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A Review on Magnetic Properties, Synthesis , Characterization, and Applications of Mn-Ni Fe2O4 Ferrites.

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A Review on magnetic properties, synthesis, characterization, and applications of Mn-Ni Fe_2O_4 Ferrites.

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Abstract

Due to its numerous uses in a variety of fields, researchers are very interested in the study of characterization and synthesis of Mn-Ni ferrites. A group of soft magnetic materials called Mn-Ni ferrites have excellent electrical, magnetic, and optical characteristics. High coercivity, saturation magnetization, permeability, permittivity, resistivity, low power losses, and permeability values are among the characteristics of Mn-Ni ferrites. Mn-Ni ferrites are useful because of their usage in different fields. These ferrites are useful in the biomedical area, in transducers, in electronic applications, transformers, and in inductors are all made using Mn-Ni ferrites. Additionally, magnetic fluids, sensors, and biosensors utilize these ferrites.

Keywords: composite, supercapacitor, energy density, ferrites, power density

Introduction

Iron oxide (Fe_2O_4) is a type of ceramic compound that can be chemically coupled with one or more other metallic elements to form ferrites. They are one of the rare materials with both ferrimagnetic and electrically nonconductive qualities, which means they can be magnetized or drawn to a magnet [1]. Based on their magnetic coercivity, ferrites can be categorized into two families. 1. Hard ferries. 2. Soft ferrites. High coercivity hard ferrites are challenging to demagnetize [2]. Moderator magnets, loudspeakers, and tiny electric motors are used to create magnets. On the other hand, Low coercivity is found in soft ferrites. They are used to create ferrite cores for inductors, transformers, and a variety of microwave components in the electronics sector. The chemical compound barium ferrite, often known as BaFe or BaM, has the formula $BaFe_2O_4$ [3]. Magnetic stripe cards and loudspeaker magnets both contain similar ferrite elements. Ferrite compounds offer great corrosion resistance and are quite inexpensive

because they are mostly constituted of iron oxide. In 1930, Tokyo Institute of Technology scientists Yogoro Kato and Takeshi Takei created the first ferrite compounds [4].

Supercapacitors have energy storage gadget because of their potentially promising uses memory backup systems, and mobile electronic devices as well as their ability to provide energy densities [5]. According to their charge storage techniques, supercapacitors of electrochemical capacitors are categories into two types. Name of first is electric double-layer capacitor , where capacitance is produced by the storage of electrostatic charge [6]. The second group is known as a pseudo capacitor, which uses faradaic reactions but functions more like a capacitor. Due to their diverse valence states, excellent corrosion resistance, good electrochemical stability [7], environmental friendliness, and mild magnetization, ferrites are regarded as a leading material for energy storage. Due to their adjustable structural property, spinel ferrites like $MnFe_2O_4$, $CuFe_2O_4$, $CoFe_2O_4$, $MgFe_2O_4$, and $NiFe_2O_4$ are of more interest [8]. At spinal ferrites, oxygen ions form a cubic tight packing with divalent in octahedral and trivalent ions in tetrahedral positions [9]. Spinel ferrites are a dominant force in the pseudo capacitive phenomenon of energy storage because of the synergetic impact of iron (Fe) and metal ions, which results in a greater number of redox processes and high capacitance. In addition to different oxidation states, ferrite's efficient 3D structure can offer 3D diffusion routes for improved ion transportation [10].

