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Araştırma Makalesi / Research Article

Investigations on $LaFeO_3$ Thin Film Using Sol–Gel Technique for Magnet Technology

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Abstract

In this study, lanthanum Ferrite ($LaFeO_3$) thin films were prepared by sol-gel method for magnet technology. With this context, precursor solutions with low contact angles were synthesized from all nitrate salts of the respective cations (La, Fe), using methanol as solvent and citric acid as chelating agents. The obtained gel films were dried at heat-treated at 500 ^{o}C for 10 minutes in air. The oxide thin films were annealed at 850 ^{o}C for 60 and 120 minutes and 1000 ^{o}C for 120 minutes in air. DTA/TG results revealed that endothermic and exothermic reactions are observed at temperature between 29 ^{o}C and 450 ^{o}C due to solvent removal, combustion of carbon based materials and oxidation of La and Fe. The spectrum of La-Fe precursor film annealed at 850^{o}C and 1000 ^{o}C shows an absence of absorption bands corresponding to organics and hydroxyls. $LaFeO_3$ phase was found as well as pure perovskite with low intensity from XRD patterns. It was found that surface morphologies of the film with homogeneous structures. The thermal, phase, microstructural and magnetic properties of the obtained samples were determined by TG/DTA, FTIR, XRD, SEM, XPS, wetting angles and VSM. The results show that sustained perovskite polycrystalline films were grown on the (100)-oriented Si substrates. In addition, the films show strong ferromagnetic behavior.

Keywords

$LaFeO_3$; Sol-gel; Magnetic properties

Manyet Teknolojisi için Sol-jel Tekniği Kullanılarak $LaFeO_3$ İnce Film Üzerine İncelemeler

Özet

Bu çalışmada, manyet teknolojisi için Lantanyum Ferrit ($LaFeO_3$) ince filmler sol-jel yöntemi kullanılarak hazırlanmıştır. Bu kapsamda, düşük temas açısına sahip başlangıç çözeltileri metanol çözücüsü ve sitrik asit kompleksleşme ajanı kullanılarak ilgili katyonların (La, Fe) tümü nitrat tuzlarından sentezlenmiştir. Elde edilen jel filmler, hava ortamında 500 °C de 10 dakika boyunca ısıl işlem ile kurutulmuştur. Oksit ince filmler hava ortamında 850 ^{o}C'de 60 ve 120 dakika ve 1000 ^{o}C'de 120 dakika süreyle tavlandı. endotermik ve ekzotermik reaksiyonların gözlendiği DTA / TG sonuçlarında 29 ^{o}C ve 450 ^{o}C arasındaki sıcaklıklarda çözücü uzaklaştırma, karbon esaslı materyallerin yanması ve La ve Fe'nin oksitlenmesi tespit edilmiştir. 850 °C ve 1000 °C'de tavlanmış La-Fe başlangıç film spektrumu, organik ve hidroksillerin görüldüğü absorpsiyon bantlarının yok olduğunu göstermektedir. $LaFeO_3$ fazının yanı sıra XRD sonuçlarından düşük şiddetli saf perovskite pikler elde edilmiştir. Homojen yapılı yüzey morfolojisine sahip film gözlenmiştir. Elde edilen örneklerin termal, faz, mikro yapısal ve manyetik özellikleri TG / DTA, FTIR, XRD, SEM, XPS, ıslatma açısı ölçüm cihazı ve VSM ile belirlenmiştir. Sonuçlar sürekli Perovskite çok kristalli filmlerin (100) yönlü Si altlıklar üzerine büyütüldüğünü göstermiştir. Buna ek olarak, filmler güçlü ferromanyetik davranış göstermektedir.

Anahtar kelimeler

$LaFeO_3$; Sol-jel; Manyetik özellikler

1. Introduction

Perovskites have been thoroughly studied with concern both applied and various areas of material science. (Tejuca and Fierro 1993). In particular, perovskites have been also thoroughly studied in recent years because of their relatively inexpensive cost and thermal stability, which make them potential choices to rare metals in peripheral power generation (NOx and unburned

hydrocarbons control). Much attention has especially been paid to lanthanum based perovskite oxides (Saracco et al. 1998; Poplawski et al. 2000). Furthermore, ferroelectrics can be made in various forms, including ceramics, single crystals, polymers and thin films increasing their exploitability (Yamamoto 2000). Perovskite ferroelectric materials all have the general chemical formula ABO_3, where A and B are cations. Typically the A cation will be around 1,2–1,6 Å in radius (similar to the oxygen ions) whilst the B cations perovskite-type oxides have attracted great interest in areas with high dielectric constant capacitors. (Monterrubio-Badillo et al. 2006). In our present work, $LaFeO_3$ has been synthesized by the sol–gel technique and characterized for magnet technologies. The effect of the calcination step on the phase constitution progression of this material is presented.

