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Abstract

Microwave-assisted route for the synthesis of nanomaterials has gained importance in the field of synthetic technology because of its faster, cleaner and cost effectiveness than the other conventional and wet chemical methods for the preparation of metal oxide nanoparticles. In the present work, synthesis of metal oxide nanoparticles viz., $\gamma$-$\text{Fe}_2\text{O}_3$, NiO, ZnO, CuO and Co-$\gamma$-$\text{Fe}_2\text{O}_3$ were carried out by microwave-assisted route through the thermal decomposition of their respective metal oxalate precursors employing polyvinyl alcohol as a fuel. The metal oxide nanoparticles are then characterized for their size and $\gamma$ to $\alpha$ (in $\gamma$-$\text{Fe}_2\text{O}_3$) transition and structure by employing powder X-ray diffraction (XRD) pattern, high-temperature X-ray diffraction (HTXRD) pattern and Fourier transform infrared (FT-IR) spectral studies. The morphology of the samples ranged from nanorods to irregular-shaped particles for different metal oxide samples on the basis of scanning electron microscopy and transmission electron microscopy images. Frequency-dependent dielectric study of the ferrite samples ($\gamma$-$\text{Fe}_2\text{O}_3$ and Co-$\gamma$-$\text{Fe}_2\text{O}_3$) showed a similar behaviour, where the dielectric constant decreased rapidly with increase in frequency. Possible explanation for this behaviour is given.

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Keywords: Metal oxides; Nanomaterials; Microwave-assisted route; Morphology

1. Introduction

Metal oxides are of interest to many scientific and technological disciplines. In particular, nanostructures of these materials have attracted considerable interest as they exhibit materials properties that differ strongly from those of the bulk phases [1]. These particle size effects enable tailoring the materials to a wide range of applications including magnetic ferrofluids, electronics and catalysis. Typical metal oxides of interest include semiconducting or metallic oxides of the type ZnO, TiO$_2$, NiO, Fe$_2$O$_3$, doped $\gamma$-Fe$_2$O$_3$ and Cr$_2$O$_3$ [2].

New synthetic routes for the preparation of ultrafine and nanosized metal oxides to obtain defined properties are under constant investigation and some of them include sol–gel [3], metal oxide chemical vapour deposition [4], coprecipitation [5], microemulsion [6], by hydrolysis in polylol medium [7] and decomposition of the precipitates prepared from non-aqueous precipitation routes [8]. These methods are employed producing precursor powder with an intimate mixture of initial constituents so as to require lower calcinations temperature. Here, the critical factor can be evaporation of solvents due to inhomogenity and formation of segregated phases. Many of these methods involved in the synthesis of metal oxides are tedious, some of them time consuming with many reaction steps and often in many cases a small quantity of material could be synthesized and also the formation of agglomerates can not be ruled out. Sekar and Patil [9] have reported the use of single precursor (metal hydrazinate complexes) for synthesis of metal oxide nanoparticles; however, this procedure has limitations of obtaining metal oxide nanoparticles in very less quantity and the synthesis reaction is highly exothermic in nature.

The microwave-assisted route is yet another method for the synthesis of metal oxides and has been gaining significance in the synthesis of oxide nanomaterials [10].
Microwaves have been used for the acceleration of organic chemical reactions for some time, because the method is generally fast, simple, energy efficient and less time consuming [11]. Unfortunately, the exact nature of microwave interactions with reactant during the synthesis of materials is somewhat unclear and speculative. However, energy transfer from microwaves to the material is believed to occur either through resonance or relaxation, which results in rapid heating. Clark and Sutton [12] have reviewed various aspects of microwave applications reported in the literature. Now a days, several reports have appeared which explain the microwave synthetic route [13,14]. Many microwave preparations reported in the literature have been made on the laboratory scale of only a few grams [15–17]. These preparations have been made with the use of domestic microwave ovens operating at 1 kW (2.45 GHz frequency). However, the use of higher power levels for synthesis of ceramics for specialized applications have also been reported [18,19].

Looking into the difficulties in the encountered synthesis of metal oxide nanoparticles, use of single-pot synthesis/ single-type precursor synthesis is thought to be beneficial on many counts, some of which include; employing a similar procedure reduces the number of precursors to be chosen, which helps in better understanding of the synthetic procedure. When the synthetic procedures are chemically understood, their reproducibility is easily attained. Also, once the synthetic route is understood, extending the procedure for syntheses of other metal oxide nanoparticles will be easier. Hence, a single synthetic procedure will then be a model synthetic approach. Keeping these criteria in view, the present investigation to obtain different metal oxide nanoparticles in a simple/ efficient route is undertaken and is being reported here.

