



An Aqueous Sol-Gel Route to $MNbO_3$ (M=Li, Na, K) Fibers

P. NIU

Department of Chemistry, Dezhou University, Dezhou, P.R. China

Corresponding author: Tel: +86 534 8987866; E-mail: np68@sina.com

(Received: 27 September 2011;

Accepted: 14 June 2012)

AJC-11586

Alkali metal niobate $MNbO_3$ (M=Li, Na, K) fibers have been prepared by the aqueous sol-gel route using the freshly precipitated hydrated niobium oxide and alkali metal acetate as starting materials, citric acid as chelating agent and hydrogen peroxide as catalyst. The green fibers and its revolution at elevated temperature were also studied with thermogravimetric analysis, infrared spectra, X-ray diffraction, scanning electron microscopy and transmission electron microscopy techniques. Scanning electron microscopy and transmission electron microscopy results showed the as-prepared fibers were of the order of 3-5 μm in diameter, in which the particle size was *ca* 40-50 nm.

Key Words: $MNbO_3$, Aqueous sol-gel route, Fibers.

INTRODUCTION

In past decades, nanoparticles have been extensively studied since their physical properties are entirely different from those of the bulk states. The fibrous materials composed of nanoparticles can offer distinct properties such as anisotropy, high thermal stability and excellent flexibility and extend the applications in micro devices including sensors, hydrophones transducers and innovative optical modulators¹. So far, a rich variety of techniques and methods have been developed to prepare fibers including sol-gel², electrolysis³ and template-based synthesis⁴. The sol-gel process has evolved as a powerful approach to produce various oxide fibers on account of its homogeneity of reactant ion, the lower processing temperature, purity for products and the control of stoichiometry.

As a technological important class of inorganic materials, $LiNbO_3$ exhibits excellent ferroelectric, piezoelectric and pyroelectric properties², thus making it promising in surface acoustic wave (SAW), electrooptic devices, electrooptic modulators, harmonic generators and parametric oscillators. $NaNbO_3$ is antiferroelectric at room temperature with high dielectric constant at Curie temperature⁵, which has potential application in piezoelectric devices and acoustic transducers⁶. $KNbO_3$ shows outstanding electrooptic, nonlinear optical, photorefractive and acoustic properties⁷, which can be applied in surface acoustic wave (SAW), optical waveguide and holographic storage systems⁸. Many methods, such as sol-gel process⁹⁻¹¹, co-precipitation¹², hydrothermal synthesis¹³ and Pechini's method^{7,14}, have been explored to prepare the alkali metal niobate powders and films. Fiberization of these niobate materials might endue them with potential application in

microdevices. There are, however, few reports on the preparation of alkali metal niobate fibers² so far.

To make full use of the virtue of sol-gel process, the current paper reported a new system to prepare $MNbO_3$ fibers, in which low cost hydrated niobium oxide and citric acid were employed as original materials. In comparison with the previous work on the preparation of fibers materials by the sol-gel method, this aqueous route to $MNbO_3$ fibers has advantages over the use of a low-toxicity precursor, operation at ambient atmosphere without protection of nitrogen and the significant cost savings. This process offers a novel simple route to the fabrication of $MNbO_3$ fibers.

EXPERIMENTAL

Niobium oxide (Nb_2O_5 , chemical grade) was purchased from Guangdong Guanghua Sci-Tech Co. Ltd., and used without further treatment. Lithium acetate, sodium acetate and potassium acetate were obtained from Sinopharm Chemical Reagent Co. Ltd., China. Citric acid (CA) was obtained from Xilong chemical plant of Shantou, hydrogen peroxide (H_2O_2 , 30 %) obtained from Shanghai Jinlu Chemical Co. Ltd., China. Concentrated ammonia aolution (25-28 %) and hydrofluoric acid (HF, 48 %) were purchased from Shandong Bangde Chemical Limited Liability Company. All other chemicals were analytical pure and used as received.

