Dependence of stoichiometry of lithium niobate nanocrystals on initial lithium to niobium ratios in the synthesis step

K Veenhuizen	extsuperscript{1}, G A Stone	extsuperscript{2}, B Knabe	extsuperscript{3,4}, K Buse	extsuperscript{3,4} and V Dierolf	extsuperscript{1}

	extsuperscript{1} Department of Physics, Lehigh University, 16 Memorial Drive East, Bethlehem, PA 18015, USA
	extsuperscript{2} Department of Materials Science and Engineering, Pennsylvania State University, Millennium Science Complex, University Park, PA 16802, USA
	extsuperscript{3} Department of Microsystems Engineering (IMTEK), University of Freiburg, Georges-Köhler-Allee 102, 79110 Freiburg, Germany
	extsuperscript{4} Fraunhofer Institute for Physical Measurement Techniques IPM, Heidenhofstrasse 8, 79110 Freiburg, Germany

Email: kjv212@lehigh.edu

Abstract. Ferroelectric nanocrystals show promise for application in forming hybridized nonlinear materials with liquid crystals. It is well known that bulk single crystals of lithium niobate (LiNbO\textsubscript{3}) are most easily grown in a congruent (lithium-deficient) form but can also be grown in a stoichiometric form. This is controlled by the specific growth conditions and the stoichiometric ratio $\rho = \frac{M_{\text{Li}}}{M_{\text{Li}} + M_{\text{Nb}}}$, where M is the molar fraction. This work explores the dependence of the stoichiometry of LiNbO\textsubscript{3} nanocrystals on the value of $\rho$ in the synthesis step. Batches of LiNbO\textsubscript{3} nanocrystals were synthesized using a sol-gel method. The nanocrystals were analysed via SEM and Raman spectroscopy to gain information about their morphology, stoichiometry, defect content, and phase. For bulk crystals, previous work has demonstrated that the spectral widths of specific Raman modes strongly depend on $\rho$. For the nanocrystals, the Raman spectra indeed reveal that the resultant nanocrystal stoichiometry depends on the initial $\rho$ used in the synthesis step. In addition, a close examination of the Raman spectra reveals the presence of an extra phase in batches with $\rho \geq 55\%$. Somewhat counterintuitively, this phase is identified by its Raman spectra to be LiNb\textsubscript{3}O\textsubscript{8}, a relatively lithium-poor phase compared to LiNbO\textsubscript{3}. Avoiding this extra phase, we find that high quality, roughly spherical LiNbO\textsubscript{3} nanocrystals can be synthesized for $\rho$ between 52 and 54%.

1. Introduction
Ferroelectric nanocrystals show promise in supplementing materials such as liquid crystals and photoconductive polymers [1]. A hybrid material is created where the nanocrystals improve an essential property of the primary material, for example the photoconductivity of a polymer [1]. An important aim is to improve some property of the primary material without any noticeable drawback due to the nanocrystals’ presence [1]. For the nanocrystals to fulfill this purpose, there should be a uniformity of the resultant nanocrystal product in terms of morphology, stoichiometry, and phase.

In this work, a variety of LiNbO\textsubscript{3} nanocrystal batches made from different initial stoichiometric ratios were analyzed using SEM imaging and Raman spectroscopy. A fundamental concern of this work was to observe whether varying the initial stoichiometric ratio could control the final nanocrystal product. A question we seek to answer is, if the variation of the initial stoichiometric ratio influences...
the morphology, stoichiometry, or phase of the final product, then what initial stoichiometric ratio is ideal for applications?

2. Experimental Procedure

Nanocrystals of LiNbO$_3$ were synthesized using a double alkoxide sol-gel method that has been discussed in detail in previous publications [2]. Niobium ethoxide and lithium ethoxide are dissolved in ethanol and refluxed for 24 h. The solution is then slightly cooled and hydrolyzed by distilled water for an additional 24 h. The precipitate is dried and calcined. The product then underwent planetary ball milling in oleic acid before being suspended in water.

The initial stoichiometric ratio

$$\rho = \frac{M_{Li}}{M_{Li} + M_{Nb}}$$

is varied, and batches are created with values of $\rho$ spanning 40 to 60% (40, 45, 50, 52, 54, 55, 56, 58, and 60%). Here $M_{Li}$ and $M_{Nb}$ are the molar fractions of the compounds.

The nanocrystals are characterized by SEM imaging and Raman spectroscopy. The morphology of the nanocrystals were observed via SEM. For Raman scattering measurements, nanocrystals are prepared in liquid suspension contained between glass slides as well as dried onto the surface of a glass slide. The confocal Raman microscope (figure 1) utilizes an Ar ion laser (Coherent Innova 70) operating at 488 nm, and light is collected in a backscattering geometry. Single mode fibers act as the excitation and collection pinholes. Spectra from dried nanocrystals are collected at a temperature of 4 K using an objective with numerical aperture 0.50. Spectra from suspended nanocrystals are collected using an oil immersion objective. The numerical aperture (NA = 1.32) of the oil immersion objective is sufficiently high to enable optical trapping of the nanoparticles. In such an optical tweezer, a dense collection of nanocrystals coalesces around the laser focus, resulting in a strong Raman signal from the cluster of nanocrystals.

