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Synthesis, characterization and evaluation of reflectivity of nanosized $CaTiO_3$/epoxy resin composites in microwave bands

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Abstract. Microwave absorbing materials play a major role in electromagnetic interference and compatibility measurements in anechoic chambers. Nanocrystalline calcium titanate (CT) was synthesized by hydrothermal method and further composites of CT/epoxy resin were fabricated as thin solid slabs of four different weight ratios. The composite material was analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM), which reveals that CT was observed to be in the monoclinic phase with an average crystallite size of 24 nm. The reflectivity measurement of the composite materials was carried out by the transmission/reflection method using a vector network analyzer R&S: ZVA40, in the X- and Ku-bands. The effective permittivity and permeability of the samples was also computed with the help of measured transmission and reflection coefficients. The results show that CT with equal weight of epoxy resin provides –30 dB at 8·5 GHz in the X-band and –19.5 dB at 18·0 GHz in the Ku-band. Reflectivity was found to be better than –10 dB for 2·2 GHz and 1·9 GHz for X-band and Ku-band, respectively and encourages use of it as potential microwave absorber material.

Keywords. Anechoic chamber; calcium titanate; electromagnetic interference; epoxy resin composites; microwave/radio frequency absorber.

1. Introduction

Due to the proliferation of complex, high speed electronic systems in the last few decades, absorption of unwanted microwave energy, i.e. electromagnetic interference (EMI) is a renowned problem (Craig 1993) that needs to be addressed at all frequency levels. Consequently, overexposure of EMI could cause harm to biological systems (Bhanu 2003), hence efforts are in progress to nullify the same.

The amount of absorption provided by different materials and composites varies with various factors. A suitable microwave absorbing material may be realized by adding lossy fillers and/or magnetic particles with high ability to absorb EMI radiation to a light weight, physically and chemically stable matrix (Sohel *et al* 2009). In our study, the epoxy resin was selected as matrix material, owing to its thermal stability and low dielectric property at microwave frequency (Xiaodong *et al* 2007). Also the electrical properties have to be stable over a wide frequency range (1–20 GHz) and temperature range of (–50 to 150°C) for better performance.

Since the speed of the signal travelling through the dielectric material is inversely proportional to the square root of dielectric constant, materials with low dielectric constant and loss tangent $<10^{-3}$ are required for high frequency applications beyond S-band (Rajesh *et al* 2009). The $CaTiO_3$ (CT) is reported as a good microwave dielectric material with permittivity ~160 and an acceptable quality factor ~8000 at 1.5 GHz (Pashkin *et al* 2005).

Calcium titanate with its perovskite structure has been reported with low dielectric loss, ranging from 1×10^{-4} to 6×10^{-4} depending (but slightly) on temperature, with a dielectric constant of 30 to 120 (Pivovarova 2002) especially at microwave frequencies. Hence they have also been used as dielectric material in ceramic capacitors (Hiroshi and Junichi 1994).

Literature review shows that there is less amount of work carried out on CT, more so in the nano regime at higher microwave frequencies as absorbers (Pashkin *et al* 2005). Thus, efforts were focused in this direction. In the present work, nanocrystalline CT has been prepared by hydrothermal method (Pinatti *et al* 2009; Silva *et al* 2009) and the synthesized nanopowders fabricated into composite with epoxy resin. Further, it has been characterized by XRD and TEM. Scanning electron microscopy (SEM) was also carried out to validate the homogeneity

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in the composite. The microwave absorption properties of these composites have been studied.

The effective permittivity and permeability of the samples were computed with the help of measured transmission and reflection coefficients (James *et al* 1990; Jeffrey and Michael 1996; Abdel *et al* 1997; Kim *et al* 2007) using the vector network analyzer R&S: ZVA40. The sample performance versus frequency and other results obtained are further analyzed for the viability of the composite as microwave absorber in applications such as anechoic chamber, radars etc.

