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# Preparation and Investigations of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ Ferrite Nanofiber Membranes by Needleless Electrospinning Method

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The preparation of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ nanofiber membranes by simple and versatile needleless electrospinning technique is presented. The single phase of spinel ferrite membrane was obtained after conventional thermal treatment of polyvinyl alcohol (PVA)/metal nitrate precursors at 800 °C for 4 h in air. The formation of single-phase fibers was characterized using differential scanning calorimetry accompanied with thermogravimetric analysis. The surface morphology, microstructure and crystal structure were investigated by scanning electron microscopy, X-ray diffraction and transmission electron microscopy. The magnetic properties of the fibrous samples measured in the temperature range from 2 to 300 K verify a soft magnetic behavior, which is quite typical for ferrimagnetic spinel-type ferrites.

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## 1. Introduction

Iron-containing transition metal oxides are the subject of extensive investigations. Ferrites possess unique magnetic, magneto-optical, magnetoresistive, thermal, electric and mechanical properties such as ferrimagnetism, high thermal conductivity, high electrical resistivity, controllable saturation magnetization, moderate thermal expansion coefficients, energy-transfer efficiency [1]. These properties make ferrites suitable for numerous device applications, including circulators, oscillators, phase shifters for microwave region, sensors, magneto-optic sensors, anode materials for batteries, catalysts, and sensors in space applications, lasers, phosphorescent sources, black and brown pigments. Since these materials do not exhibit cytotoxicity, they would be suitable also for biotechnological applications. One-dimensional nanostructures have received considerable attention due to their tunable mechanical properties such as high mechanical strength, toughness, and Young's modulus [2]. Moreover, they usually have a high surface-to-volume ratio which makes them useful for potential applications such as nanodevices, sensors, solar cells, photonics and multiferroic materials, molecular sieves, high-temperature insulation, catalysis, biomedical separation, and microwave absorbers [3, 4]. The cost-effective and simultaneously quite versatile technique for a preparation of nanostructured fibers in a large scale is electrospinning method [4, 5]. In this work we present the synthesis and experimental conditions of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ fiber preparation by needleless electrospinning technique. The single phase of spinel ferrite membrane was obtained after conventional thermal treatment of polyvinyl alcohol(PVA)/metal nitrate precursors at 800 °C for 4 h according to the results obtained from differential scanning calorimetry accompanied with thermogravimetric analysis (TG/DSC). The spinel structure membrane was verified by X-ray diffraction (XRD) analysis. The fibers morphology was visualized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The field and temperature dependences of mass magnetization of the fiber samples were measured in the temperature range from 2 to 300 K.

## 2. Experimental materials and methods

The $Ni_{0.2}Zn_{0.8}Fe_2O_4$ nanofiber membranes were prepared as follows. The precursor solution for the electrospinning was prepared by mixing of 7 wt% water solution of PVA (Acros Organic, Mw = 146,000–186,000 g/mol) with appropriate amount of metal nitrates (Acros Organic, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$). The molar ratio of $Ni^{2+}/Zn^{2+}/Fe^{3+}$ ions was set to 0.2/0.8/2 in order to maintain the molar ratio in the resulting ferrite $Ni_{0.2}Zn_{0.8}Fe_2O_4$. Subsequently, 0.03 vol.% of acetic acid (Sigma Aldrich, 99.7%) was added to the prepared solution. The prepared solutions were electrospun by Nanospider $^{TM}$ NS Lab (ELMARCO) equipped by needleless electrospinning technology. The applied voltage was 80 kV, the spinning distance between spinning and collector electrodes was in a range of 130–140 mm. The electrospinning was performed at ambient temperature with a relative humidity of 50%. After electrospinning, the electrospun composite nanofiber mats were dried at 90 °C for 15 min. The pure single phase spinel ferrite ($Ni_{0.2}Zn_{0.8}Fe_2O_4$) was obtained after annealing of precursor fibers in air at atmospheric pressure, at 800 °C for 4 h with a heating rate of 10 °C/min.

The surface morphology and microstructure of precursors and final ferrite nanofiber membrane was studied by SEM/FIB (ZEISS AURIGA COMPACT). The thermal

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decomposition of the samples was analyzed by DSC supplemented with thermogravimetric analysis (JUPITER STA 449-F1 NETZSCH). The phase and crystallinity of calcined membranes were investigated by a X-ray diffraction analysis (XRD, PhilipsX' PertPro, Cu $K_\alpha$ radiation). The substructure of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ nanofibers was observed by TEM (JEOL 2100F). Magnetic measurements were carried out by the magnetic properties measurement system (MPMS XL5 Quantum Design). The hysteresis loops and temperature dependences of mass magnetization of the fibrous samples were measured in the temperature range from 2 to 300 K.

