Materials Science & Engineering B 231 (2018) 40–56

Contents lists available at ScienceDirect

Materials Science & Engineering B

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

Effect of MWCNTs on piezoelectric and ferroelectric properties of KNN composites

Nandini R. Nadar[a], Krishna M.[a,*], Suresh A.V.[b], Narasimha Murthy H.N.[a]

[a] Research and Development Centre, Department of Mechanical Engineering, R.V. College of Engineering, Bangalore 560059, India
[b] Department of Mechanical Engineering, BMS Institute of Technology & Management, Bangalore 560064, India

ARTICLE INFO

Keywords:
KNN
MWCNT
Microwave sintering
Piezoelectric
Ferroelectric
Dielectric

ABSTRACT

The aim of the research work was to investigate the effect of multiwall carbon nanotubes (MWCNTs) reinforcement (0.3–1.2wt.%) on functional properties of microwave sintered Potassium sodium niobate (KNN) composites. Sintered composites are characterized for crystal structure, morphology and temperature stability of piezo-electric, ferroelectric and dielectric properties. KNN composites showed perovskite phase with improved tetragonal symmetry, fine grained porous microstructure, reduced dielectric loss and enhanced effective permittivity. The optimum functional properties and thermal stability obtained for KNN-MWCNT (0.9 wt.%) composites over the range of 20–100 °C, makes the idea of using the addition of MWCNTs to KNN ceramics an interesting approach in searching new structures for temperature stability.

1. Introduction

Ceramic piezoelectric materials find applications in various electronic devices such as sensors, transducers, actuators, micro motors, magneto electric sensor, high power transformers and for energy harvesting due to their robust functional properties [1–3]. Among piezoelectric ceramic materials, potassium sodium niobate (KNN) gained much interest due to its high curie temperature and good electrical properties [4,5]. The presence of morphotropic phase boundary (MPB) between two orthorhombic phases for KNN system shows good piezoelectric and ferroelectric properties similar to standard lead zirconate titanate piezoelectric materials [6,7]. KNN sintered samples showed piezoelectric charge co-efficient (d_{33}) value of 80-160pC/N using solid state method [8,9], 85 pC/N for microwave sintering [10] and 148 pC/N for spark plasma sintered ceramics [11]. But instability of KNN phase above 1140 °C and volatile nature of alkali components at higher temperature restricted them to a limited application.

To overcome the high temperature instability many researchers [12–15] have investigated different dopants on KNN ceramics. This was doped using alkaline (Li^{+}, Ba^{2+}, La^{3+}, Bi^{3+}) and transition (Ti^{4+}, Sb^{5+}, Ta^{5+}) elements to enhance functional properties by shifting the polymorphic phase (PPT) transition temperature. Lithium modified KNN samples showed d_{33} value of 235 pC/N, kp – 44% with the presence of MPB between orthorhombic and tetragonal phases [16]. Extended work by zhang [17] showed the enhanced d_{33} value of 298 pC/N, k_p – 34.5% and ε_r – 945 by adding antimony with lithium doped KNN ceramics, for orthorhombic crystal structure without the presence of MPB. Lithium, antimony and tantalum doped KNN system brought a major breakthrough for reporting d_{33} of 300 pC/N by reactive templated grain growth method (RTGG) [18]. Despite the superior piezoelectric responses, doped KNN ceramics showed the temperature dependent properties with poor stability of the poled domain state. The drastic reduction in phase transition temperature at $T_C \approx 300$ °C and an additional phase transformation at 200 °C degrades the piezoelectric properties of doped KNN ceramics significantly [16]. Hence there is a wide scope for further investigations even though some notable works have been reported [15–19].