$MnFe_2O_4$, $CuFe_2O_4$, $LiFe_2O_4$, and $MgFe_2O_4$ are only a few of the spinel Ferrites that have been researched as electrode materials for supercapacitors [11]. Low electrical conductivity and early deterioration brought on by reversible redox reactions continue to be obstacles for the materials. People have investigated nanocomposite compounds ferrites with conducting polymers, conducting materials and carbon compounds, as a way to get around this [12]. Researchers have also looked into the polymer and graphene nanocomposite as electrode materials. For instance, $MnFe_2O_4$ was explored with graphene. Mesoporous manganese nickel ferrite and rGO are being assessed for synergistic charge storage in the current investigation [13]. There are several ways to create the ternary nanocomposite. Ferrites compounds are often prepared using traditional ceramic techniques, which have some limitations such as very high hardening temperatures. Hydrothermal process, co-precipitation [14], glass crystallization, mechanical alloying, and sol-gel procedures are only a few examples of non-traditional synthetic pathways that are utilized to make nanocrystalline ferrites. However, the majority of these techniques are not viable from an economic standpoint for mass production [15].

High magnetic permeability and minimal hysteresis losses are well-known characteristics of the $NiFe_2O_4$ and $MnFe_2O_4$ ferrites [16]. There have been several attempts to explore the magnetic, electrical, and structural characteristics of these two types using bulk samples and thin films [17]. In several earlier investigations, migration of cations between sites between ionic substitution was taken into account. Transition metal oxides(TMO) are attractive materials for the use in sensors and solar cells, and more useful as supercapacitor electrodes because of faradaic redox reactions [18].

For instance, the electrochemical performance has been greatly enhanced by mixed metal oxides, such as Mn/Zn, Mn/Ni, Zn/Ni/Co, and Ni/Co/Mn oxides [19]. Complex metal oxide-based materials are increasingly appealing to develop because of high specific capacitance and less cost [20]. The outstanding magnetic, and electrical properties of spinel ferrites to display electrochemical stability and make them one of the most intriguing metal oxides. Numerous binary metal oxide ferrites (MFe_2O_4), such as $NiCo_2O_4$, $MnFe_2O_4$, and $CoFe_2O_4$, have been investigated for use in supercapacitor applications [21]. Spinel ferrites can also be mixed ferrites, which are combination of divalent metal ions with a variable materials. As a result, it is important to consider whether mixed ternary-transition-metal ferrites (A_2B_{1-X} Fe_2O_4) are appropriate for the difficult field of supercapacitors [22]. Due to their low cost of $CuCoFe_2O_4$, $NiCoFe_2O_4$, and $NiCuFe_2O_4$ have been demonstrated for supercapacitors. There are also reports on $MnCoFe_2O_4$, $MnZnFe_2O_4$, and nevertheless, mixed ternary-transition-metal ferrites merit further study before being used in practical, commercial settings [23].

The magnetic, electrical, and characteristics of nano ferrites are altered by variations in cation concentration and sintering conditions, which results in a broad range of applications. Additionally, Mn-Ni ferrite cations affect the form, morphology, electrical, and magnetic properties [24].

What is the main aim of the review?

The main objective is to work on the properties, synthesis, and methods of characterizing. While there are many excellent review articles on magnetic nanoparticles and the field of magnetic nanostructures is very broad, Mn-Ni ferrites represent a unique subset of nanoparticles due to the intense interest in soft ferrites among scientists [25]. Additionally, this paper addresses the best synthesis method for using Mn-Ni ferrites in a particular application

and critically analyses other ways. We briefly address various techniques for the synthesis of Mn-Ni ferrites, including sol-gel, co-precipitation, traditional ceramic, hydrothermal, citrate precursor, solid-state reaction, auto-combustion, and microemulsion [26].

Synthesis methods of Mn-Ni Ferrites

Top-down and bottom-up are the two ways to create nanoparticles. Top-down processing breaks down a bulk substance into nanoparticles. This process has several drawbacks, including the common use of metal oxides, the high temperature required for the reaction, the inhomogeneity of the end products, the existing impurities, a wide size dispersion, and flaws in the surface structure. A bottom-up technique results in the formation of nanoparticles from tiny atomic building pieces[27]. This is the best approach for creating nanoparticles since the end products are uniform, utterly pure, and have a small size range [28]. Mn-Ni ferrite nanoparticles are made using several different synthesis methods, including sol-gel, polyol, co-precipitation, hydrothermal, auto-combustion, and ceramic processing. The structural, electrical, and magnetic properties of Mn-Ni ferrite can be improved by doping other elements or oxides. When rGO was doped in Mn-Ni ferrite, it was discovered that the overall power loss per volume had improved [29].

