Crystallite sizes of the calcined (400°C, 2 h) NdFeO$_3$ powders.

Heat treatment temperatures	Crystallite size from $d_{[111]}$ line (Å)		
	TEAC method	Ferricyanide method	(2·5 PVA + urea) method
600°C (2 h)	Amorphous	Amorphous	340
900°C (6 h)	450	510	510
1400°C (2 h)	420	510	510

Amorphous: represents that the powders are X-ray amorphous i.e. the crystallite sizes < 200 Å.

Table 5. Maximum magnetization (σ_m) values for the calcined (400°C, 2 h) GIO powders obtained at 15 KOe.

| Preparative route	σ_m (emu/g) for the GIO powders, heat-treated at various temperatures			
	650°C (3 h)	730°C (3 h)	900°C (6 h)	1400°C (2 h)
TEAC	1·253	1·345	1·335	1·310
(2·5 PVA + urea)	1·271	1·275	1·257	1·302
Ferricyanide	1·328	1·328	1·053	1·332

Saturation magnetization (σ_m) values for the GIO single crystal is equal to 1·046 emu/g (Moskvin and Sinitsyn 1973).

size control. The TEAC method gives rise to finer particles with better particle size control. The (2·5 PVA + urea) method is suited for the preparation of the RIO powders at relatively lower external temperatures.

3.3 *Rare earth iron garnet*

The precursors of the RIG materials, prepared through the TEAC, (2·5 PVA + urea), and (2·5 PVA, nurea) methods, are observed to be X-ray amorphous. They remain amorphous even after calcination at 450°C for 2 h. All the precursors are observed to crystallize into the garnet phase through an intermediate nucleating phase of the respective orthoferrite and α-Fe$_2$O$_3$. Increase in the heat-treatment temperatures

facilitates the transformation

$$3RFeO_3 + \alpha\text{-}Fe_2O_3 \rightarrow R_3Fe_5O_{12}.$$
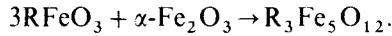
(i) The (2·5 PVA, nurea) route realizes the formation of almost pure RIG system at faster rates and at lower external temperatures (around 900°) compared to the other two methods. However, through all the routes the RIG phase is realized as the dominant oxide phase after heat-treatment around 800°C to 900°C.

(ii) With increase in the heat-treatment temperatures up to 1100°C, the crystallite/particle sizes show an increase along with an increase in the fraction of the RIG phase in all the systems.

(iii) The average particle sizes observed from TEM at low heat-treatment temperature (600°C) of the RIG powders are 20–25 nm for the TEAC method, around 30 nm for the (2·5 PVA + urea) method, and about 35 nm for the (2·5 PVA, nurea) method. High temperature (900°C) heat-treatment of the RIG powders, results in higher particle sizes: 60–70 nm for the TEAC method, and 120–140 nm for the (2·5 PVA + urea) and the (2·5 PVA, nurea) methods. The IEM studies also reveal that distributions in particle sizes for the RIG powders prepared through all the three routes are narrow.

(iv) At low heat-treatment temperatures (600°C), the agglomeration observed is high for the powders through the TEAC method, while the (2·5 PVA + urea) and (2·5 PVA, nurea) methods result in porous agglomerates. With heat-treatments at higher temperatures (900°C) the RIG powders through the TEAC method result in the formation of porous-clusters, and those prepared through the (2·5 PVA + urea) and (2·5 PVA, nurea) methods result in the formation of ragged and angular particles with agglomeration to some extent.

(v) The room temperature magnetic measurements show that TEAC method results in RIG powders with much lower values of maximum magnetization (σ_m, at 12 KOe) compared to the RIG powders through the PVA evaporation routes. The magnetization values for all the RIG systems are low at low heat-treatment temperature (600°C). The values, in general, are observed to increase within the heat-treatment temperatures and approach the saturation magnetization of the bulk sample.

(vi) The highest values of maximum magnetization (δ_m) at 12 KOe, obtained for the RIG powders, which are prepared through the TEAC, (2·5 PVA + urea) and the (2·5 PVA, nurea) routes, follow the following order:

$$(\sigma_m)_{TEAC} < (\sigma_m)_{(2\cdot5\,PVA,\,urea)} < (\sigma_m)_{(2\cdot5\,PVA,\,nurea)}.$$

Of all the three routes, (2·5 PVA, nurea) method results in almost single phase RIG system with highest formation rate and at the lowest temperature (900°C). These powders also result in the highest values of magnetization, with particle sizes ranging between 120–140 nm. The TEAC method results in finest particles (60–70 nm) though the fraction of RIG phase formation is lower than the PVA evaporation routes.

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