FERROELECTRIC PLZT FUNCTIONALIZED GRAPHENE OXIDE PIEZOELECTRIC NANOCOMPOSITES FOR ENERGY HARVESTERS, SENSORS, ACTUATORS AND BIOMEDICAL APPLICATIONS

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Abstract - This poster presentation highlights the development of Graphene Oxide nanocomposites integrated by ferroelectric PLZT for energy, sensors and actuator, and biomedical smart (both sensing and actuating) applications. The Graphene Oxide (GO) reduced by PLZT were synthesized and characterized for phase formation and nanostructure, dielectric and piezoelectric properties. PLZT was prepared by mixed oxide method and nano powders by ball mill, while GO and FGO (i.e., PLZT integrated GO) nanocomposites were prepared by Hummer’s method. Predominantly, tetragonal phase was witnessed in pure PLZT. GO could enhance surfacial properties. In other words, on one hand GO enhances large surfacial contributions to the prototype due to its 2D flakes supporting to functionalized PLZT particles, on the other hand, GO’s interaction with hosts’ β phase piezoelectric nature resulting in competitive piezoelectric properties. The piezoelectric charge coefficient d33 = 197x10^-12 C/N for pure PLZT whereas FGO had shown 218 x10^-12 C/N were found in these nanocomposites, which could be possible candidates for energy, sensors and actuator and biomedical applications.

Index Terms - Biomedical applications, Graphene Oxide, Ferroelectric PLZT, dielectric and piezoelectric properties.

I. INTRODUCTION

Lead Lanthanum Zirconate Titanate known as PLZT a ferroelectric ceramic material with ABO3 structure near morphotrophic phase boundary has shown significant properties and unusual behavior under applied electric fields and/or by varying temperature which has been used in several applications, energy harvesting, sensors and actuators [1-3]. This system can be tailored or customized for different properties. Historically speaking, the materials synthesized were suited for appropriate applications. However, in recent days, materials and routes are tailored for desired applications.

Graphene oxide contains a range of reactive oxygen functional groups through chemical functionalizations which renders it a good candidate for use in biomedical applications. Graphene Oxide has been extensively known for its surfacial properties and significant excellent electronic, electrical and mechanical properties for sensors and biomedical applications [4-7]. Graphene oxide sheets were subjected to chemical reduction prepared via The Hummer’s method uses a combination of potassium permanganate and sulfuric acid. Hummer’s method which were electrically characterized as a function of temperature and external electric fields [8]. Among different methods the chemical reduction of graphite oxide technique showed promising results [9-10]. The most common source of graphite used for chemical reactions, including its oxidation, is graphite flakes, which is a naturally occurring mineral that is purified to remove heteroatomic contamination [11]. A detailed discussion of results with respect to GO variation in PLZT system is given in results and discussion section.

This paper highlights the influence of ferroelectric PLZT functionalized Graphene Oxide piezoelectric nanocomposites and its impact on phase genesis, microstructural evolution, dielectric and piezoelectric properties were investigated for Energy Harvesters, Sensors, Actuators and Biomedical Applications. Our optimized composition was selected for this study, which was further modified by Graphene Oxide to achieve 2D Nanocomposites of Graphene Oxide reduced by ferroelectric PLZT for sensors, actuators, energy harvesting and biomedical applications. We have presented our first results in brief in this conference. Extended studies of this system are under progress in order to explore further functional properties of ultra-thin 2D Graphene Oxide nanocomposites.

II. EXPERIMENTAL

2.1 Synthesis of PLZT:

In brief, PLZT was synthesized by using PbO, La2O3, ZrO2, TiO2 through mixed oxide method, sintered the powders at 1225°C for 3 h and the samples were cooled to the room temperature in the furnace to obtain PLZT sintered powders. Please refer this reference for complete PLZT ceramics process [12].
2.2 Synthesis of Graphene Oxide (GO) by Hummer method:
Analytical reagent grade materials of 18g of graphite powder was mixed to 480ml of concentrated H_{2}SO_{4} and then 62g of KMnO_{4} was added slowly by magnetic stirring and cooling, so that the temperature of the mixture will not be lowered to 20°C. Then this mixture was stirred at 35°C for 2h, and then de-ionized water (920mL) was added. After 1 h, the reaction was terminated by the addition of a large amount of de-ionized water and 30% H_{2}O_{2} solution (50mL), causing violent effervescence and an increase in temperature to 100°C, after which the color of the suspension changed to bright yellow. The suspension was washed with 1:10 HCl solution in order to remove metal ions by filter paper and funnel. The paste collected from the filter paper was dried at 60°C, until it becomes agglomeration. The agglomeration was dispersed into de-ionized water in static state for 2-3 hours and slightly stirred by glass bar. Then the suspension was washed with much de-ionized water until the pH is nearly 7. The paste collected on the filter paper was dispersed into water by ultrasonicated. The obtained brown dispersion was subjected to 30 min. of centrifugation at 4000 rpm to remove any unexfoliated GO using centrifuge with a rotor. The GO platelets were obtained by dehydration at 60°C in air (Ref: Review on GO-piezo composites by Koduri Ramam under preparation).