2. Experimental

2.1 *Materials*

All the chemicals used were of analytical reagent (AR) grade quality. The epoxy resin was procured from Shimo Resin Pvt. Ltd. under the trade name SHIMOREZ-400, its density at 25°C being 1·11 g/ml, viscosity at 25°C being 12 ± 0·3 Pa.

2.2 *Synthesis of calcium titanate*

The nanocrystalline CT powders were prepared by hydrothermal technique (Moon *et al* 2003; Ohba *et al* 2004; Li *et al* 2009) using chloride precursor salts as source for Ca and Ti ions. The reaction was carried out in an indigenous autoclave at a pressure of 75 kg/cm^2 for 3·5 h in a highly alkaline pH of ~13·5 maintained by the addition of mineralizer KOH. The white compound obtained was dried for 24 h in a vacuum oven.

2.3 *Preparation of composite slabs*

The composites were fabricated by varying weight ratios of CT with epoxy resin as given below.

(a) CT and epoxy resin (CT 1) – 1 : 10 wt.%
(b) CT and epoxy resin (CT 2) – 1 : 5 wt.%
(c) CT and epoxy resin (CT 3) – 1 : 2 wt.%
(d) CT and epoxy resin (CT 4) – 1 : 1 wt.%

These composites were prepared by mixing appropriate quantities of CT, epoxy resin and hardener in a beaker that was heated on a hot plate at 80°C with continuous stirring for two hours. After cooling, the homogeneous slurry was made into rectangular slabs having dimensions 34 × 22 × 1 mm^3 and dried under IR lamp.

2.4 *Analysis*

Figure 1 shows the XRD of the composite CT/epoxy resin with 1 : 1 wt.% using Philips make PAnalytical XRD machine. The peaks exhibit line broadening. Major peaks have been indexed that confirm monoclinic phase formation of calcium titanate powder and its crystalline nature. Unreacted precursor peaks related to minor quantities of TiO_2 have been marked. The diffraction at lower angles is observed due to the epoxy resin matrix. The extent of broadening of CT peaks has been described by (β), the full width at half maximum (FWHM) intensity of the peak. The crystallite size (S) was calculated by substituting the value of 'β' into Scherrer's equation (Temyoshi and Namikawa 1999)

$$\text{Particle size, } S = \frac{0{\cdot}9\lambda}{\beta\cos\theta}, \quad (1)$$

where λ is the wavelength (= 1·5406 Å), θ is the diffraction angle in degree, and β is the full width at half maximum (FWHM).

The particle size calculated for individual peaks is shown in table 1.

The average crystallite size using Scherrer's equation is found to be 24 nm. The instrumental contribution of 0·05° has been accounted for by using silicon as standard while calculating the average crystallite size. The TEM images (figure 2) were observed with the help of Philips CM-200 instrument having an accelerating voltage of 200 kV. The TEM of CT nanoparticles appear to be crystalline and platelet-like in appearance with particle sizes varying between 25–50 nm.

The SEM image of CT4 composites which were firstly gold coated was scanned on a JEOL-JSM-6360A analytical scan station. The slabs were observed to have homogeneous distribution of CT nanoparticles over the

