Article type : Article

Corresponding Author Email ID: frank.clemens@empa.ch

Preparation and characterization of potassium sodium niobate nanofibres by electrospinning

Tony Lusiola¹, Lovro Gorjan¹, Frank Clemens¹

¹ – Empa - Überlandstrasse 129, 8600 Dübendorf, Switzerland.

Abstract

In this work we describe the electrospinning of (K,Na)NbO₃ fibres and the effect of calcination temperature on the final phase composition. The envisaged application is for the fabrication of ferroelectric sensor hybrid materials. A solution of potassium acetate, sodium methoxide and niobium ethoxide dissolved in methanol, acetylacetone and acetic acid was mixed with polyvinylpyrrolidone (PVP) dissolved in methanol, producing a viscous solution for electrospinning. Confirmation that the proposed equation on the average diameter of fibres produced from high viscosity solutions was larger than that of a lower viscosity solution was made. A scanning electron microscopy (SEM) study showed the fibres to be cylindrical, smooth with diameters of around 400 nm and an aspect ratio >1000. The electrospun fibres were calcined from 700 °C to 1050 °C observing the fibre morphology. With increasing calcining temperature, the grain size increased. The calcined (K,Na)NbO₃ nanofibres were brittle and generally found to display the ‘necklace effect’.

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1111/ijac.12883

This article is protected by copyright. All rights reserved.

Keywords

Electrospinning, ferroelectric lead-free ceramic, potassium sodium niobate, polyvinyl pyrrolidone.

• Introduction

Ferroelectric materials exhibit a wide array of functional properties e.g. piezoelectricity, pyroelectricity, non-linear dielectric behaviour, high non-linear optical activity and switchable polarization. Ferroelectric materials in fibre form can be incorporated into smart ceramic-polymer composites. The main advantage to the use of fibres instead of monolithic ferroelectric ceramics is the improvement attained by the design flexibility of the composites. To increase the performance of the active nano-elements, a higher aspect ratio is necessary, as 1D nano-fibre structures with high length to diameter ratios can increase the electromechanical coupling in nano-composites and enable more adsorption of molecules on the larger surface of nano-material based sensors.

1D ferroelectric materials have possible applications in high performance nano-generators and high-density ferroelectric random access memory (FeRAM), due to their suitability as ultra-thin sheets of nanofibers, which are handy for miniaturization, thus generating worldwide interest in this field. They possess unique properties directly associated with size confinement and low dimensionality, allowing fabrication of smaller components arranged into more complex assemblies, i.e. 'bottom-up' construction of nano-devices. It is generally accepted that quantum confinement of electrons by the potential wells of nanometer-sized structures may provide one of the most versatile and potent means to control the electrical, magnetic, optical and thermoelectric properties of solid state functional materials, according to Xia *et al.*

Electrospinning enables the production of ceramic nano-fibres with diameters ranging from tens of nanometers to micrometers using a mixture of polymers, metal alkoxides or inorganic salts. Electrospun fibres are relatively defect-free at a molecular level, structurally and have a high length-to-diameter ratio, enabling the production of high-mechanical-performance composite materials. Disadvantages related to electrospinning include, difficulty in controlling the shapes of the fibres and

low yields. Figure 1 shows a schematic diagram of the electrospinning process.

Figure 1: An illustration of the electrospinning setup which involves the use of a high voltage applied between the needle attached to a syringe and a collector.

The high voltage plays a key role during the electrospinning process, highlighting the importance in understanding the polarity between metallic needle and collector. Depending on the type of power supply and electrode connection, electrospinning leads to different fibre diameters and deposition areas. Nano-fibres prepared by the electrospinning process exhibit extremely high piezoelectric voltage constant, high bending flexibility and high mechanical strength. The use of nano-fibres in the assembly of 1D nano-structures enables the fabrication of flexible, portable, highly efficient devices with low frequency vibrational nature. It is generally difficult to separate single fibres and disperse them homogeneously in a polymeric matrix as the electrospun fibres form a non-woven tissue, however Regonini *et al.* demonstrated, on electrospun TiO_2 fibres, the separation of the fibres by ultrasound probe and composite fabrication by a doctor blade process. Pre-sintering enables some degree of atomic mobility and with the high porosity of the electrospun fibre system, coarsening occurs to a higher degree.

