Bull. Mater. Sci., Vol. 40, No. 2, April 2017, pp. 301–306. © Indian Academy of Sciences.
DOI 10.1007/s12034-017-1368-2

# Reduced-graphene-oxide-and-strontium-titanate-based double-layered composite: an efficient microwave-absorbing material

**SUKANTA DAS[1,2], S K SAHU[2], RAMESH ORAON[1], P C ROUTRAY[2], H BASKEY[3] and G C NAYAK[1,*]**

[1]Department of Applied Chemistry, Indian Institute of Technology (Indian School of Mines) Dhanbad, Dhanbad 826004, India
[2]Integrated Test Range (ITR), Chandipur 756025, India
[3]DMSRDE, Kanpur 208013, India

MS received 8 October 2015; accepted 2 July 2016

**Abstract.** **Microwave-absorbing materials based on reduced graphene oxide (r-GO)/strontium titanate were prepared by embedding in epoxy matrix. R-GO and strontium titanate were synthesized and characterized before composite fabrication. Microstructures of the constituent elements were studied by scanning electron microscopy and X-ray diffraction (XRD). Microwave absorption capabilities of the composite absorbers were investigated using a Vector Network Analyser in the range 8–12 GHz. A maximum reflection loss of −7.5 and −16.4 dB was obtained at 9.3 and 12.08 GHz, respectively, for 2% (w/w) r-GO-loaded epoxy composites. A maximum attenuation of −12.8 dB at 9.3 GHz was obtained for the strontium titanate/epoxy composite. However, double-layer composite with r-GO/strontium titanate/epoxy composition showed the maximum reflection loss of −15.1 dB at 9.47 GHz and −9.65 dB at 12.3 GHz. All the results are discussed in terms of complex permeability and permittivity. The study revealed that intrinsic conductivity and polarization of the r-GO particles and dielectric polarization of the strontium titanate within epoxy matrix contribute to the microwave absorption.**

**Keywords.** **Composite; absorption; reflection loss; dielectric; double layer.**

## 1. Introduction

Development of microwave-absorbing materials precisely is an essential part of the work related to stealth technology for all defence platforms. The secondary use of these composite materials is to reduce electromagnetic interference (EMI). In recent years researchers are focused on developing microwave absorbers in X-band region (8–12 GHz). Graphene is an important candidate with two-dimensional configuration and honeycomb lattice consisting of carbon. It has been an important material due to its electrical conductivity, mechanical stiffness, chemical stability, large specific surface area, low density and excellent electromagnetic response [1]. It is difficult to synthesize and maintain the stability of single-layer graphene with atomic thickness. Multi-layer graphene (MLG), consisting of a stacked layer of graphene of a few nanometer thickness, is easy to synthesize and can be utilized in the area where bulk material is required. Strontium titanate is another strong candidate for microwave absorber formulation with high dielectric constant ($\varepsilon_r$) value [2]. In strontium titanate, each $Sr^{2+}$ ion is coordinated by 12 $O^{2-}$ ions whereas $Ti^{4+}$ ions are six-fold coordinated by $O^{2-}$ ions; each of the $Sr^{2+}$ ions is surrounded by four $TiO_6$. Hence, while a covalent bonding exists in $TiO_6$ between O and Ti, an ionic bonding holds the $Sr^{2+}$ and $O^{2-}$ ions. Hence, strontium titanate has mixed ionic–covalent bonding properties. This nature of chemical bonding leads to a unique structure, which makes it a model electronic material and can be a potential microwave absorber that can absorb microwave both by ionic conduction and dipolar interaction. Out of very few works Sudhakar and Das [3] reported the use of graphene/$Fe_3O_4$/TPU-based composite for microwave absorption and showed a maximum reflection loss (RL) of −9.7 dB at 12.4 GHz. Most of the works reported the use of graphene-based composite as EMI shielding materials. Liang *et al* [4] reported the use of graphene/epoxy composite for EMI shielding effectiveness and showed a maximum 21 dB shielding within the X-band region. Eswaraiah *et al* [5] reported the use of graphene/PVDF composite for EMI shielding and showed 20 dB shielding achieved when loading of graphene was 5%. Hartomy *et al* [6] studied EMI shielding and microwave absorption capability of graphene/natural rubber and showed that a maximum shielding effectiveness of −34 dB is achieved with this material.