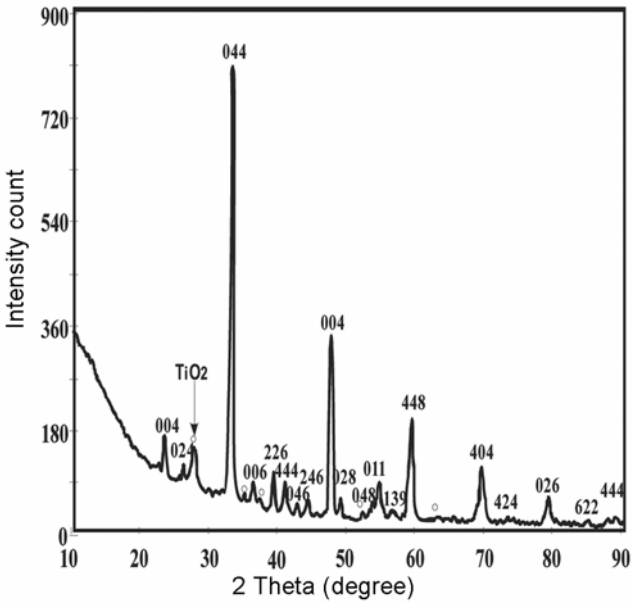

Figure 1. X-ray diffraction pattern of CT/epoxy powder.

epoxy resin matrix and occur as fine particle agglomerates as shown in figure 3.

3. Measurements

The performance characteristics of composites were studied by the transmission/reflection method (Hiroshi and Junichi 1994) using a vector network analyzer R&S: ZVA40, in the X-band and Ku-band frequency ranges of 8 GHz to 18·5 GHz. Initially, the vector network analyzer was calibrated with an open circuit, a short circuit and the matched load. The transmission and reflection properties of the samples ($S_{11} = S_{22}$ and $S_{12} = S_{21}$) were measured by the waveguide method. The sample or material under test was placed into the WR90/WR62 waveguide flanges. Utmost care was taken while coupling the co-axial to waveguide adapters with the waveguide flange. Figure 4 shows the configuration of the practical measurement setup for measuring the *S*-parameters. The performance characteristics of the materials were recorded on the basis of the reflection from the material and transmission through the material (Afsar *et al* 1986; Chen *et al* 2004). Figure 5 shows the photo picture of the flange holding the sample.

Table 1. Average particle size for CT (1 : 1)

hkl	θ (deg.)	cos θ	FWHM β (Rad) ($\times 10^{-03}$)	Particle size S (nm)
004	11·6	0·98	6·7	21·1
024	13·0	0·97	6·1	23·3
044	16·6	0·96	7·0	20·7
006	18·6	0·68	6·7	30·4
226	19·6	0·65	7·3	29·3
444	20·5	0·94	5·5	26·7
046	21·3	0·93	6·7	22·2
246	22·1	0·62	7·9	28·4
004	23·8	0·92	8·2	18·6
028	24·5	0·91	6·7	22·7
048	26·8	0·89	5·2	29·6
011	27·3	0·89	8·5	18·5
139	28·2	0·88	10·4	15·0
448	29·6	0·87	7·6	21·0
404	34·7	0·82	7·6	22·2
424	37·4	0·79	5·2	33·2
026	39·5	0·77	9·9	18·1
622	42·5	0·74	17·2	10·9
444	44·7	0·71	4·7	41·8
Average particle size (n.m): 24.0				

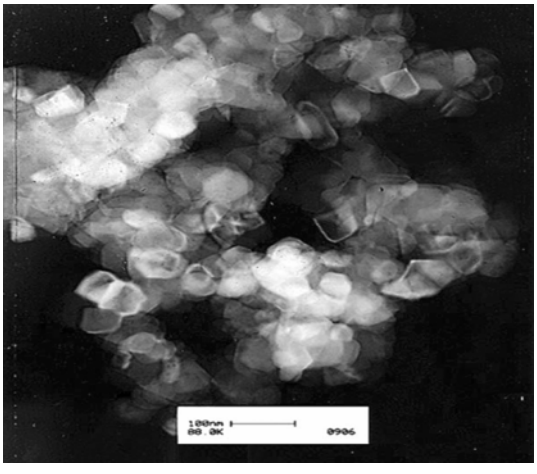

Figure 2. TEM of hydrothermally synthesized $CaTiO_3$.