2. Material and Method

All substances used in this study are analytical grade and are used without further purification. Deionized water is used in all experiments. $LaFeO_3$ samples were prepared by a sol–gel method. Before coating process, ultrasonically cleaned substrate is dipped in methyl alcohol solvent for wetting the surface and to obtain adhesion of solution. After the substrate preparation, the powder of $La(NO_3)_2.6H_2O$ (Biochem) and $Fe(NO_3)_3.9H_2O$ (Merck) were dissolved in methyl alcohol one by one. Then 3 Ll of citric acid and 1 mL of ethanol was added to the metal salt and solvent mixtured solutions under magnetic mixing. The final solutions were formed through the hydrolysis of La and Fe metal salts after vigorously stirring at room temperature for a 12 hour period at 100 rpm. The solution was spinned (The Laurell EDC-650-15B Spin coater) onto Si wafers to be thin film.

Before coating process, wettability properties of the solution were determined using contact angle measurement machine (Meter-CAM 100, KSV Instruments Ltd.). A dense amorphous film is coated on Si substrate. After spin coating process, the obtained gel coatings were dried at 300 ^oC for 10 min, heat treated at 500 ^oC for 5 min and subsequently annealed at 850 ^oC for 60 and 120 minutes and 1000 ^oC for 120 minutes with 3 ^oC/min heating regime in air to obtain the final thin films (see Table 1 for more details). Thinner coatings were obtained by repeating this process with 5 times dropped solution over and over again before annealing process.

Table 1. Sol-gel coating parameters**.**

Coating	Spin rpm	Drying (^oC), t(min)	Heat (^oC), t(min)	Anneal (^oC), t(min)
$LaFeO_3$	100	300, 10	500, 10	850, 60
$LaFeO_3$	100	300, 10	500, 10	850, 120
$LaFeO_3$	100	300, 10	500, 10	1000, 120

Thermal analyses of the La- and Fe-based xerogel dried at 150 ^oC for 30 minutes in air were evaluated at a heating rate of 10 °C/min under oxygen atmosphere using a DTG-60H Model Differential Thermal Analysis - Thermogravimetry (DTA - TG) machine in order to gain decomposition and phase formation, and to obtain an optimum heat treatment regime for drying, heat treatment and annealing processes. Prior to DTA-TG measurement of the xerogels, they were weighted as approximately 20 mg and then put into crucible. In these experiments, Al_2O_3 powder with 60 µm was used as a reference material

Fourier Transform Infrared (FTIR) spectra of the solutions, gel and film samples were recorded using Perkin Elmer FTIR spectrometer. X-ray diffraction (XRD) patterns of the thin films were performed by using a Thermo-Scientific, ARL-K_α diffractometer with a CuK_α irradiation (wavelength, λ=0.15418 nm). X-ray Photoelectron Spectroscopy (XPS) characterization of the films was carried out with a Thermo Scientific K-Alpha Surface Analysis. Magnetic properties of the sample was determined using a Dexing Magnet - Vibrating Sample Magnetometer (VSM).

3. Results

Figure 1 shows wetting angle images of $LaFeO_3$ based solutions containing citric acid at 850 ˚C (34˚)

and 1000 ˚C (32˚). Citric acid was added 3 mL to prepare solution for obtaining more wetting on Si surface. Since the results are less than 90°, there is no inconsistency about wettability between substrates and solution.

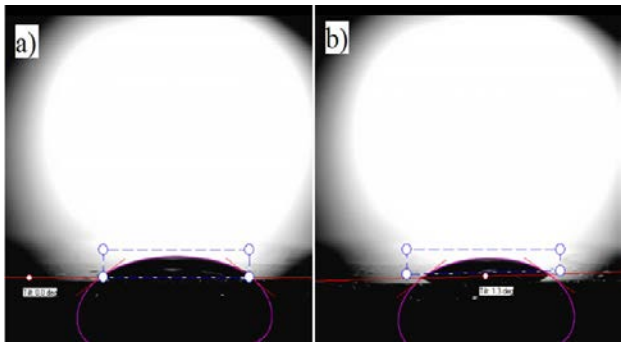

Figure 1. Wetting angle images of $LaFeO_3$ based solutions a) containing citric acid at 850 ˚C (34˚) and b) 1000 ˚C (32˚).

