Synthesis and Characterization of Potassium Sodium Nioabte, a Lead-Free Ferroelectric

Dmitriy Davydovich

Physics and Chemistry, University of the Sciences

NNIN REU Site: Penn State Nanofabrication Laboratory, The Pennsylvania State University, University Park, PA
NNIN REU Principal Investigator: Dr. Susan Trolier-McKinstry, Material Science and Engineering, The Pennsylvania State University
NNIN REU Mentor: Aaron Welsh, Material Science and Engineering, The Pennsylvania State University
Contact: ddavydovich@mail.usciences.edu (or mitay22@yahoo.com), set1@psu.edu, ajwelshprr@gmail.com

Abstract:

Many ferroelectrics used in today's devices are lead-based materials, because they exhibit high piezoelectric and dielectric properties. Due to the volatility and toxicity of lead, these materials pose environmental and health concerns. For the past decade, many scientists have began working towards lead-free alternatives. This allows the material to be integrated on bio-related devices. One of these promising materials is potassium sodium niobate (KNN). This material shows higher piezoelectric and ferroelectric properties than its lead-free competitors. Thus the main goal of this project was to design a solution, which could be laid as a thin-film to be utilized for microelectromechanical devices. We created an array of solutions with different concentration and additives such as chelating agents, stabilizers, and dopants. Currently nine solutions have been deposited via a chemical solution deposition technique. The crystal structure of the films was characterized by x-ray diffraction (XRD). The microstructure of the films was also investigated through the use of a field-emission scanning electron microscope (FESEM). They are now ready for further electrical testing.

Introduction:

Potassium sodium niobate is a lead-free material known to show high ferroelectric and piezoelectric properties. Its crystal structure develops a spontaneous dipole, which can be reoriented under an applied electric field or mechanical stress. This allows it to transform mechanical energy into electrical energy and vice versa. Its properties allow it to store large amount of charge and release it when needed without having a large charge leak. However, since this is a new material, various ways of improving its properties are still being discovered. Using several different synthesis methods, a set of KNN films was created; each had different additive and its varying concentration.

Experimental Procedure:

There are several different ways to fabricate KNN. The process chosen involved two alkali precursors: sodium and potassium acetate. The precursors were mixed in 2-methoxy ethanol, which is a polar organic solvent. The next precursor added was niobium ethoxide. These chemicals were mixed inside a nitrogen glove box and then were set to reflux for four hours at 115°C. Since this solution was very reactive with moisture, the synthesis was conducted in a low humidity environment. After the reflux, the solution was distilled at 130°C until the needed molarity was attained.

For modification of the solution, acetyl acetone was used as a chelating agent. It was introduced to limit the alkali volatility. Varying concentrations of acetic acid were used as a stabilizing agent to prevent moisture reactivity. Finally copper was used as a doping agent to limit the oxygen vacancies and increase ferroelectric properties.

The solution was then deposited on a platinum-coated silicon wafer. The film was spun onto a wafer at 3000 rpm for 30 seconds. After spinning, it was dried at 200°C for five minutes, followed by a pyrolysis at 400°C for five minutes. Then the film was placed into a rapid thermal annealer and was annealed at 550°C for five minutes. This procedure was repeated until there were 7-10 layers of film on the wafer. Then the wafer was annealed for 30 minutes at 700°C in a furnace.

Following the annealing, the solution was first characterized using FESEM in order see the microstructure and the approximate thickness of the film. The film was then subjected to XRD testing to see if all the proper KNN perovskite phases were present. After the XRD testing, the height of the film was verified with contact profilometry. For electrical testing, platinum electrodes were placed on the surface. The film was then etched with KOH all the way to the bottom electrode and was tested for its electric properties.

Results:

The first solution that was fabricated was 0.2 M. As seen in Figure 1, when deposited, it showed a good microstructure with a uniform grain size. The XRD confirmed the KNN peaks, and subsequent profilometry tests showed that the film was 400 nm thick. Primary electrical tests showed a fairly

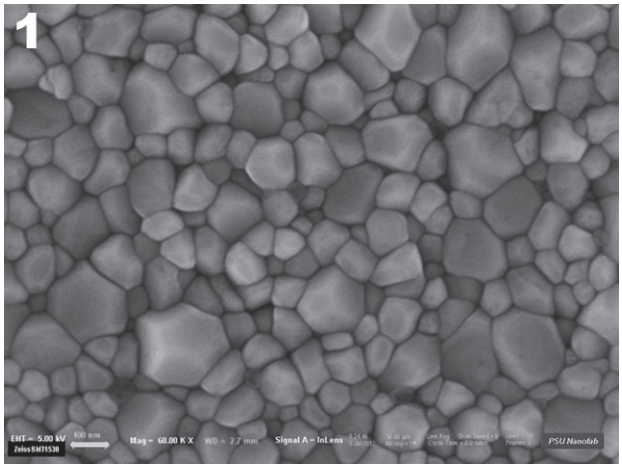

Figure 1: 0.2 M KNN film, 400 nm thickness.

