An investigation into microwave absorption properties of carbonyl iron/La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$ ($x = 0, 0.2, 0.4, 0.6, 0.8$) nanocomposites

To cite this article: Daniz Motmaen et al 2018 Mater. Res. Express 5 086107

View the article online for updates and enhancements.

Related content
- Enhanced microwave absorption properties of epoxy composites containing graphite nanosheets@Fe$_3$O$_4$ decorated comb-like MnO$_2$ nanoparticles
  Xiaogang Su, Jun Wang, Bin Zhang et al.
- Co/graphite based light weight microwave absorber for electromagnetic shielding and stealth applications
  Azizurrahaman Ansari and Mohammad Jaleel Akhtar
- Low content Ag-coated poly(acrylonitrile) microspheres and graphene for enhanced microwave absorption performance epoxy composites
  Bin Zhang, Jun Wang, Xiaocheng Chen et al.
An investigation into microwave absorption properties of carbonyl iron/La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$ (x = 0, 0.2, 0.4, 0.6, 0.8) nanocomposites

Daniz Motmaen$^1$, Abbas Kianvash$^1$ and Hussein Shokrvash$^2$

$^1$ University of Tabriz, Iran
$^2$ University of Maragheh, Iran
E-mail: hsh190@gmail.com

Keywords: microwave absorption, carbonyl iron LSMCO, nanocomposites, electromagnetic absorbers

Abstract
The nano-sized of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$ (x = 0, 0.2, 0.4, 0.6, 0.8) LSMCO powders were synthesized using a simple sol-gel method. For measuring microwave absorption properties, micro-sized carbonyl iron (CI)/LSMCO composites were prepared with the weight ratio of 75:5. The composite materials in the form of paints were applied on an aluminum substrate with a coating thickness of 0.7, 0.9 and 1.1 mm, respectively. Phase analysis of the products, morphology observation of particles, analysis of the element composition, the magnetic properties of the powders and the thickness of 0.7, 0.9 and 1.1 mm, the average absorption properties were increased. Phase analysis of the products, morphology observation of particles, analysis of the element composition, the magnetic properties of the powders and the electromagnetic (EM) wave parameters were determined using x-ray diffraction analysis (XRD), field emission scanning electron microscopy (FE-SEM), dispersive spectroscopy (EDS), magnetometer (VSM) and vector network analysis (VNA), respectively. According to SEM observations, the average diameter of the La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$(x = 0, 0.6) powders is about 30 and 36 nm, respectively. Room temperature magnetization results show a soft magnetic and ferromagnetic behavior of the CI, LSMCO powder. The CI/La$_{0.7}$Sr$_{0.3}$Mn$_{0.6}$Co$_{0.4}$O$_3$ composite showed a maximum reflection loss of—9.6 dB at 11.38 GHz with the thickness of 0.9 mm. By increasing the thickness of coating from 0.7 to 1.1 mm, the average absorption properties were increased.

1. Introduction

In recent years, the usage of electromagnetic (EM) absorbers with wide absorption bandwidth, low density, high compatibility and thin thickness have been investigated due to EM pollution and interference problems [1–3]. The microwave absorbers are designed to absorb the radiation and reduce the reflection. Strong absorption and weak reflection will lead to a large negative value of reflection loss (RL) [4]. Dielectric and magnetic loss, impedance match of EM and structural design are the important factor affects the absorption of EM waves [1]. The EM absorbers are classified into a magnetic and dielectric absorbers according to their loss fillers and generally are fabricated by adding absorbents to a matrix. n general, the absorbing characteristics of a material depend on the complex permittivity ($\varepsilon' - \varepsilon''$), complex permeability ($\mu' - \mu''$), frequency and coating thickness. Impedance match of EM in wide absorption bandwidth could be obtained only by using a magnetic material or a dielectric material; so, materials with different structures [5, 6] which are the combination of magnetic and dielectric materials, multi-layer and core/shellStructures are designed for this purpose. Hybrid-type absorbers could be achieved in a single layer absorbent with excellent absorption properties [7, 8]. Various EM absorbers, such as carbonyl iron/BaTiO$_3$ [9], carbonyl iron/Fe$_3$O$_4$ [10], graphene oxide/flake carbonyl iron powders/polyaniline composites [11], epsilon Fe$_3$N/epoxy and carbonyl iron/epoxy composites [12], carbonyl iron/MnO$_2$ composite have been investigated at recent decade [13].

