Ferroelectric and ferromagnetic nanofibers: synthesis, properties and applications

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Abstract
As first time, ferroelectric (Ba$_{0.85}$Ca$_{0.15}$)(Ti$_{0.9}$Zr$_{0.1}$)O$_3$ (BCTZ), biocompatible (Na$_{0.5}$K$_{0.5}$)NbO$_3$ (NKN), and ferromagnetic Y$_3$Fe$_5$O$_{12}$ (YIG) nanofibers were synthesized by sol-gel assisted electrospinning technique. Non-woven, bead-free 100 μm long fiber mat was formed from close-packed nanocrystals after calcination in air at 800°C (BCTZ and NKN) and 1100°C (YIG). BCTZ fibers are 200 nm in width whereas NKN and YIG fibers have smaller 50-100 nm diameter. X-ray diffraction and Raman spectroscopy show that BCTZ and NKN crystallized in tetragonal and rhombohedral polar phases in the vicinity of morphotropic phase boundary. Room temperature ferromagnetism in YIG fibers is indicated by a well formed M-H hysteresis loop with about 70% of remnant magnetization to the saturated value reached at 150 Oe. Broad band microwave spectroscopy revealed strong asymmetry of the shape of ferromagnetic resonance lines that conforms to a three orders of magnitude shape aspect ratio of YIG nanofibers.

Keywords
properties, synthesis, ferromagnetic, ferroelectric, applications, nanofibers

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Ferroelectric and Ferromagnetic Nanofibers: Synthesis, Properties and Applications

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Key words: Sol-Gel, Electrospinning, Electrical Polarizability, Ferromagnetic Resonance, Biocompatibility.

Abstract. As first time, ferroelectric (Ba0.85Ca0.15)(Ti0.9Zr0.1)O3 (BCTZ), biocompatible (Na0.5K0.5)NbO3 (NKN), and ferromagnetic Y3Fe5O12 (YIG) nanofibers were synthesized by sol-gel assisted electrospinning technique. Non-woven, bead-free 100 μm long fiber mat was formed from close-packed nanocrystals after calcination in air at 800°C (BCTZ and NKN) and 1100°C (YIG). BCTZ fibers are 200 nm in width whereas NKN and YIG fibers have smaller 50-100 nm diameter. X-ray diffraction and Raman spectroscopy show that BCTZ and NKN crystallized in tetragonal and rhombohedral polar phases in the vicinity of morphotropic phase boundary. Room temperature ferromagnetism in YIG fibers is indicated by a well formed M-H hysteresis loop with about 70% of remnant magnetization to the saturated value reached at 150 Oe. Broad band microwave spectroscopy revealed strong asymmetry of the shape of ferromagnetic resonance lines that conforms to a three orders of magnitude shape aspect ratio of YIG nanofibers.

1. Introduction
Quasi one dimensional materials including nanofibers, nanowires, nanobelts and nanorods have attracted intensive interest of scientist recently. Ferroelectric and ferromagnetic materials as functional compositions have been employed to invent or improve nanoelectronic, nanophotonic and nanogenerator devices [1-3].

Using piezoelectric nanofibers as the building blocks in nano-generators and nano-sensors makes them promising candidates for energy harvesting [4-6]. X.Chen et.al. designed and fabricated a high efficiency nanogenerator based on Pb(Zr,Ti)O3 nanofibers which produced 1.6V output [6].Recently, a Pb-free piezoelectric ceramics system Ba(Ti0.80Zr0.20)O3- x(Ba0.70Ca0.30)TiO3 ( abbreviated as BZT-x BCT, x= molar fraction of BCT) reported by W.Liu et.al. Demonstrated a high piezoelectric coefficient d33 about 600 pC/N in Morphotropic Phase Boundary (MPB) region at x= 50 [7]. Regarding to its high piezoelectric performance it would be a promising candidate to use as a piezoelectric segment in generators and sensors.

3D and fibrous structures of the electrospun ferroelectric nanofibers in addition to their response to the external electric field and ultrasound vibrations, enhanced the tissue and neural tissue regeneration
Sodium potassium niobate composition has been studied intensively since it was discovered in 1949 and showed a good potential as a biocompatible ferroelectric material. Yttrium iron garnet \( \text{Y}_3\text{Fe}_5\text{O}_{12} \) (YIG) as a high frequency passive low loss and possessing a unique magneto-optical property has been used extensively in optical communication and magneto-optical devices. The magnetic phenomenon in this material can be employed in different applications including drug delivery and DNA transportation.

