Journal of Atomic, Molecular, Condensate & Nano Physics
Vol. 2, No. 2, pp. 101–108, 2015
ISSN 2349-2716 (online); 2349-6088 (print)
Published by RGN Publications

http://www.rgnpublications.com

Comparative Studies of $MgFe_2O_4$ Nanoparticles Synthesized using Different Precursors by Sol Gel Auto Combustion Method

Research Article

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Abstract. Nanostructured powder of $MgFe_2O_4$ was prepared by sol gel auto combustion method using two different precursors. It is an ultimate combination of slow and sustained gel formation and subsequent combustion. In this work, our aim is to synthesize nanoparticles of $MgFe_2O_4$ using different precursors and to compare their relative characteristics and also to investigate that which combinations have result in better properties. The precursors of the solid were obtained from different gels of metal nitrates and metal nitrate, metal acetate with glycine used as an oxidizer and a fuel having pH value of 2 and 6, respectively. During our keenly observed processing, it was reproducibly noted that in the case of acetate-nitrate gel the self-propagation temperature was approximately 120 °C-130 °C while in the case of nitrate- nitrate gel the self-propagation temperature was approximately 180 °C-200 °C. The crystal structure, shape and grain size of the nanoparticles had been compared by XRD, SEM and TEM. VSM was used to investigate the magnetic properties of obtained powder. The hysteresis curves indicated the ferromagnetic behavior of the samples at room temperature. FTIR supports the absorption value of octahedral and tetrahedral sites.

Keywords. Nanostructured; $MgFe_2O_4$; Hysteresis; FTIR; Self-Propagation; Hysteresis

PACS. 34.

Received: March 21, 2015 **Accepted:** November 28, 2015

1. Introduction

Having versatile application in different technologies spinal type Ferrite with general formula AFe_2O_4 (A=Zn, Cd, Co, Mg, Mn, Ni etc.) used as model materials and provide us an opportunity for better understanding of the magnetic properties at nanoscale [26]. Magnesium ferrite have a special position among all the ferrites as it exhibit ferromagnetic and semiconductor properties and considered as magnetic semiconductor [4,25,27] It is widely used in electrical and microwave industry also used in computer, recording devices and magnetic cards [2,14,17,27]. In medicine like treating tumors [27], magnetic drug carrier [21] contrast agent in magnetic resonance imaging and magnetic refrigeration [9] photo catalysis [3], as gas sensors [23] and, have good photo electrical properties [25]. The above applications depend upon microstructure and surface properties of the fine powder obtained during the method of preparation [10]. The available methods for the synthesis of magnesium ferrite includes solid state reaction, sol-gel, micro emulsion, co precipitation method etc [23]. In this paper we have described the synthesis of $MgFe_2O_4$ using low cost procurers by sol gel auto combustion method. It is a simplest and economical method which produces highly pure nanoparticles in a short interval of time in the form of fine brown burnt powder of ferrite. Combustion reaction is a self-sustaining exothermic reaction which allows the system to heat quickly there by reaching high temperature even in the absence of external heat source [20]. This obtained burnt fine powder were characterized by using XRD, FTIR, VSM SEM and TEM at room temperature. Traditionally in this method metal nitrate salts are used as reactants and glycine (NH_2CH_2COOH) [16], urea ($CO(NH_2)_2$) [6] and citric acid ($C_6H_8O_7$) [33] are used as a fuel for combustion.

In our present investigation, the sol gel auto combustion method is being employed for the comparative study of the structure, morphology, size and magnetic characteristic of the obtained nano powder at room temperature formed by using mixture of different precursor with Glycine as fuel. Glycine is an organic fuel which possesses high heat of combustion and provides a platform for redox reaction during combustion [6,9,10,16,23,33].

2. Experimental Analysis

In this experiment $MgFe_2O_4$ (magnesium ferrite) powder were prepared using sol gel auto combustion method. Precursors used were of high purity AR grade of Ferric nitrate [$Fe(NO_3)_3.9H_2O$] (99%), Magnesium Nitrate [$Mg(NO_3)_26H_2O$], AR grade (98%) and Magnesium Acetate AR grade (98%) with Glycine [NH_2CH_2COOH] AR grade (98%) as a fuel.

