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Sol–gel processing and magnetic properties of nickel zinc ferrite thick films

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Abstract

Nickel zinc ferrite $Ni_{0.36}Zn_{0.64}Fe_2O_4$ (NZF) thick films have been synthesised using a dip coating sol–gel process. The coating sol has been formed from NZF powders dispersed in the NZF raw sol. A suitable processing temperature for the preparation of NZF composite films with reasonable magnetic properties has been found to be 400°C. The magnetisation of NZF films increased and coercive force decreased with the processing temperature. Typical values of magnetisation and coercive force of the NZF films have been found to be Ms = 110 emu/cm^3 and Hc = 20 Oe, respectively. The sol–gel method combined with dispersion of ceramic NZF particles in starting sols has been proved to be useful for producing thick nickel zinc ferrite films.

Keywords: A. Sol–gel processes; C. Magnetic properties; D. Ferrites; D. Spinel

1. Introduction

Spinel type ferrites including Ni–Co or Ni–Zn compositions are of great interest due to their potential applications in microelectronics, magneto-optics and as a microwave device components [1–3]. Optical fibre structures composed of magnetostriction material such as nickel, metallic glass or ferrite and optical fibre have been used for the development of magnetic field sensors [4–6]. It is a known fact [5–7] that nickel ferrites doped by various transition metals can exhibit a relatively high magnetostriction comparable to that of ferromagnetic metal such as nickel. For example, the calculated magnetostriction coefficient d_{33} for nickel zinc ferrite with the composition of $Ni_{0.36}Zn_{0.64}Fe_2O_4$ has been found [6,7] to be 4–5 orders of magnitude greater than that of $NiFe_2O_4$ or $CoFe_2O_4$. One then may expect that such material applied as a film on optical fibre would have a high response to low magnetic fields what may be particularly useful for magnetic field sensors.

Various compositions of nickel zinc ferrites (further denoted as NZF) have been fabricated especially by solid-state sintering or thermal decomposition techniques [8–11] whereas the usage of sol–gel methods has been reported only scarcely [12,13]. Sol–gel technique offers excellent composition control, low temperature processing and short fabrication times at comparatively low cost. One of disadvantages of the sol–gel method, however, consist in a fact that only a small thickness (approx. up to 200 nm) of high quality film can be achieved per one coating cycle and several coating cycles are necessary when thick films are required. One of the way to make thick layer is to form a composite material. Several papers have reported the preparation of cermets [14] or sol–gel polymeric composites [15,16]. Lead zirconate titanate (PZT) and ZrO_2 thick films have been synthesised [17] using the dispersion of ceramic powders in the sol containing zirconium alkoxides.

This paper deals with thick films of NZF based on composite materials consisting of ceramic powders of NZF dispersed in matrices prepared by the sol–gel method. The main goal of the paper was to prepare NZF films with sufficient thicknesses both on flat and

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fibre substrates which could be potentially used for the development of fibre-optic magnetic field sensors. The preparation conditions and crystallographic and magnetic properties of NZF films with the particular composition of $Ni_{0.36}Zn_{0.64}Fe_2O_4$ have been investigated.

2. Experimental

2.1. Chemistry of the thick film fabrication

Thick NZF films have been synthesised by dispersing nickel zinc ferrite powders in a properly composed solution which tends to gel when heated. Powders were made by hydrothermal ageing of hydroxides (powder type A) and by co-precipitation technique [16]. Powders made by the latter method were calcined either at temperature of 600°C (powder type B) or at 1000°C (powder type C) in air atmosphere.

Iron (III) nitrate nonahydrate $Fe(NO_3)_3.9H_2O$, nickel nitrate hexahydrate $Ni(NO_3)_2.6H_2O$ and zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ were used as precursors (Aldrich Co., ACS grade) for the preparation of the starting sol. Iron nitrate was dissolved in the mixture of ethylene glycol (EG) and 2-methoxyethanol (2-MOE) at room temperature. Nickel and zinc nitrates were dissolved in 2-methoxyethanol or ethanol at 60°C and mixed together with iron nitrate solution. This solution was heated to 70°C while stirring for 5 min. To adjust sol rheology a small portion of glycerol was added to the above solution. Ferrite powder of various types (A, B and C) was then dissolved in mixture of EG/2-MOE and added to the solution so that the target concentration of solid particles was between 15 and 20 wt%. The final solution was vigorously shaken and mixed in ultrasonic cleaner for 20 min to disperse particles sufficiently. Films were made by dip coating of glass substrate using withdrawal speed typically from 20 to 30 cm/min.