Present work reports the synthesis of metal oxide nanoparticles using metal oxalate precursors employing microwave-assisted route. In search of a suitable economic fuel, our use of polyvinyl alcohol (PVA) has shown promising result in the conversion of metal oxalate precursors to its respective metal oxides having nanodimensions and possessing interesting morphologies. Metal carboxylates as precursors are chosen, as they are understood act as to model compounds in chemical reactions [20]. Some of the possible reasons for employing PVA as a fuel in the present studies are PVA has broad melting and decomposition temperatures, which are widely separated. Metal oxalate precursors are well dispersed in the molten PVA on its melting, and also PVA is known to be good surfactant and a dispersant. Hence, the precursor will be well dispersed in the molten PVA which is a much needed phenomenon in combustion process. PVA has alcoholic groups that can bind to precursor particles so as to facilitate the chemical reaction. The combustion reaction is exothermic with evolution of large amount of gases, which results in converting the precursors to partially decomposed form. Further, microwave heat treatment for the partially decomposed form is found essential for the complete conversion to nanoceramics. The characterization of the prepared metal oxides was undertaken by employing structural (X-ray diffraction (XRD), high-temperature X-ray diffraction (HTXRD)), spectroscopic (Fourier transform infrared (FT-IR)) and surface morphological (scanning electron microscopy (SEM) and transmission electron microscopy (TEM)) techniques.

Ferrites are, in general, called as dielectric materials and their dielectric constant decreases with increase in frequencies. It is interesting to observe the changes in dielectric value of the nanoferrites and its behaviour with variation in frequencies. Hence, this study is also being reported here and the possible explanation is given for the results observed.

2. Experimental part

2.1. Materials and methods

Ferrous ammonium sulphate hexahydrate, nickel sulphate, zinc sulphate, copper sulphate, cobalt sulphate, oxalic acid and other chemicals employed in the present study were of AR grade. PVA of molecular weight 125,000 was obtained commercially.

2.2. Preparation of precursors

The hydrated metal oxalate precursors viz. ferrous oxalate, nickel oxalate, zinc oxalate, copper oxalate and cobalt (Co)-doped ferrous oxalate were prepared by dissolving equimolar proportions of the respective metal salts (sulphates) and oxalic acid in minimum volume of water and was stirred for about 15 min on a magnetic stirrer. The different metal salts show different coloured precipitate at different pH range of 2–6. The precipitates of respective metal oxalates were washed with cold distilled water till it was free from the respective sulphate and excess oxalic acid and finally, the precipitate was washed repeatedly with dry acetone and then dried under vacuum.

2.3. Syntheses of nanosized γ-Fe2O3, NiO, ZnO, CuO and Co-γ-Fe2O3

Syntheses of the above nanoceramics were carried out by employing microwave-assisted route as follows.

The prepared metal oxalate precursors were mixed with PVA in the weight ratio 1:5 individually and ground well using pestle and mortar. The mixture was transferred into a crucible and ignited in an electrical oven individually. The dispersed phase ignited with the evolution of large volume of gases. Here, PVA reacts with the precursor and only a partially decomposed product (possible having high dielectric constant) was obtained, after the complete evolution of gases. The temperature of the process does not exceed 300 °C at any time. Chemical and physical characterisation of the partially decomposed products did not give any confirmable phases. The possible reason for a
partially decomposed product formed may be attributed to the low temperature of the reaction giving rise to the insufficient energy needed for complete conversion. However, as all the samples possessed high dielectric constant, hence are treated in a microwave oven to get the desired product. This partially decomposed product was placed in a domestic microwave oven having frequency 2.45 GHz for about 0–30 min at various power levels 0–90% [10]. The solids burn by producing different coloured light depending upon the metal present in the carboxylate precursors and leaving behind respective metal oxides.

2.4. Calculation of crystallite size from X-ray diffraction

Detailed knowledge of crystallite size, shape and strain in a finely divided powder often helps to correlate many physical properties of a system undergoing transformation in a solid-state reaction. X-ray line broadening analysis provides a method of finding bulk average size of coherently diffracting domains and r.m.s. strain. The average crystallite size \( D \) from X-ray line broadening has been calculated using the Scherrer equation [21,22].

\[
D = \frac{0.9\lambda}{\beta_{1/2} \cos \theta},
\]

where \( \lambda \) is the wavelength of the X-ray beam, \( \beta_{1/2} \) is the angular width at the half-maximum intensity and \( \theta \) is the Bragg angle.