4. Observations

The reflection characteristics versus frequency were recorded for all four samples, viz. CT 1 through CT 4, that has been shown in figure 6. The testing frequency bands were chosen from 8 GHz to 12·5 GHz (X-band) and 12·5 GHz to 18·5 GHz (Ku-band). As reported by

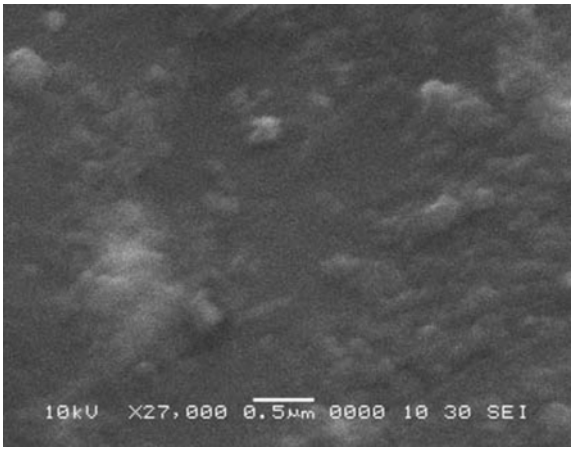

Figure 3. SEM of composite of CT/epoxy.

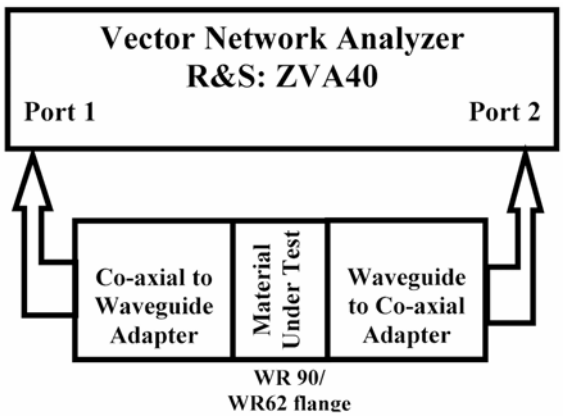

Figure 4. Measurement setup.

Xiaodong *et al* (2007), the epoxy resin has been presumed to be transparent to electromagnetic waves. Therefore, the amount of CT added alone exhibits the response as shown in figure 6.

The minimum reflection coefficient noted for samples CT1 through CT4 in the X-band have been noted as –20·3 dB at 10·3 GHz, –29·1 dB at 9·3 GHz, –18·1 dB at 9·2 GHz and –30 dB at 8·5 GHz, respectively. The reflection coefficient of composite of CT/epoxy resin with 1 : 1 wt.% (i.e. CT4) exhibits better performance in X-band as compared to others. Its reflection coefficient below –10 dB was obtained in the frequency range of 8·0 to 10·2 GHz and for the total bandwidth of 2·2 GHz.

Similarly, in the Ku-band these values have been noted as –21·6 dB at 18·1 GHz, –19·4 dB at 14·0 GHz, –18·9 dB at 14·0 GHz and –19·5 dB at 18·0 GHz, respectively. The reflection coefficient of CT2 exhibits better performance in terms of wider bandwidth of 2·0 GHz and the CT1 provides minimum reflectivity of –21·6 dB at 18·1 GHz. However, the overall performance of CT4 in Ku-band is promising as compared to others. The results obtained for all four samples are summarized in table 2.

This result of better reflectivity has been noticed for an equal concentration of CT and epoxy, *prima facie* seems to be counter-intuitive. However, it can be explained as follows. In the present study, two port measurements of S_{11} and S_{21} have been carried out using the reflection/loss method. Therefore, the reflectivity is solely governed by the impedance mismatch between the free space and the sample. The larger reflection loss for the CT4 sample thus indicates a better matching of impedance.