Preparation of $MNbO_3$ fibers: The hydrated niobium oxide was prepared according to literature¹⁵ in which Nb_2O_5 (99.5 %) was selected as niobium source. The freshly prepared hydrated niobium oxide was dissolved in citric acid (CA) solution with the molar ratio Nb: CA=1:2, to which H_2O_2

(30 %) solution was added as catalyst with the molar ratio $H_2O_2: Nb = 0.6$. The mixture was stirred at 70 °C for 2 h to form a yellow solution, which indicated the formation of peroxy-niobium complexes in the solution. The transparent solutions were mixed with excess amounts (10 %) alkali metal acetate aqueous solution to compensate the volatilization of metal at the high treated temperature. Then the mixture was stirred for another 2 h. The yellow solution was left in open air at 70 °C on water bath and the viscosity increased with the evaporation of water and the sol became spinnable after 4 days. The gel fibers were drawn when the glass rod immersed into the sol and pulled it up.

Characterization: Sol viscosity was analyzed by cone-and-plate rheometer on RS75 (HAAKE company, Germany) at room temperature. To find an optimal firing temperature of the gel fibers, thermogravimetric analysis was performed using TGA/SDTA851^e module from METTLER TOLEDO in oxygen flow with a heating rate of 20 °C/min. In order to confirm the phase composition of $MnNbO_3$ fibers treated at various temperatures, X-ray diffraction was conducted on Rigaku D/Max 2200PC diffractometer using CuK_{α} radiation and graphite monochromator in the range of 20-70° with a scanning rate of 8°/min. The infrared spectra of the products were recorded using KBr pellet technique from 400-4000 cm^{-1} (FTIR, Nicolet ZOSX) so as to detect the revolution of gel fibers. The surface morphology $MnNbO_3$ fibers were observed by a scanning electron microscopy (SEM, JEOL JXA-840). Transmission electron microscopy (TEM) images of $MnNbO_3$ fibers, which were acquired on TEM, JEM-1200EXII at an accelerating voltage of 100 kV, were used to detect the size of the particles in the fiber.

RESULTS AND DISCUSSION

Preparation of the spinnable sol and gel fibers: The hydrated niobium oxide has low solubility in excess citric acid and dissolution rate is very slow. To promote its solubility and shorten the dissolution time, the appropriate amount of hydrogen peroxide was chosen as catalyst in present work. The amount of hydrogen peroxide plays an important role in the dissolution process. If the molar ratio of H_2O_2 to Nb is less than 0.5, the hydrated niobium oxide cannot dissolve entirely even though the reaction temperature is prolonged. With the increase of the molar ratio, the hydrated niobium oxide is diffused in very short period. However, it causes a great deal of air bubble in the final spinnable sol. So the appropriate molar ratio of H_2O_2 to Nb was chosen as 0.6.

Aged time is also affected by the ratio of the evaporation area to the sol volume and the aged temperature³ in the conversion process of solution to spinnable sol. The aged time is delayed with the decreasing of evaporation area and aged temperature. On the other hand, increasing aged temperature can shorten the aged time, but the spinnability of obtained sol is poor. In present experiment, the spinnable sol is obtained after the as-prepared 180 mL solution aged with an evaporation surface area 130 cm^2 for 4 days at 70 °C.

The acquired sol property was also studied. Fig. 1 gives the rheological curves of the $MnNbO_3$ sols. Within the range of shear rate, the shear stress increases linearly with the shear

rate and the sol viscosity is independence of shearing stress at constant temperature. From this result, it can be concluded that the obtained sol is a typical Newtonian fluid, which complies with the Newton's law of viscosity. With the evaporation of the solvent, the increasing of the sol viscosity suggests that the linear or chain-like polymer has formed through the hydrolysis and polycondensation reaction. The sols with the viscosity of 15, 10, 12 Pa·s for $LiNbO_3$, $NaNbO_3$, $KNbO_3$, respectively, show excellent spinnability and this is also measured from the ability of fiberization of the sols by dipping a glass rod and pulling it up by hand. Under these viscosities, the fibers can be drawn as long as 30 cm.

