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Influence of metal precursor on the synthesis and magnetic properties of nanocrystalline $SrFe_{12}O_{19}$ thin films

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ABSTRACT

The effects of metal precursor on the structure and magnetic properties of strontium hexaferrite ($SrFe_{12}O_{19}$) thin films synthesized by polymeric precursor method have been investigated. Fourier transform infrared, thermal analyses, X-ray diffraction, scanning electron microscopy and vibrating sample magnetometer techniques were applied to evaluate the microstructure, composition, crystallite size and magnetic properties of the $SrFe_{12}O_{19}$ thin films. The films synthesized from metal nitrate precursor offered the single phase $SrFe_{12}O_{19}$ with the crystallite size of 42 nm and isotropically magnetic properties of M_s=267 emu/cm^3, M_r=134 emu/cm^3, and H_c=4790 Oe after calcination at 800 °C. The films obtained from metal hydroxide and metal chloride precursors exhibited higher coercivities, 6063 and 5047 Oe, respectively, due to the smaller particle size; however, they were not single phase strontium hexaferrite.

1. Introduction

Strontium hexaferrite $SrFe_{12}O_{19}$ (SrM) with magnetoplumbite structure is a traditional permanent magnetic material which is widely used in electro-acoustic devices, electrical motors, electricity generators, etc. However, its films can be potentially used in high density magnetic recording media due to their large uniaxial anisotropy, and excellent chemical and mechanical stability. Furthermore, unique features such as high magnetic anisotropy, narrow anisotropy field distribution, and large resistivity arouse a lot of research interests for applications in self-biased microwave nonreciprocal devices, such as isolators and circulators. In most of these applications, *c*-axis perpendicular orientation following with perpendicular magnetic anisotropy is desirable [1]. Quite a lot of film deposition methods have been tried to fabricate highly textured films, such as sputtering [2], pulsed laser deposition [3], metallorganic chemical vapor deposition [4]. However, these physical vapor deposition methods need relatively expensive devices. At the same time, cheaper chemical methods were also suggested. Sol gel method based on the Pechini-type reaction [5] was widely used to produce nanoparticles and thin films [6]. The principle of the Pechini process is based on the ability of weak polybasic acids such as citric acid to chelate metallic ions. The chelates can undergo polyesterification with polyhydroxyl alcohols such as ethylene glycol to form a polymeric precursor [7]. The polymeric precursor is then deposited onto suitable substrates by spin coater in order to make thin films. The homogeneous distribution of metallic ions and low diffusion distances result in lower calcination temperature, and thus smaller crystallites. Some efforts have been carried out to modify the sol gel process parameters such as Fe/Sr molar ratio [8], pH [9], and citric acid content [10] for achieving the finer crystallites.

In the present work, the effects of starting metal salts on the chelated species, thermal decomposition of polymeric precursors, phase evolution, microstructure and magnetic properties of strontium hexaferrite thin films were investigated.

2. Experimental procedure

The starting materials were $Fe(NO_3)_3 \cdot 9H_2O$ (> 99%), $Sr(NO_3)_2$ (> 99.99%), $FeCl_3 \cdot 6H_2O$ (> 99%), $SrCl_2$ (> 99%), $Fe(OH)_3$ (> 99%), $Sr(OH)_2$ (> 99%), citric acid ($C_6H_8O_7$) (99%), ethylene glycol ($C_2H_4(OH)_2$) (> 99.5%) and ammonia (25 wt%). The sols were prepared by dissolving the different metal salts and citric acid in deionized water at which the molar ratios of CA: total metal cations and Fe/Sr were 1:1 and 10:1, respectively [8–10]. After homogenization, ethylene glycol was added to the solution while citric acid: ethylene glycol ratio was 2:3 in mass. The pH was also adjusted to 7 using ammonia under continuous stirring which resulted in a clear transparent precursor solution. The precursor solution was then heated at 80 °C to obtain a desired viscosity. Finally, this homogeneous solution was spin coated onto Si(100) substrate of 12×12 mm^2 at 3000 rpm for 15 s. After each coating,

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the film was dried in air at 200 °C for 30 min and was preheated at 450 °C for 1 h to remove the organics. The process was performed four times to achieve the film thickness of around 900 nm. At the end, the films were calcined at 800 °C for 1 h in air. Heating and cooling rates of 5 °C/min were applied to prevent cracking of the films.

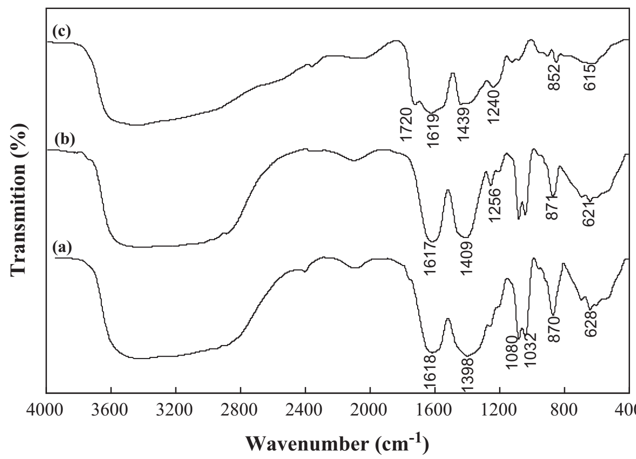

Fig. 1. FTIR spectra of the precursor solutions with different metal precursors (a) nitrate, (b) hydroxide, and (c) chloride.