2.5. Density measurement

2.5.1. Density evaluation from X-ray data

The X-ray density of the samples have been computed from the values of lattice parameters using the formula [23]

\[
d = \frac{8M}{Na^3},
\]

where 8 represents the number of molecules in a unit cell of a spinel lattice, \( M \) the molecular weight of the sample, \( N \) the Avogardo’s number and \( a \) the lattice parameter of the sample.

The lattice constant for the structure was calculated using the equation

\[
d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}.
\]

2.5.2. Tap density

The as prepared metal oxides were crushed in an agate mortar and a known amount of this powder was filled into a graduated cylinder of 25 ml capacity. The cylinder was tapped until the powder level remains unchanged. The volume occupied by this powder in the tube was noted. The ratio between the weight of the substance and the volume gives the tap density. The procedure followed here is as per our earlier work for understanding the tap density of \( \gamma \)-Fe₂O₃ samples synthesized from different precursors [24].

2.5.3. Powder density

The powder densities were determined using Archimedes principle [25] with a pycnometer of 25 ml capacity and xylene as a liquid medium. The following weights were taken and used in the density calculation.

\[
\rho_{\text{sample}} = \frac{(W_2 - W_1)\rho_{\text{sol}}}{(W_4 - W_3) + (W_2 - W_1)},
\]

where \( W_1 \) is the weight of the bottle (g), \( W_2 \) is weight of the bottle + substance (g), \( W_3 \) is weight of the bottle + substance + xylene (g), \( W_4 \) is weight of the bottle + xylene (g), \( \rho_{\text{sol}} \) is density of xylene and \( \rho_{\text{sample}} \) is the density of sample.

2.6. Characterization

The XRD patterns were obtained employing a Geol JDX-8p spectrometer using CuK\( \alpha \) radiation. The X-rays generator was operated at 30 kV and 20 mA. The scanning range, \( 20/\theta \) was selected. The scanning speed of 1°/min was employed for precise lattice parameter determination. HTXRD patterns were obtained by Philips X-Pert- PRO. The shape, size and microstructure of the prepared metal oxides were examined using Leica-440 Cambridge Stereoscan, scanning electron microscope image. The SEM was operated at 20 kV. The samples were made conducting by the sputtering of gold using a Poloron DC “sputtering unit” operated at 1.4 kV and 18–20 mA. The TEM images were obtained by Technai-20 Philips transmission electron microscope. The transmission electron microscope was operated at 190 kV. The FT-IR spectra of metal oxides were recorded on a Perkin-Elmer FT-IR spectrophotometer (Model 1000) in the range 400–4000 cm\(^{-1}\). Dielectric measurements were taken on a HP-4192A impedance analyser for samples prepared in the pellet form of 1 cm of diameter and 1 cm in thickness.

3. Results and discussion

3.1. X-ray diffraction studies

The XRD patterns of the synthesized metal oxides are shown in Figs. 1–5. The samples produce diffraction pattern with large number of peaks. The \( d \)-spacing values of all the samples matches well with standard JCPDS files of their respective metal oxides and are given in Table 1. Unit cell parameters were obtained by least-square refinement of the powder XRD data. XRD study reveals that the products are monophasic metal oxides with cubic spinel structure having nanosized particles; the values in the parenthesis indicate respective Miller indices.
3.2. High-temperature X-ray diffraction studies

HTXRD is carried out to know the Curie transition temperature (γ-Fe$_2$O$_3$ to α-Fe$_2$O$_3$) of one of our sample i.e., γ-Fe$_2$O$_3$. Fig. 6(a–f) show the indexed HTXRD pattern of γ-Fe$_2$O$_3$ at different temperatures i.e., at room temperature, 100, 200, 300, 375 and 450 °C, respectively. The lattice parameters are in good agreement with the data reported in the literature (JCPDS file 4-755).

![Indexed XRD pattern of the synthesized γ-Fe$_2$O$_3$ and inset shows the TEM image of γ-Fe$_2$O$_3$.](image)

Fig. 1. Indexed XRD pattern of the synthesized γ-Fe$_2$O$_3$ and inset shows the TEM image of γ-Fe$_2$O$_3$.

