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# Synthesis and Characterization of Lanthanum-Doped Barium-Ferrite/Poly-*o*-toluidine Composites

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Electro-magnetic functionalized lanthanum-doped barium-ferrite(BL) particles synthesized by sol-gel selfpropagation high temperature, The final materials of lanthanum-doped barium-ferrite/poly-*o*-toluidine (BL/POT) composites have been successfully synthesized by in suit chemical polymerization. Crystal structure, morphology and magnetic properties of composites were studied by X-ray diffractometer, Fourier transform infrared spectroscopy, transmission electron microscopy and vibrating sample magnetometer. The results showed that the lanthanum-doped barium-ferrite particles size are 80-100 nm and the lanthanum-doped barium-ferrite/poly-*o*-toluidine composites size are at the range of 750 nm and when the doped $La^{3+}$(x = 0.04), there have the best Ms of the $BaLa_xFe_{12-x}O_{19}$/poly-*o*-toluidine composites.

**Key Words: Conducting polymer, Barium ferrite, Rare earth, Composites, Magnetic properties.**

## INTRODUCTION

Recently, interest is focused on the ferrites nanocomposites that have combined magnetic and electrical properties. M-Type barium hexaferrite is an ideal material for the development of electromagnetic attenuation at microwave band, due to the high saturation magnetization, large anisotropy field, excellent chemical stability and high microwave magnetic loss[1-3]. It seems that small rare earth (RE) additions play an important role in modifying structure and magnetic properties of ferrites due to the magnetocrystalline anisotropy in the rare earth doped compounds and the rare earth-Fe interaction (4*f*-3*d* coupling)[4]. Till now, some researches have been carried out about the preparation and magnetic properties of ferrites. But the effect of La doped on the structure, grain size, morphology and magnetic properties for La-barium- ferrites was reported less. Spinal ferrites and hexagonal ferrites are well known as traditional granular microwave absorbers, which have been utilized as the most frequent absorbing materials in various forms[5]. The frequently used electro-magnetic wave absorbers include ferrites[5,6], conducting polymer[7,8], carbon nanotubes[9], *etc*.

On the other hand, some physical and chemical approaches have been employed to fabricate ferrites nanocomposites. Among these synthetic strategies, sol-gel technique and in suit chemical polymerization has been widely used[7,10-12], However, sol-gel technique offers excellent composition control, low temperature processing and short fabrication time at comparatively low cost.

In this article, an investigation was made to obtain lanthanum-doped barium-ferrite (BL) particles synthesized by sol-gel selfpropagation hightemperature, The final materials of lanthanum-doped barium-ferrite/poly-*o*-toluidine (BL/POT) composites synthesized by *in situ* chemical polymerization. it revealed the influence of La doping on the obtained samples and the polymer influence of composites of electromagnetic properties.

## EXPERIMENTAL

Lanthanum nitrate [$La(NO_3)_3 \cdot 9H_2O$], barium nitrate ($Ba(NO_3)_2$), ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$], ferric chloride ($FeCl_3$) and citric acid were all analytical grade and used as received. *o*-Toluidine was of reagent grade from commercial sources and distilled under reduced pressure before used. Other reagent were also analytical grade.

**Preparation of La-doped barium-ferrite:** $BaLa_xFe_{12-x}O_{19}$ (x = 0.00, 0.04, 0.08, 0.12) composites were prepared by a simple sol-gel self propagation high temperature synthesis (sol-gel-SHS) method. in a typical procedure, stoichiometric amounts of $La(NO_3)_3 \cdot 9H_2O$, $Ba(NO_3)_2$ and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in a small amount of deionized $H_2O$, citric acid was then added to the mixture solution of $La^{3+}$ and $Fe^{3+}$ to chelate these ions. The molar ratio of citric acid to metal ions used was 1:1. Ammonia was added to adjust the pH value to 7, the clear solution obtained was slowly evaporated at 80 ºC under constant stirring, forming a viscous gel. The gel were dried at 90 ºC under vacuum and then the xerogel precursors

were combusted to formed brown loose powders. The hexaferrite $BaLa_xFe_{12-x}O_{19}$ particles were thus obtained after grinding.