Method 1

In this process the solution of magnesium nitrate hexa hydrate Mg $(NO_3)_2.6H_2O$, Ferric nitrate nanohydrate Fe $(NO_3)_3.9H_2O$ and of glycine (NH_2CH_2COOH) each with 20 ml of deionized water was prepared in the molar ratio of 1:2:3. Here, $Fe(NO_3)_3.9H_2O$ and Mg $(NO_3)_2.6H_2O$ were used as an oxidants and glycine as a surrounding fuel which is responsible for the combustion reaction. Initially the solution of magnesium nitrate was mixed with ferric nitrate solution in a beaker and was magnetically stirred for 20 minutes without heating. The glycine solution (chelating/combustion agent) was then added to the solution of nitrates. Again the mixture was stirred for ten minutes. At that time the pH of the solution was 3. Then this resulting mixture was placed on preheated hot plate at temperature 70 °C and it is gradually heated for several hours to reach and maintain at the temperature of the mixture approximately 80 °C, where the xerogel was formed with continuous stirring at this temperature. After the formation of this sticky gel the temperature of the hotplate was again gradually raised reaching approximately to 180 °C-200 °C where by self-ignition ensued at one part of the gel engulfing the entire gel within few seconds resulting in complete combustion and the formation of brown fluffy powder of magnesium ferrite.

Method 2

The starting material for the synthesis of magnesium ferrite was ferric nitrate and magnesium acetate $(CH_3COO)_2Mg.\ 4H_2O$ with glycine in the same ratio as above and the pH of the solution was 6. A similar procedure was followed where we observed that the self-combustion in this case begins quite earlier at considerably lowered temperature, approximately 120 °C-130 °C shortly resulting in complete combustion and formation of dark brown fluffy powder of magnesium ferrite. In this experiment two different precursors were taken for the reaction, and lowering of self-combustion temperature in the later methodology has been reproducibly noted as an important observation in our experiment.

Infra-red measurements were carried out over the wavenumber range of 400-4000 cm^{-1} using a PerkinElmer RX1 FTIR spectrophotometer with potassium bromide (KBr) pellets. TEM samples were prepared by dispersing samples in ethanol then dropcast on carbon formvar coated copper grids and the images were acquired using an FE-Technai G2 system operated at an accelerating voltage of 300 kV. VSM was done on Microsense, ADE-Model EV9, and SEM images were acquired by JEOL-JSM-6610LV.

3. Results and Discussion

Characterization of material is very important because the structural and magnetic properties of the ferrites have been reported to depend upon the processing details of the preparation methods [18]. The XRD pattern of as-synthesized $MgFe_2O_4$-prepared powder by sol-gel auto combustion method is shown in Figure 1. It consists of well-resolved peaks, which confirms the crystalline and monophasic nature of the prepared material. The diffraction peaks at hkl plane (220), (311), (400), (422), (511), (440), (620) and (533) conformed the formation of spinel structure of the ferrite [7,25]. The data were collected in a 2θ range from 10 ° to 80 ° at a step size of (0.02s). It is found that crystal structure to be cubic with space group (SG) Fd-3m and a lattice parameter 8.3902 Å and cell volume is 590.64 in case of nitrate salts and 8.3893 Å and cell volume is 590.45 in case of nitrate-acetate salt for the ferrites structures. The obtained data was matched with reported data of $MgFe_2O_4$ from JCPDS file (pattern: 01-071-1232) S.G:Fd-3m (227). The average crystalline size of $MgFe_2O_4$ nanoparticles as burnt powder for both the precursors were obtained using Scherer's equation [8] which were approximately 27 nm and 30 nm in case of nitrates and nitrate-acetate precursors respectively. Low combustion temperature and low hydrolysis temperature could produce nanocrystallite magnetic ferrite in single step [31].

