Synthesis of Coaxial CoFe2O4 – (K0.5Na0.5)NbO3 Nanotubes by Sol-gel Technique Using Inexpensive Templates

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ABSTRACT

Magnetoelectric (ME) coupling, one of the most intriguing aspects of multiferroics, may arise directly between two or more ferroic orders as in single phase multiferroics or indirectly via strain. Strain intermediate ME coupling requires intimate contact between ferromagnetic (magnetostrictive) and ferroelectric (piezoelectric) materials in the form of composites, epitaxial heterostructures or laminates. Coaxial 1-D nanocomposite structures are proved to have large interfacial contact, enhanced strain effect and heteroepitaxy compared to thin film multilayers.

In this work we report the synthesis of a novel core shell CFO/KNN nanotubes by a modified template based sol-gel method. Potassium sodium niobate (KNN) is a promising lead free piezoelectric candidate with outstanding properties such as high Curie temperature (Tc~ 400 ºC), considerable d33 (300-400 pC/N)and high electromechanical coupling coefficients. The flexibility of 1-D niobate based perovskite structures were proved to be feasible for self powering nanodevices that harvests its operating energy from the environment. Enhanced magneto crystalline anisotropy and high Piezo-magnetic coupling coefficient (~1)of CFO is also make them favorable for getting good ME response in heterostructure forms. Hence multilayered 1-D nanostructures using CFO and KNN were fabricated by sol-gel method using commercially available AAO template and an inexpensive(PES) membrane

Keywords: magneto-electrics, nanotubes, core shell, niobates, lead free

1 INTRODUCTION

Research on multiferroic materials, where two contrasting order parameters such as magnetism and ferroelectricity coexist, started more than a century ago. [1] Magnetoelectric (ME) coupling, one of the most intriguing aspects of multiferroics, may arise directly between two or more ferroic orders as in single phase multiferroics or indirectly via strain.[2] Strain intermediate ME coupling requires intimate contact between ferromagnetic (magnetostrictive) and ferroelectric (piezoelectric) materials in the form of composites, epitaxial heterostructures or laminates.[3] Coaxial 1-D multiferroic nanocomposite structures are proved to have large interfacial contact, enhanced strain effect and heteroepitaxy compared to thin film multilayers.[4]

In this work we report the synthesis of a new 1-1 composite coaxial nanostructures containing multilayers of CFO/KNN nanotubes by a modified template based sol-gel method. Potassium sodium niobate (KNN) is a promising lead free piezoelectric candidate having uncovered outstanding properties such as high Curie temperature (Tc) beyond 400 ºC, considerable d_{33} of 300-400 pC/N and high electromechanical coupling coefficients. The flexibility of 1-D niobate based perovskite structures were proved to be feasible for self-powering nanodevices that harvests its operating energy from the environment.[5] The high Piezo-magnetic coupling coefficient near to 1 and enhanced magneto crystalline anisotropy of CFO is also favorable for getting good ME response in CFO/KNN heterostructures. Hence multilayered 1-D nanostructures using CFO and KNN are fabricated by sol-gel method using commercially available AAO template and a novel polymer membrane.

2 EXPERIMENTAL DETAILS

KNN/CFO multilayer nanotubes are synthesized using stabilized precursor sols of $K_{0.5}Na_{0.5}NbO_3$ (KNN) and $CoFe_2O_4$ (CFO).

For the preparation of KNN precursor sol, sodium ethoxide, potassium ethoxide and niobium ethoxide is used as starting chemicals and a mixture of 90 % 2-methoxy ethanol, 5 % ethanol and 5% ethylene glycol is used as the solvent. A light yellow colored transparent sol is obtained. For the synthesis of $CoFe_2O_4$ (CFO), cobalt nitrate and Ferric nitrate are weighed in the molar ratio 1:2 and dissolved in 50% ethylene glycol+50% ethanol. The sol viscosity and concentration is adjusted and optimum viscosity and concentration are estimated.

A Novel template named as Poly ethylene sulphone (PES) membrane (pore diameter .22µm) and commercially available anodized alumina (AAO) templates (pore diameter 100 nm) are used for the fabrication of 1-D nanostructures. The deposition of nanotubes is effected by pore wetting of the porous membranes via capillary action and subsequent pyrolysis. Annealing helps in the decomposition of sol into gel and finally into the metallic oxide form.

Phase structure characterization of composite CFO/KNN, CFO, KNN powders prepared from precursor sols and CFO nanotubes in PES membrane is carried out by X ray diffraction (XRD) using Cu *K*α radiation. For morphological studies scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM) are used. Optical properties of the prepared samples are separately studied by UV-Vis spectroscopy. In order to characterize magnetic properties of CFO nanotubes inside AAO templates SQUID magnetometer is used.

3 RESULTS AND DISCUSSION

Figure 1 shows the X-Ray Diffraction pattern (XRD) of CFO, KNN, and CFO-KNN composite powders.

