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Barium titanate flakes based composites for microwave absorbing applications

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Abstract

Barium titanate (BT) has attained research focus in recent past owing to considering its high dielectric constant and stealth capabilities in microwave region. Shape effects of BT viz. powder, micron size flakes, nano particles and nanotubes have been studied vastly for its stealth capabilities. Present study aims at the preparation of millimetric size barium titanate flakes (BTFs) via controlled sol-gel process followed by tape casting. BTFs were mixed in varied weight ratio (50–90 wt.%) with polyurethane resin to fabricate composite laminates. Electromagnetic properties measurement in X and Ku band revealed high values of real and imaginary permittivity. Reflection loss measurements demonstrated more than 20 dB loss in wide frequency range (11.4–13.6 GHz). For single layer microwave absorber, reflection loss values have been calculated and it is observed that calculated and measured reflection loss values are in good agreement to each other. Developed material can find applications in broadband radar signature reduction.

Keywords: *barium titanate flakes, dielectric properties, microwave absorbers*

I. Introduction

Microwave absorbing technology is critical for military purposes and has got range of applications in civil sector. Salisbury screen and Jaumann absorbers were purely structural treatments to evolve radar absorption which led to bandwidth and bulk issues respectively. Of late research focus has diverted towards the development of new materials with stealth capabilities [1]. The role of radar absorbing materials (RAM) is to reduce the radar signatures of a target by coating RAM on its surface. The RAM encompasses parameters like design, weight, thickness, absorptivity, environmental resistance, mechanical strength for particular end application. In most of the earlier efforts, development of RAM based on magnetic materials using magnetic loss phenomena was widely attempted. Ferrites and carbonyl iron powder (CIP) are the contemporary materials being researched actively but they suffer from drastic reduction in permeability in microwave region [2,3]. This demerit of magnetic materials has been compensated by molecular composition and compounding with other materials which still remains heavy owing to the higher density of ferrites and CIP [4]. In the case of ferroellectric and dielectric materials, permeability remains constant throughout the frequency range and their larger propagation constant enables wave absorber to be made thinner. These absorbers being purely dielectric, polarization and conductive losses are the main mechanism for absorption of microwaves.

In general, microwave absorption characteristic of a dielectric material depend on their complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$), electromagnetic impedance matching with free space and microstructure of the absorber. Barium titanate (BT) is one such ferroelectric material exhibiting high dielectric constant. Extensive research has been conducted on the synthesis, morphology, ferroelectricity, and permittivity properties of BT [5,6]. The characteristic feature of BT is that the Ba^{2+} and O^{2-} ions form a face centered cubic (*fcc*) lattice with Ba^{2+} at the corners and O^{2-} at the face centers. The Ti^{4+} ion sits in the octahedral interstices formed by six O^{2-} ions. At room temperature, there is possibly minimum energy position for the Ti^{4+} ion, which is off-centered and therefore gives rise to permanent electric dipoles formed with six O^{2-}.

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The relaxation phenomenon in BT primarily occurs in the GHz range which can be characterized by a decrease in dielectric constant and peak in the dielectric loss with increasing frequency. Thus, it is anticipated that the BT might be used as lossy filler in microwave region and the same has been validated by Chen *et. al*. [7,8].

It is evident that shape of microwave absorbent plays an important role in the microwave absorption properties [9]. For the exploitation of shape effects, various structures of BT such as random shaped micron size flakes [10], nanoparticles [11] and nanotubes [12] have been studied. In the present study, we have fabricated millimetric size of barium titanate flakes (BTFs) using improvised sol-gel and tape casting method for the first time. To get wider interaction in X and Ku band, dimensions of fabricated BTFs are chosen by the order of millimeters. Micro structure and morphology of the fabricated BTFs have been studied and confirmed by X-ray diffraction (XRD) and scanning electron microscope (SEM). For the optimum absorption of microwaves using developed composite laminates, higher loading (50, 60, 70, 80 and 90 wt.%) of BTFs were mixed in polyurethane (PU) resin. Electromagnetic (EM) properties ($\varepsilon_r = \varepsilon' - j\varepsilon''$ and $\mu_r = \mu' - j\mu''$) and reflection loss of the composite laminates were measured in the X and Ku band using precise free space measurement method. Reflection loss of the fabricated composites have been calculated and compared with the measured results.

