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# Investigations of superparamagnetism in magnesium ferrite nano-sphere synthesized by ultrasonic spray pyrolysis technique for hyperthermia application

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ABSTRACT

In this paper, we present the synthesized of magnesium ferrite ($MgFe_2O_4$) nano-spheres by a single-step ultrasonic spray pyrolysis (USP) technique from the aqueous metal nitrate precursor solution without any organic additives or post-annealing processes. The effects of different pyrolysis temperatures on the particles size, morphology and their superparamagnetic behavior have been investigated to evaluate the heat generation efficiency in an AC magnetic field. The X-ray powder diffraction spectra of $MgFe_2O_4$ nano-spheres synthesized at the pyrolysis temperatures of 600, 700, 800 and 900 °C exhibited single phase cubic structure and obtained mean crystallite size (primary particles) of 4.05, 9.6, 15.97 and 31.48 nm, respectively. Transmission electron microscopy (TEM) confirms that the particles consisted of aggregates of the primary crystallite had densely congested spherical morphology with extremely smooth surface appearance. Field emission electron microscopy (FESEM) reveals that the shape and size of the nano-spheres (secondary particles) does not change significantly but the degree of agglomeration between the secondary particles was reduced with increasing the pyrolysis temperature. The average size and size distribution of nano-spheres measured using electrophoretic scattering photometer have found very low polydispersity index (PDI) for all samples. The field dependent magnetization studies indicated superparamagnetic nature for the particles having crystallite size i.e. 4.05 and 9.6 nm and exhibited ferromagnetic nature for 15.97 and 31.48 nm. It is also demonstrated that, as the pyrolysis temperature increases, the saturation magnetization of the $MgFe_2O_4$ nanopowders increases due to enhancement of crystallites. The shift in Curie temperature is well described by the finite-size scaling formula. The magnetically loss heating values of selected samples in crystallite size of 9.6 and 15.97 nm were investigated by measuring the time dependent temperature curves in an external alternating magnetic field (370 kHz, 1.77 kA/m). The more heat generation ability was obtained for 9.6 nm in crystal size because of minimum squareness ratio with coercivity in superparamagnetic range. The results reported in this study are useful to find out of superparamagnetic limit for the preparation of $MgFe_2O_4$ nanopowders.



## 1. Introduction

Nanosized spinel ferrites are very important magnetic materials which exhibit interesting physical, electrical and magnetic properties that are significantly different from those of their bulk counterparts [1–6]. Since recently, ferrites have also been focus of extensive studies for their use in not only technological applications but also in various biomedical fields [7,8]. The effectiveness applicability of these ferrite nanoparticles is significantly influenced by their physical factors such as the size, shape, surface to volume ratio, purity of the system and the interactions between

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the particles [9,10]. Among the various ferrite compounds, magnesium ferrite ($MgFe_2O_4$) nanoparticles is one of the most important functional soft magnetic materials. It has excellent chemical stability with inverse spinel structured, which have found a number of modern technological applications in microwave devices, catalysis, adsorption, gas and humidity sensor, ferrofluid technology, fuel cells, magnetic core of coils and also used in an inorganic pigment [11–13]. Aono et al. [14] found that $MgFe_2O_4$ has the highest heating ability compare to other commercial ferrite powders of $MFe_2O_4$ (M=Mg, Mn, Fe, Co, Ni, Cu and Sr) in alternating magnetic field which is one of the interesting applications in hyperthermia therapy. In addition, these $MgFe_2O_4$ nanoparticles would be suitable for the use in the human body, because the elements present in these material are nontoxic [15]. To apply this material for hyperthermia applications, synthesis of particles in superparamagnetic range is required which is purely size dependent [16]. If particle size is reduced below the critical size, its coercivity $H_c$ and remanence $M_r$ will be negligible and the area of hysteresis loop is almost vanished which exhibit superparamagnetic behavior [17]. These features make superparamagnetic nanoparticles very attractive to deliver a dominant heat generation mechanism due to the relaxation losses [18]. The critical diameter of a spherical particles for the superparamagnetic to ferrimagnetic transition of magnetic materials can be expressed as:

$$D_{s\to F} = \left[\frac{6K_B T \ \ln\left(t_m f_0\right)}{\pi K}\right]^{1/3} \tag{1}$$

where $k$, $f_0$, $k_B$, $T$ and $t_m$ are anisotropy constant, frequency constant, Boltzmans constant, temperature and time of measurement, respectively [19]. Barati and coworkers have estimated the critical particle size (15 nm) for $MgFe_2O_4$ nanoparticles at room temperature [20]. However, the heat generation ability of these materials is strongly influenced by particle size, particle size distribution with high degree of monodispersity. Therefore, vital importance is given to synthesis $MgFe_2O_4$ solid spheres with narrow size distribution in order to accurately formulate the optimum particle size which is suitable for magnetic hyperthermia.