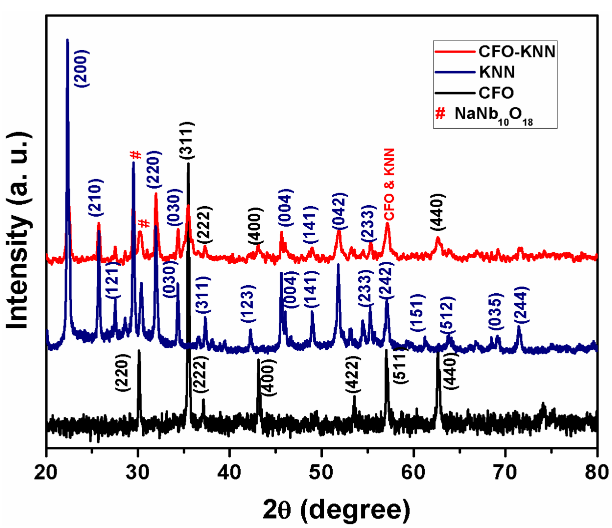

Figure 1: XRD patterns of CFO, KNN and composite CFO-KNN powder prepared from the precursor sols.

XRD pattern is indicative of the well-formed spinel phase cobalt ferrite and monoclinic perovskite structure of KNN with small traces of orthorhombic phase. Additional peaks apart from perovskite KNN at ~ 29.4º and 30.2º is observed due to the formation of #$NaNb_{10}O_{18}$.

High resolution XRD of CFO nanotubes shown in figure 2 inside PES membrane also confirmed CFO spinel phase.

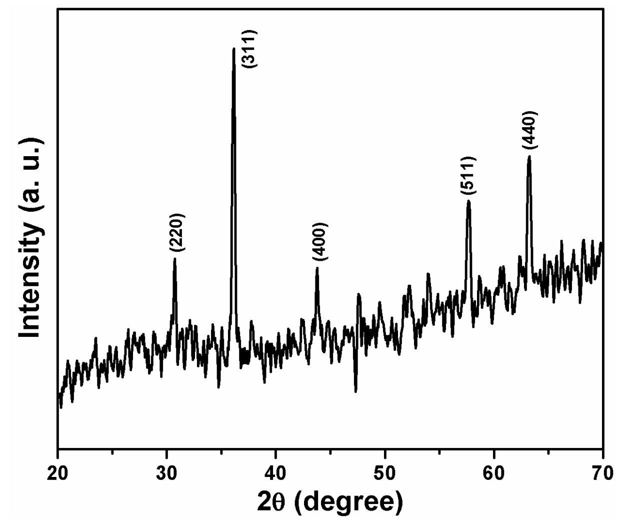

Figure 2: XRD patterns of CFO nanotubes in PES membrane.

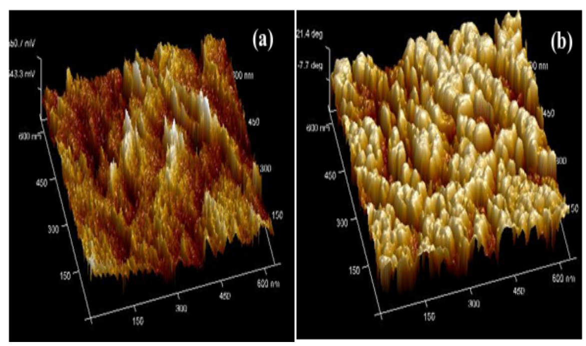

Figure 3: AFM images of (a) & (b) CFO-KNN nanotubes inside AAO templates.

The surface analysis of CFO-KNN nanotubes inside AAO template is carried out using AFM. Topographical images shown in figure 3 (a) & (b) clearly indicate the formation of 1-D nanostructures.

Figure 4 (a) & (b) shows the surface SEM of the empty AAO template (diameter 100 nm) and CFO-KNN nanotubes grown inside AAO template. From the surface morphology, the diameter of CFO-KNN multilayer nanotubes is found to be ~ 185 nm. CFO nanotubes fabricated in AAO template with high aspect ratio and diameter ~ 150 nm is shown in figure 4 (c). The formation of nanostructures using inexpensive PES template is confirmed and CFO branched nanowhiskers with diameter 235 nm is shown in figure 4 (f).

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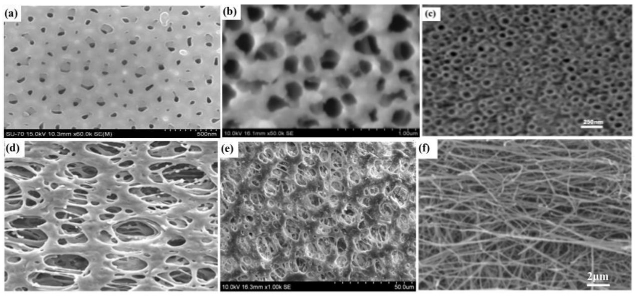

Figure 4: SEM image of (a) Empty AAO template, (b) AAO templates (100nm) filled with CFO-KNN nanotubes, (c) CFO nanotubes inside AAO template (d) Empty PES membrane (Millipore), (e) CFO-KNN nanostructure inside PES membrane and (f) CFO branched Nanowhiskers in PES membrane (Template dissolved in Phosphoric acid, then suspended in alcohol).

