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Highly-efficient electromagnetic interference shielding and microwave dielectric behavior of a (Bi_2O_3 + B_2O_3)-doped MWCNT/$BaTiO_3$ ceramic nanocomposite

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A B S T R A C T

Microwave dielectric properties along with electromagnetic interference shielding effectiveness (EMI SE) of a multi-walled carbon nanotube (MWCNT)/barium titanate ($BaTiO_3$) nanocomposite are investigated in this paper. Appropriate amount of sintering additive (Bi_2O_3 + B_2O_3) was doped into some nanocomposites to reduce the sintering temperatures. The dielectric properties of the nanocomposites with various MWCNT and sintering additive contents were evaluated at different microwave frequency ranges. It was found that the incorporation of optimized amount of (Bi_2O_3 + B_2O_3) can give rise to significantly good dielectric properties. Results also indicated that incorporation of 6 wt% (Bi_2O_3 + B_2O_3) into 1.5 mm-thick nanocomposite containing 8 wt% MWCNT led to an EMI SE greater than 28 dB, suggesting this novel nanocomposite as a promising candidate for microwave absorption and electromagnetic interference applications.

1. Introduction

As one of the novel one-dimensional materials, carbon nanotubes (CNTs) have been employed in applications such as mechanical reinforcement fillers, nanoscale semiconductor devices, capacitors, hydrogen storage and smart sensors. These extensive applications originate from CNT's unique structure as well as its excellent electrical, thermal, mechanical and chemical stability properties [1–6].

Recently, incorporation of CNTs into metal, ceramic or polymer matrix has been thoroughly investigated and a wide range of various properties have been concluded. Nanocomposites with absorbing properties are the most interesting materials owing to their possible application in electromagnetic interference (EMI) shielding, satellite communication and radar technologies [7–11].

Barium titanate ceramic is one of the most important perovskite substances with extensive application in preparation of multilayer capacitors (MLCCs), dynamic random access memory (DRAM) along with positive temperature coefficient of resistivity (PTCR), piezoelectric sensors, ferroelectrics, and non-linear optical devices. The advanced above mentioned applications have been developed due to high permittivity and convenient ferroelectric-paraelectric transition characteristics of barium titanate [12–15].

EMI shielding theory implies that electromagnetic interference shielding effectiveness (EMI SE) improves with increasing the electrical conductivity of the material. Multi-walled carbon nanotube (MWCNT) exhibits excellent intrinsic electrical conductivity. Content and dispersion of MWCNT as well as its ability to form a proper conductive network inside the nanocomposite can increase the conductivity; hence, EMI performance will obviously improve by addition of MWCNT. On the contrary, $BaTiO_3$ ceramic has high complex permittivity and dielectric constant. Therefore it was chosen as the matrix material since it increases the complex permittivity of nanocomposites which, in turn, positively influences the EMI shielding property. In addition, considering the advantages of $BaTiO_3$ and MWCNTs, the EMI shielding behavior is significantly improved. Based on these properties, a MWCNT/$BaTiO_3$ composite can be a promising candidate in microwave absorbing and EMI applications with specific microwave attenuation characteristics [16–22].

In previous work, a novel MWCNT/$BaTiO_3$ ceramic nanocomposite was prepared and successfully sintered at low temperature based on liquid phase sintering mechanism using (Bi_2O_3 + B_2O_3) as the sintering aid [23]. It was found that use of an optimal amount of (Bi_2O_3 + B_2O_3) can lower the sintering temperature from 1200 to 950 °C. This novel nanocomposite offers several advantages such as high dielectric constant, low sintering temperature and low electrical resistivity which highlight its applicability in EMI shielding within the microwave frequency range.

In this regard, the aim of present study is to investigate the dielectric properties of MWCNT/$BaTiO_3$ nanocomposite sintered by (Bi_2O_3 + B_2O_3) sintering aid at microwave frequency range. Furthermore, the

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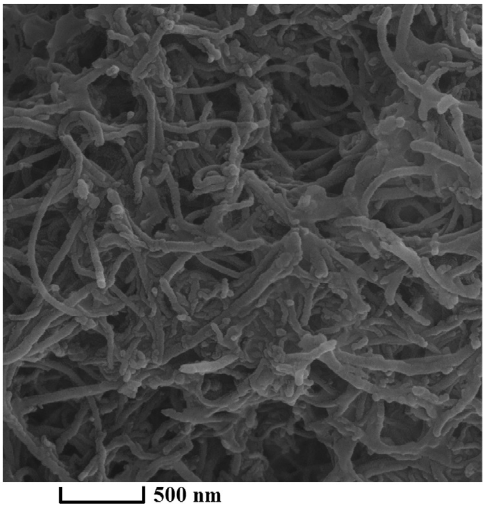

Fig. 1. SEM image of the MWCNTs used for the synthesis of the nanocomposite.

effects of MWCNT content as well as various amounts and compositions of the sintering aid on the microwave dielectric behavior and potential EMI applications are discussed.

2. Experimental procedure

Synthesis of MWCNT/$BaTiO_3$ nanocomposite through a two-step mixing technique involved application of various chemicals including reagent grade barium titanate (Merck), bismuth trioxide (Merck), boron trioxide (Merck), sodium dodecyl sulfate (SDS; Merck) and COOH-functionalized MWCNTs (US Research Nanomaterials; USA). Ethyl alcohol (Merck) was also applied as a chemical mixture medium. Moreover, fine powdered crystals of $BaTiO_3$ (purity ≥ 99%) with a density of 6.08 g/cm^3 were used. The density of MWCNTs was 2.1 g/cm^3 with purity of ≥ 98%. SEM image in Fig. 1 shows the morphology and structure of MWCNTs. Based on the HRTEM analysis reported by US Research Nanomaterials, the purchased MWCNTs had an external diameter of 20–30 nm, internal diameter of 5–10 nm and length of 10–30 µm.

