Biocompatible Er:(Na,K)NbO3 nanofibers

N P Markova¹, A M Grishin¹,²,³
¹Petrozavodsk State University, Petrozavodsk 185000, Russia
² KTH Royal Institute of Technology, Stockholm-Kista SE-164 40, Sweden
³ INMATECH Intelligent Materials Technology, Skärholmen SE-127 51, Sweden

Abstract. Dense homogeneous fabric composed from continuous bead-free erbium-doped sodium potassium niobate (Er:NKN) 100 μm long and 100-200 nm in diameter nanofibers was sintered by sol-gel calcination assisted electrospinning technique. Er doping with the concentration of 2 at.% provides readily detectable room-temperature broad-band photoluminescence (PL) centered at \( \lambda_{PL} = 0.55 \) and 0.98 μm being pumped, respectively, with 532 and 785 nm lasers. Electric field induced resistance switching and strong electric rectification effect were found in nanoporous sandwich Au/Er:NKN/Pt capacitive cell. Memristor-type current-voltage \( I-V \) characteristics originate from the electrochemical migration of oxygen vacancies at the \( n \)-type Er:NKN oxide/high work function Pt cathode junction interface.

1. Introduction
Ferroelectric sodium potassium niobate (hereinafter NKN) ceramics was patented and FDA-approved (U.S. Food and Drug Administration) as a biocompatible material for implants.¹ Thorough toxicology tests showed there were no any bacterial products (endotoxin) appear as well as viability of human monocytes was not negatively affected by the presence of NKN ceramics. In this paper, we report electrical and optical properties of Er-doped NKN nanofibers. Erbium doping promises new photonic applications to (Na,K)NbO₃ ceramics which is already abundantly supplied with piezoelectric, electrostrictive, low microwave loss voltage-tunable dielectric, and electro-optic properties.

2. Experimental details
In this work, fabrication of Er:NaₓK₁₋ₓNbO₃ fibers was performed by the electrospinning method. Electrospinning is a simple and inexpensive method for producing nanofibers with submicron and nanometer diameters. At first, fibers are formed by injecting onto metallic collector a stream of polymer – precursors solution in electrostatic field. Then, fibers are subjected to drying and annealing at high temeparture to vaporize a polymer and to crystallize a rest of inorganic material. Actually, electrospinning is a version of the sol-gel technology.

To prepare NKN precursor solution by the sol-gel method, sodium NaO₂C₂H₃×H₂O and potassium KO₂C₂H₃×3H₂O acetates were mixed in 2-methoxyethanol CH₃OCH₂CH₂OH at room temperature and stirred for 1 hour to achieve a clear and transparent solution. Niobium ethoxide C₁₀H₂₅NbO₅ and erbium nitrate pentahydrate Er(NO₃)₃×5H₂O (chosen with the concentration of 2 at.%) were dissolved at room temperature in acetyl acetone C₅H₈O₂ (used as a chelating agent), stirred for 1 hour, then added to the Na/K precursor solution, and continued stirring for 24 hours in a closed cap glass ware. Finally, to prepare the solution for the electrospinning, high-molecular polyvinylpyrrolidone PVP (PVP, 0.05 g/ml) was added and completely dissolved in the precursor mixture.
Viscous polymer stream was ejected from a plastic syringe pump NE-300 that feeds PVP/Er:NKN solution at a constant rate of 0.5 mL/hour in electric field of 1.8 kV/cm applied between metallic needle and aluminum foil collector (Figure 1). Bead-free composite polymer-hydrolyzed Er:NKN precursor fiber mat was collected from the surface of the collector and dried at 100 °C in nitrogen atmosphere for 12 hours. After drying, as-spun mat consists of interlaced binder-contained jelly-like 350 nm thick threads with a smooth surface (Figure 2). After the process of electrospinning, to remove a polymer binder, the annealing of obtained fibers was carried out in a high-temperature vacuum furnace OTF-1200X in air at 800 °C. The rate of heating/cooling was 5 °C/min.