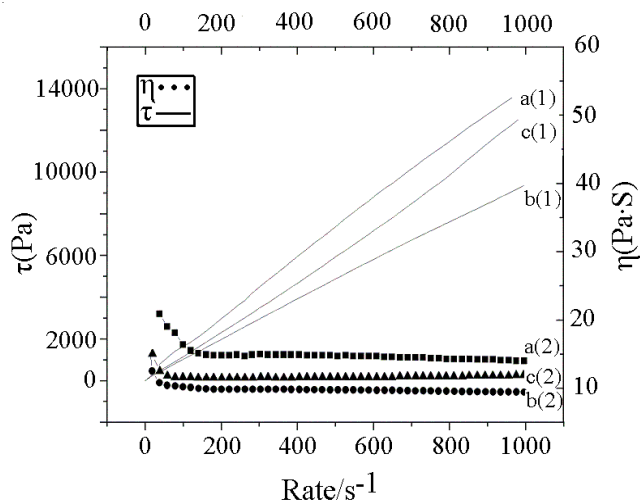


Fig. 1. Rheological curves of the $MnNbO_3$ sol (a) $LiNbO_3$, (b) $NaNbO_3$ and (c) $KNbO_3$.

Transformation of gel fibers to $MnNbO_3$ fibers: The thermal gravimetric curves of green fibers are shown in Fig. 2. The first one below 270 °C is originated from the evaporation of adsorbed and coordinated water molecules and free acetic acid, accompanying a relative weight loss of 21.3, 20.0, 15.8 % for $LiNbO_3$, $NaNbO_3$, $KNbO_3$, respectively. The weight loss occurred in the temperature range from 270 to 410 °C for $LiNbO_3/NaNbO_3$ and 500 °C for $KNbO_3$ is assigned to decarboxylation of citrate and oxidation of carbon and hydrogen in citrate precursor. In this stage the mass losses is related to the decomposition of complex formed from niobium and citrate. In the following stage, the decomposition goes to further, which might be owing to the decomposition of intermediate¹⁶. This step takes place between 410 °C and 500 °C for $LiNbO_3/NaNbO_3$. While for $KNbO_3$ the last weight loss defers to 670 °C. There is no significant weight loss above 500 °C for $LiNbO_3/NaNbO_3$ and above 670 °C for $KNbO_3$, which indicates that the organic compounds are eliminated completely before those temperatures. The residue inorganic segment content is 32.0, 35.1, 40.2 % for $LiNbO_3$, $NaNbO_3$, $KNbO_3$, respectively. The increasing of the solid content can be explained as an increase of relative atomic mass. The difference of fibers in thermal behaviour may be ascribed to the difference of intrinsic structure.

The XRD patterns of $MnNbO_3$ fibers calcined at various temperatures for 1 h in air are given in Fig. 3. From Fig. 3a and b, the $LiNbO_3$ and $NaNbO_3$ fibers are amorphous at 400 °C.

The characteristic peaks of LiNbO_3 and NaNbO_3 are observed until the temperature above 450°C . KNbO_3 fiber (Fig. 3c), however, is amorphous until 500°C and the diffraction peaks at 550°C suggest the crystallization onset of KNbO_3 phase. The diffraction peak intensity of MNbO_3 increases as the sintered temperature increasing. The higher the calcination temperature is, the higher the crystallinity of MNbO_3 fibers is. The well-crystalline MNbO_3 fibers are detected at 600°C for $\text{LiNbO}_3/\text{NaNbO}_3$ and 700°C for KNbO_3 without appearance of intermediate phase in this stage. The organic segment is eliminated completely taking the TG results into account. The drastic change of onset crystalline temperature also indicates that the intrinsic structure of $\text{LiNbO}_3/\text{NaNbO}_3$ and KNbO_3 is different, which agrees well with the TGA results. The XRD patterns of calcined fibers are characteristic of the hexagonal phase for LiNbO_3 and orthorhombic phase for NaNbO_3 ¹⁷ and KNbO_3 ¹³.