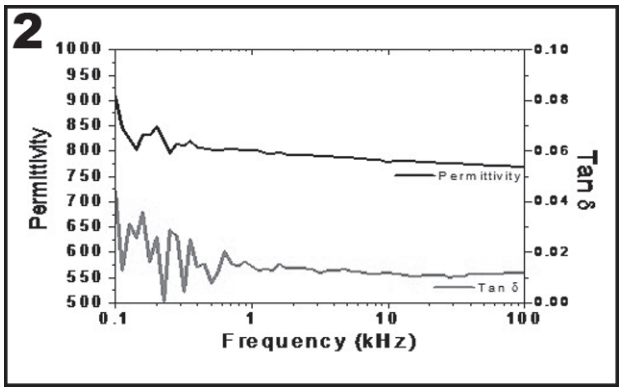

Figure 2: Permittivity and loss tangent of the 0.2 M KNN.

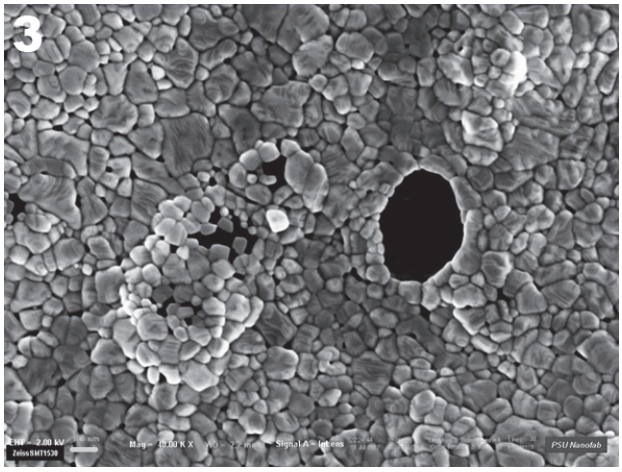

Figure 3: 2:1 KNN:acetylacetone film exhibiting high porosity.

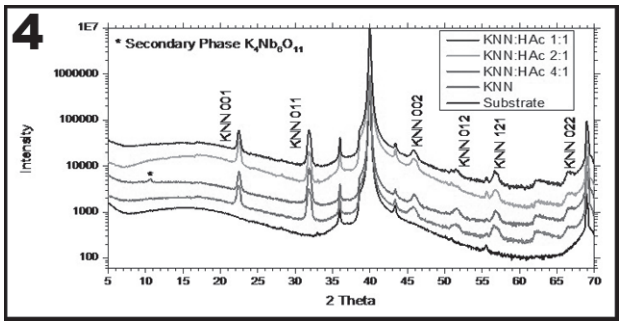

Figure 4: X-ray diffraction plot for films with acetic acid.

high permittivity of 786 at 10 kHz. In addition to that, the loss tangent, at the same frequency, was a low 1.2% as seen in Figure 2. However, when the solution was tested for its ferroelectric properties, the polarization was not able to be switched due to the sample breaking down at low fields. The hysteresis loop was not formed and the solution was deemed dielectric. This was attributed to its small thickness.

The following solutions that were fabricated were 0.4 M. The solution without additives showed an uneven grain size distribution in its microstructure. To counter that acetyl acetone was initially added. However, a low concentration of acetyl acetone did not improve the microstructure. In addition to that, as shown in Figure 3, a higher concentration of acetyl acetone introduced porosity into the films, and thus was deemed unusable. Solutions containing acetic acid showed improved microstructure as the amount of acid increased. The most promising were 33% and 50% by volume. The XRD showed all KNN peaks with an additional peak as seen in Figure 4, which was a potassium deficient secondary phase due to the volatilization of the potassium upon crystallization. The final set of solutions, containing copper acetate, showed that if acetic acid was added, then the combination of the two gave a good microstructure and improved electrical results.

Future Work:

In the future, we are trying to eliminate porosity from the microstructure of the film. Most of the focus will be geared towards improving the ferroelectric properties of KNN and making it comparable to its lead-based competitors. The final goal is to integrate this novel material into biomedical devices.

Conclusions:

After synthesis and characterization of KNN, it has been found that the solution shows high variability in microstructure based on the different additives. Both films with additives such as acetic acid and acetyl acetone, and films without additives have been fabricated and characterized using FESEM, XRD and profilometry. The last step of characterization is the electric testing, which is still in progress. If the tests show positive results then these films/solutions will be incorporated into an ingestible sensor device.

Acknowledgments:

I would like to thank my P.I. Dr. Susan Trolier-McKinstry, the STM group and my mentor Aaron J. Welsh. In addition to that I would like to thank the National Nanotechnology Infrastructure Network Research Experience for Undergraduates Program and the National Science Foundation for funding my research and providing me with this amazing opportunity.