II. Experimental procedure

2.1 Preparation of BT by sol-gel method

Barium titanate (BT) powder was synthesized using sol-gel process [13]. Titanium-tetra-isopropoxide ($Ti(OC_3H_7)_4$) and triethanolamine (TEA) were mixed in appropriate molar ratio with methoxy ethanol solvent (100 ml) and refluxed for 2 hrs at 80 °C. Separate solution of 1 mol barium was prepared by dissolving 2,4-pentadionate salt of barium in methoxy ethanol. Mild heating was done for complete dissolution of salt. The barium metal salt solution was slowly transferred to the titania sol. The resultant sol was refluxed for another 6 hrs till complete hydrolysis. After hydrolysis the sol was stirred for 6 hrs and aged for 6 days. Then a light yellow transparent gel was obtained. The gel was dried at 90 °C for 6 hrs in order to obtain xerogel. The xerogel was calcined at 900 °C for 2 hrs which is the optimum temperature for calcination to obtain pervoskite phase considering the fact that at this temperature no $BaCO_3$ or new phase of $BaTiO_4$ is detected [10].

2.2 Preparation of BTFs

Barium titanate flakes (BTFs) of size 3 mm × 2 mm × 0.2 mm were prepared by tape casting process. The obtained BT powder was mixed with 20 wt.% of 50:50 ethanol and methyl ethyl ketone (MEK) solution. Additionally 1.0 wt.% of fish oil was added as deflocculant agent and the mixture was ball-milled in a plastic jar with zirconia grinding media for 24 hr. 4.0 wt.% of santicizer was added to the resultant slurry as a plasticizer to increase the flexibility in dried tape. Finally, 4.0 wt.% of poly ethylene glycol (carbowax- 400), 13.9 wt.% of acryloid binder and 0.73 wt.% of cyclohexanone was added to the slurry. The slurry was further ball milled for another 24 hrs for complete homogenization. This slurry was then de-aired in vacuum and tape casted on "Mylar" carrier film using tape casting machine. The process has been optimized by adjusting doctor blade gap and casting speed. The 0.2 mm thick, 150 mm wide green tape obtained after air drying was cut into millimetric size flakes (3 mm × 2 mm) that were initially heat treated at 550 °C for burning the binder and then annealed at 1250 °C for 1 hour.

2.3 Fabrication of microwave absorbing composites

To fabricate the microwave absorbing composites of size 150 mm × 150 mm × 3 mm, the annealed BTFs were gently mixed with PU resin in five different weight ratio i.e. 50:50, 60:40, 70:30, 80:20 and 90:10. The PU resin used is a two-pack polyurethane matrix that consists of polyol-8 (Ciba-Geigy, Switzerland) and hexamethylene diisocynate (E-Merk, Germany) mixed in 50:50 ratio.

2.4 Microwave measurements

The BTFs based microwave absorbing composite laminates were fabricated as per free space measurement system (HVS make) requirements for the measurements of EM properties and reflection loss from 8.2 to 18 GHz. The complex scattering parameters of the samples that correspond to the reflection (S_{11} or S_{22}) and transmission (S_{21} or S_{12}) were measured employing vector network analyser (Agilent make). The complex permittivity ($\varepsilon' - j\varepsilon''$) and permeability ($\mu' - j\mu''$) were determined from the scattering parameter using Agilent software module 85071. The terminated one-port technique was used to measure the reflection loss (R_L) in decibel, where R_L is given by ($-20 \log_{10}|S_{11}|$).