Typical DTA and TGA curves of the sample obtained drying at 150°C for 30 min in air from xerogel solution is shown in figure 2. The sample was heated at regime of 5 °C min^{-1} from 29 to 950 °C. The DTA pattern shows one endothermic peak at 85°C, two exothermic peaks at about 270, 390 and three weak exothermic peaks at about 180, 200 and 500 °C.

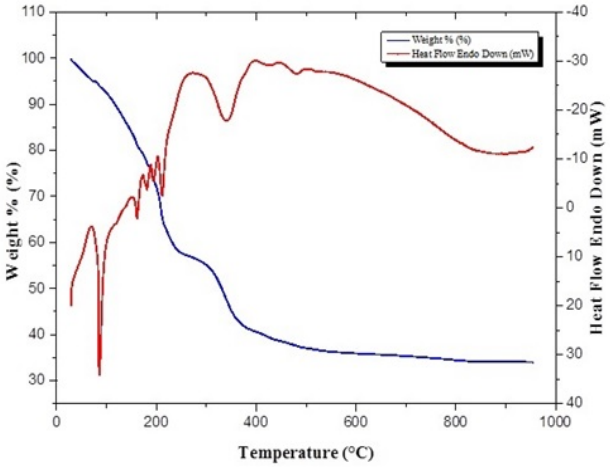

Figure 2. Typical DTA and TGA curves of the sample obtained drying at 150°C for 30 min. in air from xerogel solution.

The TG curve shows two major weight loss areas at the temperature between 29-200 °C and 200-450 °C. The first weight loss stage from 29 to 200 °C concomitant with an endothermic reaction and an exothermic reaction can be explained to the elimination of the residual water and a fractional burnout of citric acid and ethanol sequence. The second weight loss at the temperature between 200 and 450 °C concomitant with a poor exothermic reaction matches to the decomposition of remaining organic compounds. The weight loss values were determined to be ~72 % totally. The remaining weight loss from 450 to 750 °C was concomitant with a short exothermic peak. It may be determined to the constitution of the $LaFeO_3$ structure. According to these, results, process temperatures such as combustion, oxidation and phase formation were chosen as 300°C, 550°C and 850-1000°C, respectively (Gupta et al. 1995).

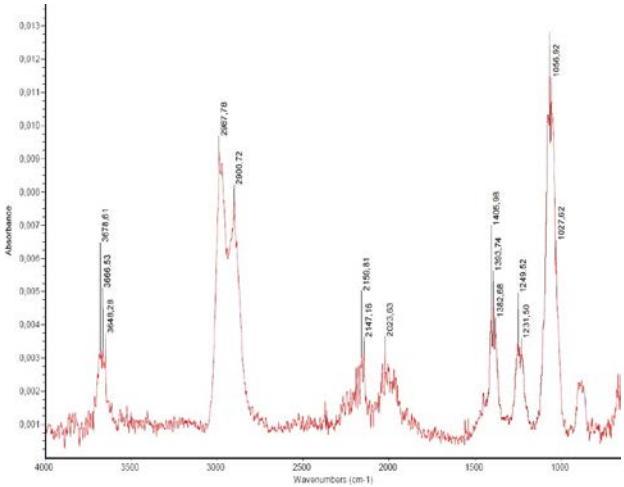

Figure 3. FTIR spectra of La- and Fe-based samples heat treated at 25°C (as recieved from solution), 150 °C for 30 min (xerogel).

The FTIR spectra of La- and Fe-based samples heat treated at 25 °C (as recieved from solution), 150 °C for 30 min (xerogel) and 850 °C which are saved in between 650–4000 cm^{-1} are indicated in figure 3. The large absorption band at 3660 cm^{-1} is related with the O–H vibration of intermolecular hydroxyl bonds. The apparent absorption band at 1050 cm^{-1}, 1250 cm^{-1} and 1390 cm^{-1} can be determined to the vibrational mode of carbon stretching. The stretching band 2000 cm^{-1} and 2150 cm^{-1}, this should be due to N=N link, but it has to be link with La or Fe cations to get a IR vibration (Silva and Soares 2009). The wide band around 2900 $cm^{-1}$and 3000 cm^{-1} in figure 3 correspond to the hydroxyl group. From the above spectroscopic observations

it was suggested that the as-prepared gel comprises of an intermediate/complex of citric acid, methanol, and metal ions. The band at 850 cm^{-1} suits to nitrate ions (Silva and Soares 2009). The bands shifting is so light that it is only realized when compared to peaks of heated compounds at 150 and 850 °C. This might be because of the insignificant effect of temperature on the distribution of ions in the material (Kivana et al. 1997).