When electromagnetic waves are transmitted through different media, magnitude of the wave length changes with respect to thickness of different layers [7,8]. Destructive interference may occur if the transmitted wave length is half of the incident wave length, which is represented as follows:

$$2r = \left(n + \frac{\lambda_1}{2}\right), \quad (1)$$

*Author for correspondence (nayak.g.ac@ismdhanbad.ac.in)

where $r$ is the thickness of the absorber, $\lambda_1$ is the wave length of the incident electromagnetic wave and $n$ is a constant that depends upon the properties of the microwave-absorbing structure. For a single layer, $n$ value is considered as 0 and thickness of the absorber can be expressed as follows:

$$r = \frac{\lambda_1}{4}, \tag{2}$$

where $\lambda_1$ is the wavelength inside the single layer and can be expressed as $\lambda_1 = \lambda_0/\sqrt{\varepsilon_r}$. Wavelength in the free space is expressed as $\lambda_0$ and $\varepsilon_r$ is the dielectric constant. Hence thickness of the single layer can be expressed as follows:

$$r = \frac{\lambda_0}{4\sqrt{\varepsilon_r}}. \tag{3}$$

In this research work special focus has been given to develop dielectric single-layer microwave-absorbing materials based on reduced graphene oxide (r-GO) and strontium titanate embedded within epoxy matrix. Moreover, in this work double-layer microwave-absorbing materials were developed based on multi-layer r-GO/epoxy (bottom layer) and strontium titanate/epoxy (top layer) structure, which enhanced the microwave absorption capability of the composite materials.

## 2. Experimental

### 2.1 *Synthesis of r-GO*

R-GO was synthesized by chemical reduction of graphene oxide, prepared by modified Hummer's method, as reported by Stankovich *et al* [9]. In a typical procedure 1 g graphene oxide was taken in a 2 litre round bottom flask with 1 litre water. Then the solution was sonicated for 30 min using an ultrasonic bath till a clear solution was obtained without any visible particles. Subsequently hydrazine hydrate (10 ml) was slowly added to the solution with continuous stirring. Then the solution was heated at 90°C for 6 h in an oil bath to complete the reduction of graphene oxide. The product was isolated by filtration, washed with water and ethanol and finally dried in vacuum at ambient temperature.

### 2.2 *Synthesis of strontium titanate*

Strontium titanate was synthesized by the sol–gel auto-combustion method as reported by Klaytae *et al* [10]. Initially desired amounts of strontium nitrate and citric acid were dissolved in a beaker with deionized water. Titanium nitrate solution was added to this with constant stirring. The entire solution was heated at 80°C for 6 h for gel formation. Then the gel was heated to 250°C to start the auto-combustion process. Finally the combustion product was calcined at 500°C for 3 h to get crystallinity. Finally the strontium titanate powder was subjected to further characterization and composite preparation.

### 2.3 *Development of microwave-absorbing structure*

In this study, three composite microwave absorbers were fabricated by blending r-GO and strontium titanate into epoxy matrix following the previously reported method [11]. An r-GO-based single-layer composite absorber was prepared by dispersing 2 wt% of r-GO in epoxy matrix along with a curing agent. A single-layer composite absorber having strontium titanate/epoxy composition was prepared by dispersing strontium titanate at a concentration of 50% (w/w) into epoxy matrix along with a hardener. A double-layer composite absorber was prepared with top layer composed of strontium titanate (50% (w/w)) and bottom layer of r-GO (2%) in epoxy matrix; here the top layer acts as an impedance-matching layer. The purpose of the top layer is to achieve high permittivity for dielectric loss and that of the bottom layer to achieve conductivity for dissipation. In all the composites, epoxy resin YD-128 (derived from Bisphenol-A and of medium viscosity) and hardener TETA were used in 9:1 ratio. The particles were first mixed mechanically with the matrix followed by sonication for 15 min to enhance dispersion. Finally the matrix with fillers was poured into a mould having dimensions 23 mm × 10 mm × 2 mm, which was backed with a conducting metal sheet. Any air entrapment was removed by applying vacuum. Curing was carried out at room temperature to avoid surface crack. The double-layer composite was prepared by first pouring the bottom layer into the mold and the top layer was poured over it after 10 min, to avoid any intermixing of the two layers.