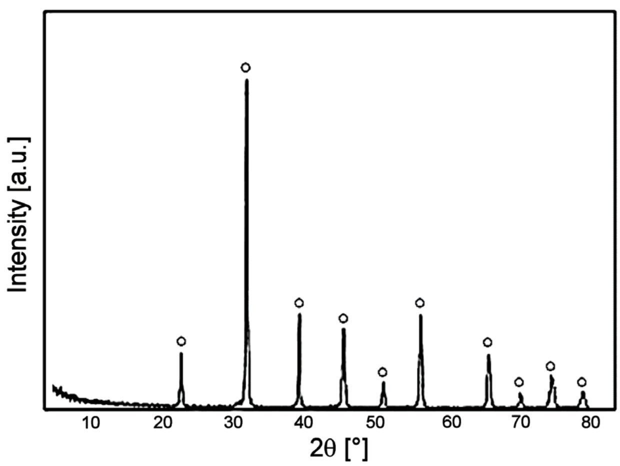
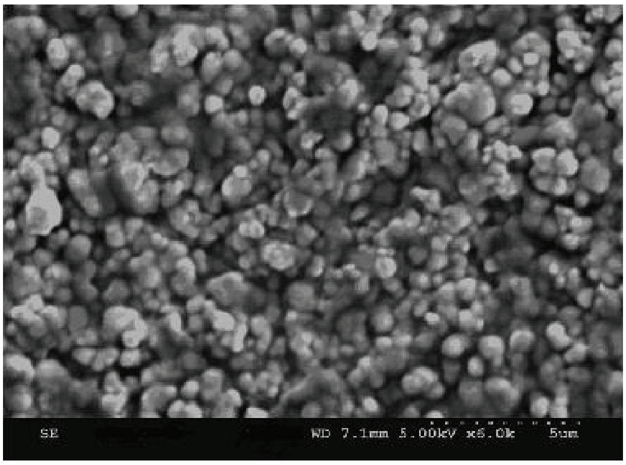
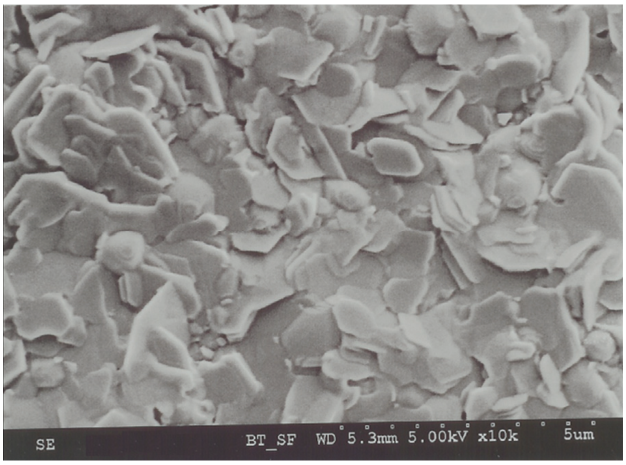


Figure 1. XRD pattern of $BaTiO_3$ prepared by sol-gel method



a)



b)

Figure 2. SEM images of green $BaTiO_3$ flakes (a) and annealed $BaTiO_3$ flakes (b)

III. Results and discussion

3.1 Structural analysis

Phase formation of BT was ascertained by X-ray diffractometer (Rigaku, Miniflex) using Cu-K_α radiation (30 KV and 20 mA, scan rate 2 °C/min). Figure 1 shows the XRD pattern of $BaTiO_3$, main peaks of barium titanate are at 2θ = 22.23°, 31.51°, 38.90°, 45.36°, 51.08°, 56.28°, 65.78°, 70.38°, 75.07° and at 79.43°, which exhibits tetragonal pervoskite structure. Size and morphology of barium titanate grains for the green BT and annealed BTFs samples were analysed on fresh fractured surface by scanning electron microscopy (Carl Zeiss SEM). The SEM image of green BT shows two kinds of nodular morphology. Smaller nodular crystallites belong to BT powder with an average particle size of 0.5 µm while bigger one to resin binder as shown in Fig. 2a. The evolution of microstructure, grains in BTF which occur during annealing process has also been studied by SEM. BTF was annealed from 1100 °C to 1250 °C and it is established that at 1250 °C, grain size of the order of 1.0 µm having platelet like morphology was observed as shown in Fig. 2b, which is the optimum size of grains for maximum dielectric constant [14].

3.2 Electromagnetic properties

Figures 3 and 4 show the real and imaginary part of permittivity of BTF-PU composites for flakes concentration of 50, 60, 70, 80 and 90 wt.%. Fabricated composites are purely non magnetic, their real and imaginary parts are in the vicinity of one and zero hence omitted in the figures. In the case of permittivity both real and imaginary spectra showed dispersion behaviour in all the samples. Principally, real and imaginary values of permittivity exhibit concomitant with respect to BTFs concentration in the composites. It is evident from the measurements that there is a gradual rise in the real and imaginary part of permittivity with respect to the concentration of BTF. For example, the sample with BTF concentration of 50 wt.% has demonstrated real part in the range of 10–15 and imaginary part in the range of 8–12, whereas the sample with BTF concentration of 90 wt.% showed real part in the range of 33–42 and imaginary part in the range of 18–23.