Electrospinning technique is a sol-gel based, versatile and straightforward method to fabricate the nanofeatures i.e. nanofibers and nanotubes that recently, has been employed extensively to produce oxides and ceramics nanostructures i.e. \( \text{Pb(Zr,Ti)}_3\text{O}_3, \text{BaTiO}_3, \text{MgFe}_2\text{O}_4, \text{TiO}_2, \text{CoFe}_2\text{O}_4 \) nanofibers.

In this paper we review our recent achievements on synthesis and characterization of ferroelectric BZT-BCT (BCTZ), biocompatible \( \text{(Na}_{0.5}\text{K}_{0.5})\text{NbO}_3 \) (NKN), and ferromagnetic \( \text{Y}_3\text{Fe}_5\text{O}_{12} \) (YIG) nanofibers were synthesized by the electrospinning technique.

2. Experimental details
Sol-gel assisted electrospinning technique was employed to synthesize the BCTZ, NKN and YIG nanofibers.

2.1 Ferroelectric nanofibers

2.1.1 BCTZ nanofibers
BCTZ precursor solution was prepared by dissolving barium acetate and calcium acetate in glacial acetic acid at 60 °C followed by mixing the Ti and Zr solution from dissolved titanium isopropoxide and zirconium propoxide in ethanol. In order to prepare the BCTZ solution for the electrospinning, 350 mg of polyvinylpyrrolidone (PVP) was dissolved in BCTZ precursor solution and stirred for 1 hour in a closed caped glass bottle. The transparent and viscous solution was transferred into a plastic syringe.

Electrospinning was carried out by applying 15 kV to the metallic needle of the syringe pump while the solution was fed with 0.5 ml/hour rate. A non-woven and bead-free nanofibers containing hydrolized BCTZ precursor and PVP were collected from the surface of the aluminium foil used as a collector placed at 9 cm below the needle. Crystallized nanofibers were achieved by drying at 100 °C for 1 hour followed by calcination at 800 °C for 1 hour in air.

2.1.2 NKN nanofibers
To prepare the NKN precursor solution, potassium acetate and sodium acetate were mixed in 2-methoxyethanol at room temperature and stirred for 1 hour to achieve a clear and transparent solution. Niobium ethoxide was dissolved in acetyl acetone at room temperature and stirred for 1 hour (acetyl acetone was used as a chelating agent) and then added to the Na/K precursor solution and continued stirring. NKN solution was stirred for 12 hours in a closed cap glass ware at room temperature. Polyvinylpyrrolidone (PVP, 0.035g/ml) was added to the precursor mixture to prepare the solution for electrospinning. The solution was transferred to a plastic syringe with a metallic needle. Electrospinning was carried at 1.8 kV/cm electric field strength between the metallic needle and aluminum foil collector located 8cm below the needle. Crystallized nanofibers were achieved by drying at 100 °C for 1 hour followed by annealing at 800°C for 1 hour in air.

2.2. Ferromagnetic nanofibers
Iron nitrate \( \text{Fe(NO}_3)_3\times9\text{H}_2\text{O} \) and yttrium acetate \( \text{Y(O}_2\text{C}_2\text{H}_3)_3\times\text{H}_2\text{O} \) were used as starting materials. The yttrium and iron salts precursors were dissolved in 10 ml solvent contained deionized water: methanol with 2:1 volume ratio, respectively. After stirring for 1 hour at room temperature, a red and transparent solution was achieved. The molar ratio of \( \text{Fe}^{3+} : \text{Y}^{3+} \) was maintained at 5:3. In order to prepare the solution for the electrospinning, 0.035g/ml of polyvinylpyrrolidone polymer was added to
the YIG precursor solution and continued stirring for 1 hour. The viscous solution was transferred into a plastic syringe.

The electrospinning was carried out by applying 15 kV to the metallic needle of the syringe pump which fed YIG solution at a constant rate of 0.3 ml/h. The as-spun nanofibers containing hydrolyzed YIG precursor and PVP were collected from the surface of the aluminum foil collector placed 10 cm below the tip of the needle and dried at 100 °C for 30 minutes. Synthesis was finalized with the calcination at 1100 °C for 1 hour in air.