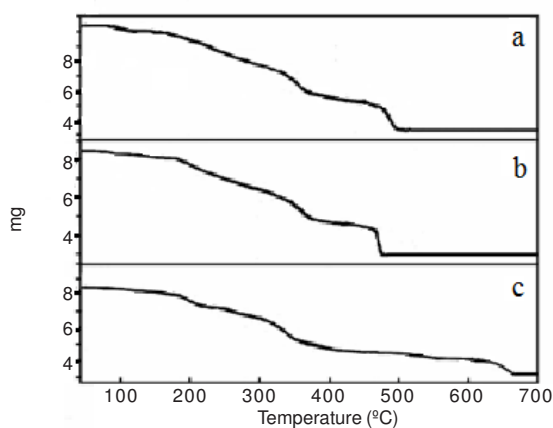


Fig. 2. TG curves of the gel fibers (a) LiNbO_3 , (b) NaNbO_3 and (c) KNbO_3

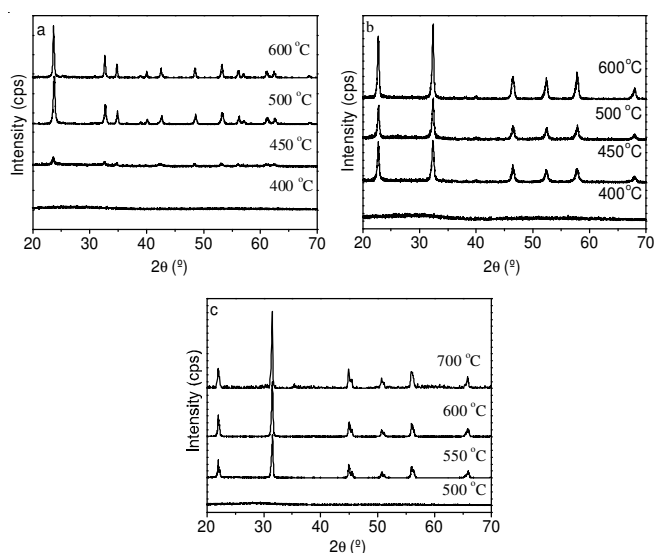


Fig. 3. XRD patterns of MNbO_3 fibers heat treated at different temperature for 1 h (a) LiNbO_3 , (b) NaNbO_3 and (c) KNbO_3

Fig. 4 shows the IR spectra of the green fibers and the fibers sintered at different temperatures. The broad bands at $3450\text{--}3430\text{ cm}^{-1}$ for MNbO_3 gel fibers originates from stretching mode $\nu(\text{OH})$ of the noncoordinated hydroxyl group in the citric acid. The bands around $3232, 3200, 3187\text{ cm}^{-1}$ and a shoulder

around $1654, 1659, 1657\text{ cm}^{-1}$ for $\text{LiNbO}_3, \text{NaNbO}_3$ and KNbO_3 gel fibers, respectively, are owing to the stretching $\nu(\text{OH})$ and bending $\delta(\text{OH})$ mode of adsorbed water. The bands of hydroxyl group and adsorbed water disappear with heat-treating. The asymmetric (ν_{as}) stretching vibration of $\text{C}=\text{O}$ appears at $1724\text{--}1719\text{ cm}^{-1}$. The typical absorption bands at $1569, 1561, 1563$ and $1393, 1394, 1394\text{ cm}^{-1}$ are attributed to the asymmetric (ν_{as}) and symmetric (ν_{s}) stretching vibration of carboxylate group of $\text{LiNbO}_3, \text{NaNbO}_3$ and KNbO_3 , respectively. The $\text{C}\text{--}\text{C}$ stretching mode at $931, 930, 927\text{ cm}^{-1}$ can be clearly identified for the $\text{LiNbO}_3, \text{NaNbO}_3$ and KNbO_3 gel fibers. The peaks at $863, 862, 861$ and $699, 698, 699\text{ cm}^{-1}$ are assigned as the vibration of the methylene group in the organic ligand. With the sintered temperature increasing, the citrate group peaks vanish gradually. The minor peaks at $1500\text{--}1400\text{ cm}^{-1}$ in the MNbO_3 fibers obtained at 600°C for 1 h are assigned to the CO_3^{2-} which is not detected by XRD. The metal oxide bands are observed at $612\text{--}400\text{ cm}^{-1}$ and shift to the higher wavenumber with the increasing of the heat-treated temperature. The blue shifts can be related to the increase in crystallinity from gel fibers to composite fibers.