3.3. Crystallite size and density

The crystallite size of the samples calculated from XRD data is given in Table 1. It is observed from the Table 1 that, all the samples have different crystallite sizes, which is supposed to depend on solid-state transformation reactions, which generally adopts the habit of its precursors [26]. Thus, the conversions of the parent precursors into its respective oxides are considered to be topotactic in nature, indicating that the synthesis of precursors with very small...
particle sizes would be required for obtaining nanosized metal oxide samples. However, it must be pointed out that the crystallite size is not the only important factor influencing the properties of ceramics, but the particle shape is also a crucial factor for magnetic and other electronic applications of the nanomaterials [27]. The density of the samples calculated from XRD data, tap density and powder density is given in Table 1. It is interesting to observe from the Table 1 that, all the samples have approximately same density. Possible reason may be attributed to their average shape which might have similar surface area as seen from SEM images (Figs. 1–5(a and b)); any change in mass might have been compensated by volume changes which resulted in almost same packing fraction thus resulting in similar tap density for all samples.

3.4. Scanning electron microscopy

The particle morphology of the prepared ceramic materials were studied by using SEM images.

Inset of Fig. 1(a and b) shows the particle morphology of $\gamma$-Fe$_2$O$_3$ samples at low and high magnification,
respectively. The particles are mostly irregular shape with a nanometer range. Some particles are found as agglomerates. Flakes of agglomerates of γ-Fe₂O₃ nanoparticles are also observed. The particles of γ-Fe₂O₃ show irregular-shaped blocks of sub-microdimensions.

Inset of Fig. 2(a and b) shows the SEM of the as synthesized NiO sample at low and high magnification, respectively. The nanosized nickel oxide particles form globular aggregates of microdimensions. These aggregates are almost similar throughout indicating uniform particle dimension (shape and size). However, in the higher magnification, some smooth solid blocks are observed. These smooth blocks may be due to very close packing of the nickel oxide nanoparticles.

Inset of Fig. 3(a and b) shows the SEM of the as synthesized ZnO sample from its oxalate precursor at low and high magnification, respectively. Self-assembled nanorods of zinc oxide, forming globular network with microdimensions, are observed. On higher magnification, some nanosized spherical particles are also observed along with the nanorods of zinc oxide.

Inset of Fig. 4(a and b) shows the SEM images of the as synthesized CuO sample at low and high magnification, respectively. Some particle agglomerates with globular shape are also observed. The high-magnification images clearly shows the presence of nanorods along with globular-shaped particles.

Inset of Fig. 5(a and b) shows the SEM images of the as synthesized Co-γ-Fe₂O₃ sample at low and high magnification. The irregular flower-like structures are observed in the image along with the presence of some rod-shaped particles.

From the above observation of SEM images, it may be concluded that all the ceramic materials showed nanosizes, forming different shapes and sizes of agglomerates starting from nanospheres to nanorods. The finer details of the dimensions and shapes have to be structured employing TEM results of the samples.

3.5. Transmission electron microscopy

The nanocrystalline nature of the microwave-assisted nanoceramics was further confirmed by TEM images. The bright-field TEM images represent the basic powder morphology of the smallest visible ultrafine particles that might be identified with the crystallites or their aggregates.

Inset of Fig. 1 shows the TEM image of γ-Fe₂O₃ sample. The particles of needle-shaped (acicular images) structure of γ-Fe₂O₃ of width 50 nm (1:10) are observed. It may be envisaged that this type of morphology of the γ-Fe₂O₃ will have applications in magnetic recording media.

Inset of Fig. 2 shows the TEM image of the synthesized NiO sample. This image shows that the particles have

| Metal oxides  | JCPDS file no. | Crystallite size (nm) | Density (kg/m³)          |
|--------------|----------------|-----------------------|--------------------------|
| γ-Fe₂O₃      | 4-755          | 26.2                  | 4998 5048 3518           |
| NiO          | 47-1049        | 32.8                  | 4936 5021 3604           |
| CuO          | 05-0661        | 23.8                  | 4945 4992 3621           |
| ZnO          | 36-1451        | 32.2                  | 4990 5026 3720           |
| Co-γ-Fe₂O₃   | 03-0864        | 49.0                  | 4988 5050 3520           |

Fig. 5. Indexed XRD pattern of the synthesized Co-γ-Fe₂O₃ and inset shows the TEM image Co-γ-Fe₂O₃.
separated into individual particles from their agglomerates noticed on SEM images. From the TEM images we can understand that the individual NiO particles are nanosized and spherical, and that they retain their morphology when giant agglomeration takes place.

