Optical spectroscopy of trivalent chromium in sol-gel lithium niobate

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We report on the characterization of sol-gel derived lithium niobate via trivalent chromium probe ions, a study that is motivated by recent reports on the synthesis of high quality sol-gel lithium niobate (LiNbO₃). In order to assess the quality of sol-gel derived LiNbO₃, we incorporate Cr³⁺ during the hydrolysis stage of the sol-gel process. A comparison of the Cr³⁺ emission and photoexcitation data on both sol-gel and melt-grown LiNbO₃ shows that the sol-gel derived material is highly stoichiometric.

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The need for sol-gel derived ferroelectric coatings and films for electro-optical and piezoelectric applications is driving the research for high quality sol-gel lithium niobate (LiNbO₃). Recent reports concentrate on optimizing the sol-gel process with the aim of producing high quality films with preferred orientation. X-ray diffraction and ICP have been the primary techniques to assess stoichiometry of the samples. To our knowledge, optical probes, such as Cr³⁺ ions, have not been used to characterize the sol-gel samples, although this approach has been very successful to show fundamental differences between congruent and stoichiometric melt-grown LiNbO₃. The Cr³⁺ ion is particularly suited to study the quality of LiNbO₃, because it is arguably the most studied optical impurity, has a spectrum that is very sensitive to the possible lattice sites and disorder in LiNbO₃, and can be readily incorporated in an early stage of the sol-gel process. In addition, chromium doped lithium niobate has stimulated much interest due to the broadband near infrared luminescence of the chromium ions, with the ultimate goal of developing a tuneable laser in the visible range through frequency doubling within the active medium.

In the current work, we study the optical Cr³⁺ transitions between the 4A₂ groundstate and the lowest 4T₂ and 4E excited electronic states. These transitions are characterized by broad absorption and emission bands for the spin allowed transition, and spectrally narrow lines for the spin-forbidden transition, respectively. These transitions provide information on the stoichiometry and disorder of the sol-gel material, and allow a comparison to the detailed study of LiNbO₃ samples grown from melt.

For the sample synthesis, we combine 1 M solutions of lithium and niobium ethoxides in ethanol such that the ratio of Li:Nb is 1:1. An appropriate amount of Cr(NO₃)₃ is then dissolved in water (in this study the Cr:Li ratio was 0.001:1). Under constant stirring, the water-chromium solution is slowly added into the mixed ethoxide. After an initial release of ethanol, the solution is capped and aged for several days. The aged solution is then dried at room temperature until a fine white powder has formed. The powder samples are finally heated in air to 800 °C for two hours to remove excess water and organic complexes. The calcined powders are characterized by x-ray diffraction utilizing Cu K-alpha radiation; a typical pattern is shown in Fig. 1. All observed diffraction peaks can be attributed to lithium niobate, and we find no evidence for alternate phases such as Li₀.88H₀.12NbO₃.

The optical experiments are carried out with the powder sample mounted in an Oxford Instruments temperature variable cryostat. For emission measurements the sample is excited with a HeNe laser at 632.8 nm. The broadband emission was collected with reflective optics and analyzed with a Bruker 66v FTIR spectrometer. Photoexcitation measurements were performed by mounting the cryostat directly into the sample space of a modified Cary 14 spectrophotometer. In both the broadband emission and photoexcitation experiments, the emitted light was collected through appropriate filters and imaged onto a liquid-nitrogen cooled InGaAs detector. For the photoexcitation, a lock-in amplifier was used.
for signal-to-noise enhancement.

Experimental results for the sol-gel LiNbO$_3$:0.1%Cr$^{3+}$ sample are shown in Fig. 2. The excitation spectrum (Fig. 2, left) observed at $\lambda_{\text{det}} \geq 900$ nm shows the characteristic $^4A_2 \rightarrow ^4T_2$ and $^4A_2 \rightarrow ^4T_1$ broad absorption bands around 655 nm and 480 nm, respectively, as well as the spin-forbidden $^4A_2 \rightarrow ^2E$ transition around 726 nm. The emission spectrum (Fig. 2, right) shows the $^3T_2 \rightarrow ^4A_2$ emission band under HeNe laser excitation ($\lambda_{\text{ex}} = 632.8$ nm).

