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Enhanced microwave absorption of $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ based composites with added carbon black

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Abstract

Composites consisting of carbon black (CB) particles, $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ (LSMO) powder, and epoxy resin were prepared for development of a high performance microwave absorber. This study investigated the influence of adding amounts of LSMO powder (60, 70, and 80 wt%) on complex permittivity, complex permeability, and reflection loss for CB (5 wt%)-epoxy composites. The variation of complex permittivity and complex permeability with frequency of the composites was measured by the cavity perturbation technique in the range of 7–14 GHz. It was found that the real part of the complex permittivity increased with increasing LSMO addition and the imaginary part of the complex permeability decreased with increasing frequency. The microwave absorption results indicated that the composite filled with 5 wt% CB particles and 80 wt% LSMO powder had the best absorption performance. The maximum reflection loss was −23.63 dB at 7.87 GHz and the absorbing bandwidth at −10 dB was 1.75 GHz with a matching thickness of 5 mm.

Keywords: A. Powders: solid state reaction; B. Composites; C. Magnetic properties; D. Perovskites; E. Functional applications

1. Introduction

Electromagnetic (EM) waves in the GHz range are increasingly utilized in wireless telecommunication systems (such as mobile phones, laptops, tablets, and local area networks), radar systems, and satellite broadcast systems [1]. Unfortunately, severe electromagnetic interference (EMI) problems accompany the extensive use of electronic devices and components, and information security during the operation of local area networks and personal digital assistants is always a concern. To overcome the EMI pollution problem, the study and development of microwave absorbing materials has attracted much interest in recent years [2].

Perovskite-structured manganese oxides $R_{1-x}A_xMnO_3$ (R: trivalent rare earth element; A: divalent alkaline earth element) are extensively studied because of their colossal magnetoresistance effect and the ordering of spin, charge, and orbitals [3]. Among these manganese oxides, those in the La_{1-x}(Ca, Sr, Ba)$_x$MnO$_3$ system, in particular $La_{1-x}Sr_xMnO_{3\pm\delta}$ (LSMO), exhibit a strong magnetism and low resistivity at room temperature, characteristics that make them promising candidates for application as microwave absorbing materials [3,4]. Carbon black (CB), on the other hand, is used as the conductive filler in composites for EMI shielding and EM wave absorption applications, due to its electrical conductivity, chemical resistance, low density, and reasonable cost [2,5]. Both LSMO and CB have been used as filler in microwave absorbers and exhibited good absorption in a high frequency range, such as the X-band frequency range [4,5].

In a microwave absorber, the excellent microwave absorption property is attributed to good wave impedance matching, which enhances dielectric loss and/or magnetic loss [2]. Therefore, complex absorbers that include both dielectric loss and magnetic loss fillers may offer high reflection-loss and wide frequency-range microwave absorption. In this study, we prepared a hybrid type microwave absorbing composite. It was a mixture of CB particles for dielectric loss and LSMO powder for magnetic loss. The goals of this study were to produce a high performance X-band microwave absorber and to investigate the influence of LSMO filler changes (varied from 60

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to 80 wt%) on the electromagnetic parameters (permittivity and permeability) and reflection loss of CB/LSMO composites.

2. Experimental

$La_{0.7}Sr_{0.3}MnO_{3-\delta}$ (LSMO) powder was synthesized by the conventional mixed-oxide process. High-purity La_2O_3, $SrCO_3$, and Mn_2O_3 powders were used as the raw materials. The raw materials were weighed, mixed, ground, and then calcined at a temperature of 1100 °C for 8 h to form crystalline LSMO powder. The nano-sized carbon black (CB, Vulcan XC-72) particles were obtained from Cabot Corporation (USA). The composite samples for measuring complex permittivity and permeability were prepared by dispersing the CB particles and LSMO powder in epoxy resin. The epoxy resin (CMA1-K02, Pentad Scientific Corporation, Taiwan) was formed by mixing 98 wt% resin and 2 wt% hardener. The mixing ratio of CB particles to epoxy was maintained at 5 wt% and the LSMO powder was varied at 60, 70, and 80 wt%. The cylinder sample for measuring the electromagnetic parameters was 2 mm in diameter and 3 mm in length.