**Preparation of $BaLa_xFe_{12-x}O_{19}$/POT:** Poly-*o*-toluidine (POT)-$BaLa_xFe_{12-x}O_{19}$ nanocomposite was prepared *via in situ* polymerization. In a typical synthesis, definite amount of *o*-toluidine and $BaLa_xFe_{12-x}O_{19}$ (x = 0.00, 0.04, 0.08, 0.12) nanoparticles were dissolved in 100 mL of 1.5 mol/L HCl. The hydrochloric acid of the mixed $(NH_4)_2S_2O_8$ was added drop-wise into the precursors solution for 6 h and the then the obtained black precipitate was washed sequentially with distilled water and hydrochloric acid.and dried at 80 ºC under vacuum for 12 h to get the powder of POT/$BaLa_xFe_{12-x}O_{19}$ nanocomposites.

**Characterization:** The structure of $BaLa_xFe_{12-x}O_{19}$/POT composites using X-ray powder diffraction (XRD) (Rigaku Smart Lab operated at 40 kV and 35 mA using $CuK_\alpha$ radiation k = 1.54059 Å) and Fourier transform infrared (FT-IR) spectra (a Perkin-Elmer BX FT-IR infrared spectrometer in the range of 4000-400 $cm^{-1}$). The morphology of $BaLa_xFe_{12-x}O_{19}$/POT composites characterized by transmission electron microscopy (TEM) (a FEI Tecnai G2 Sphera microscope. A drop of diluted sample in alcohol was dripped on the TEM grid). The magnetization measurements were carried out in an external field up to15 kOe at room temperature.

## RESULTS AND DISCUSSION

**XRD analysis of $BaLa_xFe_{12-x}O_{19}$/POT:** Fig. 1 shows that X-ray diffraction analysis of the $BaLa_xFe_{12-x}O_{19}$/POT (x = 0.00, 0.04, 0.08, 0.12). Fig. 2(a-d) shows characteristic peak centered in the range of 2θ = 20-65º and there have a broad diffraction peak centered in the range of 2θ = 20-28º that inform the amorphous characteristics of $BaLa_xFe_{12-x}O_{19}$/POT. These peaks are more intense in $BaLa_xFe_{12-x}O_{19}$/POT and $BaLa_xFe_{12-x}O_{19}$. These peaks correspond to internal doping of La and coated with POT. XRD pattern of $BaLa_xFe_{12-x}O_{19}$/POT shows the diffraction peaks of the composites are sharp and have a shift in positions as compared to $BaLa_xFe_{12-x}O_{19}$, which revealed that the $BaLa_xFe_{12-x}O_{19}$ were coated with the POT.

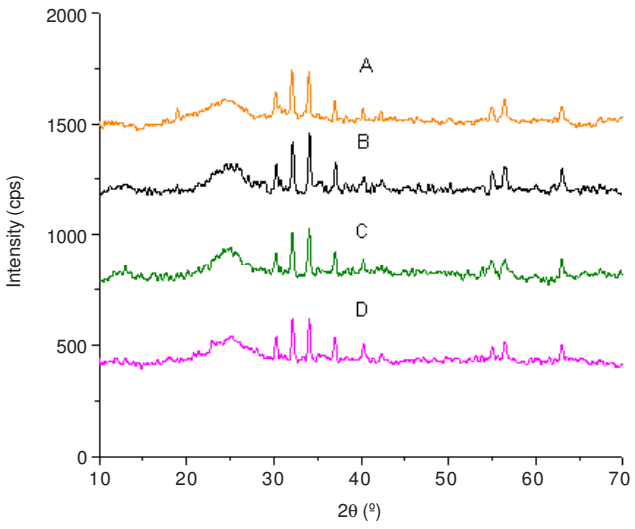



Fig. 1. X-Ray diffraction patterns of $BaLa_xFe_{12-x}O_{19}$/POT (a) x = 0.00, (b) x = 0.04, (c) x = 0.08, (d) x = 0.12

