Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Dielectric transition and ferroelectric properties of graphene oxide-barium titanate nanocomposites

T. Kavinkumar[a], P. Senthilkumar[b], S. Dhanuskodi[b], S. Manivannan[a,*]

[a] Carbon Nanomaterials Laboratory, Department of Physics, National Institute of Technology, Tiruchirappalli, 620 015, India
[b] School of Physics, Bharathidasan University, Tiruchirappalli, 620 024, India

ARTICLE INFO

Article history:
Received 25 July 2016
Received in revised form
11 November 2016
Accepted 11 November 2016
Available online xxx

Keywords:
Graphene oxide-barium titanate composite
Electrical properties
Micro capacitor
Dielectric constant
Ferroelectricity

ABSTRACT

Graphene oxide (GO)-barium titanate (BT) composite was prepared through sonication process at room temperature. The temperature dependent dielectric properties and transition of GO with different pellet thickness were studied. Electrical properties of GO-BT composites with different weight percentages of GO and BT (2:1, 1:1 and 1:2) from 30 to 200 °C were investigated. The dielectric constant was calculated as 3701 and 1296 for GO(2)-BT(1) and GO(1)-BT(1) composites respectively which are higher than that of BT at 1 kHz. The improvement of ε' is attributed to the formation of microcapacitors by GO sheets segregated by BT particles. Curie temperature of BT was suppressed in the composites and effect of GO on the dielectric properties of the composite is predominant. The dielectric peaks of GO at 50 and 170 °C were gradually shifted to high and low temperatures respectively with increasing BT content. Furthermore, polarization (P) vs electric field (E) was measured at room temperature specifying the decrease in ferroelectricity of composites from that of BT, indicating the highly conducting nature of these samples. The increasing content of GO in composite leads to decrease in remnant polarization because the introduction of GO would weaken the ferroelectricity of the composite. The present findings suggest that the new composite can be useful for fabrication of flexible electronic devices and high dielectric-based electronic and energy storage devices.

1. Introduction

High dielectric constant with low loss materials has attracted much attention due to their significant use in power capacitors in portable energy storage devices, electrical and electronic industries [1–4]. In recent years, there has been increasing interest in ferroelectric-based composites due to their enhanced performance, easy processing and flexibility [5–7]. Barium titanate (BT) is a perovskite mineral exhibiting ferroelectricity and has been used in capacitors due to its high dielectric constant [8,9]. The dielectric performance of BT has great variability with different dopants, morphology, preparation conditions, contribution of grain boundaries and internal material layers. Several methods have been suggested to enhance its dielectric properties. One such important approach is filling ceramic matrices with a small volume fraction of conductive materials such as metal particles and carbon materials to generate excellent energy storage capacity [10,11]. For instance, by combining ceramics materials with carbon materials like GO, graphene and carbon nanotubes possess special dielectric properties such as elevated dielectric constant and electrical conductivity, which leads to embedded capacitor applications [12,13].

GO based composites have attracted much attention because of its flexibility and high mechanical strength, which leads to many potential applications such as mechanical actuators and electronic devices. Thus, by incorporating GO the dielectric constant of BT can be significantly improved which may benefit to the fabrication of high energy density capacitors. Recently, Li et al. showed that the polyvinylidene fluoride (PVDF) composites with high dielectric constant and low loss tangent was obtained by loading relatively low content of graphene-encapsulated BT hybrid fillers. It is suggested that the dielectric constant of composites with 30 vol% of BT-reduced GO is 67.5 whereas the values for BT-GO/PVDF and BT/PVDF composites are 57.7 and 38.3 respectively at 1 kHz [12]. Shen et al. investigated the dielectric behaviour of three-phase graphene/BT/PVDF composites films. With the addition of GO, the dielectric constant of the composites mildly increases from 9 for 0 wt% of GO to 11 for 1.0 wt%. More substantial increase in dielectric constants was observed for the composite filled with reduced GO (rGO), i.e., from 9 for 0 wt% to 20 for 1.0 wt% [14]. Wang et al. reported the dielectric properties of functionalized rGO-BT/PVDF

* Corresponding author.
E-mail address: ksmani@nitt.edu (S. Manivannan).