In order to achieve these appreciable properties, the size and morphology of $MgFe_2O_4$ have been investigated by using various synthetic methods such as coprecipitation method [21], sol–gel method [22], mechanochemical processing [23], combustion method [24], microwave hydrothermal method [25] and polymerization method [26]. Some of this solution based methods have complicated steps and unfortunate grain growth with necking of particles can usually occur during the calcination step or post-annealing process in atmospheric environment [27]. In case of ultrasonic spray pyrolysis, nanoscale particles can be yielded in the desired size regime ranging from below the superparamagnetic limit to the monodomain limit with various advantage such as good crystallinity, chemical homogeneity, high purity, short reaction time and available for mass production [28–33].

In the present study, we report the synthesis of nanocrystalline $MgFe_2O_4$ as dried powders by using USP technique without any organic additives or post-annealing processes. To obtain superparamagnetic phase of synthesized particles, the influence of different pyrolysis temperatures on the structural, morphological and magnetic properties was investigated. The results of investigation were analyzed to study the AC magnetically induced heat generation ability which will show better efficiency for hyperthermia application.

## 2. Materials and methods

### 2.1. Materials

In this study, all reagent grade chemicals were used without further purification. Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) and iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) were selected as a precursor chemicals because of their relative high solubility in water. Deionized water was chosen as the solvent. Both produced by Kanto Chemical Co. Tokyo, Japan with high purity (99%).

Initially, the magnesium and iron nitrate were dissolved separately in distilled water at concentration of 0.04 and 0.08 M respectively to achieve the Mg/Fe molar ratio 1:2. The resultant nitrate solution was obtained by mixing these two solutions together in 1:1 volumetric proportion. The final solution was continuously stirred for 12 h using a magnetic stirrer which was used as the precursor solution for spray atomization in the particle synthesis via ultrasonic spray pyrolysis method.

### 2.2. Synthesis technique

The $MgFe_2O_4$ un-sintered nano-spheres were prepared using the home built ultrasonic spray pyrolysis system. The schematic diagram of this system is shown in Fig. 1. The system consists of atomizer, quartz reactor and powder collector chamber. The mist of prepared precursor solution was generated in the three neck round flask by ultrasonic vibrator (Honda Electronics Co. Ltd., Aichi, Japan) with selected resonant frequency of 1.6 MHz and the resulting droplets are then carrying into the tubular quartz reactor by a carrier gas. The length and diameter of the quartz reactor are 1500 mm and 31 mm, respectively. $N_2$ was used in this experiment as the carrier gas and the total carrier gas flow rate was controlled at 3 l/min by using a mass flow controller (Model RU-100, Lintec co. Ltd., Shiga, Japan). The dynamic (continuous) reduction took place in the quartz tube reactor which is located in the three zone electrical heated tubular furnace (ASH, Model ARF-50KC, Kobe, Japan) each 300 mm in length with temperature controller (Chino Corporation, Model-SU, Tokyo, Japan) of $\pm 1$ °C enabling flexibility in the production of the experimental temperature distributions which led to decomposition of precursor mist and generation of $MgFe_2O_4$ particles. The droplet evaporated, decomposed and/or crystallized in the quartz reactor [30]. The product particles are deposited on the filter paper as substrate which is placed in the funnel at the outlet of the reactor, while the water vapor and off-gases are discharged through an exhaust line. A vacuum pump (having a capacity of 15 $m^3$/h) was used to put the reactor under slight vacuum to discharge the water vapor and exhaust gases to vent at the downstream. The sample holder and the connection part were both kept at 100 °C by tape heaters. Thermocouples were inserted near the surface of the atomizer, the surface of the reactor and the sample holder location to monitor an axial profile of temperature for duration of the experiment. During this

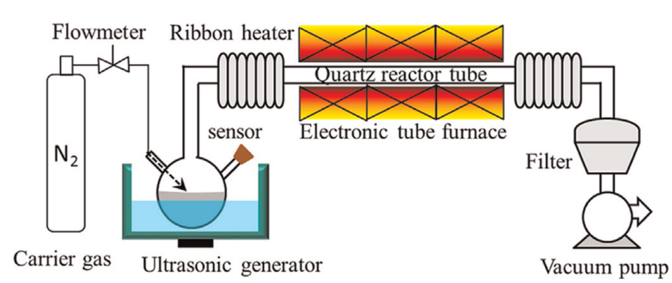


**Fig. 1.** Schematic drawing of experimental apparatus for the synthesis of $MgFe_2O_4$ nano-spheres by ultrasonic spray pyrolysis system.