Inset of Fig. 3 shows the TEM image of ZnO sample with particles of size 10 nm, further that the finer resolution is not possible under existing experimental conditions. The particles seem to be closely joined forming agglomeration. These results are in concurrence with observations made by SEM images of this sample.

Inset of Fig. 4 shows the TEM image of the as synthesized CuO sample. Particles of approximately 10 nm dimensions with spherical-shaped particles are observed. These particles are very closely joined together to form fine nanospheres.

Inset of Fig. 5 shows the TEM image of as synthesized Co-\gamma-Fe₂O₃ sample. Very fine particles of <10 nm compactly packed to form the irregular flower-like particles as noticed on SEM images are observed. From these TEM images, we can conclude that fine nanoparticles of the ceramic materials are obtained by employing microwave-assisted synthetic route.

3.6. Infrared spectroscopy

Infrared studies were performed aiming to ascertain the metal-oxygen and nature of the synthesized metal oxide ceramics. Metal oxides generally give absorption bands below 1000 cm⁻¹ arising from inter-atomic vibrations. FT-IR spectra of the samples \gamma-Fe₂O₃, NiO, ZnO, CuO and Co-\gamma-Fe₂O₃ are shown in Fig. 7(a–e). The \gamma-Fe₂O₃ sample shows the absorption in the region 3100, 1080, 550 and 450 cm⁻¹. The peak at 3100 cm⁻¹ corresponds to water of adsorption and the peak at 1080 cm⁻¹ is due to the presence of some overtones. The peaks at 550 and 450 cm⁻¹ correspond to the metal-oxygen vibrational modes of the spinel compound; also the two peaks are characteristics of
spinel compounds [28]. These two peaks are sharp and are of strong intensity. The NiO, ZnO, CuO and Co-γ-Fe₂O₃ sample also shows similar metal-oxygen vibrational frequencies. All the prepared samples show vibrations in the region 385–690 cm⁻¹ which are assigned to metal-oxygen stretching vibration and broad peaks observed at 1600–1640 and 3100–3600 cm⁻¹ are due to water of hydration. The metal-oxygen frequencies observed for the respective metal oxides are in accordance with literature values [29].

3.7. Dielectric behaviour

The dielectric properties of ferrites are dependent upon several factors, including the method of preparation, chemical composition and grain structure or size. We report here the dielectric constant and its variation with frequencies for γ-Fe₂O₃ samples prepared from different precursors have been reported earlier [30,31]. Fig. 8(a–b) shows the frequency-dependent dielectric behaviour plot of γ-Fe₂O₃ and Co-γ-Fe₂O₃ samples, respectively. The initial
The dielectric constant of Co-γ-Fe$_2$O$_3$ has considerably decreased when compared with the initial value of γ-Fe$_2$O$_3$ sample. This behaviour is felt unexpected, as Co-doped γ-Fe$_2$O$_3$ should possess higher resistance. However, it may be explained with caution that particle shape (morphology) and size (agglomerations) has played a significant role. The dielectric polarization between Fe$^{3+}$ and Co$^{2+}$ ions in the spinel lattice decreased and a possible electron jump between these ions leads to higher conductivity value in Co-doped γ-Fe$_2$O$_3$, thereby lowering the dielectric value. The rapid decrease in the dielectric value of both the samples as frequency is a general feature of all the ferrites [30,31]. The interesting part here is the observation of comparatively higher dielectric value of Co-γ-Fe$_2$O$_3$ when compared with γ-Fe$_2$O$_3$ at higher frequencies. The higher dielectric constant of Co-γ-Fe$_2$O$_3$ sample indicates the freezing of the polarization between Fe$^{3+}$ and Co$^{2+}$ ions. A detailed understanding of this phenomenon would be future aspects of our work at a later stage.

4. Conclusions

In this study, we envisage a simple and efficient synthetic procedure in the synthesis of different metal oxide nanoparticles choosing a single precursor. The use of PVA as a fuel in the synthesis is new and the present synthetic procedure may be applied for the synthesis of other metal oxides and even for the synthesis of mixed metal oxide nanoparticles. This procedure may be extended for large-scale synthesis of metal oxide nanoparticles. The results obtained from crystallite size from XRD and TEM images confirm the nanocrystalline nature of the synthesized products. The particle shape and size plays a significant role in the dielectric properties of the metal oxides.

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