Carbon nanotube (CNT) reinforced PZT-PVA 0–3 composite yielded with an increase of 61.3% in peizo-electric charge coefficient (19.8 pC/N), 67% increase in dielectric constant and 89% increase in dielectric loss factor [20,21]. CNT reinforced 1–3 piezoelectric composite had significant piezoelectric and elastic moduli with good frequency responses [22]. Peizo-damping epoxy-matrix composites developed with CNT and PZT contributed to transformation of noise and vibrations to electrical energy, along with shorting of generated electrical current to the external circuit [23]. Non-covalently functionalized graphene oxide (rGO) reinforced polyvinyl alcohol (PVA) composites showed tremendous improvement in its mechanical and thermal properties [24], The interfacial properties of epoxy resin composites enhanced significantly due to layer by layer grafting of CNTs onto carbon fibre

* Corresponding author.
E-mail address: krishnam@rvce.edu.in (M. Krishna).

https://doi.org/10.1016/j.mseb.2018.09.001
Received 7 August 2017; Received in revised form 7 January 2018; Accepted 20 September 2018

surface [25], Carbon Nano adsorbents have attracted tremendous interest for metal ion removal from wastewater due to their extraordinary aspect ratios, surface areas, porosities, and reactivities [26]. The robust electrostatic attraction developed in polystyrene/nanocarbon composites helped in achieving ultralow percolation threshold with enhanced conductivity, making a guideway for manufacturing conductive polymer based composites [27]. Polyvinylidene fluoride (PVDF) / polyacrylonitrile (PAN) / multiwalled carbon nanotubes functionalized COOH (MWCNTs-COOH) nanocomposites have shown significant enhancement in impedance and electrical conductivity of PVDF-PAN/MWCNTs composites for a wide frequency range at different temperatures [28]. Epoxy nanocomposites reinforced with SiO_2/MWCNTs helped in developing electrically insulted composite, paying a way for toughen the polymers for electric insulating applications [29].

Even though CNT is a potential candidate for tailoring functional properties of piezoelectric ceramics, no research works are focused on developing CNT reinforced KNN piezoelectric ceramic materials. Hence MWCNT may be a good reinforcement candidate to empower the functional properties of ferroelectric ceramic materials. KNN ceramics is now a potential candidate for intelligent sensing applications such as wheeled mobile robots (unmanned driving car) [30], Multi leap motion / hand tracking sensor (intelligent robots) [31], multi-source power system in electric vehicles based on PI-PD controller [32], virtual sensors, human to machine frame work for requested power demand etc., thereby embedding intelligence in applications [33].

The objective of the present work is to synthesize MWCNT reinforced KNN composites through microwave sintering assisted solid state route. The sintered composites were characterized to determine the effect of MWCNT on crystal structure, microstructure and temperature dependent functional properties of KNN composites such as piezoelectric, ferroelectric and dielectric properties.

2. Materials and methods

The raw materials used for synthesizing $(K_{0.5}Na_{0.5})\ NbO_3$ – MWCNT composites are given in Table 1.

2.1. Synthesis of KNN crystalline powders

The elemental powders of Na_2CO_3, K_2CO_3, Nb_2O_5 were precisely measured to yield desired composition of $(K_{0.5}Na_{0.5})\ NbO_3$ system and were preheated at 200 °C for 2 h. The preheated elemental powders were subjected to mechanical alloying in a Retsch, GmbH planetary ball mill PM 200 (GmbH) for 15 h. This planetary mono mill has a disc speed of 650 rpm and is programmable for both cycle time and reversing cycles. Milling was carried out with a ball to powder (BPR) weight ratio of 10:1 in a sealed stainless-steel vial using 10 mm stainless steel balls. Milling was performed at a speed of 300 rpm to avoid excessive heating and consequent crystallization of synthesized powder. Ten minutes of idle time after every thirty minutes of milling was programmed to avoid excessive heating of the vial. Reversed milling was used after each cycle of milling. A total of carefully weighed 30 g of powders were added to the vial for the reaction with 3 – 4% of acetone as a process control agent. To avoid adhesion of the powders to the vial, 1 ml of acetone was added after seven hours for every 7–10 cycles of milling.