## 3. Results and discussion

### *3.1. Structural analysis*

The thermal decomposition of PVA/metal nitrate precursor fibers was evaluated according to DSC/TG measurement. Figure 1 shows the characteristic thermal analysis curves of the polymer solution containing metal salts with PVA. It is evident from TG curve that the largest weight mass loss was recorded at the temperature 151.5 °C which invoked a rapid decomposition of PVA and auto-self-combustion process accompanied by evolution of volatile-by product. The highest exothermic peak was observed at this temperature. A more gradual release and weight loss takes place in the temperature region 500–1000 °C consistent with the burning-out of metal salts. The exothermic peaks at 607 °C, 702 °C, and 940 °C indicate the crystallization of spinel structure of NiZn ferrite fibers, after which the final nanostructured morphology is formed.

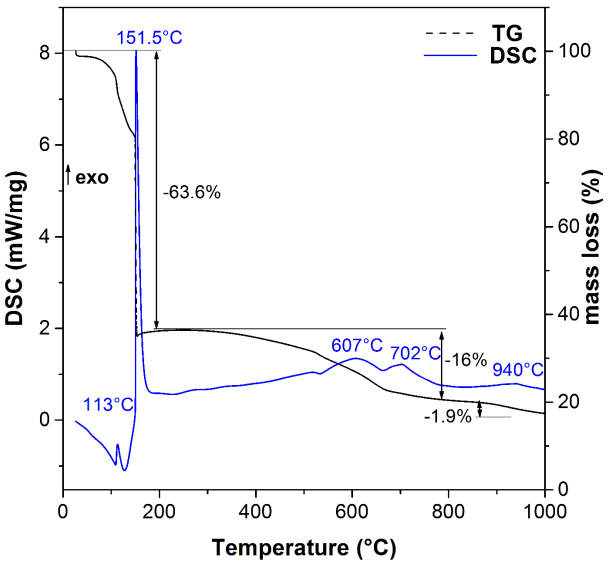


Fig. 1. TG-DSC analysis of PVA/metal nitrates precursors.

The crystal structure of the final membranes was investigated through an analysis of XRD pattern shown in Fig. 2. After sintering of precursors at 800 °C for 4 h in air

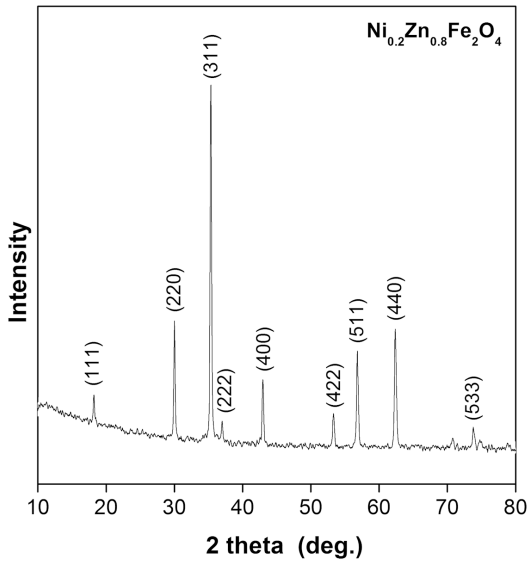


Fig. 2. XRD pattern of spinel $Ni_{0.2}Zn_{0.8}Fe_2O_4$ nanofiber membrane.

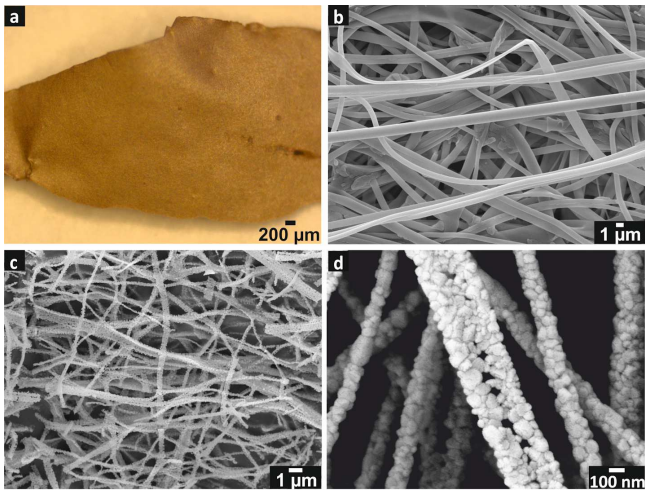


Fig. 3. Optical image of final ferrite membrane (a), SEM images of composite precursors (b), final fiber membrane (c), and detail of polycrystalline porous fibers (d).

characteristic diffraction peaks were identified as (111), (220), (311), (222), (400), (422), (511), (440), (533) and represent the main crystal planes in the pure spinel crystals. Some insignificant additional peaks of other phases were observed in the XRD pattern, which indicates a high purity of the membrane.

