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Nanostructure and magnetic properties of magnesium ferrite thin films deposited on glass substrate by spray pyrolysis

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ABSTRACT

The spinel $MgFe_2O_4$ thin films were prepared on the glass substrates at T_S=400 °C by the spray pyrolysis deposition method. Structural and magnetic properties of the calcinated thin films at different temperatures were also investigated. By changing the calcination temperature from 400 to 600 °C, the crystallite size increased from 10 to 15 nm and the crystallinity of the films improved slightly. Thickness of the films calcinated at 400 and 600 °C were 0.648 and 1.473 μm respectively. However, the surface morphology of the films did not change considerably. Magnetic measurements, when the applied magnetic field was in parallel and perpendicular directions, showed the isotropic magnetic nature of the prepared films and their magnetic properties increased with the increment of calcination temperature. The H_c value of thin films calcinated at 400 °C was about 168 Oe.

1. Introduction

The spinel-type ferrites are too important due to their many applications in technology and industry. Among magnetic ferrites, magnesium ferrite with unique magnetic properties has a significant advantage. This ferrite is a soft magnetic n-type semiconductor and has many applications in catalysis [1–4], brown pigments [5], high-density recording [6], gas sensors [7], transformers, magnet core of coils and ferrofluids [8–12]. In recent years, considerable attention was attributed to the production of its nanostructures because of their different properties from bulk materials [13–15]. Thin films are the suitable type of nanostructures which have many applications due to their easy using and have more efficiency in comparison with other nanostructures. Thin films are produced using many methods including chemical vapor deposition (CVD) [16,17], sputtering [18,19], vacuum evaporation [20,21], pulsed laser evaporation [22,23], hydrothermal technique [24,25], sol–gel [26,27], ferrite plating [28] and spray pyrolysis [29,30]. The spray pyrolysis is not only an easy method but also a cheap one, which can be used to produce many types of thin films in air. This method has the production capability of highly mixed thin films with two or more compounds, since their initial compounds are mixed in solution forms. Furthermore, it can be possible to prepare doped thin films with very accurate percentage of raw materials by spray pyrolysis route. Controllable size, uniform distribution of grains size and high speed are the other advantages of this method in comparison with other methods. The full description of spray pyrolysis method (SPD) was reported in works of other authors. Wu et al. classified this method into five essential steps [31]. Also, Viguie et al. categorized the SPD method in four sections based on reaction occurring at the surface of substrate [32].

In the other work, we synthesized nanoparticles of $MgFe_2O_4$ by using the sol–gel auto combustion method [33]. To our knowledge, there is no report about producing of magnesium ferrite thin films using spray pyrolysis approach. Therefore in this study an attempt has been made to investigate the structural and magnetic properties of thin films, which were fabricated using the aforementioned method.

2. Experimental procedure

To fabricate magnesium ferrite thin films, iron nitrate ($Fe(NO_3)_3\ 9H_2O$) and magnesium nitrate ($Mg(NO_3)_2\ 6H_2O$) were used as the mineral reactants and deionized water as the solvent. Iron and magnesium nitrates were solved separately in deionized water at concentration of 0.08 and 0.04 M respectively. The final solution with yellow color was obtained by mixing these two solutions together in 1:1 volumetric proportion. Thin films were deposited on glass substrates and were put on the hot plate of the apparatus by a holder. The substrate temperature was controlled

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using a thermocouple which was connected to a glass substrate. A solution was atomized by a high pressure air. In order to produce a suitable thin film, the deposition process of spray should be repeated several times. It is also necessary to wait some seconds between each time of deposition process in order to get thermal equilibrium on the surface of thin films. The spray rate, the distance between nozzle to substrate and substrate temperature affect the characterization of the produced thin films. Therefore, the spray rate, the distance between nozzle to substrate and substrate temperature have been considered constant and were 10 cc/min, 30 cm and 400 °C respectively. The effects of these parameters are being studied and will be published elsewhere subsequently. The conditions of deposition process are shown in Table 1. The obtained thin films were calcinated at 400 °C, 500 °C and 600 °C for 2 h with rate of 180 °C/h.

The structural properties of thin films were analyzed by the X-ray diffraction (XRD; model D8 Advance Bruker) using Cu Kα radiation (λ=0.154056 nm). The range of 2θ was from 25° to 80° with the scanning speed of 0.02 °s^{-1}. Morphology of the films and their grains size were also investigated using the scanning electron microscopy (SEM; model Hitachi S-4160). The magnetic properties at room temperature were measured using the vibrating sample magnetometer (VSM; model Lake Shore 7400).