**FTIR spectra analysis:** In the Fig. 2 shows that the FITR spectrograms of $BaLa_xFe_{12-x}O_{19}$/POT composites. In the spectrum of Fig. 4, the broad band between 1591-1582 $cm^{-1}$ can be assigned to the ketone structure of C=C characteristic peak. the peaks between 1502-1494 $cm^{-1}$ can were assigned to the Benzene structure of C=C characteristic peak the peaks at approximately 1261 and 312 $cm^{-1}$ were attributed to the characteristic stretching vibrations of C=N the peaks at approximately 1112 and 1130 $cm^{-1}$ are attributed to the characteristic flexural vibrations of saturated C-H of protonation reaction. The broad band between 830-811 $cm^{-1}$ were attributed to the the LB-ferrite replace the 1,2,4-aniline the peaks at *ca.* 2920 $cm^{-1}$ are attributed to the characteristic stretching vibrations of saturated C-H of methyl of poly-*o*-toluidine.

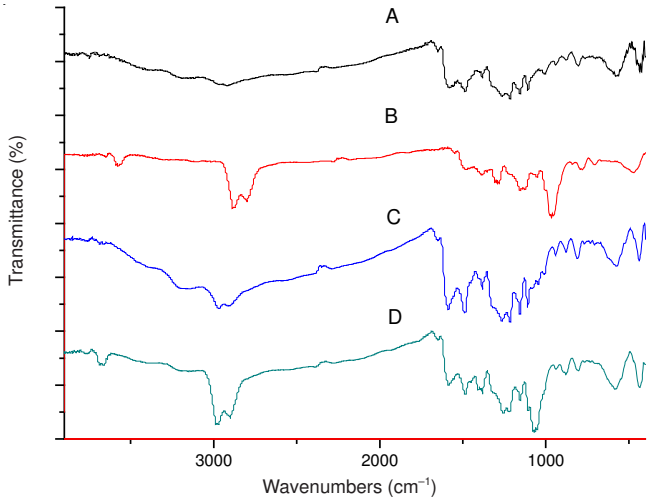
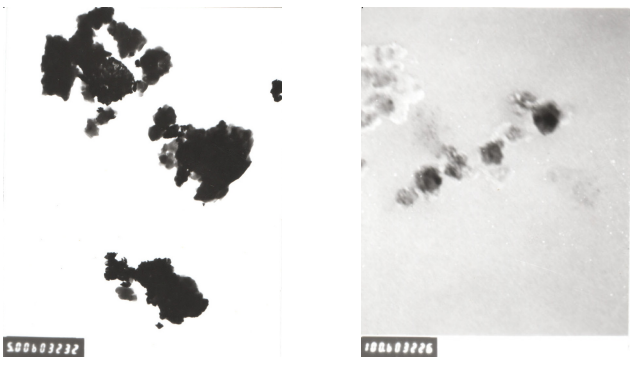



Fig. 2. FI-IR spectra of $BaLa_xFe_{12-x}O_{19}$/POT. (a) x = 0.00; (b) x = 0.04; (c) x = 0.08; (d) x = 0.12

**TEM:** The morphology and size distribution of $BaLa_{0.04}Fe_{11.96}O_{19}$ and $BaLa_{0.04}Fe_{11.96}O_{19}$/POT were analyzed using TEM. The image of $BaLa_{0.04}Fe_{11.96}O_{19}$ particles (Fig. 3a) informs that the size of particles is in the range of 80-100 nm. the image of $BaLa_{0.04}Fe_{11.96}O_{19}$/POT particles (Fig. 3b) informs that the size of particles is at the range of 750 nm. This makes it rather difficult to make an average size estimation from the micrographs. The TEM images of $BaLa_{0.04}Fe_{11.96}O_{19}$ compared with the $BaLa_{0.04}Fe_{11.96}O_{19}$/POT particles size, it can be proof that the POT are well coated the La-Ba-ferrite and these particles exhibit polycrystalline character.



