Facile Preparation of Magnesium Ferrite Film via a Single-source Precursor Route

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A magnesium ferrite film has successfully been fabricated by sintering a single-source Mg–Fe^{II}–Fe^{III} layered double hydroxide (LDH) precursor at 900 °C. It is shown that the obtained ferrite film exhibits a promising superparamagnetic behavior.

Magnesium ferrite ($MgFe_2O_4$) is a widely studied material that finds applications in many areas including magnetic recording, catalysis, sensor, and adsorption. In recent years, nanosized magnesium ferrites prepared by various methods have been intensively investigated and shown to exhibit markedly different magnetic properties from the bulk ferrites, such as particularly interesting superparamagnetic behaviors.[1–8] With the current trend toward miniaturization of magnetic products, numerous studies have focused on the development of new methods for preparation of high-quality ferrite films. Several methods including facing-target sputtering, pulsed laser deposition, metallorganic chemical vapor deposition, and spray pyrolysis have been used to prepare such films.[9–12] These techniques require expensive vacuum equipments and complicated processing, which increases the cost of the films. Other techniques such as sol–gel/slurry processing[13] and roll-spray ferrite plating[14] have also been used to prepare ferrite films. Although the sol–gel/slurry process gives highly homogeneous films and allows easy control of composition and lower sintering temperatures, production costs of the films are still relatively high since organometallic precursors and organic additives are usually required. Development of a simple, economical, and environmentally friendly fabrication process for ferrite films is essential if their potential applications are to be realized in practice. However, only a few methods for fabricating magnesium ferrite films have been reported to date. For example, an $MgFe_2O_4$ film has been prepared by a sol–gel process using metal nitrate salts as the raw materials and glycerol, formamide, and HCl as solvents,[15] $MgFe_2O_4$ epitaxial films have been formed by solid-state reactions on MgO(100) surfaces,[16] and $MgFe_2O_4$/Fe composite thin films have been obtained by soft solution processing.[17]

Layered double hydroxides (LDHs), also known as hydrotalcite-like materials, are a class of synthetic anionic clays whose structure can be described as consisting of brucite-like layers in which a fraction of the divalent cations have been replaced by trivalent cations giving positively charged sheets with charge-balancing anions between the layers.[18–21] LDHs can be described by the general formula $[M^{II}{}_{1-x}M^{III}{}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$. Our group has shown that when M^{II} is a mixture of Mg and Fe^{II} and $M^{III} = Fe^{III}$ with $Mg/(Fe^{II} + Fe^{III}) = 0.5$, the resulting LDHs may be converted to magnesium ferrite powders which have superior magnetic performance to those prepared by conventional ceramic methods.[22–24] This work aims to demonstrate the feasibility of direct conversion of LDH precursor coating to prepare a ferrite film. In this paper, we show how this process may be extended to prepare magnesium ferrite films on an α-Al_2O_3 substrate without the use of organic additive or expensive precursor. The structure, morphology, and magnetic properties of the resulting film have also been investigated.

A well-dispersed and stable suspension of Mg–Fe^{II}–Fe^{III}–CO_3–LDH was prepared by a procedure developed in our laboratory involving separate nucleation and aging steps (SNAS method)[25,26] using a precursor solution in which the molar ratio of $Mg^{2+}/Fe^{2+}/Fe^{3+} = 4/5/3$. The resulting slurry was cast on the α-Al_2O_3 substrate, and the resulting film was dried in air at room temperature for about 48 h. The film was then heated to 900 °C with a heating rate of 1 °C/min, held at that temperature for 4 h, and then slowly cooled to room temperature.

The XRD pattern of the powder scraped from the $MgFe_2O_4$ film is shown in Figure 1. The diffraction peaks can be indexed to the (220), (311), (222), (400), (422), (511), and (440) reflections of an $MgFe_2O_4$ spinel phase.[22–24] The energy dispersive X-ray spectrometric analysis (EDS) shows that the film contains the expected peaks for Mg and Fe with the ratio of Mg:Fe being 1:1.97. Thus, by tailoring the composition of the LDH precursor to ensure the ratio of Mg:Fe being 1:2 ($Mg/Fe^{II}/Fe^{III} = 4/5/3$), a single-phase magnesium ferrite film can form on the α-Al_2O_3 substrate through the oxidation of Fe^{II} to Fe^{III} during calcination in air. This is consistent with our earlier studies of the powdered materials.[22–24]

Figure 2 shows SEM images of the microstructure of LDH coating and $MgFe_2O_4$ film. From the comparison between the LDH coating (Figure 2A) and the $MgFe_2O_4$ film (Figures 2B and 2C), it can be seen that the as-prepared film is coarse but dense, whereas the annealed film is composed of spherical or elliptical grains with diameters of less than 100 nm. Figure 2D shows the SEM image of cross-sectional morphology of the $MgFe_2O_4$ film, indicating that the film thickness is of the order of 2–3 μm. In addition, the annealed film showed good adhesion with the α-Al_2O_3 substrate.