FTIR Analysis

FT-IR spectra also supported the formation of spinel $MgFe_2O_4$ structure at room temperature. Two ranges of the absorption bands: 4000-1000 and 1000-400 cm^{-1} are analyzed [15, 18]. In the range of 4000-1000 cm^{-1}, vibrations of CO_3^{2-} and moisture were observed [1]. The intensive band at 3422 cm^{-1} is due to O–H stretching vibration interacting through H bonds. The band at 2857 cm^{-1} is C–H asymmetric stretching vibration mode due to the $–CH_2–$ groups of the long aliphatic alkyl groups. The intensive band at 1636 cm^{-1} is due to the O–H stretching through H bond. The (C=O) stretching vibration of the carboxylate group (CO_2^{2-}) was observed around 1384 and 1402 cm^{-1} and the band at 1095 cm^{-1} was corresponded to nitrate ion traces [1, 13, 15, 29, 30]. In the range of 1000-400 cm^{-1} a higher frequency band appears at 561 cm^{-1} and 558 cm^{-1} which strongly suggests the intrinsic stretching vibrations of the metal (Fe and O) at the tetrahedral site, and lower frequency band at 432 cm^{-1} and 430 cm^{-1} are assigned to iron-oxygen stretching at octahedral site [15]. The remarkable increase in the intensity of the band indicates the enhancement in magnesium ferrite [19].

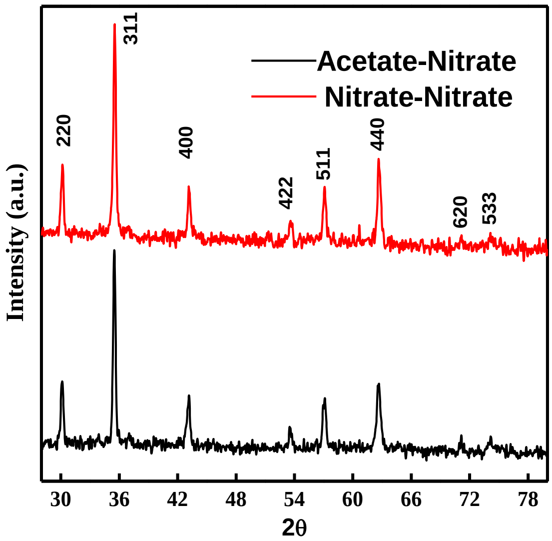

Figure 1. XRD of as synthesized $MgFe_2O_4$ powder obtained by using different precursors by sol gel auto combustion method at room temperature

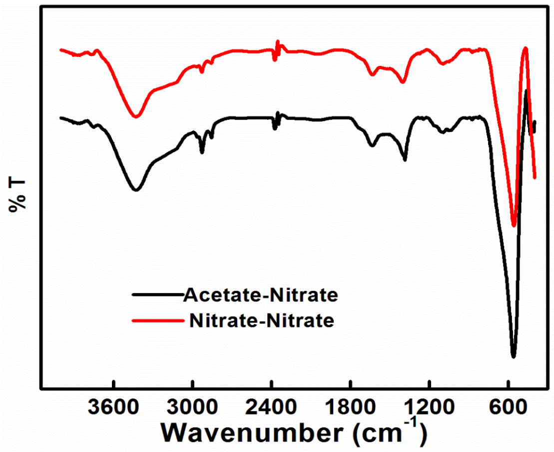

Figure 2. FTIR spectra (at room temperature) of the as synthesized nanoparticles as powder of $MgFe_2O_4$ using different processors by sol gel auto combustion method

VSM Analysis

Table 1. Data obtained using VSM of magnesium ferrite nanoparticles as burnt powder

	Ms (emu/g)	Hc (oe)	Mr (emu/g)
NT	30.9	78.7516	8.44949
AC	33.9	72.8438	7.64055

The magnetic properties of the $MgFe_2O_4$ nanoparticles as burnt powder obtained from different precursors were measured in magnetic field of 3koe. Using VSM. The saturation magnetization curves of these obtained powder at room temperature is shown in the Figure 3. The hysteresis loop indicates the typical behavior of ferromagnetic materials [12] from the above measurements, values of magnetization (Ms), remenance (Mr) and coercivity (Hc) were obtained.