(a) (b)

Fig. 3. (a) TEM images of $BaLa_{0.04}Fe_{11.96}O_{19}$ (b) EM images of $BaLa_{0.04}Fe_{11.96}O_{19}$/POT

**Magnetic properties analysis:** The magnetic parameters of $BaLa_xFe_{12-x}O_{19}$ composites determined by the hysteresis loops are given in Table-1. It is found that the electrical conductivity of the composites is strongly affected by the dopant and Ba-ferrite particles. It can be observed the best Ms when the $La^{3+}$ (x = 0.04) content, which the Ms is 80.1179444 emu $g^{-1}$. And the heteresis curve of LB-ferrite particles increase with the $La^{3+}$ content. In the Figs. 4 and 5 shows the hysteresis loops of $BaLa_xFe_{12-x}O_{19}$ (x = 0.00, x = 0.04) and LB-POT composites. The magnetization of LB-POT composites exibits a clear hysteretic behavior. The effect of the La content on the electrical and magnetic properties of the pure $BaFe_{12}O_{19}$ and the $BaLa_{0.04}Fe_{11.96}O_{19}$ composcoites. The data in Fig. 6 told that the conductivity and magnetic properties of the $BaLa_xFe_{12-x}O_{19}$ composite can be adjusted by changing the La content.

TABLE-1
MAGNETIC PARAMETERS OF $BaLa_xFe_{12-x}O_{19}$ AND COMPOSITE

| | Coercivity (Hc/Oe) | Saturation magnetization (Ms/emu $g^{-1}$) | Remanent magnetization (Mr/emu $g^{-1}$) |
|---|---|---|---|
| $BaFe_{12}O_{19}$ | 5007.83699 | 8.28138163 | 4.59140691 |
| $BaLa_{0.04}Fe_{11.96}O_{19}$ | 5023.51097 | 80.1179444 | 49.115417 |
| $BaFe_{12}O_{19}$/POT | 5274.29467 | 4.23336142 | 2.59898905 |
| $BaLa_{0.04}Fe_{11.96}O_{19}$/POT | 5556.42633 | 2.95029486 | 2.09182814 |

In addition, the pristine polymers of POT synthesized without ferrite is antimagnetic. Figs. 6 and 7, the BL-POT composites present lower value in Ms compared with BL, that is because POT chain coated on the BL particles prevents the coupled dipoles from aligning along the magnetic orientation, thus there is a tendency toward lower magneti-zation values[13].

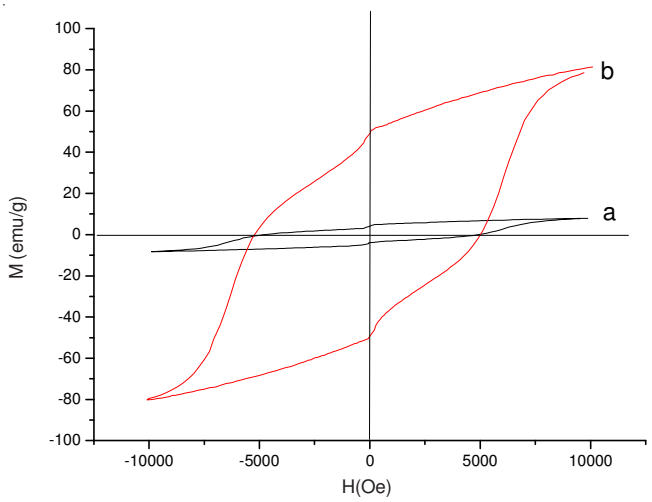



Fig. 4. Hysteresis loops for (a) $BaFe_{12}O_{19}$ and (b) $BaLa_{0.04}Fe_{11.96}O_{19}$

## Conclusion

In this study, the $BaLa_xFe_{12-x}O_{19}$ particles synthesis by sol-gel self propagation high temperature and the synthesis of LB-POT composite *via in situ* polymerization of POT with front of $BaLa_xFe_{12-x}O_{19}$ particles. XRD reveals XRD reveals $BaLa_XFe_{12-X}O_{19}$ had Hexagonal structure, and the size of LB-POT at the range of 750 nm. LB particles would be possible to tune the morphology and properties of the $La^{3+}$ content, as the