To interpret these results, they are compared to spectra obtained on standard melt-grown LiNbO$_3$:Cr$^{3+}$, lithium niobate crystals pulled from a melt with equal amounts of lithium and niobium crystallizing with a Li 3% deficit, and are referred to as congruent samples. When chromium ions are added to these melts, a 3% deficit is found by varying the contributions to the impurity absorption for each site while keeping the total constant, $C_{\alpha} = 1$. The fit shown in Fig.3 (solid line) represents a 66% Cr[Li] to 34% Cr[Nb] ratio.

In contrast to the Cr[Li] spectrum that dominates in congruent LiNbO$_3$ crystals, the sol-gel produced material has a significant contribution to the luminescence at excitation wavelengths beyond 750 nm, as evident in a shoulder in the excitation spectrum extending from about 750 nm to 800 nm in Fig.2. Fig.3 shows an expanded excitation spectrum in this region (dots). This shoulder can be attributed to chromium ions on niobium sites, Cr[Nb]. To quantify this contribution to the excitation spectrum, we measured the spectra of LiNbO$_3$:Cr$^{3+}$ crystals with and without magnesium codoping (6%).

The fit to the excitation spectrum determines the 66% Cr[Li] to 34% Cr[Nb] ratio. A careful inspection of LiNbO$_3$:Cr:Mg (insert Fig.3, dashed line) shows a small peak at 727 nm ($^4A_2 \rightarrow ^2E$ transition), due to Cr[Li]. Taking this correction into account, we arrive at relative Cr[Li] and Cr[Nb] concentrations of 0.64 and 0.36, respectively.

The substantial occupation of the niobium site by chromium ions is in marked difference to melt-grown congruent samples, where the chromium ions occupy lithium...
sites exclusively. In highly stoichiometric LiNbO$_3$ samples, grown by the HTTSSG method, we also find chromium ions on both the lithium and niobium sites, thus our results confirm reports that the sol-gel process yields highly stoichiometric samples without the intrinsic Li deficit, which is characteristic for congruent melt-grown LiNbO$_3$. In stoichiometric single crystal samples of highest quality, the zero-phonon line of the $^4$A$_2 ightarrow ^4$T$_2$ can be observed at low temperature. In our sample, this transition is broadened, which is indicative of lattice defects. Our sample also shows the optical signature of so-called high field sites, which is due to Cr$^{3+}$ ions in a strong crystal field, resulting in the $^2$E level lying below the $^4$T$_2$ level, characterized by sharp emission lines at low temperatures, and which are associated with defects in the crystal. Thus, while our results indicate that the sol-gel samples do not have the intrinsic lithium deficit of congruent melt-grown material, the overall quality of the material does not yet approach that of the highest quality single crystal material. However, with the optical absorption and emission spectra of trivalent chromium being a clear indicator of the crystal quality, systematic studies are possible to improve the quality of sol-gel derived LiNbO$_3$.

In summary, we have shown Cr$^{3+}$ ions are sensitive optical probes of the quality of sol-gel derived LiNbO$_3$. Our experiments confirm that sol-gel produced lithium niobate is highly stoichiometric and does not contain the intrinsic Li deficit of congruent LiNbO$_3$. Our results also show that our sol-gel material contains more defects than high quality stoichiometric LiNbO$_3$. With the aid of the chromium optical probe ions, experiments are under way to improve the quality of sol-gel LiNbO$_3$ and related ferroelectric materials.

[1] Shin-ichi Hirano, Y. Takeichi, W. Sakamoto, and T. Yogo, Journal of Crystal Growth 237-239, 2091 (2002).
[2] S. Cheng, X. Han, C. Kam, Y. Zhou, Y. Lam, J. T. Oh, X. Xu, and T. Chong, Applied Physics A 73, 511 (2001).
[3] G. Salley, S. Basun, A. Kaplyanskii, R. Meltzer, K. Polgar, and U. Happek, Journal of Luminescence 87-89, 1133 (2000).
[4] B. Henderson and G. Imbusch, Optical Spectroscopy of Inorganic Solids (Oxford University Press, Clarendon, Oxford, 1989).
[5] R. Byer, J. Young, and R. Feigelson, Journal of Applied Physics 41, 2320 (1970).
[6] P. I. Macfarlane, K. Holliday, J. F. Nicholls, and B. Henderson, Journal of Physics: Condensed Matter 7, 9643 (1995).
[7] K. Polgar, A. Peter, L. Kovacs, G. Corradi, and Z. Szaller, Journal of Crystal Growth 177, 211 (1997).
[8] G. Salley, Ph.D. thesis, The University of Georgia (2000).