Carbonyl iron (CI) absorbers have been attracted many researchers attention because of their low cost, large saturation magnetization and high complex permeability but has a limitation in an excellent absorption with low thickness and at low frequency [14, 15].
Perovskite-type manganites with composition $R_{1-x}A_x MnO_3$ (R: trivalent rare earth element, A: bivalent alkali earth element) have attracted many interests due to their very interesting magnetic and electric properties such as colossal magneto resistance (CMR) [16]. The application of these materials are magnetic recording products, infrared stealth and microwave absorption fields [17–21].

La$_{1-x}$Sr$_x$MnO$_3$ (x from 0 to 0.4) (LSMO) is an interesting material in the fields of microwave absorption. LaMnO$_3$ compounds show antiferromagnetic properties since there is a super-exchange interaction between ions Mn$^{3+}$. Lanthanum-strontium manganite nanoparticles (La$_{1-x}$Sr$_x$MnO$_3$) were synthesized via sol-gel method and precipitation from non-aqueous solution [22]. Shlapa et al. by use of organic compounds and non-aqueous media were shown the significantly decreasing of the crystallization temperature of LSMO nanoparticles, and the single-phase crystalline product was formed in one stage [22].

When divalent metal ions (Sr$^{2+}$) doped into La$^{3+}$ position, creates the mixed valence of the manganese ions (Mn$^{3+}$–Mn$^{4+}$), which leads to an increase in electrical conductivity and appearances the ferromagnetic properties due to double-exchange (DE) model ($\text{Mn}^{4+}$–O–Mn$^{3+}$) [23].

When the doping concentration was increased, the conductivity of the material increases, up to a certain value, the material will have conductivity as good as metal and expresses strong ferromagnetic properties. The LSMO possess high absorption, broad frequency, strong magnetism, low resistivity, Curie temperature above room temperature and low carrier density because of these advantages, many researcher investigates different kind of LSMO such as La$_{0.8}$Sr$_{0.2}$MnO$_3$/La(OH)$_3$ composites [24], La$_{0.6}$Sr$_{0.4}$MnO$_3$/polyaniline [25], La$_{0.7}$Sr$_{0.3}$MnO$_3$/carbon black [26], La$_{0.7}$Sr$_{0.3}$MnO$_3$/carbon nanotube [27].

In this research, CI/LSMCO microwave absorption properties of the composites with nanosized CI and La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$ (x = 0, 0.2, 0.4, 0.6, 0.8) powders in the frequency range of 8–12 GHz were investigated.

2. Experimental

The nanoparticles of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$ (x = 0, 0.2, 0.4, 0.6, 0.8) (LSMCO) manganite were prepared by sol-gel method. Firstly, the stoichiometric amounts of La(NO$_3$)$_3$·6H$_2$O (%99), Sr(NO$_3$)$_2$ (99%), Mn(NO$_3$)$_2$·4H$_2$O (%98.5) and Co(NO$_3$)$_2$·6H$_2$O (%99.5) were dissolved in distilled water to form a clear solution, then citric acid (%99.5) and urea (%99.5) were added to the solution as chelating agent under constant stirring. The molar ratio of metal nitrates to citric acid was 1:2. The mixed solution was slowly evaporated at 80 °C and turned into a gel. The gel was dried and decomposed at about 250 °C for 24 h. Finally, the prepared powders were annealed at 700 °C for 6 h to obtain final powders. CI powders were purchased commercially with purity of 99.999% and spherical powder shape.