In order to avoid some difficulties related to the fabrication of similar films on optical fibres, and to improve adhesion of NZF films to the substrate, fibres were precoated by 2 layers of ZrO_2 stock sol–gel solution prior to the deposition of NZF film. For optical fibres withdrawal speed of 70 cm/min was used.

Films were dried in an oven at 120°C for 5 min and then fired in a tubular furnace at 350°C between each successive coating. One to three layers were deposited and annealed at temperatures ranging from 400 to 600°C.

2.2. Scanning and transmission microscopy

Transmission electron microscopy (TEM) was used to characterise ferrite powders with respect to their particle size and overall appearance. Surface and cross-section of NZF films were examined using scanning electron microscopy (SEM).

2.3. X-ray diffraction studies

The crystallographic structure of NZF powders and films was investigated using a Siemens D5005 diffractometer with either copper or cobalt anode.

2.4. Magnetic properties

Magnetic properties were examined at a room temperature using the vibrating sample magnetometer VSM model PAR1500. Magnetisation at saturation M_s, remnant magnetisation M_r and coercive force H_c were evaluated from hysteresis curves for both NZF powders and NZF thick composite films deposited on planar substrates.

3. Results and discussion

3.1. Crystallography and TEM

Diffraction patterns of powders A, B and C are shown in Fig. 1. Typical spinel reflections can be clearly seen on all traces where the lowest peak intensities were found for the powder A. This is apparently due to the low temperature synthesis during the hydrothermal grow and hence reduced grain size. On the other hand the maximum peak intensities were measured for the powder C calcined at a processing temperature of 1000°C. However, some excess of ZnO can be observed which can be explained by the phase separation of ZnO at such high temperature (see ZnO reflections at $2\theta = 37.2°$ and 42.4°, Co anode). The lattice constant c was determined taking into account d-spacing of {311} line. The lattice constant c was calculated to be 8.393 Å for the powder A, whereas for the powder B and C the lattice constant did not differ much and was found to be 8.406 and 8.405 Å, respectively.

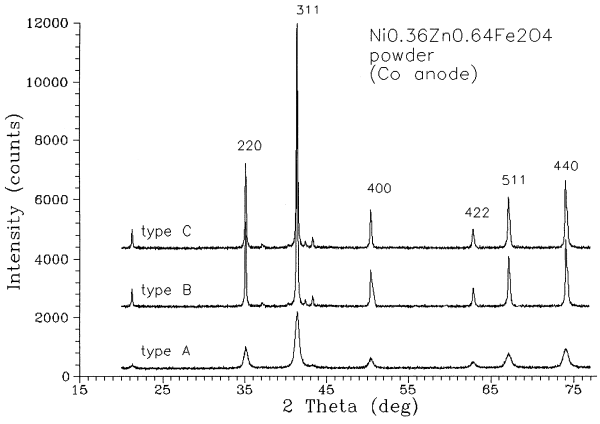

Fig. 1. X-ray diffraction pattern of the NZF powders: A, hydrothermally grown at 300°C; B, co-precipitation method, annealed at 600°C; C, co-precipitation method, annealed at 1000°C.

A diffraction pattern of composite films annealed at 300, 400 and 600°C (Fig. 2) shows no peaks attributed to ZnO or any other phase. The lattice constant $c = 8.412$ Å for the films was the biggest among the other ones which would correspond to less rigid structure observed in sol–gel matrix. Also, the lattice values correspond to unit cell dimensions of nickel zinc ferrite films as previously published by Wolska [18]. As the extended annealing around 500°C promotes the formation of hematite (α-Fe_2O_3), the processing temperatures of about 400°C were further used. Low processing temperatures for NZF films are especially important for the deposition of such layers on optical fibres because it has been found that mechanical properties of optical fibres deteriorate substantially with increasing temperature [19].

TEM photographs of powders A, B and C are shown in Fig. 3a–c, respectively. Very fine crystal structure with the particle size ranging from 10 to 30 nm have resulted from the hydrothermal grow method (powder A). This type of powder was the most easy to disperse in the starting solution. Particles with a size of several hundreds of nanometers have been found in powders B and C. The latter powder also exhibited a substantially larger portion of aggregates in the solution which were difficult to break and disperse.