## 3. Characterizations

A scanning electron microscope (SEM) was used for morphological study with an accelerating voltage of 30 kV. X-ray diffraction (XRD) studies of all the powder samples were conducted with a Regaku Ultima-III (Cu-source, $\lambda = 1.540598$) and scanning was performed in the range 10–80°. Permittivity and permeability studies of the microwave-absorbing materials were carried out with a Vector Network Analyser (VNA, Agilent, Model No. E 8364B) in X-band frequency range (8–12 GHz). The major variables of interest, impedance and RL parameters of the absorbers, were measured using an Agilent VNA (Model No. E 8362B).

## 4. Results and discussion

### 4.1 *XRD analysis*

The XRD analysis of r-GO and strontium titanate is shown in figure 1. Graphite possesses a sharp and intense peak at $2\theta$ value of 26.4° (figure 1a), which can be ascribed to the tightly bound graphitic layers [12]. However, this peak disappeared in case of r-GO due to exfoliation of graphitic layers during the redox synthesis process. XRD analysis of strontium titanate showed many sharp intense peaks. Comparison with the crystal structure database JCPDS card No. 35-0735

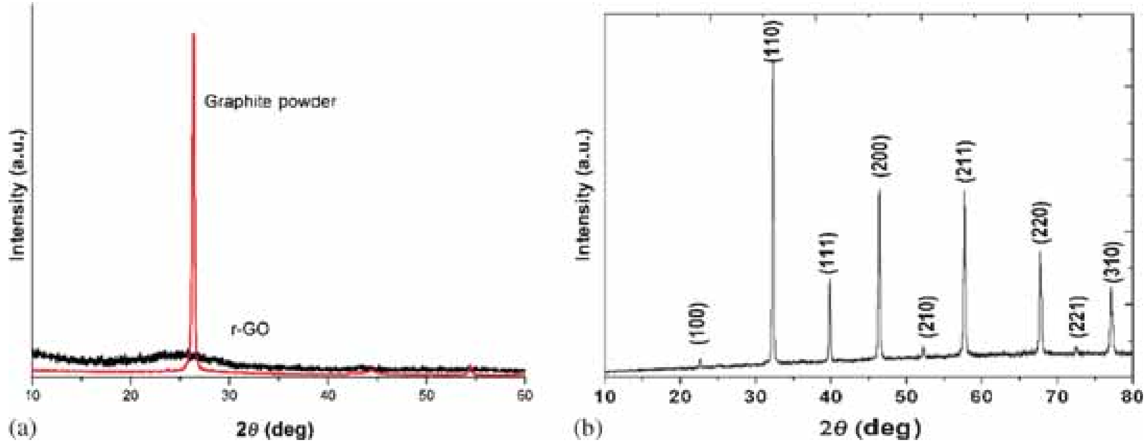


**Figure 1.** XRD pattern of (**a**) graphite and r-GO and (**b**) strontium titanate.

revealed good agreement with strontium titanate crystal planes (100), (110), (111), (200), (210), (211), (220) (221) and (310). The average crystallite diameter of the strontium titanate particles was determined to be 40.65 nm from the major diffraction peak of (110), using the well-known Scherrer's formula [13].