Techniques	Temperature (^{0}C)	Advantages	Disadvantages
Co-precipitation Technique	30-140	very simple process	Poor crystallinity
		Aqueous material media	More reaction time required
		Controlled size and morphology	
		Easily operated	
Hydrothermal process	100-200	Scalable measurement	need of special reactor
		Controlled size	More pressure required
		Aqueous media	High temperature

		High yield	High reaction time
Sol-gel method	20-200	Controlled size of ferrites	long time process
		Low cost	Medium Yield
Combustion technique	480	Less times consumed	required very high temperature
		An effective method	
		Versatile	
		Nanoparticles are homogenous	
Solid state reaction process	25	No toxic used	—
		economic	
Oxidation methods	30	Narrow size distribution	[Irregular and elongated-
		Uniform size	morphology]

Table.1 Advantages and limitations of some synthesis techniques.

Hydrothermal method

All compounds are employed without additional purification, including $Mn(NO_3)_2.4H_20$, $Fe(NO_3)_3.9H_2O$, $Ni(NO_3)_2.6H_2O$, and cetyltrimethylammonium bromide (CTAB). A hydrothermal approach was used to create the $Ni_{1-x}Mn_xFe_2O_4$ nanoparticle powders (x=0.0,0.2,0.4, 0.6, 0.8, and 1), which is comparable to our work on the features of $Ni_{1-x}Co_xFe_2O_4$ nanoparticles [30]. First, 40 ml of deionized (DI) water was dissolved using stoichiometric quantities of the components mentioned in Table 2 by stirring for around one hour. The produced nitrate mixture was then given 1 cc of a 25% ammonia solution while being vigorously stirred. The prepared mixture was then put into stainless steel autoclave that had been lined with Teflon and heated at 180 °C for 15 hours**.** The autoclave was kept at room temperature while cooling in ambient air. After numerous rounds of washing with DI water, we dried the finished product for three hours in a 70°C oven. Further characterizations were conducted using the produced powders [31]. Ferrite nanoparticles are manufactured on a large scale using the hydrothermal technique. approach has a very high yield of nanoparticles. If factors like temperature, pressure, and reaction time are carefully chosen, the outcome will be of high quality.

Co-precipitation Process

Co-precipitation process is a simple and common technique for making nanomaterials [32]. This technique produces ferrites with controlled sizes, high levels of purity, and homogeneous structures. The starting components for this approach are typically inorganic salts (such as nitrate, chloride, sulphate, etc.), [33]. It should be mentioned that the growth of crystals and the aggregation of the particles are negatively impacted by the salt content and rate of PH change.

Co-precipitation was employed by Thakur et al. to create ferrites. The raw materials for this procedure included sodium hydroxide, manganese chloride, iron (III) chloride, and nickel chloride. Pre-precipitation is followed by the collection and washing of the solid bulk. The residue is then heated to the medium's boiling point [12].To convert the hydroxides into crystalline oxides, they are calcined. 60 cc of distilled water was prepared with a 3 M solution. The PH was then maintained between 11 and 12 by adding this solution to a boiling NaOH solution and stirring for 60 minutes at 353 to 358 K using a magnetic stirrer. The sample was repeatedly rinsed with distilled water after stirring allowing nanoparticle precipitates to settle. The sample was cleaned and dried in a hot air oven, and then the dry material was ground into a powder with a mortar and pestle. chemical coprecipitation was also used to create ferrites, with the starting ingredients being a solution of $Mn(NO_3)_2.4H_2O$ and $Fe_2(NO_3)_3.9H_2O$ [34].To create homogenously, these were combined. Pre-precipitates were generated after mixing all of the starting components by quickly adding Di-ammonium oxalate while stirring continuously for 30 minutes at 45 °C. Precipitates were thoroughly cleaned before being dried for eight hours at 100 °C in an oven. Ferrites were made utilizing an in-house microwave heating setup and dried yellow precipitates [35]. This set-up was placed inside a 2.45 GHz commercial microwave oven. The temperature was increased to 450 °C. The brick was removed and kept cooling after that. The co-precipitation approach offers several benefits for synthesis and because it is a fairly straightforward process. The size and morphology of the nanoparticles that are produced are well under control [36]. Nano ferrites can be made using this process, although it takes a while. Due to the weak crystalline structure of the produced ferrite powder, this process has drawbacks.