Table 1
Specification of the materials used for synthesizing KNN – MWCNT composites.

Element	Na_2CO_3	K_2CO_3	Nb_2O_5	MWCNTs
Purity (%)	99.5	99.0	99.9	95.0
Density	2.53 g/cm^2	2.29 g/cm^2	Density: 4.6 g/cm^2	2.1 g/cm^3
Dimension				Length: 10–30μ, Surface area: above 200 m^2/gm
Supplier	Alfa Essar, U.K	Alfa Essar, U.K	Alfa Essar, U.K	Chemo pal Industries, Mumbai

2.2. Surface treatment of the MWCNTs and KNN

The MWCNTs was treated by the Fenton / UV method to oxidize, functionalize the multi-walled carbon nanotubes and were vacuum dried at 200 °C for 4 h. The filtrated MWCNTs consisted of agglomerated clusters of MWCNTs due to van der wall's forces. The MWCNTs were surface treated in ethanol and sonicated for four hours in an ultrasonicator, prior to inclusion within the KNN matrix. This non-covalent dispersion method provides surface energy to the multiwall nano tubes to overcome the Vander walls forces between them. The ball milled KNN powder for 15 h was calcined at 900 °C, 5 h to complete the reaction of the elemental powder and to obtain the desired KNN system. The calcined powder was re-milled for 2 h to avoid the agglomerations formed during solid state reaction. The measured quantity of re-milled powder was uniformly dispersed in liquid media (ethanol) by sonication at RT for 30 min.

2.3. KNN composite preparation

The uniformly dispersed MWCNTs and re-milled KNN nanopowders were ultrasonicated for a period of 2 h to obtain proper inclusion of MWCNT into KNN matrix. The obtained slurry of the KNN composite was vacuum dried, mixed with 2–3 drops of poly vinyl alcohol and was pressed uniaxially at 250 MPa to obtain composite discs of diameter 10 mm and thickness of 1.5 mm. The discs were densified between 1040 and 1120 °C for 30 min using microwave assisted sintering (Microwave furnace 1600 AC, Super (VBCC, Chennai)). The bulk densities of sintered composites were measured by density meter. The densified composite samples were polished using silicon carbide paper and dry grinding. For electrical measurements, high temperature silver paste was coated on both sides of the disc to form electrodes. For piezoelectric activation, all samples were polled in a silicon oil bath under a poling field of 2.5–4 kV/mm DC for 30 min at ambient temperature using parallel plate contact polarization method and a Spellman SL Series high voltage generator.

2.4. Characterization

The crystalline symmetry and lattice parameters were determined by using X-ray diffractometer (XRD, Rigaku Smart Lab), and expert high score software respectively. Morphology, grain size and elemental composition were evaluated on polished samples using scanning electron microscopy-EDS (SEM, ZeissSupra-40). The piezoelectric strain factors of MWCNT-KNN samples were measured by a Piezotest PM300 Pte. Ltd, from RT to 200 °C, under a field of 4 kV/mm. Capacitance, impedance and dissipation factor of specimens were measured by using semiconducting device analyzer (B1500 A), between 1 kHz and 1 MHz. Hysteresis loops were determined using precision premier II ferroelectric tester (Radiant technologies.INC), at room temperature under 5 kV/mm, AC field at 50 Hz with a unit based on sawyer-tower circuit [10]. The dielectric constant of samples was measured using a programmable impedance analyzer (HP4294A, Agilent Technologies), in the frequency range 100 Hz – 1 MHz. The electromechanical coupling factor (k_p) and mechanical quality factor (Q_m) were determined from resonance and antiresonace methods referring to IEEE standards.

3. Results and discussions

3.1. MWCNT and KNN characterization

The surface morphology and distribution of MWCNTs within ethanol after 4 h of sonication were observed with the aid of TEM images as shown in Fig. 1(a). The higher magnification image