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.11.026
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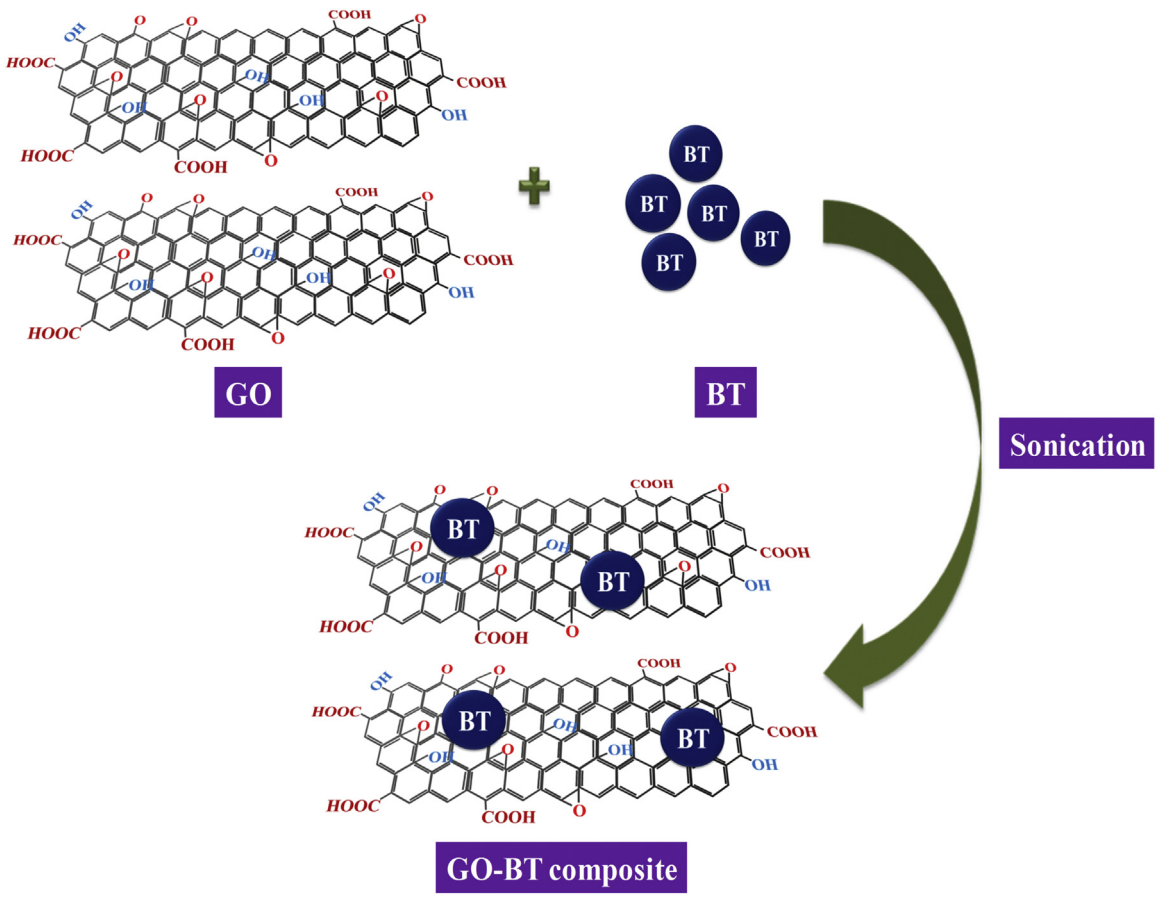

Fig. 1. Schematic diagram for the preparation route of GO-BT composite structure.

nanocomposites with high dielectric constant (65) and a relatively low loss tangent (0.35) at 1 MHz [15]. According to the literature, it is still a great challenge to develop high performance capacitors with a high dielectric constant and low loss to meet electronic device requirements. A systematic investigation on dielectric and ferroelectric properties of composites are essential to understand their functional properties. However, to the best of our knowledge, no reports have been published on the investigation on electrical and ferroelectric behaviour of GO-BT composites.

Here, for the first time we carried out the preparation and temperature dependent electrical properties of GO-BT composites with different weight percentages of GO and BT, prepared through sonication process. Moreover, the effect of thickness in the transition of the electrical properties of GO from 30 to 200 °C in the frequency range of 100 Hz–1 MHz was studied. The existence of ferroelectricity in the GO, BT and GO-BT composites through P-E loop measurement at room temperature was also analyzed.

2. Experimental details

2.1. Preparation of GO-BT composites

GO and BT were synthesized separately using modified Hummers and sol-gel methods respectively [16,17]. The desired amount of GO and BT were dispersed in the ethanol using sonication process, separately. Then, the BT suspension was poured into the GO mixer slowly. The obtained mixtures were stirred for 30 min and then transferred into a petri dish, dried at 60 °C. The weight ratio of GO to BT was controlled to be 1:1, 1:2 and 2:1. The samples were named as GO(1)-BT(1), GO(1)-BT(2) and GO(2)-BT(1) for 1:1, 1:2 and 2:1 wt%, respectively. After drying, the powders were pressed into pellets (8.0 mm in diameter and 1.0 mm in thickness) using a hydraulic press by applying uniform pressure of 20 MPa for 1 min. Subsequently, BT pellet was sintered for 3 h in a muffle furnace at 800 °C. Rest of the samples is not sintered due to poor thermal stability. Because, after sintering GO and GO-BT composite transformed into rGO-BT due to reduction of GO at high temperature. The pellets were polished and silver paste was used to make ohmic contacts on both sides of the sample. The dielectric measurement was carried out using LCR meter connected to a furnace. The density of the samples were calculated as 2.786, 5.871, 3.144, 3.682 and 4.060 g/cm^3 for GO, BT, GO(2)-BT(1), GO(1)-BT(1) and GO(1)-BT(2) composites respectively. The formation route to GO-BT composite is schematically illustrated in Fig. 1.

2.2. Characterization

Powder X-ray diffraction (XRD) pattern was recorded (Rigaku Ultima III) at a scanning rate of 4°/min in the range of 5–80° with CuKα_1 radiation (1.5406 Å). Fourier-transform infrared (FT-IR) spectra of all samples were collected using Perkin Elmer Frontier FT-IR spectrometer in the range 4000–400 cm^{-1}. Thermogravimetric analyses (TGA) were carried out in the temperature range 30–800 °C at the heating rate of 10 °C/min under N_2 atmosphere (SIINT, EXSTAR 6200). Ultraviolet-visible-near infrared (UV–vis-NIR) spectra were carried out in the range of 200–800 nm using JASCO UV–vis-NIR (Model-V-670) spectrophotometer. The microstructure of sample was obtained using LabRAM HR Evolution Raman spectrometer with an excitation wavelength of 532 nm. The morphology of GO-BT composite was investigated using a field emission scanning electron microscope (FESEM) (Quanta 250 FEG, FEI) and existence of elements in composites were determined

Please cite this article in press as: T. Kavinkumar, et al., Dielectric transition and ferroelectric properties of graphene oxide-barium titanate nanocomposites, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.11.026