The amount of power absorbed in the CT samples can be calculated using the basic relation: $P_i = P_r + P_t + P_a$, where P_i, P_r, P_t and P_a are the incident, reflected, transmitted, and absorbed powers, respectively. For example, at around 10 GHz $P_a/P_i = 0{\cdot}4$ (i.e. 40% of the incident power is absorbed in 1 mm of CT1. In a typical anechoic chamber-like situation the absorbing layer (the CT samples in our case) is backed by a conducting plate. If we assume the conducting plate to be purely reflecting, then the microwave would travel through a total of 2 mm of the CT sample (as it come out on the same side as the incident beam), causing more absorption.

From the measured reflection and transmission coefficients, the intrinsic parameters such as permittivity (ε) and permeability (μ) were computed using the Nicolson–Ross–Wier (NRW) method (Abdel *et al* 1997) as

$$\text{Permeability } \mu^* = \frac{\lambda_{og}}{\Lambda}\left(\frac{1+\Gamma}{1-\Gamma}\right), \tag{2}$$

where Γ is the reflection coefficient and λ_{og} is the guide wavelength in the free space

$$\lambda_{og} = \frac{1}{\sqrt{\frac{1}{\lambda_o^2} - \frac{1}{\lambda_c^2}}}, \tag{3}$$

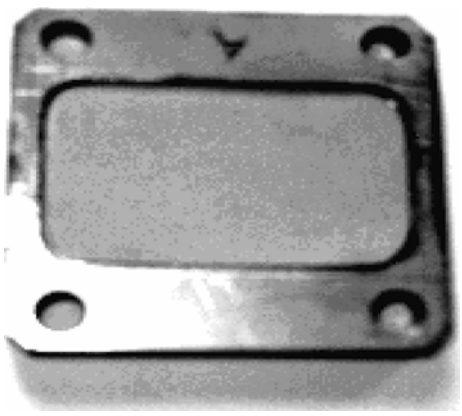

Figure 5. Photograph of the flange with sample.

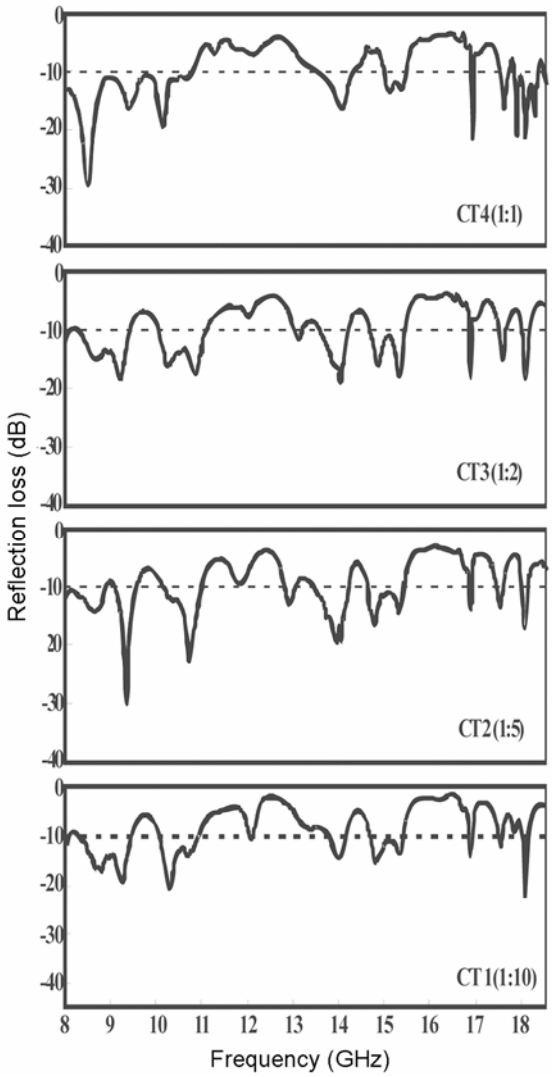

Figure 6. Performance characteristics of CT/epoxy resin composites.