### 4.2 *SEM analysis of filler particles (multi-layer r-GO and strontium titanate)*

Surface morphology of r-GO and strontium titanate analysed using a SEM is presented in figure 2. The SEM image reveals the sheet-like morphology of r-GO (figure 2a) while that of strontium titanate was found to be particle like (figure 2b). SEM images of composites are shown in figure 2c–g. Surface morphology of the r-GO/epoxy composite shows the dispersed r-Go sheets in the epoxy matrix (figure 2c), while in the strontium titanate/epoxy composite the dispersed particles are observed (figure 2d). In case of double-layered composite the layered boundary can be clearly observed in figure 2e. The marked sections of each layer were magnified and are presented in figure 2f and g. It was found that the r-GO/epoxy layer showed the sheet-like morphology due to r-GO sheets and the strontium-titanate-containing layer presented the particle-like morphology.

### 4.3 *Microwave absorption analysis*

The microwave absorption efficiency of single- and double-layer composite materials was evaluated by measuring RL of the composite. The input impedance of the *n*th layer could be computed according to the following equation [14,15]:

$$Z_{\text{in}}(n)=Z_c^m(n)\frac{Z_{\text{in}}(n-1)+Z_c^m\tan\text{h}\,\gamma(n)d(n)}{Z_c^m(n)+Z_{\text{in}}(n-1)\tan\text{h}\,\gamma(n)d(n)}, \quad (4)$$

where $\gamma(n) = j\frac{2\pi f}{C}\sqrt{\mu_n \in_n}$ is the propagation constant of the *n*th layer, $d(n)$ is the thickness of *n*th layer, $Z_c^m(n)$ is the characteristic impedance of the *n*th layer with respect to the free-space impedance ($Z_0 = 50\ \Omega$) and $c$ is the speed of light. The characteristic input impedance ($Z_{\text{in}}$) of microwave absorbers is measured and plotted for all the three composite absorbers and shown in figure 3a. Plotted data show that input impedance values of double-layer r-GO/strontium titanate/epoxy composite are close to free-space impedance value (50 Ω), which indicates that absorption performance of double-layer composite is better than that of other two composites. This observation was further supported by the RL plots. RL can be calculated by the following equation:

$$\text{RL(dB)} = 20\log\frac{|Z_{\text{in}}(n) - Z_0|}{|Z_{\text{in}}(n) + Z_0|}. \quad (5)$$

RL value <−10 dB is considered to be an accepted value for microwave absorbers [16,17]. The results obtained from RL measurements are illustrated in figure 3b, which shows variation of RL with frequency for all the three composites. All the composites have 2 mm thickness and are cut into a size to be fitted into the Network Analyser. The r-GO/epoxy composite absorber shows maximum RL of −7.5 dB at 9.3 GHz and −16.46 dB at 12.07 GHz. For the strontium titanate/epoxy composite, a RL of −12.8 dB was observed at 9.3 GHz. However, for the double-layer r-GO/strontium titanate/epoxy composite, two peaks were observed at 9.46 and 12.3 GHz, with a RL value of −15.14 and −9.65 dB, respectively. RL properties of all the composites are purely due to dielectric loss mechanisms resulting from the molecular polarization phenomenon, such as space charge relaxation and dipole rotation. To further explore the absorption mechanism, permittivity of the composite materials was measured and is discussed in the following section.

### 4.4 *Permittivity study of the composite absorber*

The real and imaginary components of permittivity for all the composite absorbers were measured and analysed [18,19] with a Vector Network Analyser in the frequency range of 8–12 GHz and are shown, respectively, in figure 4a and b. Since the developed absorber is completely dielectric in nature,