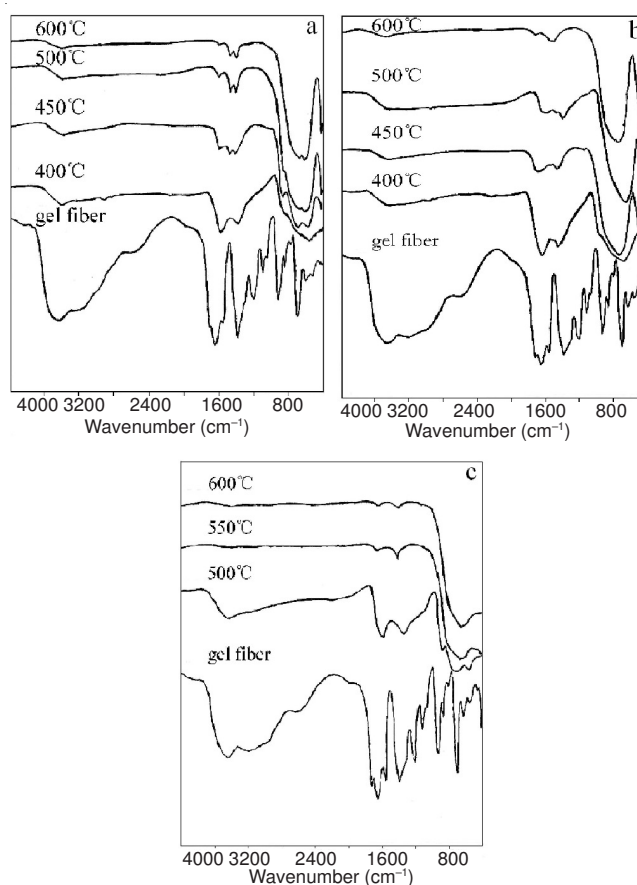


Fig. 4. IR spectra of the gel fiber and the MNbO_3 fibers obtained at elevated temperature (a) LiNbO_3 , (b) NaNbO_3 and (c) KNbO_3

Morphology and microstructure of MNbO_3 gel fibers:

Fig. 5 shows typical SEM pictures of MNbO_3 fibers in air for 1 h. The heat-treated temperature is 600°C for $\text{LiNbO}_3/\text{NaNbO}_3$ and 700°C for KNbO_3 . The surface of MNbO_3 fibers is smooth and free of cracks with uniform diameters along the axes. The diameter of sintered fibers is $3\ \mu\text{m}$ for LiNbO_3 and

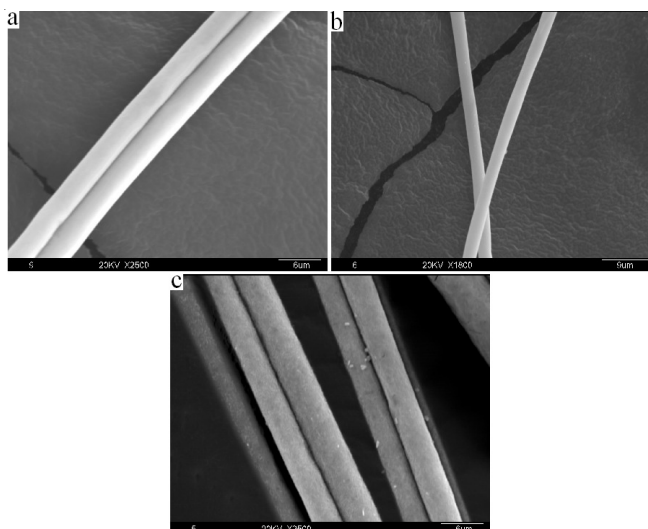


Fig. 5. SEM images of the fibers sintered at 600 °C for 1 h (a) LiNbO₃, (b) NaNbO₃ and (c) KNbO₃

5 μm for NaNbO₃ and KNbO₃ with the lengths up to 30 cm. The diameter of gel fibers decreases considerably on heating because of the decomposition of organic compound. The heating rate before the organic ingredient is removed entirely has remarkable effect on the surface morphology of fibers. It can lead to many voids in the surface if the heating rate is too fast due to the release of gas from the decomposition of the organic portion. So the optimal heating rate is selected as 0.5 °C/min prior to the decomposition of organic section. The corresponding TEM images are also given in Fig. 6. The particles consisted of MNbO₃ fibers are essentially nanometer size with a grain size about 40–50 nm.