The crystal structure of calcined LSMO powder was examined using an X-ray diffractometer (XRD, Bruker D8 SSS) with Cu Kα radiation. The morphology of the LSMO powder was observed by scanning electron microscope (SEM, Hitachi S-4800), and the element composition of powder sample was verified by energy dispersive X-ray spectrometry (EDS). The average particle size of LSMO powder was decided by the mean linear intercept, which was determined from SEM micrograph. Magnetization–magnetic field (*M*–*H*) hysteresis loop measurement was performed with a vibrating sample magnetometer (VSM, Lake Shore 7003) at a frequency of 60 Hz.

The complex permittivity and complex permeability of the composites were measured by the cavity perturbation technique using an Agilent N5230A (PNA-L) Vector Network Analyzer in frequency ranges of 7.0–12.4 GHz for permittivity measurements and 7.5–13.8 GHz for permeability measurements. The calculated equations are presented in detail in our previous study [6]. The X-band rectangular resonant cavity is constructed with a WR 284 aluminum waveguide with dimensions of 100 mm in length, 22 mm in width, and 10 mm in height (Fig. 1). According to the results of reflection loss with frequency of composites, we can evaluate their microwave absorption capabilities.

3. Results and discussion

Fig. 2 shows the X-ray diffraction (XRD) pattern of the calcined $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ (LSMO) powder. All the detected diffraction peaks were indexed satisfactorily on the basis of a rhombohedral cell [$R\bar{3}c$ (167)] of $La_{0.7}Sr_{0.3}MnO_3$ (JCPDS no. 89-8098) [7]. The XRD result clearly indicates that the as-prepared LSMO powder exhibited the pure rhombohedral perovskite phase. The inset of Fig. 2 presents the plot of the magnetic hysteresis loop of LSMO powder measured at room temperature. That hysteresis loop shows the typical

Fig. 1. Photograph of an X-band rectangular resonant cavity for measurement of complex permittivity and permeability of microwave absorbing composites.

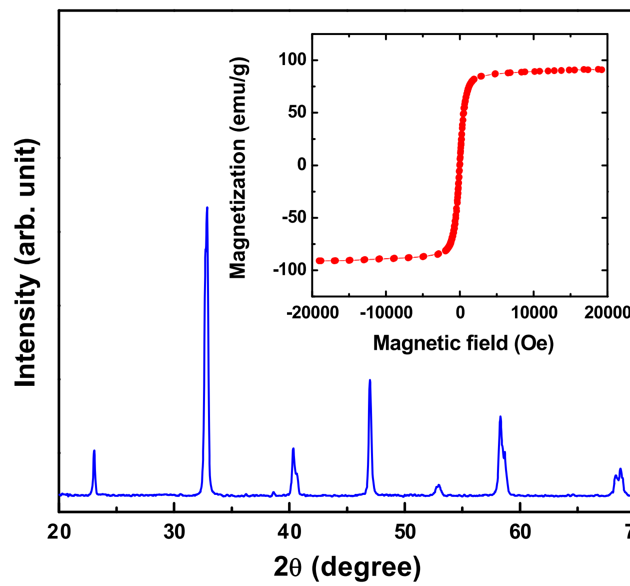

Fig. 2. XRD pattern of calcined $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ (LSMO) powder. The inset is a plot of magnetization versus magnetic field for LSMO powder.

feature of soft magnetic materials, with minimal hysteresis. The saturation magnetization and coercivity of calcined LSMO powder were about 91.0 emu/g and 15 Oe. Bayrakdar posited that soft magnetic materials achieving a saturation magnetization higher than 80 emu/g could be used for EMI and absorbing materials [1].