Table 2. Summary of results

Parameters	X-band				Ku-band			
	CT1	CT2	CT3	CT4	CT1	CT2	CT3	CT4
Frequency range in GHz with reflectivity of –10 dB or less	8.3–9.5 and 10.1–10.9	8.2–8.9, 9.1–9.5 and 10.2–11.0	8.4–9.4 and 10.1–11.1	8.0–10.2	13.8–14.2 and 14.7–15.4	13.5–14.2, 14.6–15.4 and 17.8–18.3	17.5–17.6 and 18.0–18.1	13.4–13.9, 14.6–15.5 and 17.8–18.3
Bandwidth in GHz	2.0	1.9	2.0	2.2	1.1	2.0	0.2	1.9
Minimum reflectivity in (dB)	–20.3	–29.1	–18.1	–30.0	–21.6	–19.4	–18.9	–19.5
Frequency (GHz) of minimum reflectivity	10.3	9.3	9.2	8.5	18.1	14.0	14.0	18.0

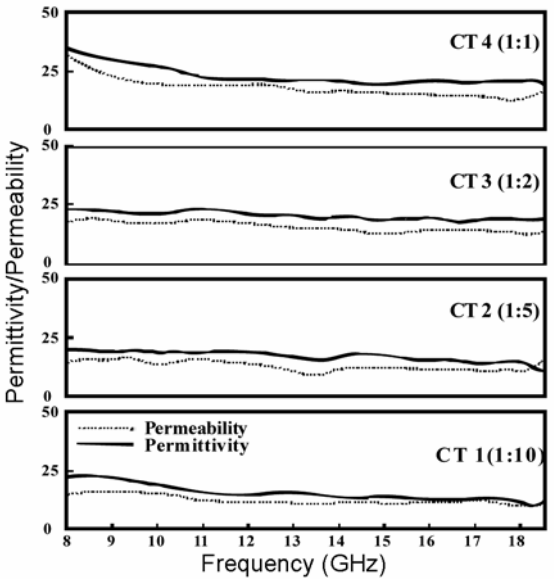

Figure 7. Permittivity and permeability versus frequency.

where, λ_o correspond to free space wavelength, λ_c correspond to cutoff wavelength and

$$\text{Permittivity } \varepsilon^* = \frac{\lambda_o^2\left(\frac{1}{\Lambda^2}+\frac{1}{\lambda_c^2}\right)}{\mu^*}, \tag{4}$$

where

$$\frac{1}{\Lambda^2} = \left[\frac{j}{2\pi d}\ln(\mathrm{T})\right]^2, \tag{5}$$

$$T = \frac{S_{11}+S_{12}-\Gamma}{1-(S_{11}+S_{12})\Gamma}, \tag{6}$$

$$\Gamma = K \pm \sqrt{K^2-1}, \tag{7}$$

$$K = \frac{S_{11}^2 - S_{12}^2 + 1}{2S_{11}}, \tag{8}$$

where S_{11} is the reflection scattering parameters, S_{12} is the transmission scattering parameters, Γ is the first reflection coefficient and T is the first transmission coefficients.

Figure 7 shows the permittivity and permeability versus frequency computed using (2) and (4) respectively. They show significant variation with frequency. The magnitudes obtained for all four composites decrease with increasing frequency, indicating that the CT can cause the dielectric loss and also the magnetic loss.

5. Summary

(I) CT nanopowder with an average crystallite size of 24 nm has been hydrothermally synthesized resulting in the monoclinic phase.

(II) Amongst the four samples prepared, CT4 with equal weight of CT and epoxy resin provides up to 30 dB absorption. Moreover, it also provides a wideband response below –10 dB.

(III) Based on the response of CT/epoxy resin composites, CT4 appears to have potential application as a microwave absorber in the X-band and Ku-band ranges that could be used in anechoic chamber.

(IV) Similar studies on other perovskite oxides such as barium titanate and strontium titanate are in process to explore the possibility of combining them for net effect in the above frequency range.

(V) Further studies on larger number of samples need to be carried out by the free space method.

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