KNN is a bio-compatible piezoelectric ceramic that is cheap with respect to other non-toxic bio-compatible Pb-free piezoelectric ceramics. It is an environmentally-friendly alternative to lead-based piezoelectric ceramics and could eventually play a comparable role to PZT in certain electronic applications in the future, with the added advantage of being bio-compatible. KNN nano-fibres would be expected to improve the ferroelectric properties of this ferroelectric material if prepared in nanofibre form due to their high diameter to length ratio. The aim of this work was the synthesis of KNN nano-fibres with different fibre diameters by the electrospinning process.

• Experimental

• Materials

Sodium methoxide, potassium acetate and the niobium ethoxide were added according to the $K_{0.5}Na_{0.5}NbO_3$ stoichiometric formula into methanol, acetic acid and acetyl acetone (ACAC) to make a 0.3 M solution. Sodium methoxide (0.006 mol), potassium acetate (0.006 mol) were added to a solution of methanol (0.247 mol) & acetic acid (0.003 mol) as a stabiliser (all from Sigma Aldrich). Niobium (v) ethoxide (0.012 mol) (Sigma Aldrich) [hygroscopic] was added to the solution together with ACAC (0.024 mol) (as a stabiliser/chelating agent for the niobium ethoxide) in a glove box under a N_2 atmosphere. A stock solution was prepared whereby the desired amount of polyvinyl pyrrolidone (PVP – M_w 1.3 million) [Sigma Aldrich] was dissolved in methanol (6 g PVP in 20 ml of methanol) at room temperature until a clear transparent solution was obtained. The PVP solution and the KNN solution were mixed normally in a 1:1 volume ratio when preparing the electrospinning solution.

• Instrumentation

The specific surface area (SSA) was determined from a five point N_2 adsorption isotherm obtained from Brunauer–Emmett–Teller (BET) measurements (Beckman-Coulter SA3100, Beckman-Coulter, USA). Electrospinning was carried out using NEU-Pro (NaBond Technologies Co., Limited - China). A Scanning Electron Microscope (SEM, Vega Plus 5136 MM, Tescan) was used to examine the electrospun fibres before and after calcination and image analysis (IMAGIC's software package) for fibre thickness determination and grain size determination, with several SEM micrographs from different points on the electrospun KNN fibre mat were collected for examination. For grain size determination at least 40 measurements were recorded to determine each figure. Investigations concerning the rheology were conducted using a Modular Compact Rheometer MCR 302 from Anton Paar. The rheological measurements were carried out using a parallel plate system (diameter 25 mm, measuring distance 0.5 mm). Phase analysis was performed using X-ray diffraction (XRD, X'Pert Pro MPD, PANalytical) on crushed fibres, to have information about the average composition.

• Electrospinning

The electrospinning was carried out on a NEU-Pro electrospinning machine and a standard domestic kitchen aluminium sheet was taped to the collection drum. The electrospinning conditions selected to produce the standard KNN electrospun fibres are reported in the Table 1.

Table 1: Shows the standard conditions used during electrospinning of (KNa)NbO₃ fibres.

Various tests were carried out to observe what the effect of changes in voltage and viscosity of the electrospinning solution would have on the resultant fibres.

The fibre mat was removed from the aluminium foil placed in a covered alumina crucible. Debinding was carried out at 600 °C for 5 h to completely decompose the PVP binder material; and calcined for 2 h with a 3 °C/min heating rate to form the perovskite KNN at 700 °C. Higher calcining temperatures were investigated, from 750 ° to 1050 °C with 50 °C increments, each with a 2 h dwell time.

• Results

High-molecular-weight polyvinyl pyrrolidone (PVP) was used as a polymeric binder for the production of KNN electrospun fibres due to its wide production range of stable lead-free fibres. Thus, using a 50:50 volume % ratio of the KNN precursor solution (in methanol) with PVP dissolved in methanol, the electrospinning of KNN fibres was successfully attempted. The fibre mats were collected (Figure 2) and characterised by SEM.

Figure 2: Image of a) electrospun fibre mat on aluminium foil; b) KNN electrospun fibre mat removed from foil.

From the standard conditions in Table 1 a fibre mat with fibres with an average diameter of 472 nm was produced.

