Synthesis of single-crystalline one-dimensional LiNbO₃ nanowires†

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Received 6th May 2010, Accepted 14th May 2010
DOI: 10.1039/c005318j

We report a large-scale synthesis of single-crystalline LiNbO₃ nanowires with diameters of 300–400 nm, containing only minor amounts of impurities, using a modified molten salt procedure. The isolated product is composed of rhombohedral-phase LiNbO₃ nanowires with the c-axis oriented along its length. Raman investigations further confirm the purity and ferroelectric order of the nanowires and are consistent with electron microscopy data.

The miniaturization of functional transition metal oxides with controllable morphology, purity, size distribution, and crystallinity has rendered them as viable candidates for a host of emerging applications as diverse as sensing, capacitance, detection, nonvolatile memory devices, pigmentation, photonics, energy storage and conversion, as well as electroceramics.1–4 Specifically, lithium niobate (LiNbO₃) is a key material in integrated optics due to its photo-stability as well as excellent nonlinear optical properties including large piezoelectric, electro-optic, and nonlinear optical coefficients.5–6 Moreover, as a potential thin-film transducer material, it has advantages over most other ferroelectric materials in that it is not only thermally, mechanically, and chemically stable but also possesses a small dielectric constant.7–9 These advantageous features have rendered these materials as viable components of devices including optical waveguides,8 voltage sensors,9 data storage media,10 and acousto-optical modulators.11

Bulk single crystals of LiNbO₃ have been synthesized in the past using the micro pull-down procedure,11 the laser heated pedestal growth protocol,14 and the Czochralski method.15 To the best of our knowledge, there have been only four prior reports of the reliable, reproducible production of anisotropic, high aspect-ratio one-dimensional (1-D) LiNbO₃ with diameters in the submicron length scale.8 However, challenges remain, particularly regarding crystallinity, growth direction, and size control.

Specifically, one group9 utilized the pyrolysis at 550 °C for 5 h of a 5 wt% lithium tetraethoxy(1-phenyl-1,3-butadiene) niobate precursor in ethanol in order to synthesize nanotubes of LiNbO₃, measuring 180 to 400 nm in outer diameter with thicknesses of a few tens of nm, within the pores of anodized aluminium oxide templates.

While this protocol maintains superb control over product morphology, as-prepared products are likely polycrystalline; moreover, the process is relatively high-temperature and utilizes a precursor that requires air-sensitive conditions to produce. A second group16 reacted a mixture of Nb₂O₅ and LiOH in the presence of various amine ligands under hydrothermal conditions at 220 °C for 1–4 days. This protocol yields smooth, monodisperse nanorods with average diameters of ~800 nm and lengths of up to 3 microns. Nonetheless, while this procedure can produce large quantities of nanorods, individual nanoparticulate sizes are still relatively large. In addition, a third group17 used a hydrothermal technique to synthesize LiNbO₃ nanowires with widths of ~50 nm and lengths of up to 3 microns. A potential limitation of this report is that as-generated nanowires tend to possess random crystallographic planes with respect to the long axis of their growth. Finally, a fourth group18 has demonstrated a solution-phase approach for the synthesis of crystalline anisotropic rod-like structures of LiNbO₃, resulting from the directed aggregation of nanoparticles during aging and with diameters of ~7 nm and lengths of up to 100 nm. While this method does not require very high temperature processing, it tends to generate polycrystalline structures.

Smaller, highly crystalline nanocrystals of LiNbO₃ measuring between ~20 and 80 nm can be produced either hydrothermally using LiOH and Nb₂O₅ as reactants,19 solvothermally in the presence of benzyl alcohol,20 mechanically with a high-energy ball milling process for up to 25 h,21 or chemically using a low-temperature sol–gel method.22 However, noticeably larger micron-scale crystals with sizes on the order of the optical wavelengths are better suited for integration into nanophotonic applications.

It is evident that while LiNbO₃, especially its 1-D formulations, can be produced, each of the prior protocols has its limitations. Therefore, in the current report, using a modified, multi-step molten salt method previously used to produce one-dimensional ANbO₃ (A = Na, K, (Na, K)),23 we were able to generate gram quantities of LiNbO₃ that were not only reasonably pure (e.g. relatively miniscule amounts of a potassium lithium niobate solid mixture as the impurity phase) and single-crystalline but also possessed smooth, well-defined edges and crystal facets. Moreover, in our syntheses, we were also able to fabricate submicron scale 1-D structures as the predominant morphological motif. It is important to note that two previous molten salt synthetic procedures, concerned with 1-D niobate production, failed to generate analogous single-crystalline, relatively pure 1-D structures of LiNbO₃.24 One potential drawback to the technique used in this paper relates to the successive high temperature steps needed for the reaction and hence, the correspondingly sizable energy requirements associated with that overall process.