Figure 4 indicates XRD patterns of $LaFeO_3$ calcined at different temperatures. XRD results show that the intensity as arbitrary unit of coated $LaFeO_3$ thin films at 1000 °C for 2 hours. (Lf1000) and 850 °C for 1 and 2 hours (Lf850) coating cycles were respectively, with experimental deflection approximately 5%. The dependence of crystal structure on the annealing temperature is illustrated in figure 4 where XRD results for diversely annealed thin films are shown. It can be seen that all these films show a $LaFeO_3$ coatings (Shimizu and Murata 1997).

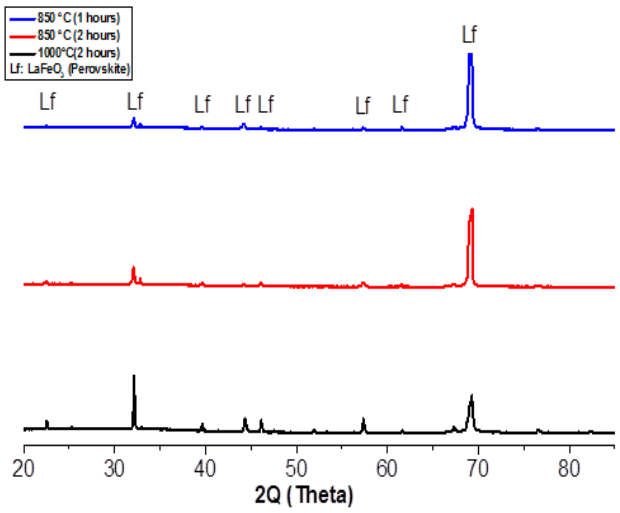

Figure 4. XRD patterns of $LaFeO_3$ nanoparticles calcined at different temperature; (Lf) $LaFeO_3$

The films were fully crystallized after annealing at 1000 °C. The XRD peaks of the annealed films are given in figure 4 $LaFeO_3$ peaks appeared clearly after annealing at 1000 °C at two theta angles of 32.8, 39.7, 44.1, 47.2, 58.2, 63.1 and 69.1. The SEM technique was employed for finding morphology of $LaFeO_3$ as synthesized thin films heated at 850°C and 1000°C.

Figures 5 and 6 show SEM images of $LaFeO_3$ thin film heated at 850°C and 1000°C at different magnifications. The particle shapes are not well defined. The coatings have micro cracks and pores.

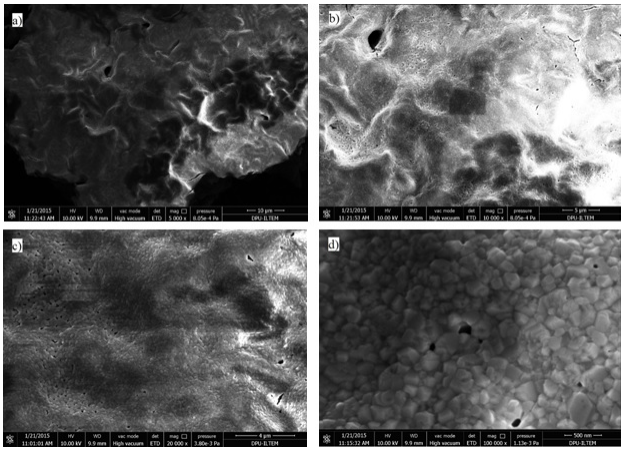

Figure 5. SEM images of $LaFeO_3$ thin film heated at 850 °C at different magnifications such as a) 5,000 x, b) 10,000 x, c) 20,000 x, and d) 100,000 x.

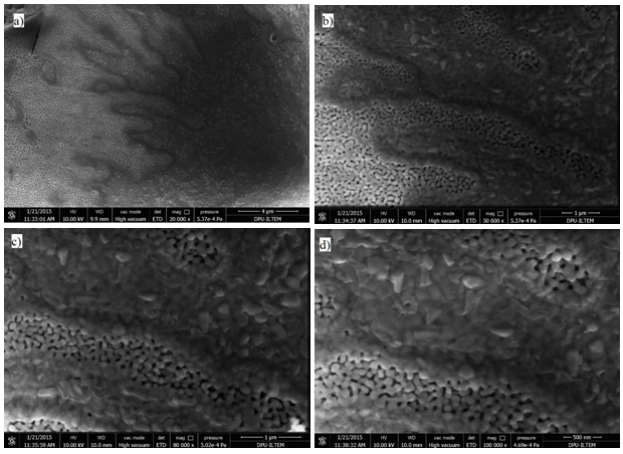

Figure 6. SEM images of $LaFeO_3$ thin film heated at 1000 °C at different magnifications such as a) 20,000x, b) 50,000x, c) 80,000x and d) 100,000x.