Field emission scanning electron microscope (FE-SEM, ZIESS Ultra 55) was used to observe the morphology and crystallinity of nanofibers. The images were taken by using 1 kV accelerating voltage at 3 mm work distance without using a conductive coating of tested fibers. Phase content and crystalline structure of the nanofibers were examined by x-ray diffraction (XRD) using Siemens D5000 powder diffractometer. Raman spectra of the BCTZ and NKN nanofibers were recorded at room temperature using 514.5 nm line of Ar-laser (HORIBA Jobin-Yvon). Scanning capacitance microscope (SCM, Dimension 3100, Vecco metrology group) was used to study the polarizability of ferroelectric fibers.

3. Results and discussion

3.1 BCTZ nanofibers

SEM images of nanocrystalline structure of BCTZ nanofibers are shown in Figure 1. Very uniform, non-woven and bead-free mat of BCTZ nanofibers were achieved by sol-gel assisted electrospinning technique. Fibers are crystallized in about 200 nm in width and several ten microns in length.

![FE-SEM image of the BCTZ nanofibers annealed at 800 °C.](image)

Figure 1. FE-SEM image of the BCTZ nanofibers annealed at 800 °C.

Figure 2(a) shows X-ray diffraction (XRD) patterns of electrospun BCTZ nano-fibers annealed at 800 °C for 1 hour. Bragg reflections are indexed according to the PDF reference cards 85-0368 for rhombohedral structure and 80-0601 for the tetragonal structure of the barium titanate [22]. The crystallite size of 18 nm of the BCTZ nanofibers calcined at 800 °C was calculated using Scherrer equation from the full width at half maximum (FWHM) value of the Bragg peak at 20 = 31.5
deg. Figures 1(b) and 1(c) show enlarged profiles of the main Bragg diffraction reflections \{110\} at 31.5 deg and \{200\} about 45 degrees in nanofibers fitted by several Lorentzian contour lines. Coexistence of the tetragonal and rhombohedral syngonies confirms nanofibers were crystallized in the vicinity of morphotropic phase boundary (MPB).

Raman spectrum of the electrospun nanofibers calcined at 800 °C is shown in figure 3. Peaks at 260, 306, 520, and 720 cm\(^{-1}\) correspond to the BaTiO\(_3\) tetragonal phase [23-26] whereas a low intensive band around 181 cm\(^{-1}\) is assigned to an \(A_1(LO)\) optical mode in rhombohedral phase of crystallized fibers [26].

**Figure 2.** (a) - XRD pattern of nanofibers calcined at 800 °C in air. (b) and (c) – fitting of the main Bragg diffraction reflections \{110\} and \{200\} in nanofibers by Lorentzian functions.

Band frequencies around 268 cm\(^{-1}\) [\(A_1(\text{TO})\)], 290cm\(^{-1}\) [\(B_{1g}(\text{TO}+\text{LO})\)], 520cm\(^{-1}\) [\(A_1(\text{TO})\)], and 720 cm\(^{-1}\) [\(A_1(\text{LO})\)] which would not be present in the cubic phase are commonly considered as the indication of the polar phases in BaTiO\(_3\) crystals [27].
Scanning capacitance microscopy (SCM) was employed to study ferroelectric properties of (Ba,Ca)(Ti,Zr)O₃ nanofibers annealed at 800 °C on the conductive substrate (Pt coated silicon wafer). SCM method enables the measurement of local capacitance at different bias voltages and superimposed ac-signals. Figures 4 (a) and (b) present, respectively, differential capacitance vs. voltage \( \frac{dC}{dV-V} \) and deflection vs. voltage curves recorded contacting the middle of individual (Ba,Ca)(Ti,Zr)O₃ nanofiber. \( \frac{dC}{dV-V} \) plot shows saturated polarization whereas the deflection-\( V \) indicates the electrostriction effect occurred during bias voltage swiping. Maximum deflection about 11 nm was achieved around 4-5 V where \( \frac{dC}{dV-V} \) curve reaches the saturation.