The EM wave-absorbing composite coatings were prepared by dispersing certain mixture of CIP and LSMCO powders into a polyester resin matrix. A uniform CI/LSMCO—polyester composite were coated on a rectangular aluminum substrate with 22.86 $\times$ 10.16 $\times$ 0.8 mm$^3$ dimention.

Phase analysis of the products, morphology observation of particles and analysis of the element composition were determined using X-ray diffraction analysis (XRD), field emission scanning electron microscopy (FE-SEM) and dispersive spectroscopy (EDS), respectively. X-ray analysis measurements were done by a x-ray diffractometer (Siemens D5000 x-ray diffractometer) using Cu (Kα) radiation ($K = 1.5405$ Å). The LEO 906, Zeiss, 100 Kv analytical TEM was used for imaging, and analyzing of synthetic samples.

The magnetic properties of the composites and the EM wave parameters (8–12 GHz) of the paints were measured using vibrating sample magnetometer (VSM) and vector network analysis (VNA), respectively.

3. Results and discussion

3.1. Structure and morphology of samples

Figure 1 shows the XRD pattern of CI and La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$ (x = 0, 0.6) powders. As shown in figure 1(a), it includes pure $\alpha$-Fe phase, with body centred cubic structure (BCC). Figures 1(b), (c) shows that, all the characteristic peaks of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$ (x = 0, 0.6) can be well indexed as a rhombohedral structure with R 3C symmetry. The particle size was estimated from the peak width of the most intense peak, using scherrer’s formula [28]:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

Where D, $\beta$, $\lambda$ and $\theta$ are particle size, the full width of the peak at half maximum in radian, the wave length of x-rays and Bragg angle, respectively.

The average crystallite size of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$ (x = 0, x = 0.6) particles using the classical Scherher formula were measured as 21 nm and 17 nm, respectively.
Figure 2 shows SEM images of CI and La\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1-x}\)Co\(_{x}\)O\(_3\) (\(x = 0, 0.6\)) powders. It could be concluded that the particles of CI are spherical, with different diameters in the average range of 1–5 µm (Figure 2(a)).

Figures 2(b), (c) shows that the La\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1-x}\)Co\(_{x}\)O\(_3\) (\(x = 0, 0.6\)) powders are nearly spherical and the average particle size is about 36 and 30 nm, respectively. The difference between particle size will be affected on the dielectric loss and electromagnetic waves absorption properties.

It should be noted that the size of the particles obtained from the (SEM) images are bigger than the Crystallite size calculated from Scherrer’s formula. Because, each particle according to its size could be formed of several crystallite. Moreover the Scherrer’s formula estimates only the average size of the crystallite grains.

### 3.2. EDX results

Figure 3 shows the EDX spectra of La\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1-x}\)Co\(_{x}\)O\(_3\) (\(x = 0, 0.6\)) nano powders. The ratio of the peaks is in good agreement with elemental composition.
Figure 2. SEM images of (a) Cl powders, La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$ (x = 0(b), x = 0.6(c)).

Figure 3. EDX spectra of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$ (x = 0(a), x = 0.6(b)) nano powders.
3.3. TEM studies

Particles morphology and distribution of phases was investigated by TEM (Electron Microscopy) LEO 906, Zeiss. TEM studies showed that obtained nanoparticles are weakly agglomerated and have small sizes (5–90 nm). The average size and distribution of the particle size are clearly shown in the figure.

The contrast produced in bright field images (BF) shows the distribution of phases with high-resolution on a nanometer scale. In figure 4(a) nanofibers of \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Co}_x\text{O}_3 \) (dark) are easily distinguished from the CI phase (bright). In figures 4(b) and (c), \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Co}_x\text{O}_3 \) nanoparticles appear in dark, while CI has a bright contrast, because they are almost parallel to the axis of the region.