The prepared composites are heterogeneous mixtures of BTFs separated by polyurethane molecules. The dielectric properties of such heterogeneous composites arise mainly due to the interfacial polarization. Another most important mechanism in the microwave frequencies is orientational polarization. Contributions from atomic and electronic polarization are negligible and ruled out because these occur above the microwave frequency range. In the case of millimetric size flakes, dipole lengths are increased and dipoles of big strength are formed which may be leading to a higher dielectric constant and a long relaxation time giving rise to a higher dielectric loss. Further, more flakes content in the composite would result in more dielectric constant and dielectric loss which is clearly reflected in Figs. 3 and 4.

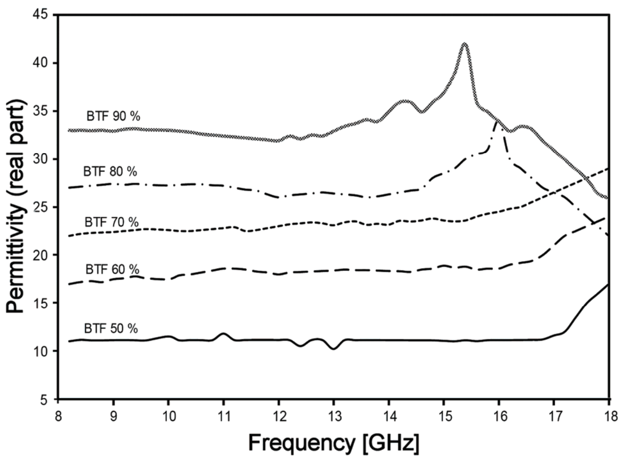


Figure 3. Real part of permittivity for different loading wt % of BTF

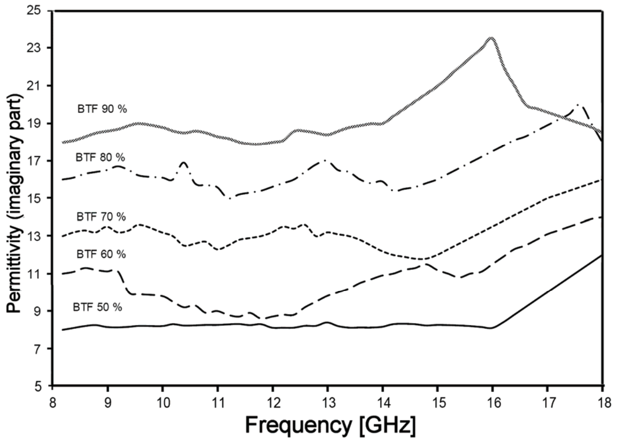


Figure 4. Imaginary part of permittivity for different loading wt.% of BTF

3.3 Microwave absorption

Samples with varied weight percent loading of BTF were prepared in polyurethane matrix. Fig. 5 shows the measured and calculated values of reflection loss. The results showed concomitant enhancement in bandwidth and reflection loss with the increment in BTF concentration. However, there is a variation at 90 wt.% loading

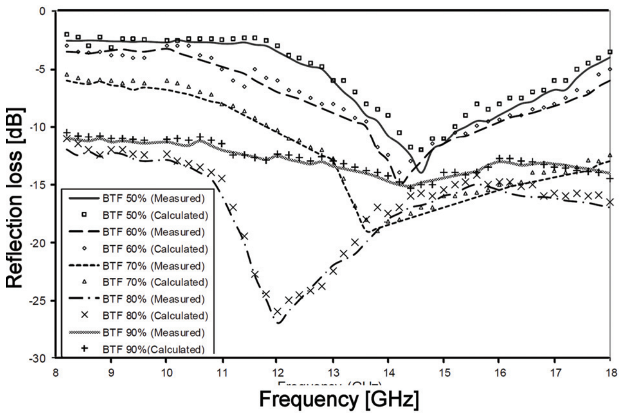


Figure - 5: Reflection loss characteristics of BTF based microwave absorbers

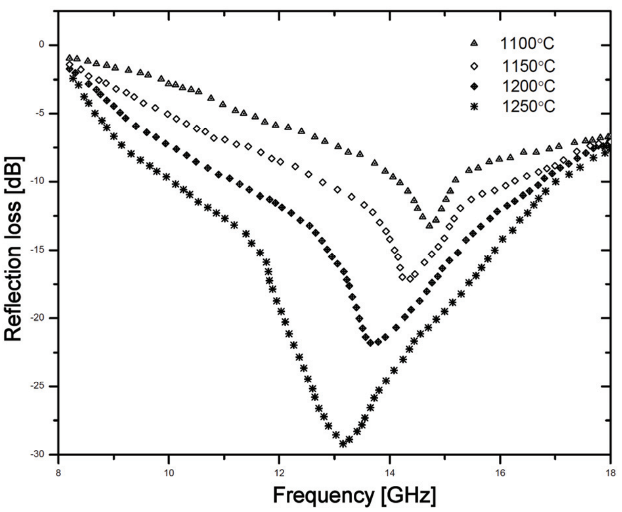


Figure 6. Reflection loss with frequency for different annealing temperature of BTF