The NZF films made from properly composed dispersions were homogeneous and had good adhesion to substrates. The surface of NZF films prepared on the basis of the powder A was smooth; however, at medium magnifications (500×) microcracks became visible (Fig. 4a). Particles up to 1 μm in diameter visible on the film surface resulted apparently from larger aggregates, formed during sol preparation, which were difficult to break apart. At high magnifications (5000×) we could estimate the width of cracks being less than 0.3 μm (Fig. 4b). The formation of microcracks may be explained by the local inhomogeneity existing throughout the film. The cross-section of two-layer NZF composite film deposited on microscopic slide shows a relatively good packing density (see Fig. 4c, magnification 3000 ×) and the film thickness per one coating cycle was estimated to be 1–1.1 μm. The cross-section of NZF three-layer film (powder A) applied on the silica optical fibre is shown in Fig. 4d. The film thickness was estimated to be 2 μm.

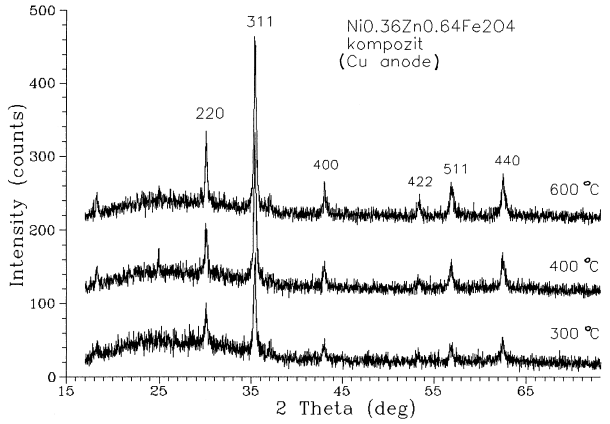

Fig. 2. X-ray diffraction patterns of NZF composites (powder A used), annealed at 300, 400 and 600°C for 5 min.

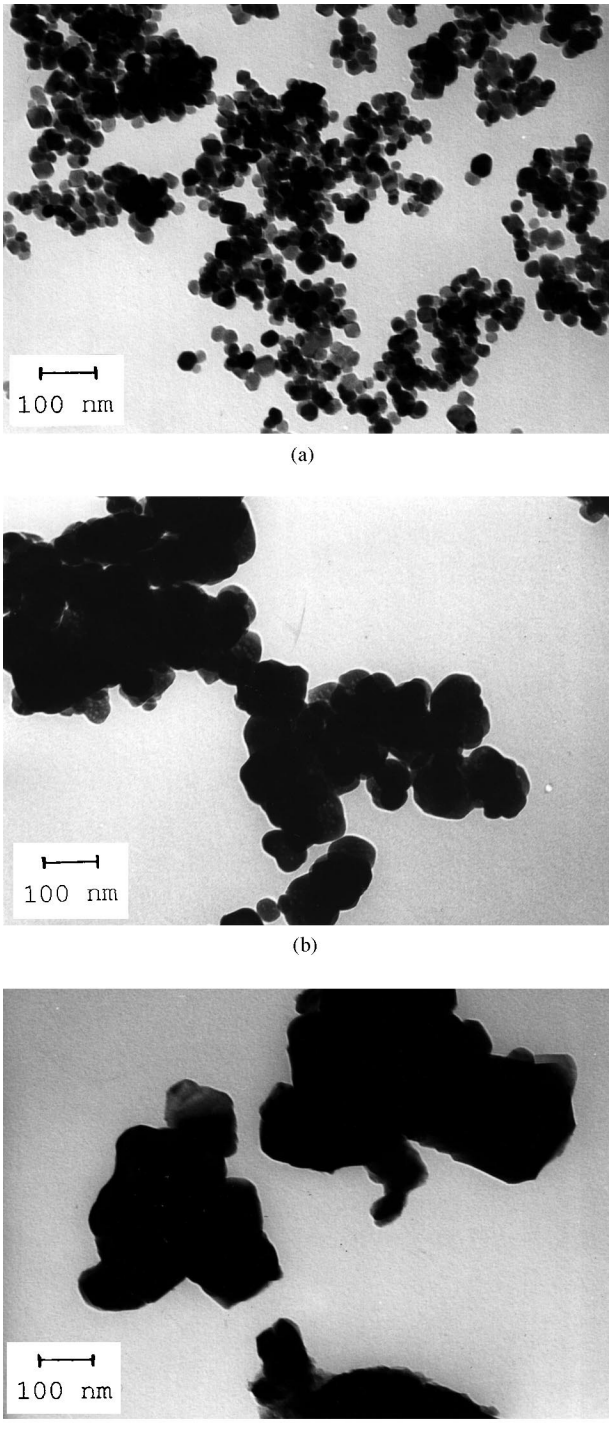

Fig. 3. TEM photograph of (a) NZF powder A; (b) powder B and (c) powder C.