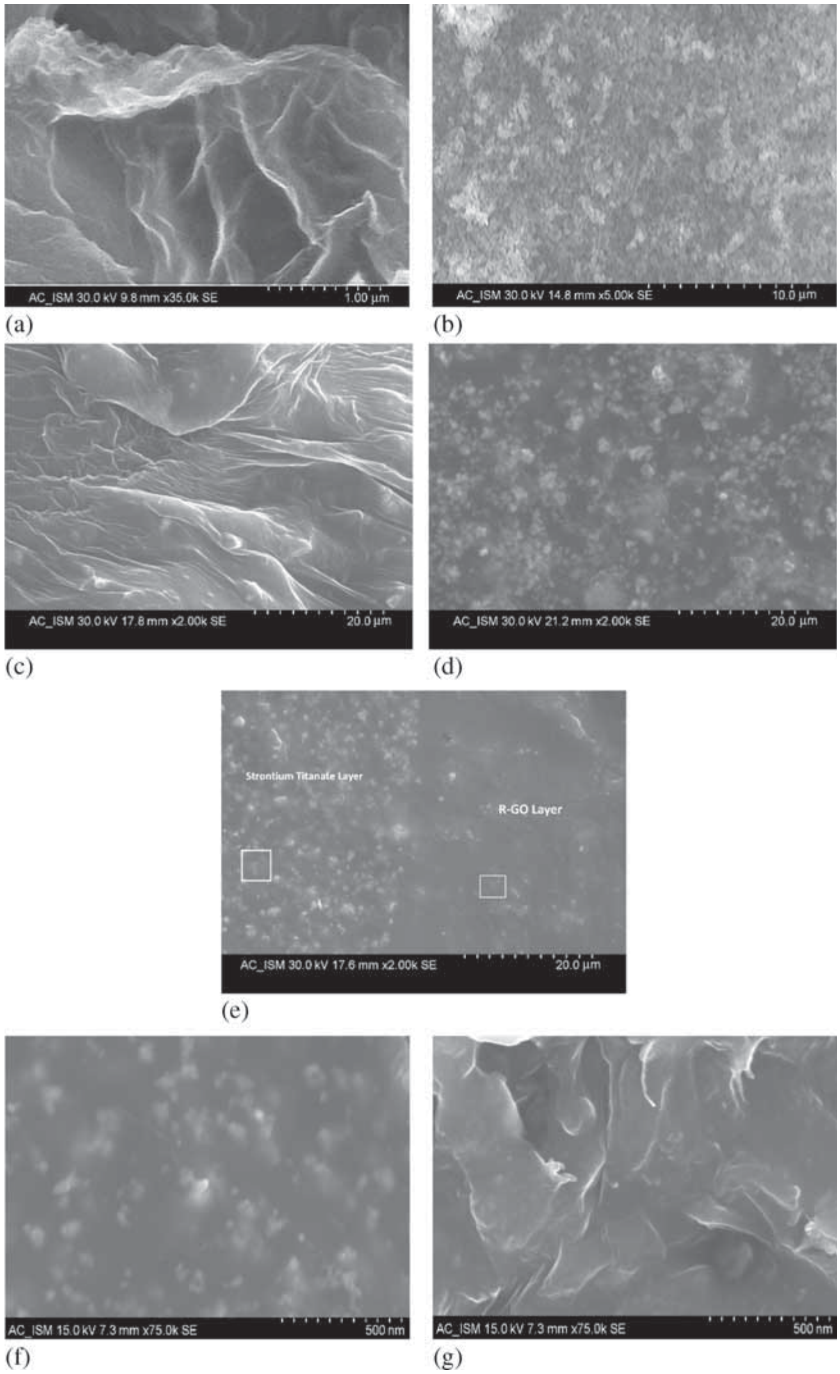


**Figure 2.** SEM images of (**a**) r-GO, (**b**) strontium titanate particles, (**c**) r-GO/epoxy, (**d**) strontium titanate/epoxy, (**e**) r-GO/strontium titanate/epoxy composites, (**f**) magnified section of strontium-titanate-containing layer and (**g**) magnified section of r-GO-containing layer.

only permittivity of the samples was measured. The imaginary component of permittivity (figure 4a) shows that the r-GO/epoxy composite has a characteristic peak at around 11.9 GHz and the same peak pattern also appeared in RL plot. This may be due to the presence of electric field, where high dielectric loss may occur due to intrinsic electrical dipole moment and polarization relaxation within the composite absorber. It was observed that the imaginary part of permittivity of strontium titanate/epoxy composite varies between 2 and 8 in the X-band frequency range. However, imaginary part of permittivity value for the double-layer r-GO/strontium titanate/epoxy composite showed peak value at 9.03 GHz for strontium titanate and 11.9 GHz for r-GO. The real part of permittivity for all the composite absorbers decreased with increasing frequency (figure 4b), which is due to increase of loss character with the increase in frequency.