which is likely attributed to the impedance mismatch. Reflection loss of 27 dB at 12 GHz has been achieved for the sample with 80 wt.% of BTF with the bandwidth of 2.2 GHz (from 11.4 to 13.6 GHz) where absorption is more than 99%. The windfall gain in properties is primarily attributed to the millimetric size of BTF resulting into wider interaction in X and Ku band. It is also observed that peak of reflection curves shifts towards lower frequency for higher concentration of BTF. Measured values of complex permittivity and permeability were used to calculate the reflection loss of samples for given thickness [15] and shown in Fig. 5. It is clear that calculated and measured values of reflection loss are in good agreement.

Figure 6 shows a typical relationship between reflection loss and frequency for BTF (annealed at different temperatures i.e. 1100 to 1250 °C) in the 8.2–18 GHz range with a thickness of 3 mm. It is observed that the width of absorption band becomes broad and the maximal reflection loss becomes large with the increased annealing temperature. It is worth noticing that BTF annealed at 1250 °C exhibits the best microwave absorption property and the maximum of reflection loss reaches to 29.22 dB at 13.15 GHz for the sample with maximal loading of BTF.

To investigate the relationship between reflection loss and sample thickness, composite laminates of BTF (annealed at 1250 °C) were fabricated in the thickness range of 1 to 3 mm and measured in 8.2–18 GHz frequency region as shown in Fig. 7. It is well reported that sample thickness has significant effects on the electromagnetic reflection loss of a wave absorbing material, it can influence the material's absorbing peak values and bandwidth. Same has been observed in our studies also and shown in Fig. 7, maximal reflection loss reaches to 27 dB at 12 GHz with a matching thickness of 3 mm. In addition, it can be found that when the thickness of sample decreases, the location of absorbing peak is shifted towards a higher frequency with reduced bandwidth and peak power.

In the recent past, various groups [16–18] have fabricated radar absorbing composites using BT as powder along with polyaniline, carbon black etc. In addition to this few groups [7,10] have also tried neat BT powder or in-situ synthesized micron size flakes in the epoxy matrix. Under this study, we have fabricated the millimetric size BTFs in a controlled fashion and mixed in PU resin which provided the better elongation and expansion. The prepared composite laminates demonstrated high reflection loss in the wide bandwidth.

IV. Conclusion

Radar absorbing composite laminates based on millimetric size of BTFs and polyurethane has been fabricated successfully for the first time. Barium titanate flakes (BTFs) were prepared by controlled sol-gel and tape

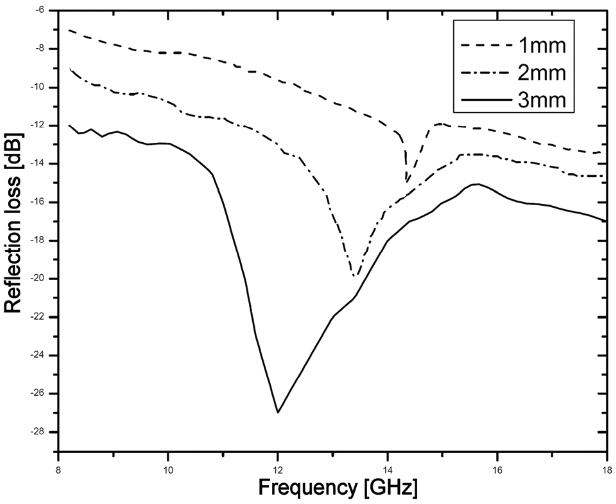


Figure 7. Reflection loss with frequency for different sample thickness of BTF composite

casting process. It was found that grain size of BTF annealed at 1250 °C is of the order of 1.0 μm, exhibited real part of permittivity in the range of 33–42 and imaginary part in the range of 18–23 in 8.2 to 18 GHz frequency region. Composite samples with 80 wt.% loading of BTF exhibited maximum reflection loss of 27 dB at 12 GHz with wider absorption bandwidth (11.4–13.6 GHz) in microwave region. This work suggests that the BTF-polyurethane composites can be used as good EM wave absorption material in wideband frequency region.

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