**Figure 4.** TEM images for \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) nanoparticles: a, b and c synthesized by precipitation from aqueous solution and annealing at 700 °C for 6 h.
4. Magnetic properties

To study the CI, LSMCO nanoparticles and composites, magnetic properties were obtained using magnetic field up to 10 kOe effectively. The results of investigations are presented in the following sections.

4.1. Magnetic hysteresis

Magnetic hysteresis loops of the CI, LSMO powders and CI/LSMCO composite with 95:5 measured at room temperature are shown in figure 5. All three samples have soft magnetic properties, because the hysteresis loops are long and narrow with low coercivity values. The saturation magnetization \( (M_s) \) values are 192.89, 31.57 and 168.12 emu gr\(^{-1}\) for CI, LSMO powder and CI/LSMCO composite, respectively. CI has excellent ferromagnetic properties. The magnetic parameters of CI, LSMO and CI/LSMCO composite, the related saturation magnetization are listed in table 1.

The critical radius of the La\(_{1-x}\)Sr\(_x\)MnO\(_3\) powder is 40 nm, when the powder size are less than 40 nm, it shows a super paramagnetic properties, but at higher grain size than the critical radius La\(_{1-x}\)Sr\(_x\)MnO\(_3\) is ferromagnetic. Thus LSMCO nano powders have superparamagnetic properties.

4.2. Complex permittivity and permeability

Figure 6 shows the frequency dependence of the real part \( (\varepsilon') \) and imaginary part \( (\varepsilon'') \) of relative complex permittivity on CI, CI/Lao.7Sr0.3MnO3 (LSMO) and CI/Lao.7Sr0.3Mn0.4Co0.6O3 (LSMCO) composites. Both the \( \varepsilon' \) and \( \varepsilon'' \) increase with the addition of LSMCO to CI in the whole range of 8–12 GHz. After the doping of cobalt to La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\), Both the \( \varepsilon' \) and \( \varepsilon'' \) values of the composite increases.

Figure 7 shows the frequency dependence of the real part \( (\mu') \) and imaginary part \( (\mu'') \) of relative complex permeability on CI, CI/LSMO and CI/LSMCO composites. With the addition of LSMCO to CI, the \( \mu' \) value increases but the \( \mu'' \) value decreases. Generally, the \( \mu'' \) value has not changed much. Increasing the dielectric loss and nearly constant magnetic loss leading to improve the EM wave absorption properties in the composite.

4.3. Microwave absorption properties

The reflection loss (RL) of samples is simulated by the transmission line theory. The RL of normal incident EM wave at the absorber surface is given by the following equation [27]:

\[
RL = 20 \log_{10} \left( \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right)
\]
Figure 6. The real and imaginary part of complex permittivity of the CI, CI/LSMO and CI/LSMCO in the frequency range of 8–12 GHz.

Figure 7. The real and imaginary part of complex permeability of Samples CI, CI/LSMO and CI/LSMCO in the frequency range of 8–12 GHz.
where $Z_0$ is the impendence of the free space and $Z_{in}$ is the input impedance of the absorber; $\mu_r$ and $\varepsilon_r$ are the relative complex permeability and permittivity, respectively; $d$ is the thickness of the absorber, $c$ is the velocity of the light and $f$ is the frequency.

Figure 8 shows the RL versus frequency in the paints coating with 80 wt% filler ($\text{CI/La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Co}_x\text{O}_3 (x = 0, 0.2, 0.4, 0.6, 0.8)$) and 20 wt% wax (resin/hardner). The coating thickness was 0.9 mm and the frequency was ranged 8–12 GHz. The weight ratio of CI to $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Co}_x\text{O}_3 (x = 0, 0.2, 0.4, 0.6, 0.8)$ in these composites was fixed 75:5.