Surface morphology of annealed nanofibers was characterized using scanning electron microscope (SEM) Hitachi SU1510. Phase content and crystalline structure were examined by X-ray diffraction (XRD) using Siemens D5000 diffractometer. Quantitative elemental analysis was performed by using SEM energy-dispersive X-ray spectroscopy (EDX) analyzer with Thermo Scientific UltraDryTM detector.

3. Conclusion
Scanning electron microscope images of as-spun and dried NKN fibers captured at accelerating voltage of 20 kV are shown in Figure 2. As-spun nanofibers have diameter of about 350 nm. After annealing diameter of fibers significantly reduced to values of about 100 nm. Nanothreads experience strong shrinkage due to the vaporization of PVP and solvents during the annealing process. Because of nitrogen and carbon presence in NKN precursor solution, big amount of these elements was expected in fibers before their calcination. Based on our recent observations of nanofibers fabrication by electrospinning using PVP, we concluded that complete polymer and solvent removal occurs at temperature around 550 °C. This was confirmed from quantitative elemental analysis of EDX spectra recorded at accelerating voltage of 10 kV. These results are collected in Table 1. After calcination, the nitrogen was not detected at all and carbon content was about 3–4 at.%. This indicates thermal decomposition of PVP into volatile substances that leaving nanofibers. In fact the concentration of the carbon content in calcined nanofibers can be even lower. Additional contamination might occurs as an unnecessary carbon deposition during EDX measurements. This is so called black box effect is commonly attributed to the oil carbon vapour from a fore vacuum pump of SEM.

Figure 3 depicts the trace of thermogravimetric analysis (TGA) during calcination of our as-spun Er-doped Er:(Na,K)NbO₃ fibers. The shape of the TGA curve is similar to that for (Na,K)NbO₃ nanofibers sintered earlier (see Ref. [4,5]). It suggests the presence of water and/or residual solvent. The main weight loss occurs below 550 °C indicating that the most of organics and other volatiles have been already removed at this temperature. Noticeable weight loss about 8 % is observed in TGA curve between 25 °C and 100 °C. This weight loss at relatively low temperatures we rely upon the water vaporization. Degradation of PVP exhibits itself at 150–250 °C and causes 15 % of weight loss.
Big and sharp step in the profile of the weight's loss change between 250 °C and 450 °C represents the pyrolysis and/or oxidation of PVP. The total loss of fibers in flowing dry air equals approximately to 63 wt% and signifies almost complete at 550 °C removal of PVP initially added to the precursor colloidal dispersion. Further annealing up to 600–800 °C leads to the crystallization of nanothreads and accomplishes synthesis of NKN fibers.

Table 1 Results of quantitative EDX elemental analysis of Er:(Na,K)NbO₃ nanofibers after calcination.

| Element | Mass concentration [%] | Mass concentration error [%] | Atomic concentration [%] | Atomic concentration error [%] |
|---------|------------------------|-----------------------------|--------------------------|-------------------------------|
| C       | 1.83                   | ± 0.22                      | 4.1                      | ± 0.35                        |
| O       | 36.58                  | ± 0.35                      | 65.32                    | ± 0.58                        |
| Na      | 8.97                   | ± 0.10                      | 11.24                    | ± 0.06                        |
| K       | 10.17                  | ± 0.08                      | 7.46                     | ± 0.05                        |
| Nb      | 37.56                  | ± 1.06                      | 10.86                    | ± 0.31                        |
| Er      | 4.89                   | ± 0.26                      | 1.02                     | ± 0.03                        |

XRD spectrum of crystallized Er-doped NKN fibers is presented in Θ-2Θ scan in Figure 4. Na₃₋₀.₃₅K₀.₆₅NbO₃ perovskite phase predominates there. The relative intensity ratios of NKN Bragg reflections 1₁₁ indicate noticeable preferential NKN(001) orientation: intensity reflection ratio I₀₀₁/I₀₁₁ = 0.90 in Er:NKN fibers compared to 0.58 in “ideal” Na₃₋₀.₃₅K₀.₆₅NbO₃ powder.³

![Figure 3](image_url) TGA trace during annealing of Er:(Na,K)NbO₃ nanofibers.