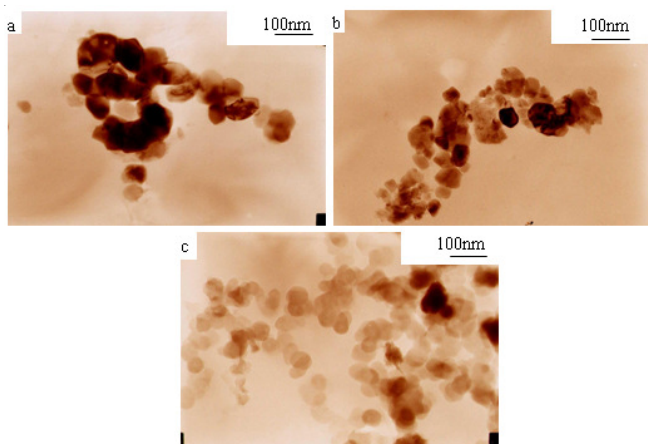


Fig. 6. TEM images of the MNbO₃ fibers obtained at 600 °C (a) LiNbO₃, (b) NaNbO₃ and (c) KNbO₃

Conclusion

MNbO₃ fibers were prepared using citric acid as stabilizer of metal ions and H₂O₂ as catalyst by an aqueous sol-gel process. In this process, H₂O₂ played an important role, which shortened the reactant time through the formation of the peroxy-niobium complexes. The obtained sol was a typical Newtonian fluid and the gel fibers could be drawn when the viscosity is up to 15, 10, 12 Pa·s for LiNbO₃, NaNbO₃, KNbO₃ sol respectively. The fibrous gel yielded crystallized LiNbO₃ and NaNbO₃ phase at 450 °C and the KNbO₃ began to crystallize at 550 °C. The MNbO₃ fibers with diameter mainly range from 3 to 5 μm and lengths up to 30 cm were obtained and the nanoparticles composed of the crystallized fibers varied between 40 nm and 50 nm.

REFERENCES

- S.H. Zhan, D.R. Chen, X.L. Jiao and C.H. Tao, *J. Phys. Chem. B*, **110**, 11199 (2006).
- S. Hirano, T. Hayashi, K. Nosaki and K. Kato, *J. Am. Ceram. Soc.*, **72**, 707 (1989).
- T. He, X.L. Jiao, D.R. Chen, M.K. Lv, D.R. Yuan and D. Xu, *J. Non-cryst. Solids*, **283**, 56 (2001).
- D.J. Walter, A. Safari, R.J. Card and M.P.O. Toole, *J. Am. Ceram. Soc.*, **73**, 3503 (1990).
- M.A.L. Nobre, E. Longo, E.R. Leite and J.A. Varela, *Mater. Lett.*, **28**, 215 (1996).
- A. Molak and J. Kubacki, *Cryst. Res. Technol.*, **36**, 893 (2001).
- B.D. Zaitsev, I.E. Kuznetsova, I.A. Borodina and S.G. Joshi, *Ultrasonics*, **39**, 51 (2001).
- C.H. Lu, S.Y. Lo and Y.L. Wang, *Mater. Lett.*, **55**, 121 (2002).
- (a) H.C. Zeng and S.K. Tung, *Chem. Mater.*, **8**, 2667 (1996); (b) V.P. Rao, D.S. Paik and S. Komarneni, *J. Electroceram.*, **2-3**, 157 (1998); (c) E.R. Camargo and M. Kakihana, *Chem. Mater.*, **13**, 1905 (2001).
- E.R. Camargo, M. Popa and M. Kakihana, *Chem. Mater.*, **14**, 2365 (2002).
- M.M. Amini and M.D. Sacks, *J. Am. Ceram. Soc.*, **74**, 53 (1991).
- S.I. Hirano and K. Kato, *Adv. Ceram. Mater.*, **2**, 142 (1987).
- C.H. Lu, S.Y. Lo and H.C. Lin, *Mater. Lett.*, **34**, 172 (1998).
- M.P. Pechini, US Patent 3330697 (1967).
- R.N. Das and P. Pramanik, *Mater. Lett.*, **46**, 7 (2000).
- N.S. Gajbhiye, U. Bhattacharya and V.S. Darshane, *Thermochim. Acta*, **264**, 219 (1995).
- S. Lanfredi, L. Dessemond and A.C.M. Rodrigues, *J. Eur. Ceram. Soc.*, **20**, 983 (2000).