The morphology of calcined LSMO powder is shown in Fig. 3(a); visible is a slightly reactive aggregated powder with an average particle size of about 1.5 μm. Fig. 3(b) displays the EDS spectrum of the LSMO powder; visible are La, Sr, Mn, and O peaks, without any impurities. The amounts in at% of the elements La, Sr, Mn, and O were found to be 16.02, 6.74, 21.67, and 55.43, respectively. It was worth noting that the concentration of O was significantly deficient as compared with the stoichiometry of the nominal chemical composition $La_{0.7}Sr_{0.3}MnO_3$. Chueh et al. reported that the oxygen deficiency could destroy and reduce magnetic properties [8].

The cavity perturbation technique is widely adopted for measurements of complex permittivity ($\varepsilon_r=\varepsilon'+j\varepsilon''$) of microwave dielectric materials [9] and complex permeability ($\mu_r=\mu'+j\mu''$) of microwave magnetic materials [10]. That

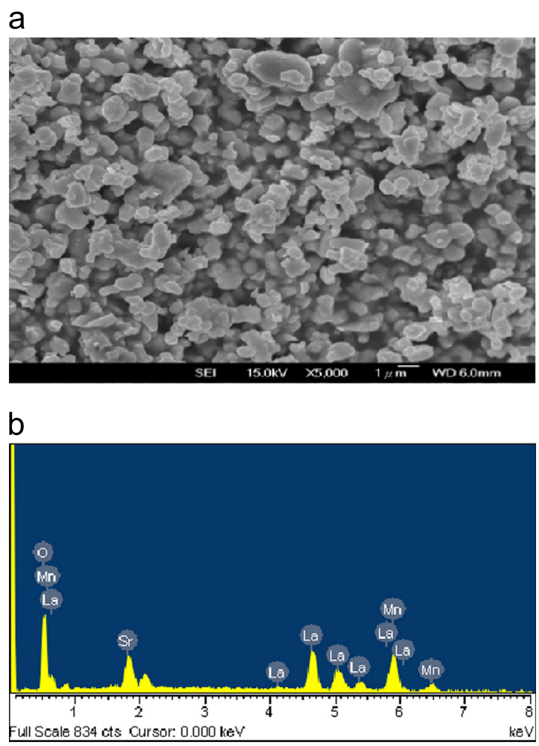

Fig. 3. (a) SEM micrograph of the LSMO powder sample and (b) EDS spectrum of the corresponding powder sample.

characterization method has attracted more interest due to its accuracy, good sensitivity, ease of configuration, and simplicity of measurement [11,12]. Therefore, it was used for measurement of the complex permittivity and complex permeability of the composites in this study. The X-band resonant cavity is excited by a TE_{10} mode and a TM_{10} mode [12]. Sweeping the frequency from 7 to 14 GHz for an empty cavity can detect four resonance peaks that are excited by the TE_{10} mode and four resonance peaks that are excited by the TM_{10} mode. Thus, only the eight-resonator frequency was used for examining the complex permittivity and complex permeability of the LSMO-based composites.

It is well known that the real parts of permittivity (ε') and permeability (μ') of materials are associated with their microwave energy storage capacity and the imaginary parts (ε'' and μ'') are measured to evaluate the ability for energy dissipation or loss [13]. Variation of permittivity and permeability of CB and CB/LSMO composites with frequency are shown in Figs. 4 and 5, respectively. In order to confirm the measured results, the samples without the filled absorber (i.e. epoxy resin samples) were also prepared and their electromagnetic parameters determined as the reference baseline. The mean complex permittivity and complex permeability of epoxy resin samples are $2.64-j0.036$ and $1.0-j0$, values that are very close to the results measured by transmission/reflection (T/R) method [6].

Fig. 4 shows the plots of complex permittivity of CB and CB/LSMO composites versus frequency. It is found that the values of complex permittivity of the CB/70LSMO and CB/80LSMO samples increased with increasing frequency in the range of 8–12.4 GHz and both values of $\varepsilon'$and ε'' slightly increased with increasing weight percentage of LSMO powder in the composites. Cheng et al. reported that increases in the permittivity of carbonyl iron/LSMO composites may be attributed to the enhancement of the interfacial polarization [14]. Fig. 4(a) also revealed that the values of ε' of the CB composites were between 4.2 and 4.6 in the whole measured frequency range. However, in Fig. 4(b), the ε'' values of CB composites are greater than those of CB/LSMO composites. The dielectric loss contains conductance loss, dielectric relaxation loss, resonance loss, and so on [13]. According to the free-electron theory, the imaginary part of permittivity (ε'') is proportional to the conductivity (σ). Thus, the CB composites with LSMO powder addition reduced the conductivity of composites, which in turn reduced the ε'' values.