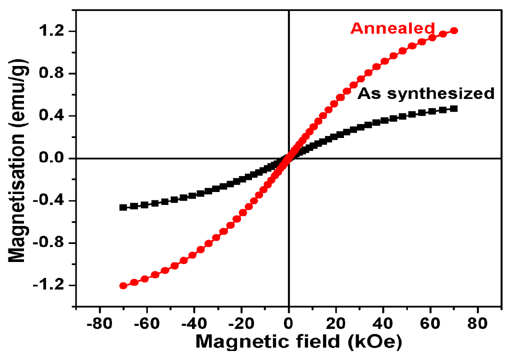

Figure 5: M-H loop of CFO nanotubes grown in AAO template (annealed at 500 ºC).

Room temperature magnetic hysteresis measurement shows that the CFO nanotube samples are magnetic with zero remanence and coercivity.

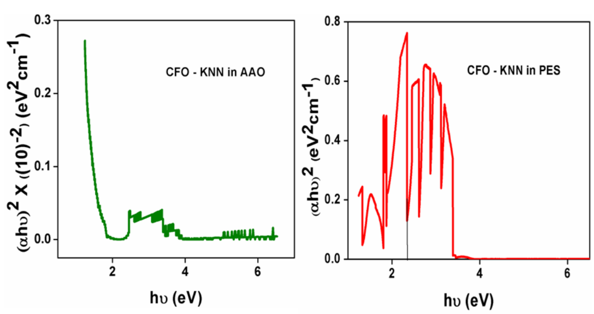

FIGURE 6. Tauc plot of CFO-KNN nanotubes in (a) AAO template (b) PES membrane.

The band structure is examined and different band edge positions are attributed to KNN nanostructures using UV-Vis spectrometry (figure 6). The absorption edges of KNN nanostructures are not modified substantially and hence it can be concluded that the nanostructures are not falling under the quantum confinement regime, as expected.

CONCLUSION

Multiwalled nanotubes of KNN-$CoFe_2O_4$ magneto electric structures are synthesized using sol gel pore wetting technique by employing two different templates of which the polymer template is highly cost effective. Structural studies showed the formation of KNN and CFO. Absorption edges for both KNN and CFO got blue shifted due to strain effect. Magnetic studies of the CFO nanotubes showed that the nanotubes are magnetic at room temperature with near zero loop loss, remanence and coercivity hinting towards the superparamagnetic nature. Electrical characterizations are in progress.

ACKNOWLEDGMENTS

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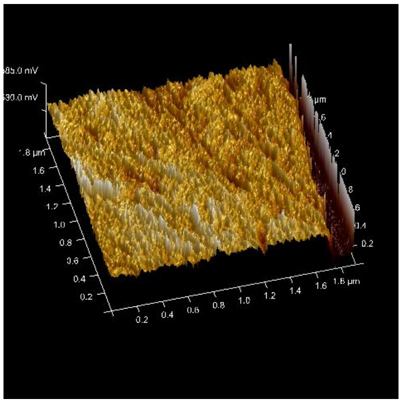
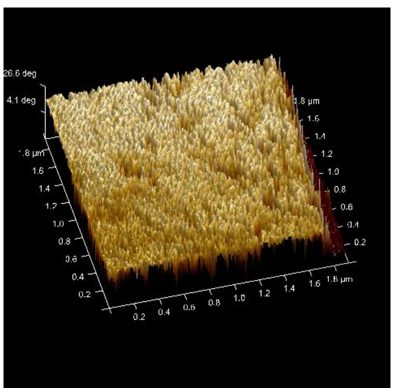
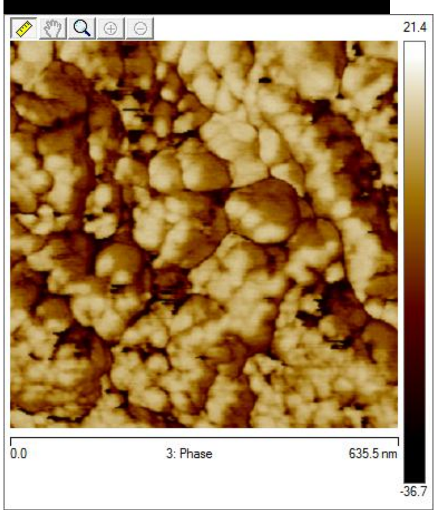
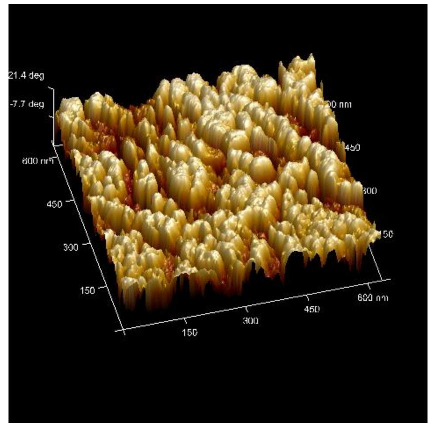
4 SUPPORTING FIGURES









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