Microscopical analysis confirmed that the final solid ferrite membranes maintain the nanofiber structure even after calcination (see Fig. 3a). The PVA/metal nitrates precursor fibers were uniform, continuous with smooth surface and diameters between 0.5 and 1.5 $\mu$m. The calcination was accompanied with two basic changes: the decrease of fiber diameter and the change of overall morphology. The thickness of final ferrite nanofibers is about 100–250 nm and the circular-shaped precursor fibers were

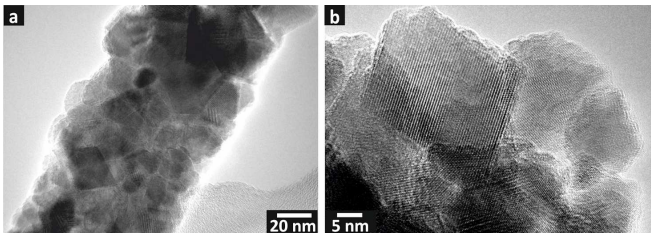


Fig. 4. TEM image of a) individual polycrystalline nanofiber and b) HRTEM image of nanoscale ferrite grains.

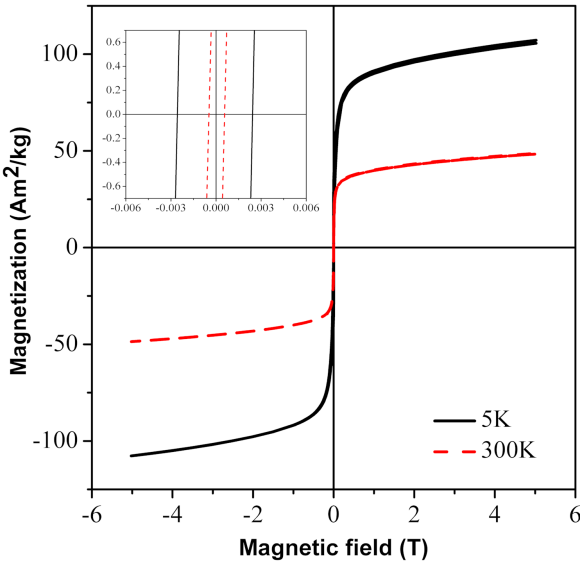


Fig. 5. Temperature dependencies of magnetization of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ nanofiber samples measured in magnetic fields 0.01 T and 1 T.

transformed into ribbon-shaped ferrite fibers. The similar ribbon-shaped structure of ferrite fibers was also reported by Fong et al. [6]. The ribbon formation can be attributed to a collapse of hollow nanofibers. The hollow nanofibers may be formed owing to a rapid evaporation of solvent. The SEM images of precursor and final nanofibers are shown in Fig. 3b–d. It can be seen that the fibers are porous and polycrystalline.

The substructure of $Ni_{0.2}Zn_{0.8}Fe_2O_4$ nanofibers has been investigated by TEM and HRTEM. TEM image of individual polycrystalline nanofibers and nanoscale ferrite grains are illustrated in Fig. 4. The fiber consists of cubic ferrite nanograins with different orientations in space and an average grain size of about 20 nm.

### *3.2. Magnetic properties*

The hysteresis loops recorded by the measurement system MPMS XL5 Quantum Design revealed soft magnetic properties of the measured nanofiber samples as exemplified in Fig. 5. The recorded values of coercivity were very low, around 2.5 mT at temperature 5 K, and below 1.3 mT at the room temperature (it is not possible to determine exactly the coercivity at room temperature using this equipment). The temperature dependences of the magnetization measured in magnetic fields 0.01 T and 1 T are displayed in Fig. 5. It can be seen from this figure that the prepared nanofiber membranes exhibit quite characteristic thermal dependences of the magnetization, which are typical for ferrimagnetic spinel-type ferrites with two antiparallel oriented sublatice magnetizations [7, 8].

## 4. Conclusions

The pure single-phase spinel $Ni_{0.2}Zn_{0.8}Fe_2O_4$ nanofiber membranes have been successfully synthesized via needleless electrospinning method and conventional thermal treatment of the precursor fibers at 800 °C. The membranes consist of polycrystalline continuous nanofibers with typical diameter ranging in between 100 and 250 nm. The presented results imply that the needle-less electrospinning combined with calcination is simple, inexpensive, and perspective technique for a production of ferrimagnetic membranes.

## Acknowledgments

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