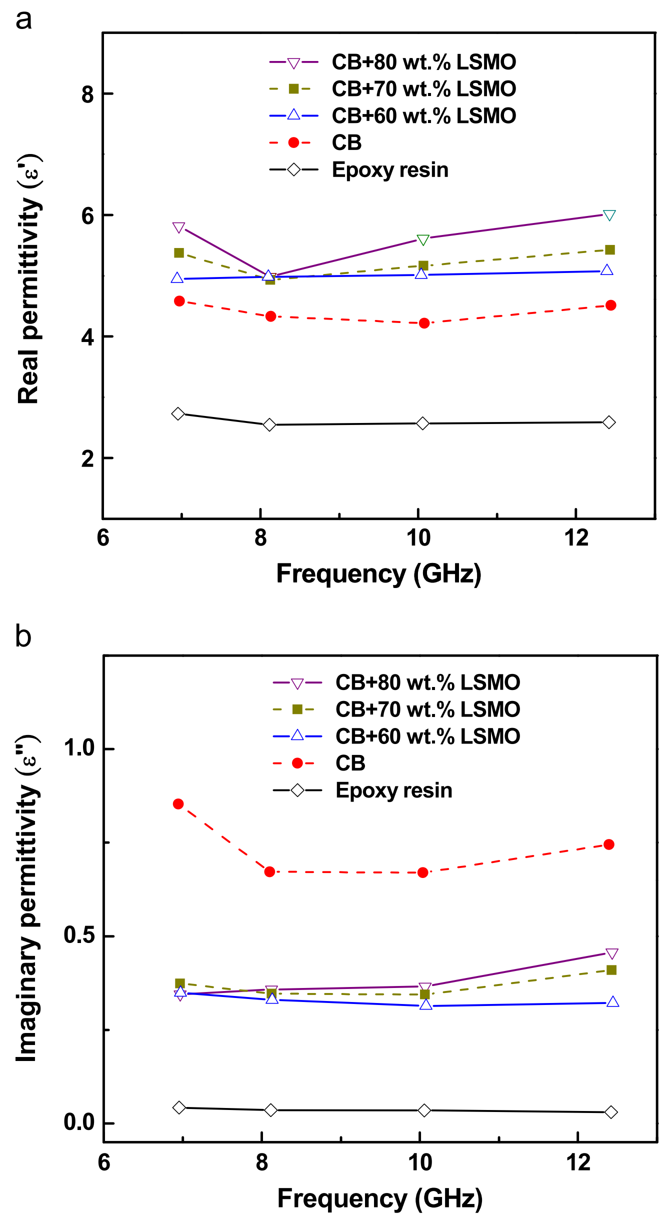

Fig. 4. Variation of complex permittivity of CB and CB/LSMO composites with measured frequency: (a) the real part and (b) the imaginary part.