The data is analyzed using the multipeak fit utility in IGOR Pro. Peaks were fit with Lorentzian profiles and a cubic polynomial baseline. The multipeak fit is restricted to peaks with Raman shift between 100 and 500 cm$^{-1}$ to maintain high accuracy. The directional dispersion that is characteristic for the polar LiNbO$_3$ material [3] contributes to the asymmetric appearance of some peaks and somewhat reduces the accuracy of the fit. A lithium poor phase (LiNb$_3$O$_8$) was present in a few batches. It possesses a unique Raman spectrum, and so fitting was performed only when Raman spectra containing the LiNbO$_3$ signature were obtained, as the intention was to extract information from the best fit parameters on stoichiometry and presence of defects in LiNbO$_3$ nanocrystals.

![Figure 1. Schematic of confocal Raman microscope.](image-url)
3. Results

3.1. Raman spectroscopy

In previous studies on bulk single crystal LiNbO$_3$, the full-width-at-half-the-maximum (FWHM) of the E(\(\text{TO}_1\)) mode as well as the A(\(\text{LO}_4\)) mode in regards to the lithium concentration were calibrated [4]. In this work, the nanocrystals in liquid suspension are oriented in various directions and interface related effects are more relevant [5], and hence we need to focus on the E(\(\text{TO}_2\)) mode for which the directional dispersion contributes very little to its broadening [3]. Figure 2(a) shows the Raman spectra of nanocrystals in liquid suspension for a variety of the initial stoichiometric ratio while figure 2(b) displays the FWHM of the E(\(\text{TO}_2\)) mode obtained from these spectra. Raman spectra were also collected for bulk single crystal z-cut congruent lithium niobate (CLN) and z-cut near-stoichiometric lithium niobate (nSLN). The FWHM of the E(\(\text{TO}_2\)) mode for each of these bulk single crystals is drawn as a horizontal line for reference on figure 2(b). The 55% batch is seen to have the narrowest FWHM comparable to that of nSLN. All batches between 50 and 60% possess FWHM which fall between CLN and nSLN. The 40 and 45% batches show significant broadening as displayed in figure 2(a).

Figure 2. (a) Raman spectrum of liquid suspended nanocrystals for each initial stoichiometric ratio. The gray highlighted regions correspond to the wide E(\(\text{TO}_1\))–E(\(\text{LO}_2\)) and E(\(\text{TO}_4\))–A(\(\text{TO}_4\)) directional dispersion regions. (b) FWHM of E(\(\text{TO}_2\)) mode vs initial stoichiometric ratio \(\rho\) with z-cut CLN and z-cut nSLN shown for reference.
Inspecting the nanocrystal Raman spectra beyond the $E(\text{TO})_2$ mode, there is a significant contribution from the $E(\text{TO})$ modes. Mode assignments are given in table 1 using the most recent literature data [6]. Directional dispersion is evident in the $E(\text{TO})_1$-$E(\text{LO})_2$ and $E(\text{TO})_3$-$A(\text{TO})_4$ regions leading to broadened asymmetric line shapes [3]. Some $A(\text{LO})$ modes are reduced like the $A(\text{LO})_4$ mode, and $A(\text{TO})$ modes are largely suppressed, as evidenced by the absence of the $A(\text{TO})_1$ mode.

There are differences between the Raman spectra for each initial stoichiometric ratio. For the 40 and 45% batches, the $A(\text{LO})_4$ mode does not appear as a distinct peak. Looking at the $E(\text{TO})_3$-$A(\text{TO})_4$ directional dispersion region, there is a clear variation in the dispersion profile as a function of stoichiometric ratio. For values of $\rho \geq 55\%$, an intense extra mode appears at a higher energy than all the other modes at around 900 cm$^{-1}$. Other peaks not related to LiNbO$_3$ also appear, indicating the appearance of an additional phase. This phase is so dominant for the 56% batch that no data point is included in figure 2(b) for this batch.

A Raman spectrum collected from a dried sample of nanocrystals from the 58% batch is shown in figure 3(a). In such a dried sample, the orientation of the nanocrystals is random and cannot be controlled as in the case of liquid suspended nanocrystals trapped near the focus of the optical tweezer.