Sol-gel method

The synthesis of ferrite nanoparticles using the sol-gel process is a promising technique. To create nanoparticles, a chemical solution technique is used [37]. This method of synthesizing nanoparticles is cost-effective and uses moderate temperatures. With the use of pure ferrus nitrate, nickel nitrate ,and manganese nitrate as starting ingredients, De-ionized water heated to 60 °C was used to dissolve these compounds[16]. The aforementioned solution contained water that was dissolved to bring the concentration down to 0.1–0.4. Following each coating, the samples were heated for 30 minutes at 350 °C before crystallization for 60 minutes at 550 °C. Additionally, spin thermoelectric generators that need uniform magnetic and structural film deposition employ the sol-gel technique [38].

Nickel-doped Mn ferrites were created by using the auto combustion process, and a non-collinear magnetic structure was noted. It was found that the conductivity at room temperature was greater than that of pure Mn-Ni ferrite [39]. With an increase in nickel concentration, the dielectric constant and dielectric loss tangent both decreased. Better size and form control make this approach favorable, although the synthesis takes longer to complete[40]. The sol-gel method is an easy-to-use, inexpensive, and low-temperature processing method. Pure cubic spinel is the only structure present in the prepared ferrite.

Combustion method

A productive and inexpensive way to create nanomaterials is by burning them. When preparing nanomaterials, this method is straightforward, adaptable, and quick. This approach has the advantage of requiring low time and effort throughout the process. The resultant nanoparticles are uniform [41]. This technique was widely used by researchers to create Mn- Ni ferrites. In this procedure reducing agent was utilized along with iron nitrate, nickel nitrate, and manganese nitrate [42]. Normally, a solution is created by mixing all of these ingredients with deionized water and heating it on a hot plate in the air at 480°C [26].

The lattice parameter decreased when other elements were added, which could be explained by the doped elements. As a result, they prevent grain growth. The combustion process can be used to dope rare-earth metals in a single step. The Mn-Ni ferrites generated are greatly impacted by the fuel used in the combustion process [43]. Urea and glycine are typically

recommended fuels for this procedure. These fuels enable the production of homogenous nano- ferrites with precise stoichiometry.

Characterization

X-ray diffractometer (XRD), SEM, TEM, and AFM are only a few of the tools used to characterize MnNi ferrites (AFM). Measurements using the VSM, M-H loops, and ESR hysteresis loops are used to examine the magnetic characteristics of the ferrites. An X-ray diffractometer with Cu Kα radiation is used for the X-ray research. Below is a list of different formulas for calculating crystallite size, X-ray density, and lattice constant**.**

lattice constant (a): By using XRD data analysis, the lattice constant is calculated by following the formula

$$a = \frac{d_{hkl}}{(h^2+k^2+l^2)^{1/2}}$$

X-ray density calculated by using the formula

$$D_{xrd} = \frac{8M}{Na^3}$$

Experimental density (d): formula for densiy is

$$\mathbf{d} = {mass}/{volume}$$

Crystallite size (D): The Scherrer's formula to calculate crystallite size:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where D is the crystallite size, λ = 1.54056 Å is the wavelength of X-ray,is Bragg's angle and β is the FWHM value.