2.3 Synthesis of FGO : PLZT integrated GO:
Functionalized GO with equi-proportions (i.e., FGO) were synthesized from the above Hummer’s method by dispersing (during the final step of Hummer’s method) initially prepared PLZT sintered powder. GO and FGO (i.e., ferroelectric PLZT coated GO) nanocomposites were prepared by Hummer’s method.

2.4 Characterization of FGO nanocomposites:
The phase formation in PLZT, GO and FGO powders were studied with a Philips powder X-ray diffractometer (PW-1710) using CuKα radiation with a Ni filter at room temperature. The XRD patterns were recorded at a scan rate of 1°/min and 2θ = 20 to 60°. The GO and FGO powders were characterized by Transmission Electron microscope to understand shape and size of ultra thin 2D graphene oxide sheets. The above synthesized PLZT, GO and FGO powders were dispersed in equi-proportions of Poly-vinyl difluoride dissolved in DMF solvent to develop thin films and to characterize their electrical and piezoelectric properties. These films were electrodeed by air dry Ag paint to form electrodes on both sides of the films. The electroded specimens were characterized for their room temperature dielectric constant (ε_{RT}) using a 4192A HP Impedance Analyzer. DC field poled thin films were characterized for piezoelectric charge coefficient (d_{33}) by using a Berlincourt piezo-d-meter.

III. RESULTS AND DISCUSSION

XRD and Microstructural studies:
Fig. 1 represents (a) Powder X-ray diffraction patterns of pure PLZT and (b) Graphene Oxide (GO) and Functional Graphene Oxide (FGO) nanocomposites. Predominantly, a tetragonal phase was observed in pure PLZT system due to the morphotrophic phase boundary region chosen for this study. The surfacial properties could have enhanced due to the perovskite tetragonal PLZT incorporation into the GO and the patterns indicated the homogeneous diffusion between PLZT and GO nanocomposites in this system as shown in Fig 1b.

![Fig-1: Powder X-ray diffraction patterns of (a) PLZT and (b) GO and FGO.](image)

Microstructure:

![Fig-2: TEM micrographs of (a) GO and (b) FGO.](image)

Fig. 2(a) shows the Transmission Electron Micrograph of GO and and Fig 2(b) shows TEM of FGO (i.e., PLZT-FGO) respectively. The ferroelectric...
PLZT particles were dispersed randomly on the ultra thin 2D nano-sheets of graphene oxide (GO) forming as nanocomposites. The TEMs attests the clear structures of homogeneous distribution of PLZT:GO in this study.

**Electrical properties:**
The ferroelectric perovskite tetragonal PLZT showed relatively higher room temperature dielectric constant ($\varepsilon_{RT}$) of 2183 at 1 kHz. The incorporation of GO-PLZT in PVDF system resulted in enhanced dielectric constant of ($\varepsilon_{RT}$) of 2347 at 1 kHz. The dielectric behaviour could be attributed to both GO’s and PLZT’s atomic sites and inter-intra atomic homogeneous diffusion between the nanocomposites. The thin films of PLZT integrated on GO dispersed in PVDF, in which PVDF shows β-phase enriched with dielectric and piezoelectric nature, which is an added advantage to ferroelectric PLZT contribution. Further studies are under progress to tune the electronic structure of graphene via chemical edge functionalization for enhanced functional properties in these nanocomposites. Accordingly, 2D ultra thin Graphene Oxide nanocomposites reduced by piezoelectric PLZT had shown competitive piezoelectric nature in this study. This could be attributed to the piezoelectric energy conversion capability in these prototypes both due to GO’s surfacial behavior as well as strong piezoelectric activity in PLZT, and due to PVDF. In other words, on one hand GO enhances large surfacial contributions to the prototype due to its 2D flakes supporting to functionalized PLZT particles, on the other hand, GO’s interaction with hosts’ β phase piezoelectric nature resulting in competitive piezoelectric properties. The development of 2D smart nanocomposites of ultra thin flexible Graphene Oxide reduced by PLZT was achieved through hummer’s method. The piezoelectric charge coefficient $d_{33} \approx 312 \times 10^{-12}$ C/N for pure PLZT whereas FGO had shown 218 $10^{-12}$ C/N (optimum than pure GO and pure PVDF) were found in these nanocomposites, which could be potential and possible candidates for energy harvesting, sensors and actuator and biomedical applications.

**CONCLUSIONS**
Pervoskite ABO$_3$ PLZT system was integrated on GO supported to develop 2D ultra thin Graphene based nanocomposites for biomedical smart (both sensing and actuating) applications. In addition, the flexible prototypes could be developed due to the contribution of piezoelectric nature by PVDF with a β-phase and ferroelectric PLZT with tetragonal phase incorporated on the GO to generate flexible PLZT-FGO nanocomposites. These flexible PLZT-GO prototype nanocomposites could be very promising candidates for miniaturized and flexible next generation sensors, actuators, energy harvesting and biomedical smart applications.

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