The temperature dependence of the magnetization for zero field cooled (ZFC) and field cooled (FC) of the $MgFe_2O_4$ film was investigated using a superconducting quantum interference

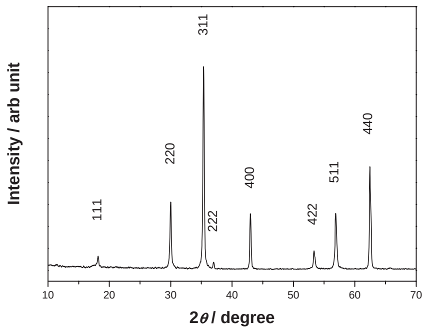

Figure 1. XRD pattern of the $MgFe_2O_4$ film.

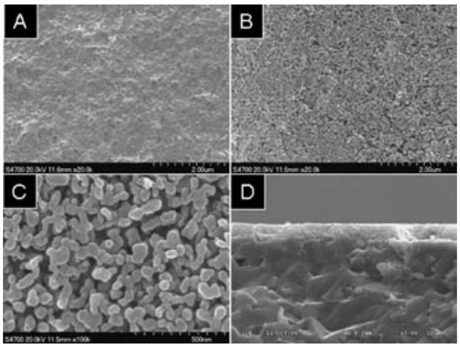

Figure 2. SEM images of Mg–Fe^{II}–Fe^{III} LDH coating (A) and $MgFe_2O_4$ film (B and C: surface; D: cross sectional).

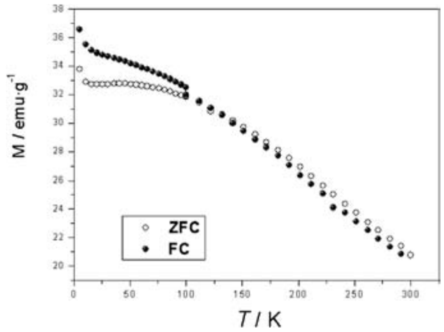

Figure 3. Magnetization–temperature curves of $MgFe_2O_4$ film.

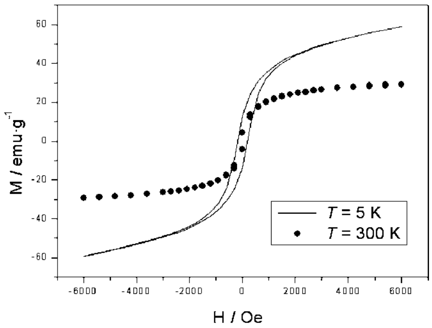

Figure 4. Magnetization versus applied magnetic field plots of the $MgFe_2O_4$ film measured at 300 K (solid line) and 5 K (solid circle).

device magnetometer (SQUID) at 100 Oe field, as shown in Figure 3. The ferrite film has a blocking temperature (T_B) of 100 K. Above T_B, the FC and ZFC magnetization data are very similar, whereas below T_B, they diverge significantly. The field dependence of the magnetization of the sample is shown in Figure 4. At 5 K, the magnetization of the $MgFe_2O_4$ film displays a clear hysteresis loop. At room temperature (300 K), however, there is no hysteresis and the magnetic moment is unsaturated even at a magnetic field of 6 kOe. It is well known that the appearance of a blocking temperature and unsaturated magnetization is indicative of superparamagnetic properties originating from the quantum effect of nanometric magnetic grains.[27] In addition, dependence of microstructure and magnetic properties of $MgFe_2O_4$ films on the annealing temperature was investigated. We have observed that the $MgFe_2O_4$ film prepared at 1100 °C is composed of larger particles which do not show superparamagnetism. It suggests that the superparamagnetic property of the film annealed at 900 °C arises from nanomagnetic grains.

In conclusion, we have realized a facile preparation of $MgFe_2O_4$ film by sintering the Mg–Fe^{II}–Fe^{III} LDH coating at 900 °C. The as-prepared $MgFe_2O_4$ film exhibits a promising superparamagnetic behavior. Most importantly, the present approach can be flexibly extended to fabricate other ferrite films, such as $NiFe_2O_4$, $ZnFe_2O_4$, and so on.

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