![Figure 4](image_url) XRD patterns in CuKα radiation of Er:NKN nanofibers annealed at 800 °C in air.

Electric properties of Er:NKN nanofibers were investigated by a measurement of current-voltage I-V characteristics. They were traced for the planar Au/Er:NKN/Au cell with 350 μm thick Er:NKN fiber fabric placed onto glass-ceramic Sitall substrate as well as for the vertical sandwich Pt/Er:NKN (260μm)/Au structure shown, respectively, in the left inset and in the main frame of Figure 5. Circular 0.95 mm in diameter ohmic Au electrodes were thermally evaporated through a shadow mask on the top of nanofiber fabric specimens.

Hysteretic character of I-V plots at weak electric field in the planar Au/Er:NKN/Au cell and positive bias voltage shift U₀ when current goes to zero indicate ferroelectric properties of Er:NKN fibers. Pt/Er:NKN/Au sandwich structure exhibits a strong rectification of direct current as well as resistance switching from low-resistance to high-resistance state with the resistance ratio of 10². Quasi-static I-V characteristics correlate with the results obtained by impedance spectroscopy carried out at frequencies up to 1 MHz.
Intensive room temperature luminescence was observed by pumping fibers with 532 and 785 nm lasers light. Photoluminescence spectra are presented in Figure 6. Excitations at 532 nm and 785 nm laser light illumination are shown with green and red colors, respectively. They produce intensive luminescence at $\lambda_{PL} = 0.55 \mu$m (Raman shift 556 cm$^{-1}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$) and within the $\lambda_{PL}$ band from 0.96 to 1.11 $\mu$m (Raman shifts from 2300 to 3750 cm$^{-1}$, $^4I_{11/2} \rightarrow ^4I_{15/2}$). Radiation of 532 nm excites Raman-active internal vibrations of NbO$_6$ octahedra that correspond to stretching $^{1}A_{1g}$ ($v_1 = 632$ nm), $^{1}E_g$ ($v_2 = 559$ nm), and bending $^{1}F_{1u}$ ($v_4 = 437$ nm) modes.

Radiation of 785 nm laser excites strong fluorescence lines with the wavelengths from 0.96 to 1.11 $\mu$m (Raman shifts from 2300 to 3750 cm$^{-1}$ in the right panel of Figure 6). They are attributed to radiative intra-$4f$ Er$^{3+}$ ion $^4I_{11/2} \rightarrow ^4I_{15/2}$ transitions. Also, $^4I_{9/2} \rightarrow ^4I_{15/2}$ transitions cause weaker PL at wavelengths from 0.83 to 0.87 $\mu$m (Raman shifts from 700 to 1200 cm$^{-1}$ in the left panel of Figure 6). In addition, $^4I_{15/2} \rightarrow ^4S_{3/2}$ and $^4I_{15/2} \rightarrow ^4F_{9/2}$ transitions clearly manifest a resonant Er$^{3+}$ ions absorption of the light reflected from Er:NKN fiber fabric. Corresponding light reflection spectrum contains two distinct pits at $\lambda = 524$ nm and 658 nm which are in respectable accord with an excitation of $^4S_{3/2}$ and $^4F_{9/2}$ energy states of Er$^{3+}$ ion.

Figure 5. Current-voltage I-V characteristics traced with Keithley 2410 SourceMeter. Main frame - in the vertical Au/NKN (260μm)/Pt/Si cell. Inset - at low voltages in the planar Au/NKN(350μm)/Au cell onto Sitall substrate.

Figure 6. Unpolarized backscattered Raman spectra of Er:(Na,K)NbO$_3$ nanofibers calcined at 800 °C in air. Excitations at 532 nm and 785 nm laser light pumping are shown with green and red colors, respectively.

4. Conclusion

Erbium doping opens up serious prospects for new photonic applications of ferroelectric (Na,K)NbO$_3$ ceramics which has already demonstrated a wide range of piezoelectric, electrostrictive, low microwave loss voltage-tunable dielectric, and electro-optic properties.

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