3.2. NKN nanofibers
FE-SEM images of as-spun binder-contained fibers after drying at 100 °C in \( \text{N}_2 \) atmosphere for 12 hours and NKN sample completely calcined at 800 °C for 1 hour in air are shown in figures 5(a) and (b), correspondingly. A bead-free and non-woven mat of nanofibers was achieved by controlling the electrospinning and annealing conditions during the synthesis procedure. The smooth surface of the dried binder-contained fibers is due to their amorphous structure. Dried fibers with average diameter about 350 nm experienced a considerable shrinkage of more than 50% and crystallized in the average diameter of 150 nm after annealing at 800 °C for 1 hour. The rough surface of the calcined nanofibers shown in inset of Figure 5(b) indicates the way how NKN plate-like nanocrystals grow on each other and compose nanofibers with several microns in length.
Figure 6(a) shows XRD pattern of the NKN nanofibers calcined at 800 °C in air for 1 hour. The pure perovskite-type and highly crystallized structure are observed in annealed sample. The XRD reflections are indexed according to the PDF reference card 77-0038 for monoclinic (Na0.33K0.67)NbO3 lattice with Pm (6) symmetry with a = c > b [28]. Crystallite size calculation using Scherrer equation from the FWHM value of the Bragg peak at 2θ = 31.9 deg, shows that nanofibers crystallized at 800 °C have a size of 42 nm. Enlarged {220} and {440} peaks at 31.9 and 66.6 deg fitted by Lorentzian functions are shown in Figs. 2(b) and 2(c). Absence of any trace of an impurity phase evidences for well homogenized and uniform structure of NKN nanofibers synthesized by electrospinning technique followed by a well controlled heating and cooling regimes.

Figure 6. (a) - XRD pattern of the NKN nanofibers calcined at 800 °C in air for 1 hour. (b) and (c) – enlarged {220} and {440} Bragg reflections fitted by Lorentzian contour lines.

Raman spectrum of NKN-nanofibers annealed at 800 °C recorded at room temperature is shown in figure 7. Comparing this spectrum with Raman spectra of NKN and K NbO3 ceramics [29-31] shows that internal vibrational modes of the NbO6 octahedra produce the Raman shift bands at frequencies above 160 cm⁻¹.
Figure 7. Raman spectrum of the NKN-nanofibers annealed at 800 °C for 1 hour in air.

Stretching mode vibration of the O-Nb-O bonds are represented by strong peaks at 569 (v1) and 616 cm⁻¹ (v3). The bands located in 270 (v2) and 438 cm⁻¹ (v3) are attributed to the bending mode of O-Nb-O bonds. The Raman signals at higher frequencies located at 804 and 860 cm⁻¹ are produced by the fundamental vibrational v1 (A1g) and v3 (F1g) modes of the short Nb=O bonds in NbO₆ octahedra [29-31].

3.2. YIG nanofibers
Morphology and dimension YIG nanofibers calcined at 1100 °C for 1 hour are displayed by FE-SEM images in figure 8. A crystallized YIG nanofiber with 100nm in diameter is shown in inset to Fig. 8.

Figure 8. High resolution SEM images of YIG nanofibers annealed at 1100°C in air.

Figure 9 shows XRD pattern of ferromagnetic YIG nanofibers annealed at 1100 °C. Bragg peaks are indexed according to the standard PDF card 33-0693. Sample was confirmed as almost a single phase yttrium iron garnet Y₃Fe₅O₁₂ with the only two noticeable orthoferrite Bragg reflections: the main
YFeO$_3$(111) at 2\( \Theta \) = 32.89 deg and YFeO$_3$(111) at 2\( \Theta \) = 25.95 deg [32]. The relative intensity ratios of all the Y$_3$Fe$_5$O$_{12}$ reflections are in a good correspondence with Y$_3$Fe$_5$O$_{12}$ powder.

**Figure 9.** XRD pattern of YIG nanofibers annealed at 1100 °C for 1 hour in air. Fibers are clamped onto single crystal Si(001) wafer.

Room temperature ferromagnetism in YIG nanofibers was revealed by tracing \( M-H \) hysteresis loops presented in figure 10(a). YIG nanofibers saturate in a weak magnetic field 150 - 200 Oe and possess high remnant magnetization at the level of 68% of saturated value.

**Figure 10.** (a) \( M-H \) hysteresis curve traced with a rate of 20 Hz in YIG nanofibers. (b) Resonance variation of the reflection scattering parameter \( |S_{11}| \) recorded for Y$_3$Fe$_5$O$_{12}$ nanofibers.

To detect very weak FMR signals from a diminutive amount of fibers, we employed broad Ferromagnetic Resonance (FMR) spectroscopy. Figure 10(b) displays FMR lines detected at 5.83 and 9.18 GHz. Resonant response reveals strong magnetic anisotropy of YIG nanofibers: non-symmetric FMR lines are inverted when external magnetic field rotates from in-plane (where fibers are aligned) to out-of-plane geometry. This effect conforms to a three orders of magnitude length-to-diameter aspect ratio of YIG nanofibers.
4. Conclusion

- \((\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3\) (BCTZ) piezoelectric and ferroelectric nanofibers were fabricated successfully at 800 °C with high aspect ratio in morphotropic phase boundary region which can be used as piezoelectric nanogenerator in nano-devices.
- Biocompatible and ferroelectric \((\text{Na,K})\text{NbO}_3\) nanofibers were synthesized with 3D structure that make them a promising candidate as scaffolds for engineering, repair, and regeneration of damaged tissue.
- Ferromagnetic yttrium iron garnet (YIG) nanofibers with about 100nm in diameter and several tens of microns in length have been synthesized and showed strong resonance response in a microwave irradiation. YIG ferromagnetic fibers have the potential to use as delivery guides for pharmaceutical drugs, protein complexes, and DNA transportation.