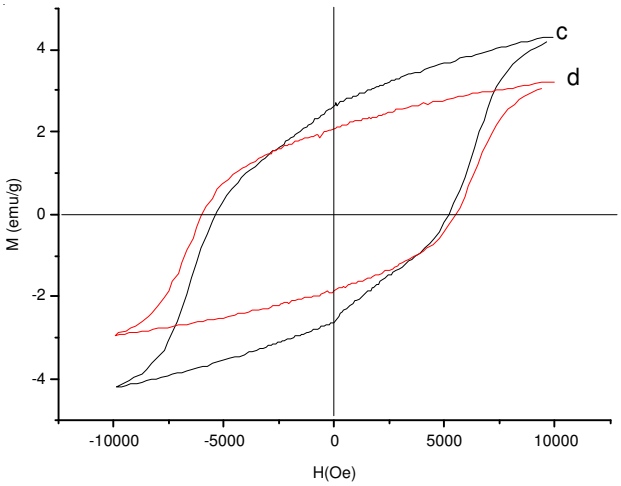



Fig. 5. Hysteresis loops for (c) $BaFe_{12}O_{19}$/POT and (d) $BaLa_{0.04}Fe_{11.96}O_{19}$/POT

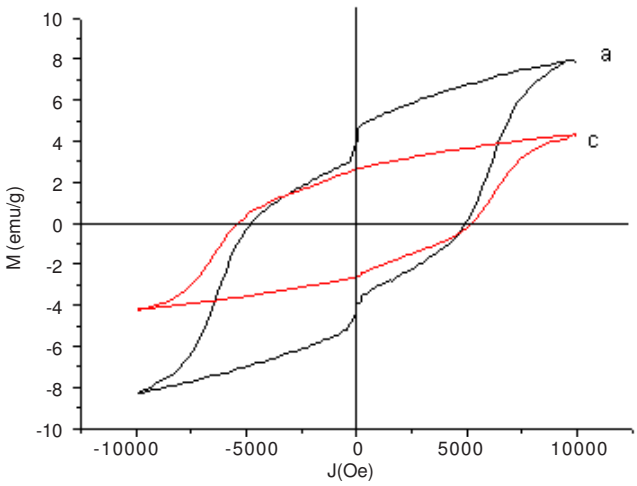



Fig. 6. Hysteresis loops for (a) $BaFe_{12}O_{19}$ and (c) $BaFe_{12}O_{19}$/POT

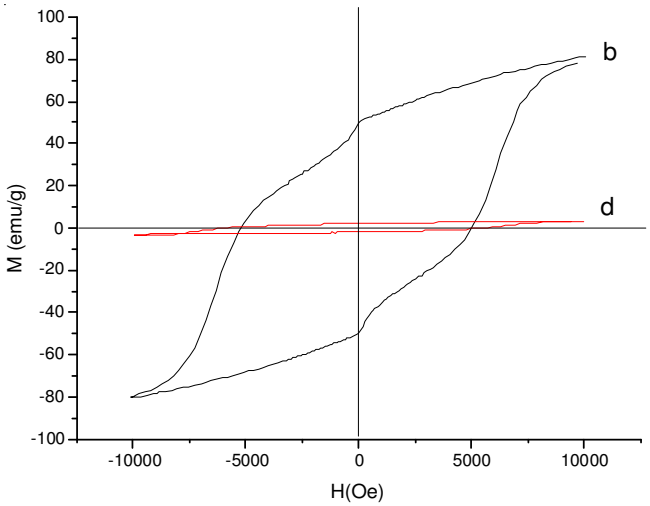



Fig. 7. Hysteresis loops for (b) $BaLa_{0.04}Fe_{11.96}O_{19}$ and (d) $BaLa_{0.04}Fe_{11.96}O_{19}$/POT

results, the best Ms when the $La^{3+}$ (x = 0.04) content, which the Ms is 80.1179444 emu $g^{-1}$. And the Hc of LB-ferrite particles increase with the $La^{3+}$ content and the magnetic properties of LB-POT have changes, which the POT is antimagnetic. It is worth mentioning that, the POT are well coated the La-Ba-ferrite and these particles exhibit polycrystalline character.

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