J. of Supercritical Fluids 113 (2016) 96–105

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

# Synthesis of nano-crystalline $NiFe_2O_4$ powders in subcritical and supercritical ethanol

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ARTICLE INFO

*Article history:*
Received 16 December 2015
Received in revised form 11 March 2016
Accepted 14 March 2016
Available online 15 March 2016

*Keywords:*
Supercritical
Subcritical
Nano-crystalline powders
Nickel ferrite
Metal oxide
Magnetic properties

ABSTRACT

Nano-crystalline nickel ferrite has a broad range of applications due to its favourable magnetic properties. Those characteristics can be significantly influenced by the synthesis pathway including methods conducted in the presence of supercritical alcohols. Nano-crystalline $NiFe_2O_4$ powders were obtained in the reaction under subcritical and supercritical conditions of ethanol. Both high pressure synthesis routes resulted in powders with smaller primary particles and higher mesoporosity than co-precipitation method. Upon the annealing treatment the average crystallite size increased while material structure remained uniform, resulting in significantly enhanced magnetic properties, such as coercivity and remanence. It was found that synthesis under supercritical conditions provides higher conversion but also material with larger average crystallite size upon annealing. The time and temperature of annealing stage significantly influenced the morphology and magnetic properties of the obtained powders.


## 1. Introduction

Nickel ferrite is fairly known and widely used material but still very interesting both to industry and academia. In essence it is a ceramic material, a mixed metal oxide with inverse spinel to mixed spinel structure, which exhibits certain magnetic properties. Over the years it has been used and investigated for applications in electronics for magnetic memory, optical devices, sensors, drug delivery systems, fuel cells and catalysts, especially in nano-size powder form [1,2]. However, since it is a ceramic material its synthesis in nano-crystaline form is still a challenge. Its properties are heavily influenced by the conditions during synthesis process; therefore selected synthesis route is crucial for its further application [1,2]. Furthermore, many desirable properties like nano-scale size and saturation magnetization are favoured by conflicting conditions [1,2]. Consequently its properties are always designed as a compromise and choice between crystallite size and shape, morphology, and quality of magnetic properties.

There is still an interest to investigate and develop novel synthesis routes, and among those the sol-gel method was found to be advantageous for obtaining powders with "fine" structural properties [3]. If followed by supercritical drying process much of the original gel network structure can be substantially preserved [3–5], taking into account that post drying heat treatment of the gels has a significant impact on the morphology and specific surface area [3–8]. Unique and adjustable properties of supercritical fluids provide good conditions for crystallization and also allow certain degree of control over the process by adjustment of only temperature and pressure [9–12]. Over the years, several techniques have been developed that utilize supercritical conditions for nanoparticles processing, techniques like Supercritical Anti-Solvent (SAS) and Gas Anti-Solvent (GAS) processes, Rapid Expansion of Supercritical Solution (RESS), as well as Solvo-thermal method, which includes high-temperature sol-gel reaction in a supercritical organic solvent [9–14]. Unlike in the conventional sol-gel process, the reaction kinetics of sol-gel reactions in supercritical fluids is not only a function of reaction temperature and reactant concentrations, but pressure as well [9]. So far nanocrystalline nickel ferrite has been successfully synthesized in near supercritical and supercritical $H_2O$ using flow systems, with primary particle size ranging from 7 to 43 nm [15–17]. Such synthesis route requires

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http://dx.doi.org/10.1016/j.supflu.2016.03.014
0896-8446/

extremely high pressures of 250–300 bar. Supercritical alcohols are often found to be good choice of solvent since they usually have low values of critical temperature and pressure, and offer an opportunity for a degree of H-bonding to be tuned as a function of density [18]. Additionally, supercritical alcohols encourage high nucleation rates with little subsequent growth of the nuclei themselves, thus their use leads to formation of very small particles [18] and the use of supercritical alcohols provides an alternative pre-annealing treatment which improves sinterability of the ceramic material and decreases required annealing temperature [18].

Reports from previous studies with simple primary alcohols under supercritical conditions show that under such conditions alcohols can display reducing properties. This reducing ability probably comes from reducing activity of free hydroxide ions present in supercritical medium, which are generated through dissociation of hydroxide group from alcohol molecules [19,20]. This ability is temperature dependent and increases with rise of temperature in the system. Utilizing this additional property of simple alcohols novel synthesis route was developed for different metal and metal oxide nano-crystalline powders [19–25]. So far mainly methanol and ethanol have been investigated and mostly for the purpose of synthesis of metal or corresponding single and mixed oxide nanoparticles from the nitrate solutions [19–25]. Other alcohols and precursors have also been studied [22,25]. Reaction conditions in such synthesis route usually include very high pressures and temperatures (~400 °C, 300 bar), necessary to enhance reactivity and reducing power of the supercritical alcohol. Magnetite nanoparticles have been synthesized utilizing supercritical MeOH at 400 °C and 300 bar [20], but to our best knowledge such synthesis route has not yet been investigated for synthesis of $NiFe_2O_4$. Such severe conditions are not suitable for the synthesis of $NiFe_2O_4$ since metallic nickel can be produced [21]. However, at lower temperatures (< 350 °C) a mixture of nickel hydroxide ($\alpha$-$Ni(OH)_2$) and Ni forms [19], which indicates that under more moderate conditions perhaps only nickel hydroxide might be formed. Consequently more moderate conditions could lead to a formation of iron and nickel hydroxides necessary for further formation of mixed oxide $NiFe_2O_4$ [19–21]. Previous reports have found that mechanism of nanoparticle formation under subcritical and supercritical conditions is mainly favoured by the solubility of the metal oxide and kinetics of the synthesis reaction. Reason for this is the impact of dielectric constant on reaction equilibrium, reaction rate and solubility, which can significantly vary around the critical point due to the change of solvent properties.