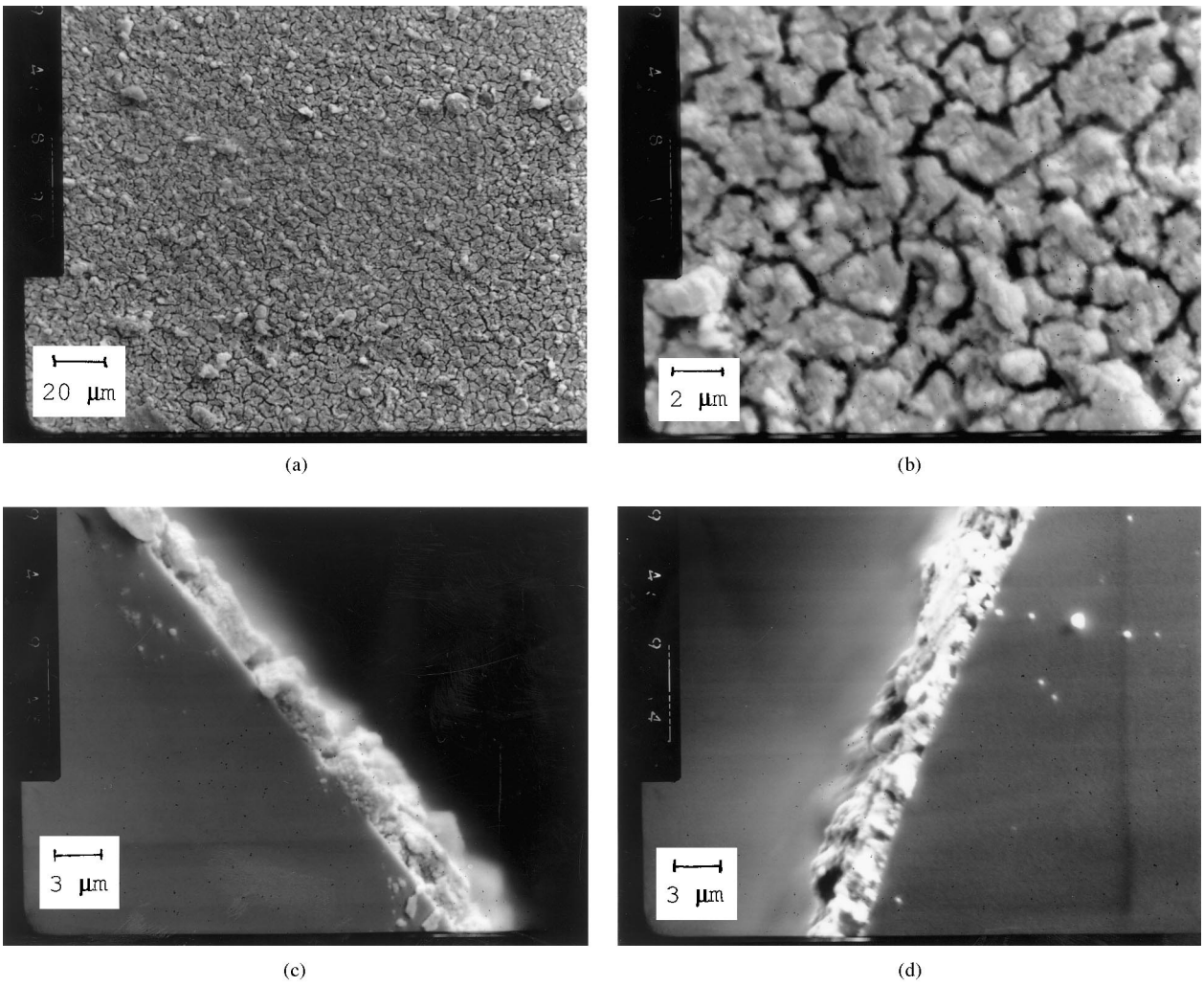

Fig. 4. SEM of the composite NZF film (powder A used) processed at 600°C: (a) film surface magnified 500 times and (b) 5000 times; cross-section of the NZF film on (c) planar substrate and (d) on optical fibre.