The flowchart of the synthesis process was presented in previous work [23]. In a typical procedure, various amounts of MWCNTs (0.25, 0.5, 1, 2, 4, and 8 wt%) were first dispersed in ethyl alcohol, and 0.6 wt% of SDS was then added to the system as a surfactant to prevent from MWCNTs agglomeration. The mixture was then subjected to ultrasonication in an ultrasonic bath with power of 200 W for 1 h at room temperature. At the same time, a specific quantity of barium titanate (as a matrix) and 2, 4, 6 or 8 wt% sintering aid (Bi_2O_3 + B_2O_3) containing 10, 30, 50, 70 or 90 mol% Bi_2O_3 were added to the system. The mixture was stirred at 1000 rpm for 15 min and again ultrasonicated for about 1 h. The acquired system was stirred at 1000 rpm for 15 min. Finally, the prepared homogeneous mixture was dried in an oven at 80 °C for 48 h. The bulk samples were prepared by pressing the dried powders into disks with diameter of 32 ± 0.5 mm and thickness of 3 ± 0.5 mm under 400 MPa pressure. Additionally, the compacted nanocomposites were sintered in a tubular furnace at 950 °C for a soaking time of 1 h in an Ar-controlled atmosphere with the heating rate of 10 °C/min.

Based on the above mentioned procedure, 4 different dispersion approaches were used: 1) without the use of any surfactant, ultrasonication or stirring processes; 2) with the use of surfactant without ultrasonication and stirring processes; 3) with the use of surfactant and ultrasonication; and 4) with the use of surfactant, ultrasonication and stirring processes.

A PNA series network analyzer (Agilent Technologies, E8361C: 10 MHz to 67 GHz) was employed to measure microwave dielectric properties of the nanocomposites, i.e. complex permittivity ($\varepsilon = \varepsilon' - j\varepsilon''$), loss tangent, and transmission and reflection scattering parameters (S_{11}/S_{22} and S_{21}/S_{12}). The wave-guide technique was applied for this measurement at room temperature and frequency ranging from 12 to 18 GHz (Ku-band). The transmission and reflection coefficients (T and R) were calculated using S_{21} (S_{12}) and S_{11} (S_{22}) measurements according to: $T = |E_T/E_I|^2 = |S_{21}|^2 = |S_{12}|^2$ and $R = |E_R/E_I|^2 = |S_{11}|^2 = |S_{22}|^2$. Furthermore, the absorption coefficient (A) was evaluated by $A = 1 - R - T$ equation. The EMI SE of the nanocomposite (expressed in dB) was indicated using the following equation [24,25]:

$$\text{EMI SE} = -10\log\left(\frac{P_t}{P_i}\right) \sim SE_A + SE_R \tag{1}$$

In which P_t and P_i are the incident and outgoing power of the electromagnetic wave, respectively. SE_A and SE_R can be determined by following equations:

$$SE_A = -10\log\left(\frac{T}{1-R}\right) \tag{2}$$

$$SE_R = -10\log(1-R) \tag{3}$$

Moreover, the two-wire method was used to measure the electrical resistivity of the samples by the help of a current source (6220 DC Keithley, OH, USA).

Finally, the microstructure and distribution of the constituents as well as their chemical compositions were investigated by employing TESCAN FE-SEM MIRAII and KYKY-SEM3200 scanning electron microscopes (SEM) equipped with an energy dispersive X-ray spectroscope (EDX).

3. Results and discussion

The variations of the real (ε') and imaginary (ε'') parts of permittivity are plotted as a function of frequency in Fig. 2(a) and (b) for the nanocomposites doped via different amounts of (Bi_2O_3 + B_2O_3)

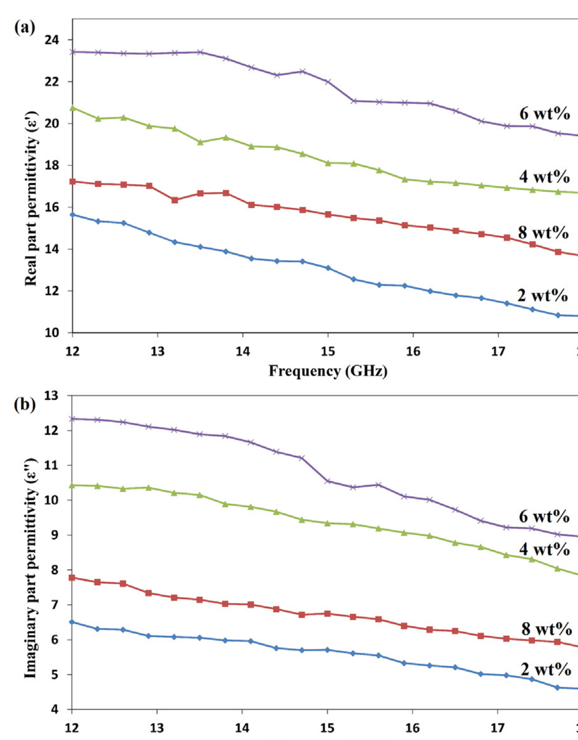

Fig. 2. (a) Real and (b) imaginary parts of permittivity for the nanocomposites containing 1 wt% MWCNT prepared by various amounts of the sintering aid containing 50 mol% Bi_2O_3.