![Raman spectrum of dried sample of nanocrystals taken from 58% batch at 4 K.](image)

**Table 1.** Multipeak fit results for 55% batch and $z$-cut nSLN.

| Raman shift (cm$^{-1}$) | Mode | $\rho = 55\%$ | Mode | Raman shift (cm$^{-1}$) | Mode | $z$-cut nSLN |
|--------------------------|------|---------------|------|--------------------------|------|-------------|
| 156.4 ± 0.2              | $E(\text{TO})_1$ | 153.4 ± 0.1  | $E(\text{TO})_1$ |  |
| 239.1 ± 0.1              | $E(\text{TO})_2$ | 238.6 ± 0.1  | $E(\text{TO})_2$ |  |
| 264.1 ± 1.0              | $E(\text{TO})_3$ | 264.4 ± 0.2  | $E(\text{TO})_3$ |  |
| 276.8 ± 0.2              | $A(\text{LO})_1$ | 275.9 ± 0.2  | $A(\text{LO})_1$ |  |
| 320.3 ± 0.8              | $E(\text{TO})_4$ | 321.2 ± 0.2  | $E(\text{TO})_4$ |  |
| 333.3 ± 0.4              | $A(\text{LO})_2$ | 334.7 ± 0.1  | $A(\text{LO})_2$ |  |
| 370.3 ± 0.4              | $E(\text{TO})_5$ | 367.6 ± 0.2  | $E(\text{TO})_5$ |  |
| 432.6 ± 0.5              | $E(\text{TO})_7$ | 432.4 ± 0.2  | $E(\text{TO})_7$ |  |

3.2. **SEM imaging**

The SEM images in figure 4 reveal that the crystallization process improved with increasing values of $\rho$. The 55, 58, and 60% batches produced a uniform collection of near spherical nanocrystals. The 40,
45, and 50% batches all produced inhomogeneous collections of nanocrystals with jagged edges. The 40% batch produced the worst nanocrystal product, characterized by large clumps and lack of uniformity in the shape of the nanocrystals.

4. Discussion
The trend of figure 2(b) shows the FWHM hits a minimum around $\rho_{\text{min}} = 55\%$. The batches with $\rho < 50\%$ have the broadest peaks, indicating high defect content and off-stoichiometric nanocrystals. The FWHM of the 50% batch is near to that of CLN and 55% is near to that of nSLN, indicating the final stoichiometric ratio of the nanocrystals is less than the initial stoichiometric ratio before synthesis.

The Raman spectrum in figure 3 is a fingerprint of a collection of randomly oriented crystallites. There are a few clear distinctions between this spectrum when compared to the Raman spectra in figure 2(a) of nanocrystals in liquid suspension trapped by the optical tweezer. The most notable differences are in the 300-350 cm\(^{-1}\) and 580-630 cm\(^{-1}\) regions.

In the case of the optically trapped nanocrystals in liquid suspension, the directional dispersion in the $E(\text{TO})_1$-$E(\text{LO})_2$ and $E(\text{TO})_8$-$A(\text{TO})_4$ regions covers the entire dispersion range, implying the nanocrystals are aligning themselves at a variety of orientations in the optical trap. However, the difference when compared to the Raman spectrum of dried nanocrystals as well as the mode assignment of table 1 reveals a preferential orientation of the nanocrystals in the optical trap.

The absence of the $A(\text{TO})$ modes combined with the strong presence of the $E(\text{TO})$ modes suggests the preferred alignment is with the ferroelectric axis of the nanocrystals roughly parallel to the light propagation axis. The dominant contributor to the alignment of the nanocrystals is the induced dipole perpendicular to the spontaneous polarization of the nanocrystals, consistent with what has been observed in a previous study of LiNbO\(_3\) nanocrystals in liquid suspension under application of an external electric field [7]. The observed alignment effect is most pronounced for those batches for which the nanoparticles were almost round and a competing alignment effect based on the geometric shape is absent.

The extra mode around 900 cm\(^{-1}\) apparent in the Raman spectra for $\rho \geq 55\%$ can be explained as a different crystal phase in the batch besides LiNbO\(_3\). Figure 5(a) displays spectra where the extra modes, including the 900 cm\(^{-1}\) mode, are indicated. Comparing these characteristic Raman spectra with earlier work on thin films in Figure 5(b) [8] leads to the conclusion that this extra phase may be LiNb\(_3\)O\(_8\) [8]. This is somewhat counterintuitive because LiNb\(_3\)O\(_8\) is lithium poor. It would be expected that when higher relative ratios of lithium to niobium are used in the synthesis step, a lithium rich phase like Li\(_3\)NbO\(_4\) would appear. Further work (beyond the scope of this paper) is needed to study this point.
5. Conclusion

It was observed that changing the initial stoichiometric ratio indeed varies the resultant nanocrystal product. Initial stoichiometric ratios with $\rho \geq 55\%$ produced uniform batches of spherical nanocrystals while batches with $\rho \leq 50\%$ produced non-uniform collections of nanocrystals. Furthermore, the FWHM of the E(TO)$_2$ was at a minimum for those batches with $\rho \geq 55\%$, indicating a near-stoichiometric LiNbO$_3$ nanocrystal product. Batches with the higher initial concentration of lithium to niobium ($\rho \geq 55\%$) also possessed an extra phase besides LiNbO$_3$. The 52 and 54% batches balance the avoidance of the extra phase while producing high quality, near-stoichiometric nanocrystals and are thus most suitable for application purposes.

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