Our detailed step-by-step reaction schematic, starting from bulk precursors, is shown in Scheme 1. First, this protocol involves the initial synthesis of precursor KNb₂O₆ nanowire reagents using
a molten salt reaction. Briefly, bulk Nb$_2$O$_5$ (Alfa Aesar, 99.9985%) was mixed with KCl (Mallinckrodt, 99.5–100%) in the presence of ethanol in a 1 : 10 molar ratio. The mixture was subsequently dried at 80°C and then heated in a tube furnace to 800°C for 3 h. Upon gradual cooling to room temperature, the sample was washed several times with hot, deionized water, isolated by centrifugation, and finally oven dried at 80°C.

Second, a quantity of these as-prepared KNb$_3$O$_8$ nanowires was stirred at room temperature in 400 mL of 2 M HNO$_3$ for 48 h, followed by washing several times with distilled water, so as to obtain H$_3$ONb$_3$O$_8$ nanowires through an exchange reaction.

Third, annealing of H$_3$ONb$_3$O$_8$ nanowires to 550°C for 1 h enabled their successful conversion to Nb$_2$O$_5$ nanowires (Fig. S1†). Nb$_2$O$_5$ nanowires were ultimately used as the direct precursors for LiNbO$_3$ nanowire synthesis in a reaction, previously explained for analogous KNbO$_3$ systems by using a combination of ‘dissolution-precipitation’ and ‘template formation’ mechanisms. Briefly, niobium oxide nanowires were ground together with Li$_2$CO$_3$ in a 1 : 1 molar ratio before being mixed with an equal weight of KCl. The resulting powder was then transferred to a porcelain boat and heated to 780°C isothermally for 10 min, prior to gradual cooling to room temperature. The ensuing product was washed several times with distilled, deionized water so as to remove any KCl, prior to dispersion in ethanol for characterization. Product yields of ~100% conversion were routinely obtained, corresponding to amounts ranging from 100 mg to >1 gram, depending on the initial quantities of the precursors used.

Fig. 1A highlights the XRD pattern and corresponding SEM image of LiNbO$_3$ nanowires, obtained from our molten salt technique. As can be observed from the XRD pattern, though there is a relatively small amount of a potassium lithium niobate solid mixture impurity, the major phase of the product is clearly crystalline LiNbO$_3$, with peak intensity ratios that correspond well with the JCPDS #85-2456 database standard. LiNbO$_3$ has a space group of...
and that the indexing is consistent with that expected for rhombohedral LiNbO$_3$ is highlighted in Table S1.† Peaks observed at 151, 237, 365, 578, 621, and 883 cm$^{-1}$ are spectroscopically identical to those of bulk and single-crystal analogues. The strongest fundamental $A_1$ TO mode, expected at 630 cm$^{-1}$, shifted to a lower wavenumber of 621 cm$^{-1}$ for our sample, an observation which may be due to a mixing of $A_1$ TO and $E$ TO modes but which is consistent with phonon propagation at an angle of 65$^\circ$ relative to the surface normal.25 Similarly, the peak observed at 870 cm$^{-1}$, expected at 883 cm$^{-1}$, can be assigned to the quasi $TO$ mode.

In conclusion, we were able to adapt an existing molten salt method23 to produce in a facile manner, for the first time, large quantities of single-crystalline LiNbO$_3$ nanowires with high purity (minimum amounts of potassium lithium niobate), smooth crystal surfaces, and controllable chemical composition at a reasonable cost.

Research (including synthesis work and personnel support) carried out at Brookhaven National Laboratory was funded by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. Moreover, research carried out (in whole or in part, such as transmission electron microscopy studies) at the Center for Functional Nanomaterials, Brookhaven National Laboratory, is also supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. SSW also acknowledges the Alfred P. Sloan Foundation for support of the diffraction and SEM work (including experimental supplies). MR specifically thanks the U.S. Department of Energy, Office of Basic Energy Sciences for support of Raman studies under contract number, DE-SC0002197.

Notes and References