From several SEM micrographs (Figure 3), it was observed that the fibres were uniform, cylindrical and smooth and the fibre mat did not have various imperfections such as droplets or flat sections.

Figure 3: Shows various SEM scans of KNN electrospun fibres produced under the

aforementioned electrospinning parameters.

- **Adjusting the viscosity**

The voltage needed to eject a charged jet from the drop at the nozzle end, depends mainly on the solution viscosity. By varying the volume fraction of the PVP solution to the KNN solution, the viscosity of the electrospinning sol was adjusted with a view to observing the effect on the diameter of the resultant electrospun fibres. A 3:2 KNN to PVP solution was prepared and the electrospun fibres compared with a standard 1:1 KNN to PVP solution volume fraction.

Figure 4: The viscosity at a constant shear rate of 300s^{-1} of two electrospinning solutions with varying volume fractions of PVP solution at a constant shear rate over time. 50:50 v.% and 60:40 v.% results in 1:1 and 3:2 composition, respectively.

Electrospinning fibre diameter depends on the viscosity of the solution according to Equation 1 confirmed by experiments by Baumgarten & He.

$$\text{Equation 1} \quad d \approx \eta^{0.5}$$

Where d is the diameter of the fibre and η is the viscosity of the solution. Thus Equation 1 predicts that the average diameter for the 1:1 KNN:PVP soln. would be larger than that of the 3:2 KNN:PVP soln. This equation was used to predict general trends rather than a prediction of specific predicted diameters in this work. This is because in order to more accurately predict the resultant fibre diameters much more information such as jet radius, jet velocity, surface density of charge, shear stress etc. is required.

Figure 5: The diameter distribution of electrospun KNN fibres from a) 1:1 PVP:KNN soln. (higher viscosity); b) 3:2 PVP:KNN soln. (lower viscosity)

With the use of image analysis software an average fibre diameter was determined from 5 scans at

5000x magnification. The higher viscosity 1:1 KNN to PVP solution average fibre diameter were found to be 472 ± 124 nm; while the 3:2 KNN to PVP soln. had an average fibre diameter of 398 ± 182 nm. The hypothesis drawn by Alves *et al.* is that increased viscosity requires higher electrical forces to overcome the surface tension and viscoelastic forces in order to stretch the fibre, implying that higher viscosity, results in thicker fibres. The results showed the effect of varying the viscosity had a small effect on the resultant fibres on this occasion, as the variance in viscosity was minimal, though the results followed the trend predicted by Equation 1.

• Adjusting electrospinning electric field

The diameter of the electrospinning jet gets smaller as it approaches the opposite pole due to -

- The evaporation of the solvent,
- The continuous stretching of the jet as a function of the electric field.

Many authors have attempted to investigate the relationship between the applied voltage and the diameter of the jet, but there is no conclusive analytical theory in the literature. However, Demir *et al.* suggested that the final diameter of the fibres under constant current flow depends on the applied voltage and from their experiments they determined that an increase in the diameter of the jet, results from an increase in the applied voltage which is the opposite of Equation 2 as suggested by He *et al.*.

$$\text{Equation 2} \quad d \approx E^{-0.5}$$

Where d is the fibre diameter and E is the applied electric field and thus predicts that increasing electrical fields result in smaller diameter fibres a trend which has been found by several other groups. For the investigation a 1:1 volume fraction PVP to KNN electrospinning solution was used. The solution was spun at different field voltages, to observe the effect on the diameters of the fibres after spinning. At high electrical fields and low viscosities, multiple jets may be formed from the Taylor cone at the tip. Similar to the equation relating viscosity to the fibre diameter, Equation 2 depends on several factors not covered by this work, in order to produce an accurate prediction of the fibre diameter.

Figure 6: SEM scan of electrospun fibres produced at a) 1.25 kV/cm, b) 1.5 kV/cm, c) 2.5 kV/cm, electric field with a distance between the needle and drum of 10 cm.