3.2. Magnetic properties

Dependence of magnetisation M in electromagnetic units per gram (EMU/g) on external magnetic field for the powder samples A, B and C is shown as the hysteresis loops in Fig. 5. It can be seen that the values of coercive force H_c for all powders are quite low where the lowest value of H_c was found for the powder A (approx. 3 Oe). This result can be related to a high content of superfine crystals in this powder and hence to a high content of single domain particles. The values of magnetisation in saturation Ms were 30, 32 and 54 EMU/gm for powders A, B and C, respectively.

The hysteresis loops for the composite films heat-treated at 300, 400 and 600°C are shown in Figs. 6–8, respectively. Sankpal et al. [11] have found the value of H_c for $Ni_{0.7}Zn_{0.3}Fe_2O_4$ bulk material (sintering of mixed oxides) to be of 1.66 Oe whereas Itoh et al. [10] for $Ni_{0.6}2Zn_{0.38}Fe_2O_4$ films published the value of H_c of around 25 Oe. The extremely low H_c values for the

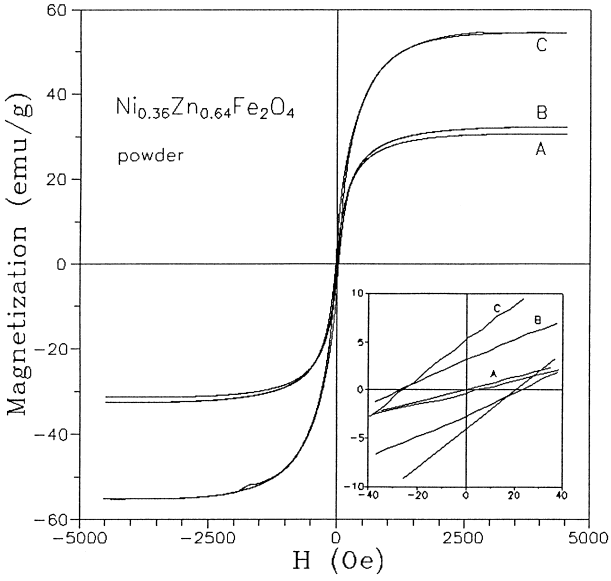

Fig. 5. The hysteresis loops for the NZF powders A, B and C; the coercive force H_c is 5, 22 and 25 Oe for the powder A, B and C, respectively.

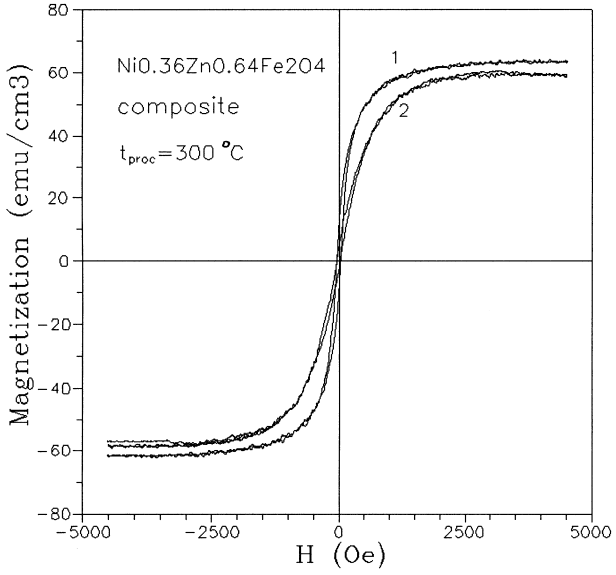

Fig. 6. The hysteresis loops for the NZF composite film (powder A used) heat-treated at 300°C; film oriented parallel (1) or perpendicular (2) to the external magnetic field.