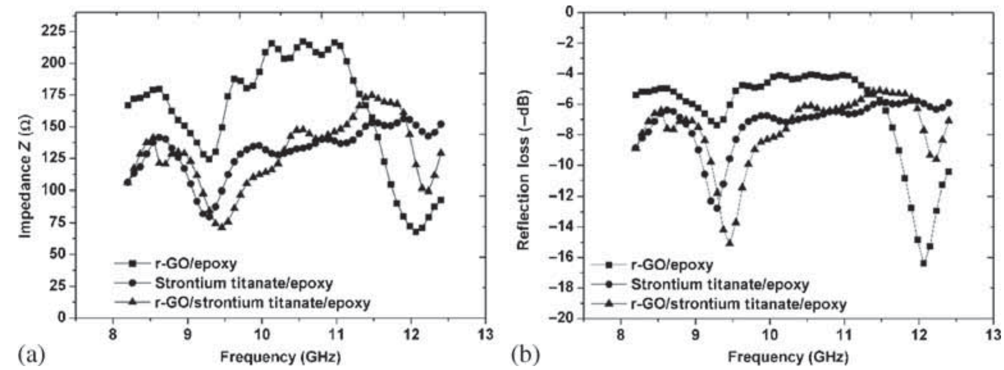


**Figure 3.** (**a**) Impedance *vs.* frequency and (**b**) reflection loss *vs.* frequency plots of all samples.

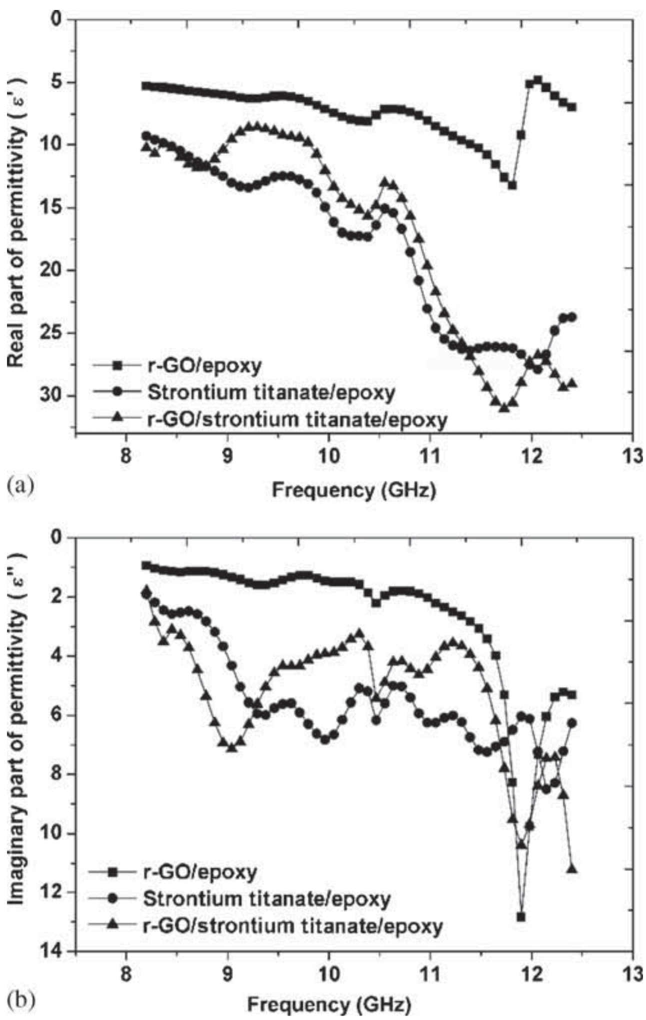


**Figure 4.** (**a**) Real part of permittivity ($\varepsilon'$) and (**b**) imaginary part of permittivity ($\varepsilon''$) of single- and double-layer absorbers.