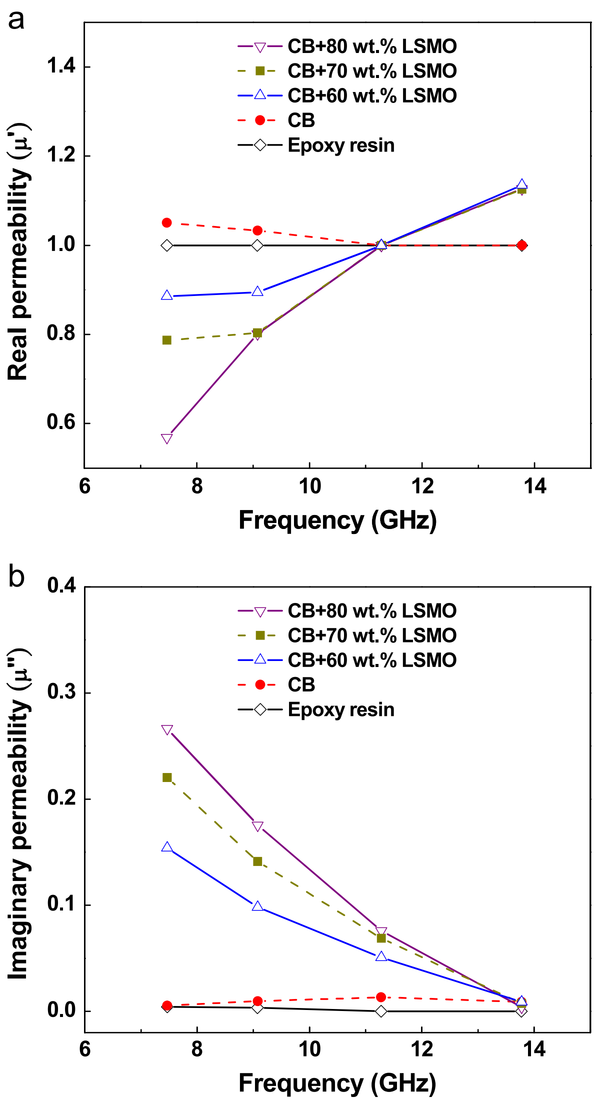

Fig. 5. Variation of complex permeability of CB and CB/LSMO composites with measured frequency: (a) the real part and (b) the imaginary part.

The real and imaginary parts of permeability are presented in Fig. 5(a) and (b), respectively. Measured results showed that the μ' values of CB/LSMO composites increased with increasing frequency in the range of 7.5–11.2 GHz, while the μ'' values decreased with increasing frequency in the whole measured frequency range. It is noted that the μ' values of the CB/LSMO composites were less than unity in the range of 7.5–11.2 GHz (Fig. 5(a)). Because the relationship between permeability (μ') and magnetic susceptibility (χ) is $\mu'=1+\chi$, that χ is negative. Such feature associates with the Neel magnetic resonance. The $LaMnO_3$ system has the feature of anti-ferromagnetism; however, the double exchange interaction between Mn^{3+}–O–Mn^{4+} ions by substituting Sr at site A will induce ferromagnetic behavior [13]. In addition, regarding the mechanism of the microwave magnetic loss, Cheng et al. described that the μ'' values of complex composites show a decreasing trend with increasing frequency, which may contribute to the low resonance frequency [14]. In Fig. 5, it can also be seen that the complex permeability of CB composites approaches the characteristics of the epoxy resin samples because the filler, CB particles, is a dielectric material.

According to the transmission line theory, the reflection loss (RL) of electromagnetic wave radiation related to the normalized input impedance Z_{in} at the surface of single-layer material backed by a perfect conductor is [15]:

$$\mathrm{RL}\ (\mathrm{dB}) = 20 \log |(Z_{in}-1)/(Z_{in}+1)| \tag{1}$$

Z_{in} is given by

$$Z_{in} = \sqrt{\mu_r/\varepsilon_r}\ \tan\ h\left[j(2\pi f d/c)\sqrt{\varepsilon_r \mu_r}\right] \tag{2}$$

where f is the frequency of the electromagnetic wave, d is the thickness of the absorber, and c is the velocity of light in the free space. It is found that the reflection loss of the microwave absorber is determined by the complex permittivity (ε_r), complex permeability (μ_r), and thickness (d). As described above, since finite measured data can be acquired only by using the cavity perturbation technique, then for evaluating variation in reflection loss with frequency of absorbing composites, some complex permittivity and permeability values were estimated by the linear interpolation method based on measured data.