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References

[1] Thomas L, Moriya R, Rettner C and Parkin S S P 2010 Science 330 1810
[2] Marti'na J I, Nogue’s J, Liuc K, Vicente J L and Schuller I K 2003 J. Magn.Magn.Mater. 256 449
[3] Ryan Tu, Zhang L, Nishi Y and Dai H 2007 Nano Lett. 7 2778
[4] Chen C Y, Huang J H, Song J, Zhou Y, Lin L, Huang P C,Y Zhang, Liu C P, He J H and Wang Z L 2011 ACS Nano 5 6707
[5] Que R, Shao M, Wang S, Ma D D D and Lee S T 2011 Nano lett. 11 4870
[6] Chen X, Xu S, Yao N and Shi Y 2010 Nano lett. 10 2133
[7] Liu W and Ren X 2009 Phys. Rev. Lett. 103 257602
[8] Weber N, Lee Y S, Shannugasundaram S, Jaffe M and Arinzech T L 2010 Acta Biomater. 6 3550
[9] Jianqing F, Huipin Y and Xingdong Z 1997 Biomaterials 18 1531
[10] Matthias B T 1994 Phys. Rev. 75 1771
[11] Hagh N M, Jadidian B and Safari A 2007 J. Electroceram. 18 339
[12] Cho C R and Grishin A M 1999 Appl. Phys. Lett. 75 268
[13] Nilsson K, Lidman J, Jungstrom K and Kjellman U.S. patent 6,526,984, March 4, 2003
[14] Jalilian A, Kavrik M S, Khartsev S I and Grishin A M 2009 J. Appl. Phys. 105 033917
[15] Zhang J, Sun W, Bergman L, Rosenholm J M, Lindén M, Wu G, Xu H and Gu H C 2012 Mater. Lett. 67 379
[16] Wang Y and Santiago-Avil’ es J 2004 Nanotechnology 15 32
[17] McCann J T, Chen J J L, Dan L, Zuo-Guang Y and X Younan 2006 Chem. Phys. Lett. 424 162
[18] Maensiri S, Sangmanee M and Wiengmoon A 2009 Nanoscale Res. Lett. 4 221
[19] Lee S H, TekmenC and Sigmunda W M 2005 Mater. Sci. Eng. A 398 77
[20] Lamastra F R, Nanni F, Camilli L, Matassa R, Carbone M and Gusmano G 2010 Chem. Eng. J. 162 430
[21] 2001 JCPDS-International Center for Diffraction Data, Cards No. 85-0368 and 80-0601.
[22] Pizani P S, Mastelaro V R, Santos C O P, Varela J A 2008 Chem. Mater. 20 5381
[23] Urban J J, Yun W S, Gu Q and Park H 2002 J. Am. Chem. Soc. 124 1186
[24] Choi Y K, Hoshina T, Takeda H and Tsurumi T 2010 J. Ceram. Soc. Jpn. 118 881
[25] Xiao C J, Jin C Q and Wang X H 2008 Mater. Chem. Phys. 111 209
[26] 2001 JCPDS-International Center for Diffraction Data, Card No. 77-0038.
[27] Thas J, Amer B, Morandi M and Mortier P 2005 Chem. Phys. Lett. 488 54
[28] 2001 JCPDS-International Center for Diffraction Data, Card No. 77-0038.
[29] Trodahl H J, Klein N, Damjanovic D, Setter N, Ludbrook B, Rytz D and Kuball M 2008 Appl. Phys. Lett. 93 262901
[30] Rubio-Marcos F, Romero J J, Martin-Gonzalez M S and Fernández J F 2010 J. Eur. Ceram. Soc. 30 2763
[31] Ge H, Hou Y, Rao X, Zhu M, Wang H, and Yan H 2011 Appl. Phys. Lett. 99 032905
[32] 2001 JCPDS-International Center for Diffraction Data, Cards No. 33-0693 (YFeO3) and 39-1489 (YFeO3)