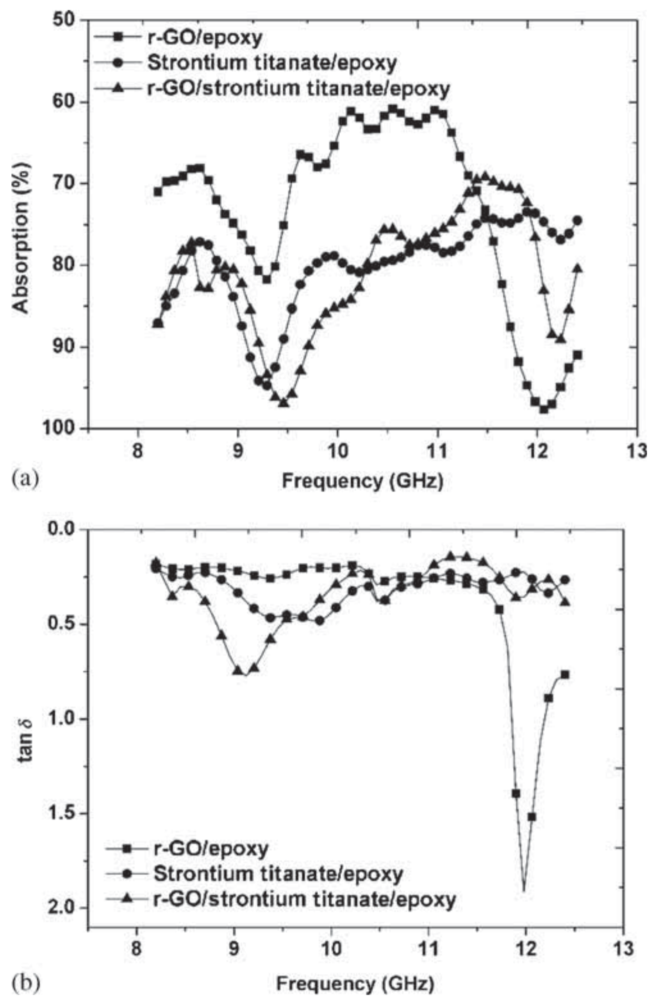


**Figure 5.** (**a**) Loss tangent ($\tan \sigma$) *vs.* frequency plot and (**b**) absorption (%) *vs.* frequency plot.

## 4.5 *Conductivity and absorption analysis*

Figure 5a shows the variation of loss tangent with the applied microwave frequency of all the composite absorbers in the X-band region. Loss tangent of the composite absorber was determined using the following equation:

$$\tan(\sigma) = \left[\frac{\varepsilon_r''}{\varepsilon_r'}\right], \tag{6}$$

**Table 1.** Comparison of reflection loss values.

| Absorber compositions | Maximum reflection loss | Remarks |
|---|---|---|
| r-GO/$SrTiO_3$/epoxy (with 2 wt% r-GO loading) | −15.10 dB at 9.47 GHz | This work |
| Graphene nanoplatelets/epoxy (with 15 wt% graphene) | −14.5 dB at 18.9 GHz | Reference [1] |
| Graphene/$Fe_3O_4$/TPU | −9.7 dB at 12.4 GHz | Reference [3] |

where $\varepsilon''$ is the imaginary and $\varepsilon'$ is the real component of permittivity. A composite absorber with $\tan \sigma \ll 1$ is classified as low-loss and low-conductivity medium with good dielectric property. A composite absorber with $\tan \sigma \approx 1$ is classified as lossy conducting medium. When $\tan \sigma \gg 1$ the absorber is classified as high-conductivity and high-loss medium. It can be seen from figure 5a that the r-GO/epoxy composite is a high-loss medium with high conductivity, whereas the composites having strontium titanate/epoxy and r-GO/strontium titanate/epoxy composition are medium-conductivity materials. The absorption capability of the microwave absorber [20,21] was determined by equation nos (7) and (8). The r-GO/epoxy composite shows absorption peaks at 9.3 and 12.05 GHz. Strontium/epoxy shows absorption peak at 9.22 GHz. The r-GO/strontium/epoxy composite shows absorption peaks at 9.44 and 12.2 GHz.

$$S_{11} = \left| \frac{Z_{\text{in}} - Z_0}{Z_{\text{in}} + Z_0} \right|, \tag{7}$$

$$\text{Absorption (\%)} = (1 - |S_{11}|^2) \times 100. \tag{8}$$

It can be observed that the double-layered composite has the maximum absorption capability in the whole X-band region with two absorption maxima, which is better than that of composites having only a single component. A comparative RL table of this work with other works has been presented in table 1, which shows the potential of developed composite materials for microwave absorption.