The aim of this study is to investigate synthesis of $NiFe_2O_4$ under subcritical and supercritical conditions of ethanol. In order to evaluate investigated synthesis routes, with respect to the properties of the obtained powders, the materials were compared to the material obtained using atmospheric conventional co-precipitation method. The impact of the annealing stage within the synthesis route was investigated in order to determine the optimal conditions of the annealing treatment.

## 2. Material and methods

### 2.1. Materials

Throughout the experiment for the synthesis of nickel ferrite following chemicals were used: $Ni(NO_3)_2{\cdot}6H_2O$ (p.a. grade, ≥98.5) purchased from Sigma-Aldrich; $Fe(NO_3)_3{\cdot}9H_2O$ (p.a. grade, 98–101.0%) supplied by Alfa Aesar GmBH; concentrated $C_2H_5OH$ (96%) purchased from Zorka Pharma Ltd and NaOH (p.a. grade, 99.0%) supplied by Merck. All chemical reagents were used as delivered, without any further purification.

### 2.2. Synthesis

#### 2.2.1. Reaction under subcritical and supercritical conditions of ethanol

Nano-crystalline nickel ferrite powders were prepared via novel synthesis route using only inorganic salts as metal oxide precursors and ethanol as solvent. Nickel(II) nitrate hexa-hydrate (2.9 g) and iron(III) nitrate nona-hydrate (8.08 g) were dissolved in 100 ml of ethanol in quantities necessary to achieve molar ratio of 1:2 of Ni:Fe in the solution. Alcohol solution was transferred to the pressure vessel (Autoclave Engineers BTRS-Jr, Division of Snap-title, Inc., Erie, PA, USA) contained within glass beaker and the pressure vessel was filled with additional amount of ethanol. Such procedure was necessary to ensure that the pores in obtained material were always filled with single phase ethanol solution (liquid, supercritical or gas) thereby avoiding formation of the two phase region (liquid-gas) in the pores [26]. The experimental procedure is shown on the phase diagram (Fig. 1). The vessel (height 130 mm, diameter 76 mm, equipped with ceramic electronically controllable heater) was then sealed and heated (heating rate 5.5 °C/min, total time of heating was 45 min) to the desired temperature. Different reaction conditions were applied in order to determine optimum conditions and to observe possible changes in reactivity.

For the purpose of this study two different synthesis routes were performed. In the route utilizing subcritical region of ethanol (red line on the diagram shown in Fig. 1) the precursor solution was kept at 200 °C for two hours while pressure in the vessel was maintained at 33.7 bar. Under such conditions ethanol is still well below its critical point (241 °C, 63 bar). In the synthesis route conducted under supercritical conditions of ethanol (blue line on the diagram shown in Fig. 1), the precursor solution was kept for 2 h at 260 °C and 72.7 bar, well above the critical point of ethanol. Upon the reaction completion, the system was depressurized to atmospheric pressure followed by gradual temperature decrease to ambient conditions.

Obtained powders were further processed and characterised, powder obtained under subcritical conditions was labelled ET-1 and powder obtained under supercritical conditions was labelled ET-2. Annealing of the powders was performed at 650 °C for 4 h, at 650 °C for 8 h, and at 900 °C for 4 h. Annealed samples were correspondingly labelled ET-1@6504 h, ET-1@6508 h, ET-1@9004 h for ET-1, and ET-2@6504 h, ET-2@6508 h, ET-2@9004 h for ET-2.

#### 2.2.2. Co-precipitation with NaOH

For the synthesis of $NiFe_2O_4$ material via conventional atmospheric co-precipitation method, the same precursor salts were applied, absolute ethanol as solvent and NaOH as precipitating agent. Precursor salts $Fe(NO_3){\cdot}9H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ were dissolved in 2l of absolute ethanol in molar ratio 1:2 (1.46 g of $Ni(NO_3)_2{\cdot}6H_2O$ and 4.04 g of $Fe(NO_3){\cdot}9H_2O$). Upon homogenisation of the solution by vigorous steering, 1.6 g of NaOH was added. The mixture was stirred for additional 15 min and then left to settle. As the precipitate slowly formed two separate phases started to appear in the mixture. On the top a clear layer of solvent formed and below a dense layer with ochre precipitate which slowly settled. The upper clear layer was periodically decanted until about 100 ml of mixture remained. The residual 100 ml of mixture was then heated to 60 °C so that remaining solvent could be removed. At the end a solid dark brown disk was obtained, which was further annealed at 900 °C for 4 h and labelled ET-3@9004 h.

### 2.3. Characterization

In order to gain insight into structure, morphology and composition of obtained powder samples several instrumental techniques were employed. Crystalline structure of the obtained powders was analyzed by X-Ray diffraction method (XRD). The samples were