XRD Analysis

The average crystallite size of all the samples, according to the analysis of the diffraction peaks, was found to be between 43 and 50 nm, indicating size homogeneity. The sample's Mn ion concentration is correlated with a slight increase in the lattice constant. The bigger Mn2+ ions (0.83) can be used to substitute the smaller Ni2+ ions,

which can be used to explain the lattice expansion. Analysis of the Williamson-Hall plot demonstrates the presence of strain in the sample due to the difference in ionic radii between Fe3+ and Mn2+ and the occurrence of cation vacancies [44].

X	d (Å)	a (Å)	V (Å3)	FWHM (degrees)	D (nm)	ε	Alg Raman shift (1/cm)
0.0	2.52	8.36	584.28	0.7233	9.36	-0.00234	687.81
0.2	2.52	8.37	586.38	0.6436	9.44	-0.00253	686.38
0.4	2.52	839	590.59	0.7460	9.12	-0.00265	677.77
0.6	2.53	8.39	590.59	0.7350	8.39	-0.00302	654.37
0.8	2.55	8.45	603.35	0.6441	10.13	-0.00242	631.21
1.0	2.56	8.480	609.80	0.3936	9.54	-0.00284	630.98

Table 2. lattice parameter a, inter-planar spacing d, unit cell volume V, etc. [30]

TEM Analysis

The particles have a size of about 50 nm and existing to be spherical. This is consistent with the crystallite size that was determined by fine-tuning the XRD data. Chemical coprecipitation maintains a consistent particle size distribution, as seen by the almost monodispersed particles in the microstructure image. Furthermore, single grain crystals are discovered to make up the particles. It shows that the nanoparticles are very crystalline. Because of the particles' increased surface energy as their size is shrunk to nano dimensions, a minor amount of agglomeration is seen. The FFT image of a small cluster of nanoparticles is displayed in the inset. The image clearly shows the 311 and 220 planes, from which the dazzling diffraction dots emerge. TEM and XRD data are in perfect agreement with one another [45].

The power densities of samples were calculated by

$$\text{Energy density} = \frac{CV^2}{2}$$

$$\text{Power density} = \text{energy density/time}$$

x	Specific capacitance (F/g)	Energy density (Wh/kg)	Power Density (W/kg)
0.0	492	35.55	497.92
0.2	601	43.41	452.98
0.4	766	55.31	476.35
0.6	988	71.34	526.25
0.8	1,152	83.18	475.28
1.0	1,221	88.16	473.96

Table 3. specific capacitance, energy density and power density

Applications

Researchers are interested in the nanoparticles synthesis and using them in different applications, including the information technology, communication, medical, and biosensors. Ferrites are used in biomedical, catalytic, and wastewater treatment, and there are numerous reviews available on their synthesis, characteristics, and uses. Mn-Ni ferrites have many uses because of their high magnetization, permeability, and low power loss [22]. Power applications, magnetic devices, fluid, radar absorbing systems, high-frequency, bio-medical, water purification, and other uses for Mn-Ni ferrites are among their range of applications.

Conclusion

Over the last 10 years, there has been a rise in the synthesis of Mn-Ni particles, with 2016 marking the year with the highest advancement. Among all synthesis techniques, the co-precipitation and sol-gel methods are the best for obtaining the fine crystallite size. The cubic spinel phase group may be seen in distinctive peaks on the XRD pattern of Mn-Ni ferrites. The prepared ferrite has a roughly spherical form, however, following doping, some distortion may be seen. The ferrite nanoparticles' spinel phase, which contains tetrahedral and octahedral sites,

was validated by FTIR spectra. When Mn-Ni ferrites are synthesized utilizing sol-gel automated processes with the appropriate quantity of nickel doping, the saturation magnetization value is at its maximum.

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