## 5. Conclusion

Strontium titanate was successfully prepared by sol–gel auto-combustion method and r-GO was prepared by reduction of graphene oxide. Single- and double-layered composites based on reduced graphene oxide and strontium titanate were prepared with epoxy matrix. XRD with a SEM confirmed the formation of strontium titanate and r-GO. It was found that microwave absorption property of the double-layered composite was larger as compared with the single-layered composite. Two reflection loss maxima were found in the case of double-layered composite in comparison with one peak for the single-layered composite. Hence, it can be concluded that the double-layered composite will be much more suitable for microwave absorption application as compared with single-layered composites.

## Acknowledgement

We are grateful for the support from Director, Integrated Test Range (ITR), DRDO, Chandipur, Odisha.

## References

[1] Wang Z, Luo J and Zhao G L 2014 *AIP Adv.* **4** 017139
[2] Lee S J, Thiyagarajan P and Lee M J 2008 *J. Ceram. Process. Res.* **9** 385
[3] Sudhakar C V and Das C K 2012 *Mater. Sci. Eng. B* **2** 368
[4] Liang J, Wang Y, Huang Y, Ma Y, Liu Z, Cai J, Zhang C, Gao H and Chen Y 2009 *Carbon* **47** 922
[5] Eswaraiah V, Sakaranarayanan V and Ramaprabhu S 2011 *J. Macromol. Mater. Eng.* **296** 1
[6] Hartomy O A A, Ghamid A A, Dishovsky N, Shtarkova R, Iliev V, Mutlay I and Tantawy F E 2012 *Mater. Sci. Appl.* **3** 453
[7] Choi L, Kim J G, Seo L S and Lee D G 2012 *J. Compos. Struct.* **94** 3002
[8] Folgueras L D C and Rezende M C 2008 *J. Mater. Res.* **11** 245
[9] Stankovich S, Dikin D A, Piner R D, Kohlhaas K A, Kleinhammes A, Jia Y, Wu Y, Nguyen S B T and Ruoff R S 2007 *Carbon* **45** 1558
[10] Klaytae T, Panthong P and Thountom S 2013 *Sci. Res. Essays* **8** 32
[11] Oh J H, Oh K S, Kim C G and Hong C S 2004 *J. Compos. Part B* **35** 49
[12] Mhamane D, Ramadan W, Fawzy M, Rana A, Dubey M, Rode C, Lefez B, Hannoyerd B and Ogale Satishchandra 2011 *Green Chem.* **13** 1990
[13] Peng E, Ding J and Xue Jun Min 2014 *New J. Chem.* **38** 2312
[14] Zhang Z, Li T, Jing D and Zhuang Q 2009 *Carbon Sci. Technol.* **3** 117
[15] Wang Y, Wang L and Wu H 2013 *J. Mater.* **6** 1520
[16] Feng Y B, Qiu T, Shen C Y and Li X Y 2006 *IEEE Trans. Magn.* **42** 363
[17] Aloia A G D, Marra F, Tamburrano A, De Bellis G and Sarto M S 2014 *Carbon* **73** 175
[18] Wang Q and Chen G 2012 *Adv. Mater. Res.* **1** 93
[19] Phang S W, Tadokoro M, Wantanabe J and Kuramoto N 2008 *Curr. Appl. Phys.* **8** 391
[20] Murugan M and Kokate V K 2011 *Bull. Mater. Sci.* **34** 699
[21] Hong Y K, Lee C Y, Jeong C K, Lee D E, Kim K and Joo J 2003 *Rev. Sci. Instrum.* **74** 1098