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# Synthesis of nanosized zinc ferrites from liquid precursors in RF thermal plasma reactor

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**Abstract**

Micro- and nanosized zinc ferrite particles were prepared in RF thermal plasma conditions. Ethanol solutions of the mixture of zinc- and iron-nitrates were used as precursors. In the experiments, effects of synthesis conditions on the properties of products were investigated. The products were characterized for chemical and phase composition, morphology and magnetic properties. Zinc ferrite particles having ferrimagnetic properties were produced which refers to formation of zinc ferrites of inverse spinel structure in particular conditions.


*Keywords:* X-ray methods; Magnetic properties; Ferrites; Spinels; RF thermal plasma

## 1. Introduction

Spinel ferrites are widely used in different industries, e.g. as adsorbents,[1] as catalysts,[2] pigments[3] and materials of devices for electronic and magnetic storage of information. Applications require nanosized ferrites in many cases. Thus, synthesis and studies on the properties of zinc ferrites is an interesting research topics now.

Ferrite spinels crystallize in face centered cubic lattice. In the normal zinc ferrite structure, $Zn^{2+}$ ions are in tetrahedral, while $Fe^{3+}$ ions are in octahedral positions. Zinc ferrites having normal spinel structure exhibit paramagnetic properties at room temperature.[4] Under extreme conditions, such as mechanochemical activation,[5] rapid quenching[6] or coprecipitation followed by annealing[7] position of $Zn^{2+}$ and $Fe^{3+}$ cations in the crystal structure can be partially or even completely reversed. The strong super-exchange interaction among these sites results in an unusually high magnetization as compared to normal spinels.[6]

Thermal plasmas, such as direct current (dc) arcs[8] and radiofrequency[9,10] (RF) plasmas offer unique advantages for the synthesis of special ceramic powders due to the easily achievable high temperatures and energy densities. In an RF thermal plasma flame the gas temperatures may exceed $10^4$ K independently of the gas composition. In addition, a high temperature gradient exists between the hot plasma flame and the surrounding gas phase. The resulting rapid quenching rate is favourable for producing fine particles with unstable structures in thermodynamic terms.

In this paper results on the RF thermal plasma synthesis of zinc ferrites from the ethanol solutions of the corresponding nitrates are presented. Aim of the study was to find correlations between plasma parameters and properties of product.

## 2. Experimental

The experiments were performed in a radiofrequency thermal plasma reactor operating at a maximum plate power of 30 kW. The experimental set-up is shown in Fig. 1. Argon was used as plasma gas with a flow rate of 20 l min$^{-1}$. The sheath gas was a mixture of Ar and $O_2$ with flow rate of 23 and 20 l min$^{-1}$, respectively.

The precursor solutions were prepared by the dissolution of analytical grade $Fe(NO_3)_3{\cdot}9H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ powders in technical grade ethanol using a magnetic stirrer. The Fe to Zn molar ratio was set to 2:1 in all cases.

The ethanol solutions of corresponding nitrate salts were injected into the plasma flame by a TEKNA suspension feeder. The solutions were atomized by argon with flow rate of

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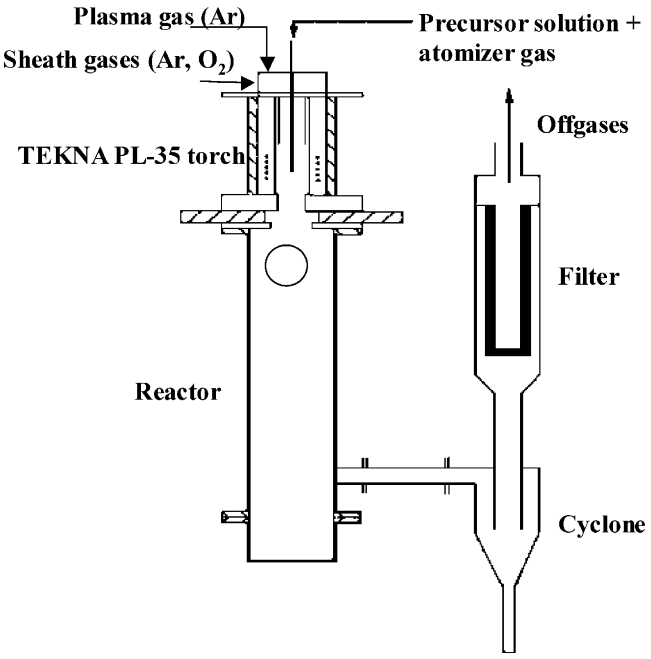


Fig. 1. Experimental set-up.