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of the synthesized $MgFe_2O_4$ thin films which calcinated at different temperatures. As shown in Fig. 1, the thin films calcinated at 400 °C are not completely crystallized and the (422) and (533) Bragg peaks with low intensity do not appear. By increasing the calcination temperature from 400 to 600 °C, these peaks appear, and the other Bragg reflection peaks become higher and narrower also. It refers to better crystallization and increasing of the crystallites size. No peaks corresponding to other phases were observed in the X-ray diffraction patterns. Our results show that the spray pyrolysis method is suitable for producing thin films of $MgFe_2O_4$ with a very small crystallite size. It is well-known that small size particles are more useful for material applications [34,35].

The crystallite size of films was estimated by using the Scherrer equation:

$$D = 0.89\lambda/\beta\cos\theta \quad (1)$$

Table 1
The conditions of deposition process.

Substrate material	Substrate temperature	Spray rate	Distance between nozzle to substrate
Glass	400 °C	10 cc/min	30 cm

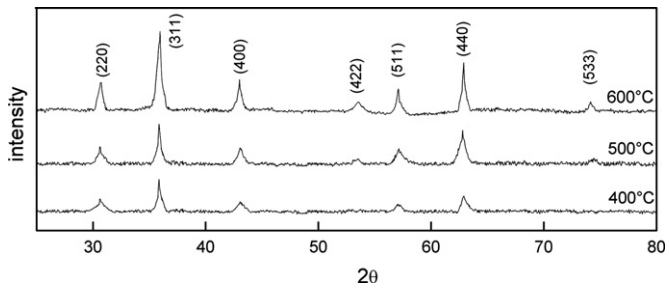

Fig. 1. X-ray diffraction patterns of $MgFe_2O_4$ thin films calcinated at different temperatures.

where λ is the wavelength of the radiation, θ is the Bragg diffraction angle and β is the full width at half maximum (FWHM) of the strongest diffraction peak (311). Due to the cubic spinel structure of thin films, the lattice parameter was also calculated using the following relationship [36]:

$$a = d_{hkl}(h^2+k^2+l^2)^{1/2} \quad (2)$$

The X-ray density was also calculated according to the following formula [37]:

$$R_{hkl} = 8M/Na^3 \quad (3)$$

where M, N and a are molecular weight of the material, Avogadro's number and lattice parameter of the crystal respectively. The structural parameters such as mean crystallite size, lattice constant and X-ray density of the thin films, which were deduced from X-ray data, as a function of calcination temperature are given in Table 2.

Fig. 2 shows SEM images of cross section of the Mg-ferrite film which are calcinated at 400 and 600 °C. Thin films calcinated at both temperatures have smooth and dense surfaces. Wu et al. reported that the surfaces of $ZnFe_2O_4$ thin films obtained from the solution with low pH were smooth. Nevertheless thin films prepared from the solution with high pH have rough surfaces [31]. Other works showed that if acetate solutions were used for production of CdS films, the surfaces would be very smooth, while using chloride solutions lead to the rough surfaces [38].

In this study the surface morphology of magnesium ferrite thin films which was calcinated at different temperatures is similar. This is probably due to using identical primary solution for deposition process of all thin films. As shown in Fig. 2, by increasing the calcination temperature, the thickness of thin films becomes greater, which is due to the growth of grains. The thicknesses of the produced films at 400 and 600 °C are 0.648 and 1.473 μm respectively.

The SEM images of thin films are shown in Fig. 3. For all samples, the grains size distribution is uniform. The grains size of the films calcinated at 400, 500 and 600 °C are about 17, 24 and 31 nm respectively. As can be seen, the variation of particles size is in agreement with the XRD results. The nanoparticles with cubic crystal are tending to grow into the spheral shape because in this configuration the surface tension is minimized [39].

Magnetic parameters of the thin film samples were measured by a vibrating sample magnetometer (VSM) at room temperature for different directions of applied field (parallel or perpendicular to the film's surface). Hysteresis loops of the $MgFe_2O_4$ thin films calcinated at different temperatures are illustrated in Figs. 4 and 5.

Saturation magnetization can be determined from extrapolation of the plot M versus $1/H$ [40]. The experimental magnetic moment values (η_B) in Bohr magnetons are calculated using the following formula [41]:

$$\eta_B = MM_S/5585 \quad (4)$$

which M and M_S are molecular weight and saturation magnetization (emu/g) of the material respectively. The magnetic parameters of samples such as saturation magnetization (M_s), coercivity field (H_c) and experimental magnetic moment (η_B), as a function of

Table 2
Structural parameters of thin films at different calcination temperatures.

Calcination temperatures (°C)	Lattice constant (Å)	Crystallite size (nm)	Cell volume (Å^3)	X-ray density (g/cm^3)
400	8.35	10.63	581.41	4.57
500	8.36	15.20	583.37	4.56
600	8.37	19.60	586.82	4.53