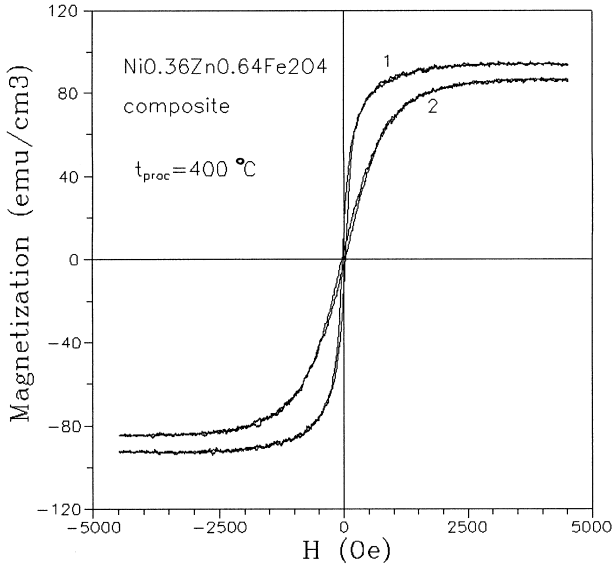

Fig. 7. The hysteresis loops for the NZF composite film (powder A used) heat-treated at 400°C; film oriented parallel (1) or perpendicular (2) to the external magnetic field.

former composition can be attributed to large grain size whereas with decreasing grain size one may expect increase in coercivity [1] as in the case of sol–gel derived thin films. Somewhat higher values of coercive force H_c for the prepared composite NZF films in comparison to those of the NZF powders are inherent to the nickel-zinc ferrite sol–gel matrix and built-up stresses existing on substrate interface. On the basis of Figs. 6–8, one can draw conclusion that the magnetisation was also dependant on processing temperatures even though the temperature of 400°C seems to be sufficient for producing good quality films.

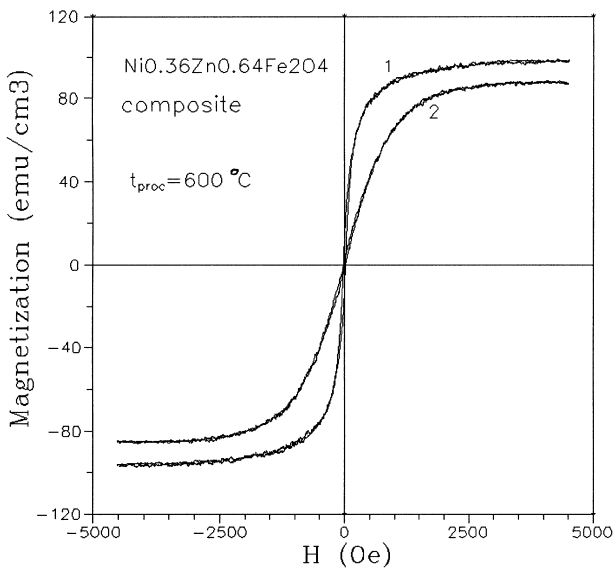

Fig. 8. Hysteresis loops for the composite film (powder A used) heat-treated at 600°C; film oriented parallel (1) or perpendicular (2) to the external magnetic field.

The shape of hysteresis loops has been found to be also dependent on the orientation of NZF films to external magnetic field H_{ext} (Figs. 6–8). By approaching the parallel orientation a value of the magnetic susceptibility χ of the films became consecutively greater and greater. This fact can be explained by a lower barrier for domain reorientation in the parallel directions. When considering an optical fibre with NZF layer deposited as the fibre jacket then the easiest direction of magnetisation would be along fibre axis. This means that with the change of magnetic field intensity along fibre axis its length will change resulting in a phase shift of light transmitted in the fibre core. Conclusively, such fibre will act as a magnetic field sensor.

4. Conclusions

1. Nickel zinc ferrite $Ni_{0.36}Zn_{0.64}Fe_2O_4$ (NZF) thick films have been synthesised using a dip coating sol–gel process. The coating sol has been formed from NZF powders dispersed in the NZF raw sol. The best dispersing capability showed powders produced by the hydrothermal grow method at 300°C.
2. A suitable processing temperature for the preparation of NZF composite films with reasonable magnetic properties has been found to be 400°C. The magnetisation of NZF films increased and coercive force decreased with the processing temperature and has been found to be $M_s = 110$ emu/cm^3 and $H_c = 20$ Oe, respectively. The lowest barrier for domain reorientation exists in parallel directions of external magnetic field and NZF film

orientation since the magnetic susceptibility increased.

3. The sol–gel method combined with dispersion of ceramic NZF particles in starting sols has been proved to be useful for producing thick nickel zinc ferrite films.
4. Further attention will be concentrated to the fabrication of the NZF thick films on single mode optical fibres and to testing of such modules in fibre-optic modulators and sensors of magnetic field.

Acknowledgements

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