The RL of the pure CI is $-5.52$ dB at 11.4 GHz. With the addition of the LSMCO content, microwave absorption properties improved. The maximum RL of $\text{CI/La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Co}_x\text{O}_3 (x = 0, 0.2, 0.4, 0.6, 0.8)$ reaches to $-8.16, -8.84, -9.03, -9.6$ and $-8.4$ dB, respectively, with a coating thickness of 0.9 mm. Therefore, the optimum RL related to the 60 at% Co-doped LSMO in the composite and the bandwidth of the RL below $-4$ dB (more than 60% absorption) of this composite was in the whole range of 8–12 GHz. It could be conclude that, after Co-doping the absorption properties improved.

The maximum RL, the related absorption frequencies and bandwidths are listed in Table 2.

Figure 9 shows the RL dependence of the $\text{CI/La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.6}\text{O}_3$ composite coating with 5 wt% LSMCO and different coating thicknesses; The detailed data were given by Table 3. By increasing the coating thickness from 0.7 to 0.9 and 1.1 mm, the maximum RL increases to $-8.84, -9.6, -10.57$ dB, respectively and the maximum absorption frequency shifts to lower frequency.

The above results can be explained by the following equation [28]:

\[
f_m = \frac{c}{2\pi\mu_r d}
\]
where $f_m$, $c$ and $d$ are the matching frequency, the velocity of light, and the sample thickness, respectively. This equation indicates that the matching frequency $f_m$ shifts towards lower frequency by increasing the thickness of samples.

The microwave absorption properties are improved by increasing LSMCO and as well as the thickness of coating.

### 5. Conclusion

La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$ (x = 0, 0.2, 0.4, 0.6, 0.8) (LSMCO) powders were successfully synthesized by the sol-gel method. A mixture of CI and LSMCO powders as magnetic absorbers were filled into polyester resin to fabricate microwave absorbing materials. The microwave absorption properties of CI/LSMCO were studied in 8–12 GHz in the paints with the different thicknesses of 0.7, 0.9 and 1.1 mm. The analysis of experimental data shows that by incorporation of Co on La$_{0.7}$Sr$_{0.3}$MnO$_3$ powder and increasing coating thickness, the microwave absorption properties are improved by incorporation of Co on La$_{0.7}$Sr$_{0.3}$MnO$_3$ powder and increasing the thickness of coating. The paint of CI/La$_{0.7}$Sr$_{0.3}$Mn$_{0.4}$Co$_{0.6}$O$_3$ with the ratio of 75:5 showed an optimum reflection loss of $-9.6$ dB at 11.38 GHz with the thickness of 0.9 mm, and the bandwidth below $-4$ dB (more than 60% absorption) was 4 GHz. By increasing the coating thickness from 0.7 to 0.9 and 1.1 mm, the RL intensity increases and the maximum absorption frequency shifts to lower frequencies. According to magnetization results, the saturation magnetization ($M_s$) values were obtained to be 192.89, 31.57 and 168.12 emu gr$^{-1}$ for the samples of CI, LSMCO powder and CI/LSMCO composite, respectively.

### Acknowledgments

This research was supported by the University of Tabriz and University of medical new technology for their obtaining and application. The appreciation for the possibility of electron microscopic studies is expressed to Aida Azami, Drug Applied Research Center.

### ORCID iDs

Hussein Shokrvash © https://orcid.org/0000-0002-2072-0676
References

[16] Wang B, Cao Q and Zhang S 2014 Effects of the incorporation of Fe on the electromagnetic and microwave absorption performance of La$_{0.5}$Sr$_{0.5}$MnO$_3$ Materials Science in Semiconductor Processing 19 101–6
[24] Cheng Y, Dai J, Zhu X, Wu D and Sun Y 2010 Preparation, magnetic and microwave absorption properties of La$_{0.5}$Sr$_{0.5}$MnO$_3$/La(0H)$_3$ composites Mater. Res. Bull. 45 663–7
[26] Tsay C Y et al 2014 Enhanced microwave absorption of La$_{0.5}$Sr$_{0.5}$MnO$_3$ based composites with added carbon black Ceram. Int. 40 3947–51