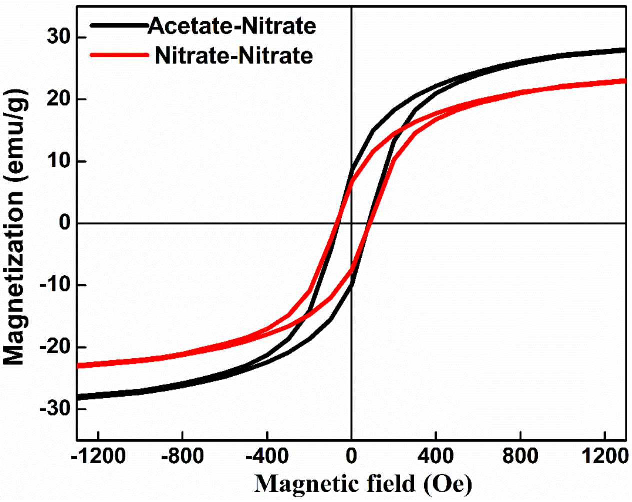

Figure 3. Hysteresis curve for soft ferromagnetic $MgFe_2O_4$ as burnt powder at room temperature

Which indicates that the magnetization in case of nitrate -nitrate mixture is 29.275 emu/g and in case of nitrate -acetate precursor it is 33.478 emu/g which close to the bulk $MgFe_2O_4$ material (approximately 30 emu/g) [22]. The calculated magnetic properties of as burnt magnesium ferrite nanopowder is shown in Table 1, it is found that the magnetic properties calculated in case of nitrate-acetate precursors had improved compared to nitrate nitrate precursors. The increase in the value of Ms is consistent with the enhancement of crystallinity. The improvement of crystallinity and the decrease of the concentration of oxygen vacancies have been considered as being responsible for the increase of the Ms and strengthens the Fe^{3+}–O^{2}–Fe^{3+} exchange interaction, and as a result improves the magnetic properties of the materials [5,28]. Mr and Hc values of the two precursors are 8.4494 emu g^{-1}, 7.64055 emu/g and 78.7516 Oe and 72.8438 Oe respectively. The coercivity in both the cases does not change significantly, which indicates that the increase in value of Ms might be resulted from the increase of the particle size and improvement of crystallinity. The reason behind this may mainly due to method of preparation [32].

SEM and TEM Analysis

The morphological study of the magnesium ferrite as burnt powder obtained from auto combustion method was done with the help of SEM and TEM. A highly and typical porous structure of the sample after auto combustion is observed to be formed. As the samples are magnetic in nature the particles are agglomerated and held together by magnetic interaction, due to the intense forces of van der Waals attraction [28].

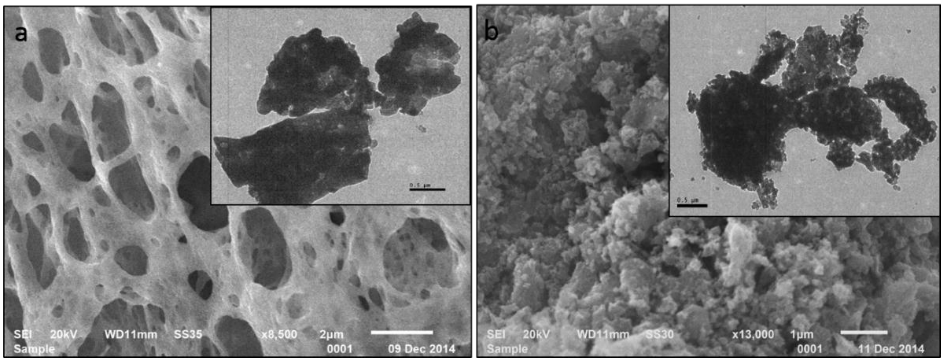

Figure 4. SEM and TEM (inset) images showing morphology (porous and agglomeration) of as burnt ferrite powder

4. Conclusions

- The result indicated that the nanopowder synthesized using acetate-nitrate precursor have comparatively better magnetization than nitrate-nitrate precursor.
- The samples were found to be cubic spinal nanoparticles conformed by XRD with crystal size approximately 29.7 nm and 27 nm in case of nitrate-nitrate and nitrate-acetate respectively.
- FTIR also indicated the purity and formation of spinal ferrite structure.
- Thus the result obtained from these structural and magnetic analysis, provided the basis for using precursor other than the traditionally employed precursors (auto combustion temprature 180-200 °C) for the synthesis of magnesium ferrite under much milder (120-130 °C) conditions.
- This work has provided a new direction for the synthesis of magnesium ferrite.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed equally and significantly in writing this article. All the authors read and approved the final manuscript.

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