The fibres produced at the machine, set at 12.5 kV (1.25 kV/cm) had an average fibre diameter of 350 ± 126 nm, the fibres produced at 15 kV (1.5 kV/cm) had an average diameter of 472 ± 124 nm and the fibres produced at an electrical field voltage of 25 kV (2.5 kV/cm) had an average diameter of 441 ± 169 nm. This result did not agree with the trend predicted by the formula suggested by He *et al.* with experimental error taken into account. Demir *et al.* and He *et al.* state that the trend is that the lower the applied voltage, the thinner the fibres that are formed, though Equation 2 indicates the opposite trend.

• Calcining electrospun fibres

The yield of the debinded KNN ceramic from the electrospinning was ~300 mg after 24 h of electrospinning time. The fibres were examined by SEM showing an unwoven mat structure at low magnification and a ‘necklace’ structure with a single grain forming the entire diameter of the fibre. The specific surface area of fibres calcined at 700 °C for 2 h was 7.38 m²/g.

Figure 7: Various SEM scans of KNN electrospun fibres calcined for 2h at 700°C.

The effect of heat treatment was examined by incremental calcining with a 2 h dwell at each temperature, starting from 700°C – 1050°C with 50°C steps in-between. KNN is known to have issues during calcination due to the volatility of K₂O during calcination (800–950 °C) leading to the production of non-perovskite structures of potassium niobate . Due to the highly porous nature of the electrospun fibre mat; vapour transport, surface and lattice diffusion from particle surfaces to the particle neck which lead to neck growth and coarsening at the expense of densification that would normally occur in non-porous multi-grained ceramics. The results of grain size analysis based on SEM scans is presented in Figure 8. The average grain size was evaluated from grain size distribution

made by the linear intersection method in which 40 grain intersections were used for each SEM scan. The grain growth kinetics were modelled according to the well accepted equation for normal grain growth – Equation 3. The exponent m depends on the mechanism (usually it has values between 2 and 4). Different values for m were checked, however all various values of m , described the data similarly. In other words, the scattering of the data is too large to select the best m value. Therefore, we used $m = 2$ for the presented calculation, which is most commonly used and is widely recognized for normal grain growth. The best fit was made by the least square linear fit on the linearized form of Equation 3. Fitting parameters of the line presented in Figure 8 are $G_0 = 200$ nm, $k_0 = 1.08 \cdot 10^9$ (nm/s)² and $E_A = 190$ kJ/mol.

Equation 3

Where G is the average grain size, G_0 is the initial average grain size, $m = 2$ was used in the results, k_0 is pre-exponential factor, E_A is the activation energy, R is universal gas constant, T is temperature and Δt is the time increment at a certain temperature.

Figure 8: The graph shows the average grain size of KNN electrospun fibres calcined for 2 h at temperatures between 700°-1050°C with the standard deviation. The dashed line shows a fitted curve according to the model described by Equation 3 and parameters written in the Figure 8.

The data indicates a large increase in grain size occurring at 1050 °C suggesting the beginning of the sintering stage (KNN normally sintered at about 1100 °C); at 700 to 750 °C barely any grain growth occurs while there is a slight rise in grain growth from 800 °C where it is thought coarsening of the grains occurs as it has been stated by De Jonghe & Rahaman that in porous ceramics, grain growth is very limited during pre-sintering, with coarsening of the grains by surface diffusion and vapour transport being the dominant factor

Figure 9: SEM scans of KNN electrospun fibres calcined for 2h at between 700°-1050°C with average grain size (GS) indicated.

It is well known that as the heat treatment temperature of ceramics increases, the grain size increases too because particles tend to coalesce increasingly as sintering temperature increases. The SEM scans (Figure 9) show how the grain size develops as the calcination temperature increases. By 900 °C, large grained particles are visible indicating a loss of the desired sub-micro particle size of the electrospun fibres. Figure 8 suggests that at between 750-800 °C the grains undergo a significant morphological change while the SEM scans (Figure 9) suggest ~850°C may be the threshold beyond which the particle size advantage gained with the use of the electrospinning technique, begins to be lost.

The XRD scans of the electrospun KNN fibre mats calcined at different temperatures is shown in Figure 10, with KNN powder prepared by the Molten Hydroxide Synthesis (MHS) method, calcined for 2 h at 700°C used as the reference for KNN.

Figure 10: XRD scans of KNN electrospun fibres calcined for 2h at between 700°-1050°C. MHS KNN powder calcined at 700°C was used as a reference. - Secondary phases.