$31\,min^{-1}$. Inlet of injection probe was positioned at distances of 83 and 103 mm, respectively, below the top of induction coil. In the tests the following parameters were varied:

- Plate power.
- Concentration of salts in the ethanol solution.
- Position of injection probe.

The experimental conditions are summarized in Table 1.

The reaction products were collected from the reactor wall. Their chemical composition was analyzed by ICP-OES (Thermo Jarrell Ash Atomscan 25). A Philips Xpert XRD apparatus operating with Cu Kα radiation was used to analyze the phase composition. The lattice parameters ($a$) of the crystalline phases were determined from the positions of relevant diffraction peaks. Composition of zinc ferrite phase was determined from the lattice parameters. Morphology of products was studied by SEM (Philips XL30 ESEM) and TEM (Philips CM20). Energy dispersive X-ray fluorescence spectroscopy (EDS; NORAN EDS system) was applied to analyze the Fe and Zn content of individual particles. Magnetization measurements were performed at room temperature by a vibrating-sample (Foner-type) magnetometer. The external magnetic field varied up to 20,000 Oe. The saturation magnetization was determined by extrapolating the linear high-field part of the magnetization curve to zero fields.

Table 2
Results of the plasma tests

| Run | Zinc ferrite ($ZnFe_2O_4$) | | Magnetite ($FeFe_2O_4$) | Saturation magnetization (emu $g^{-1}$) |
|---|---|---|---|---|
| | $a$ (Å) | $I_{rel}$ (%) | $I_{rel}$ (%) | |
| 1 | 8.440 | 100 | 54 | 25 |
| 2 | 8.441 | 100 | 57 | 26 |
| 3 | 8.441 | 100 | 13 | 20 |
| 4 | 8.440 | 100 | 84 | 28 |
| 5 | 8.438 | 100 | 35 | 20 |
| 6 | 8.438 | 100 | 31 | 28 |
| 7 | 8.438 | 100 | 51 | 32 |
| 8 | 8.438 | 100 | 23 | 16 |

$a$: lattice parameter, $I_{rel}$: relative XRD intensities (731).

## 3. Results and discussion

The experimental results are summarized in Table 2. For evaluation of experiments, the XRD intensity ratio of stoichiometric zinc ferrite ($ZnFe_2O_4$) related to magnetite ($FeFe_2O_4$) and the morphology of products were chosen. Composition of the spinel structure was determined by deconvoluting the 731 spinel reflection of X-ray diffractograms.

Products from the different runs had the same bulk Fe/Zn molar ratio as the precursor solutions (Fe/Zn = 2). Plasma treatment of precursors resulted in extensive spinel formation in all experiments (Fig. 2). Mainly spinels of zinc ferrite type were formed. However, formation of magnetite ($FeFe_2O_4$) was detected, as well. Intensity of the magnetite reflection related to that of zinc ferrite varied in a broad range (13–84%) with the experimental parameters (Table 2). Low magnetite content of the spinel phase was measured in processing of more concentrated solution at high plate power (Run 3) and also in processing less concentrated solutions at low plate power (Run 8). In both runs the injection probe was situated at the higher position (83 mm). Lowering the probe position by 20 mm resulted in the slight increase of the magnetite content (Runs 5 and 6). Highest

Table 1
Experimental conditions

| Run no. | Probe position (mm) | Plate power (kW) | Zn + Fe molar concentration (mol/l) | Feed rate (l/min) | Specific energy (kWh/mol Zn + Fe) |
|---|---|---|---|---|---|
| 8 | 83 | 15 | 1.95 | 0.018 | 7.1 |
| 2 | 83 | 15 | 3.9 | 0.014 | 4.6 |
| 4 | 83 | 25 | 1.95 | 0.021 | 10.2 |
| 3 | 83 | 25 | 3.9 | 0.014 | 7.6 |
| 6 | 103 | 15 | 1.95 | 0.019 | 6.7 |
| 1 | 103 | 15 | 3.9 | 0.010 | 6.4 |
| 7 | 103 | 25 | 1.95 | 0.019 | 11.2 |
| 5 | 103 | 25 | 3.9 | 0.013 | 8.2 |