Spectra of the sol in the range of 400–4000 cm^{-1} were measured by Fourier transform infrared (FTIR) spectrometer (Tensor 27 BURKER). The thermal decomposition behavior of the gel was examined by simultaneous DTA/TGA with the heating rate of 5 °C/min in air on the 2960 SDT V3.0F instrument. The structure of the calcined strontium hexaferrite thin films was characterized by X-ray diffraction (XRD) in θ–2θ geometry, using CuKα radiation (Philips PW-1730). The crystallite size was determined with the Scherrer equation by applying the full-width at half-maximum value of the (114) diffraction peaks [11]. The samples were also submitted to a quantitative analysis by the Rietveld method using Materials Analysis Using Diffraction (MAUD) program [12]. The relative error of Rietveld refinement method is about 5% [13]. The morphology was studied using a scanning electron microscope (CamScan, MV2300). The SEM operating voltage was 15 kV. Magnetic properties were also measured by a vibrating sample magnetometer (Lake shore 7400) at a maximum applied field of 12 kOe. The 5×5 mm^2 samples with thickness of about 0.8 μm [10] were used for VSM. Therefore, self-demagnetizing factors for in plane measurement were assumed to

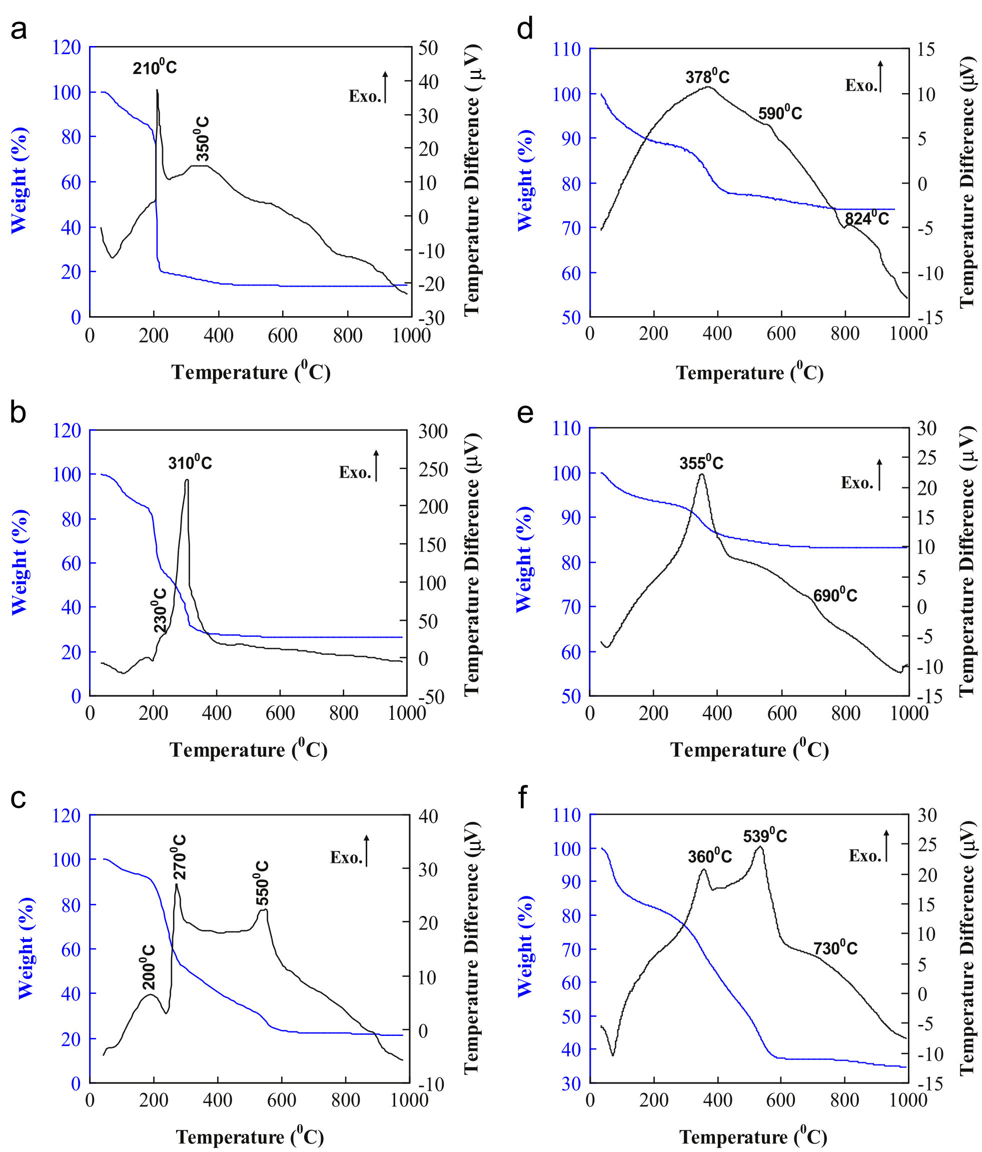

Fig. 2. DTA/TGA curves of the gels dried at 100 °C for (a) nitrate (b) hydroxide and (c) chloride precursors and DTA/TGA curves of the gels dried at 200 °C for (d) nitrate (e) hydroxide and (f) chloride precursors.