We assumed that the pores are mainly intergranular because intergranular pores can be seen on the SEM photographs. Coated film surfaces were also examined by means of SEM. The SEM examinations show that the film exhibits several microstructural defects and imperfections in a form of cracks and holes. The coating is homogeneous and the grains were distributed evenly. Film thickness was measured by ionically

etching the coated film. As it is seen from, coated surface of the film was etched ionically by focused ion beam then tilted 53° in the vacuum chamber of the SEM. It can be seen from the image, which is taken from the etched and tilted surface, that film thickness about 120 nm. The examined film was coated by dipping two times so the film thickness for each dip can be said as 60-70 nm (Silva and Soares 2009).

Figure 7 show XPS curve and results of $LaFeO_3$ heated at 850 ^{o}C respectively. In the $LaFeO_3$ the lack of peak in high energy value shows the existence of the lattice oxygen. Changing in the crystalline structure and also in the electronic structure can result from displacement of the peak for higher energy values.

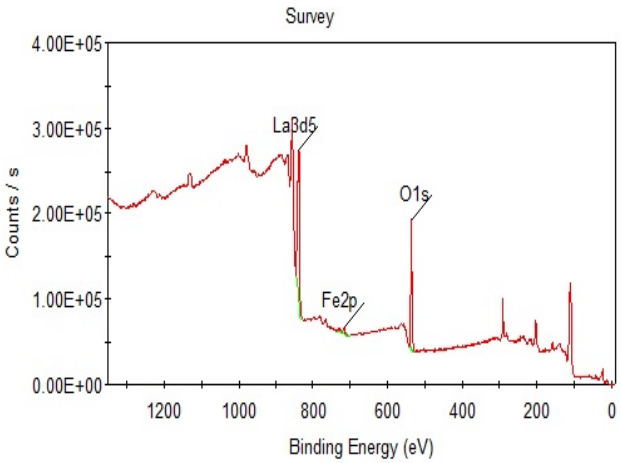

Figure 7. XPS curve of $LaFeO_3$ heated at 850 ^{o}C.

In $LaFeO_3$ film, the proportion La/Fe is 0.79, shows the non-stoichiometric $LaFeO_3$ phase with lanthanum deficiency (Sankar and Joy 2005). In order to keep the charge equilibrium, the conversion can be considered: Fe^{3+} to Fe^{4+}. Vacancies constitution results from this transition. Nevertheless, Some of lanthanum isn't incorporated in perovskite, but presented as oxide, and some of this oxide was decreased (Zampieri et al. 2002).

Hysteresis curve of magnetization were measured for the $LaFeO_3$ sample heated at 850 ^{o}C as shown in figure 8. The hysteresis loops at room temperature (27 ^{o}C) were nearly diamagnetic (Teraoka et al. 2001 and Brankovic et al. 2010). But, under the critical temperature, the films indicate soft magnetic behavior, clear from figure 8.

Sintering in O_2 atmosphere causes cation vacancies in $LaFeO_3$, resulting in an up-shift of the magnetic critic temperatures and enhanced ferromagnetic feature that arises from the canting of the antiferromagnetic sequence of spins (Ritter et al. 1997, Gupta et al. 1995, Yamaguchi et al. 2016 and Tsukasa et al. 2014).

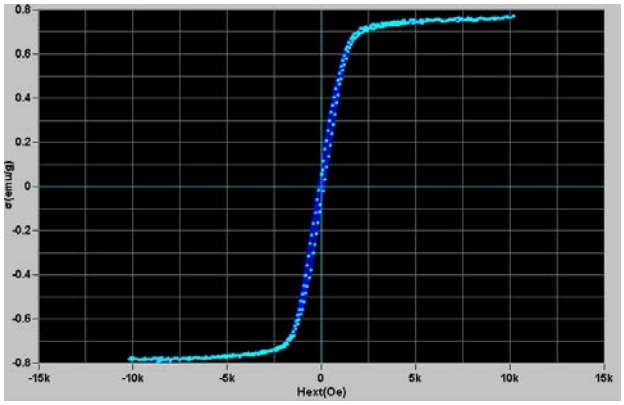

Figure 8. Hysteresis curve of magnetization were measured for the $LaFeO_3$ sample heated at 850 ˚C.

4. Conclusion

Coating of ceramic films using sol-gel has promised in depositing dense and homogenous films for new generation magnetic applications. The deposited films cling to the substrate very well. This study shows that high quality and highly dense $LaFeO_3$ thin films can be fabricated using sol-gel. Furthermore, the films show strong ferromagnetic behavior.

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