The XRD scan of material calcined at 700°C shows the KNN perovskite crystal structure. The extra phases in the XRD trace of the KNN fibres are $K_2Nb_8O_{21}$ (JCPDS 031-1060) and K_3NbO_4 (JCPDS 014-0283) that have a tetragonal tungsten-bronze (TTB) structure. The extra phases were present in all the samples indicating close phase structure of the sintered products. The presence of secondary phases indicates the need to optimise the calcining procedure, by creating an alkali-niobate rich atmosphere. At 850°C there is increased synthesis of secondary phases. The hypothesis for this is that it is well known that KNN synthesis results in alkali losses, resulting in niobate excess which leads to the creation of the aforementioned alkali niobates as secondary phases.

• Conclusions

Cylindrical lead-free, homogeneous KNN nano-fibres (diameter range 350 to 470 nm) were successfully produced using the electrospinning process. Experiments confirmed the He *et al.* equation, on the effect of viscosity of electrospun fibre diameters that the average diameter of fibres produced from high viscosity solutions was larger than that of lower viscosity solutions as stated in literature. The result of the electrical field versus fibre diameter experiments did not follow the expected trend; however, the trend with this parameter is not clear in literature one way or the other. The fibres were debinded and calcined to produce an unwoven KNN nano fibre mat which displayed a necklace structure with a single grain forming the entire diameter of the fibre when calcined at 700 °C. The average grain size, XRD and SEM data in combination suggested that 800°C was the maximum calcining temperature that could be used to obtain perovskite KNN electrospun ceramic fibres with a reduced number of secondary phases and suitable nanometre sized grains. The grain size was observed to generally increase as the heat treatment temperature increased.

Acknowledgements

The authors would like to acknowledge the COST Action MP1206 - Electrospun Nanofibres for Bio-Inspired Composite Materials & Innovative Industrial Applications and the SBFi for financing the project FerroSens C13.0143.

Figure 1: An illustration of the electrospinning setup which involves the use of a high voltage applied between the needle attached to a syringe and a collector.

Figure 2: Image of a) electrospun fibre mat on aluminium foil; b) KNN electrospun fibre mat removed from foil.

Figure 3: Shows various SEM scans of KNN electrospun fibres produced under the aforementioned

electrospinning parameters.
Figure 4: The viscosity at a constant shear rate of 300s^{-1} of two electrospinning solutions with varying volume fractions of PVP solution at a constant shear rate over time. 50:50 v.% and 60:40 v.% results in 1:1 and 3:2 composition, respectively.
Figure 5: The diameter distribution of electrospun KNN fibres from a) 1:1 PVP:KNN soln. (higher viscosity); b) 3:2 PVP:KNN soln. (lower viscosity)
Figure 6: SEM scan of electrospun fibres produced at a) 1.25 kV/cm, b) 1.5 kV/cm, c) 2.5 kV/cm, electric field with a distance between the needle and drum of 10 cm.
Figure 7: Various SEM scans of KNN electrospun fibres calcined for 2h at 700°C .
Figure 8: The graph shows the average grain size of KNN electrospun fibres calcined for 2 h at temperatures between 700°C - 1050°C with the standard deviation. The dashed line shows a fitted curve according to the model described by Equation 3 and parameters written in the Figure 8.
Figure 9: SEM scans of KNN electrospun fibres calcined for 2h at between 700°C - 1050°C with average grain size (GS) indicated.
Figure 10: XRD scans of KNN electrospun fibres calcined for 2h at between 700°C - 1050°C . MHS KNN powder calcined at 700°C was used as a reference. - Secondary phases.

Table 1: Shows the standard conditions used during electrospinning of $(\text{KNa})\text{NbO}_3$ fibres.

Electrospinning conditions using NEU-Pro (NaBond Technologies Co., Limited - China)		
Needle (gauge)	21	Inner ϕ
		0.514 mm
Syringe	10 mL	
Flow rate	0.5 mL/h	
Vol. sol. Σ mL	15 mL	
Occulation	Low	
Syringe code (set on	02	

machine)	
Voltage (applied by machine)	15 kV
Distance (nozzle to drum)	10 cm
Drum speed	3 rpm
Voltage/cm	1.5 kV/cm