Fig. 6(a) and (b) show reflection loss values as a function of frequency for CB composites filled with 60 wt% and 80 wt% LSMO powder, respectively. The thickness of CB/LSMO composites of less than 3 mm did not result in a significant reflection loss (curves (i) and (ii) in Fig. 6), and the maximum reflection losses of the CB/LSMO composite samples shifted toward the lower frequency range as the thickness of composites increased. That indicated that increasing the thickness of microwave absorber increase the absorption performance in the low frequency regions. This phenomenon can be explained by the following equation [16]:

$$f_m = c/2\pi\mu'' d \tag{3}$$

where f_m is the matching frequency (the frequency of the maximum reflection loss). A significant improvement was observed when the thickness of CB/LSMO composite increased to 5 mm as shown in the curve (v) of Fig. 6(b). In the present study, the CB composites filled with 80 wt% LSMO powder exhibited the best microwave absorption. A reflection loss of −23.63 dB was found at 7.87 GHz for an absorber thickness of 5 mm, and the absorbing bandwidth corresponding to the RL at −10 dB was 1.75 GHz.

4. Conclusions

We developed a hybrid type, X-band microwave absorbing composite by mixing carbon black (CB) particles, $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ (LSMO) powder, and epoxy resin. It was demonstrated that an effective way to change the complex permittivity and permeability and then to turn the impedance of the microwave absorber is to combine dielectric loss and magnetic loss fillers. Measured results showed that the μ' values of the CB/LSMO composites were less than unity in the range of 7.5–11.2 GHz. Increasing the amount of LSMO filler in the CB composites not only enhanced the magnetic loss in

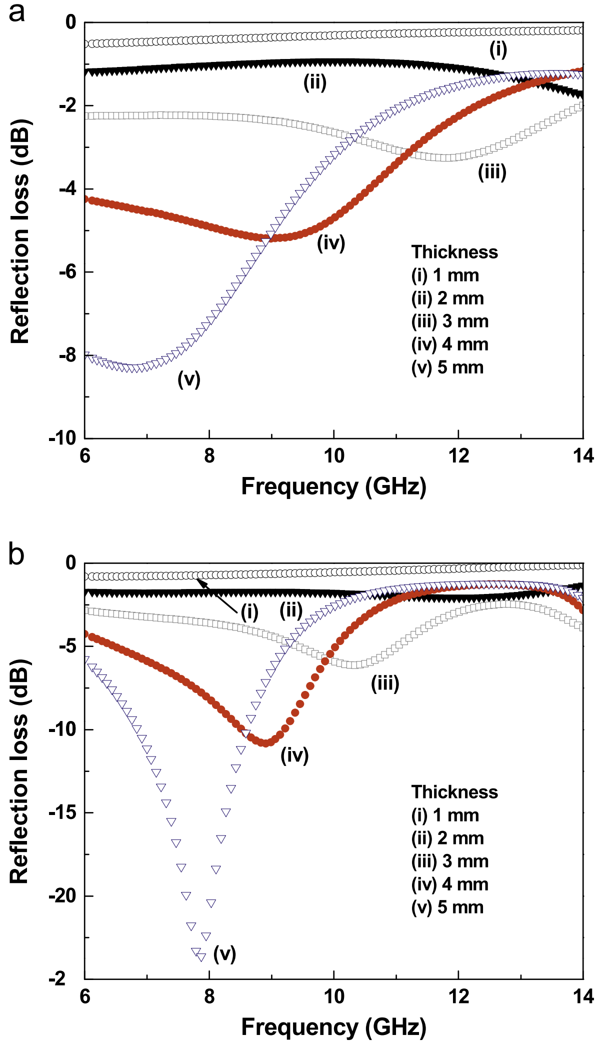

Fig. 6. The calculated reflection loss values of CB/LSMO composites with different matching thicknesses as a function of frequency. The CB composites filled with (a) 60 wt% and (b) 80 wt% LSMO powder.

the whole frequency range but also slightly increased the dielectric loss in the range of 8–12.4 GHz. In this study, the best microwave absorption of −23.63 dB at 7.87 GHz was obtained with a composite absorber containing 5 wt% CB particles and 80 wt% LSMO powder, with matching thickness of 5 mm. The absorbing bandwidth at −10 dB was 1.75 GHz for the corresponding sample.

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