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^{93}Nb NMR as a Sensitive and Accurate Probe of Stoichiometry in $LiNbO_3$ Crystals

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^{93}Nb NMR has been used to study stoichiometry variations in lithium niobate crystals. All crystals grown by the Czochralski technique are found to be lithium deficient. This may influence their susceptibility to laser damage.

The detection and measurement of variations of stoichiometry in solid-solution crystals are usually accomplished by difficult or indirect means. We have found that nuclear magnetic resonance can be a very powerful and simple technique for following changes in the stoichiometry of $LiNbO_3$ crystals. In this case, the large quadrupole coupling constant of ^{93}Nb (22.02 MHz) makes the niobium resonance quite sensitive to the defect concentration.

In order to study the change in niobium resonance with composition, specimens of lithium carbonate (99.999% from United Mineral and Chemical Corp.) and niobium pentoxide (optical grade from Kawecki Chemical and also CIBA Chemical) mixtures were hydrostatically pressed and sintered at 1100C for 2 days, then reground, repressed and resintered again at 1100C. The specimens were removed from the furnace and air cooled to room temperature in 5 min. The niobium NMR of these powders gives a second order powder spectrum. The spectra (which are derivatives of the absorption lines) for 50% Li_2O and 49% Li_2O specimens are shown in Fig. 1a,b, respectively. The large increase in the peak width of the nonstoichiometric (49%) specimen is quite evident. Even more striking is the improvement in signal to noise ratio of the 50% specimen. The half-width of the low field peak is a convenient measure of the line distortion and this width as a function of

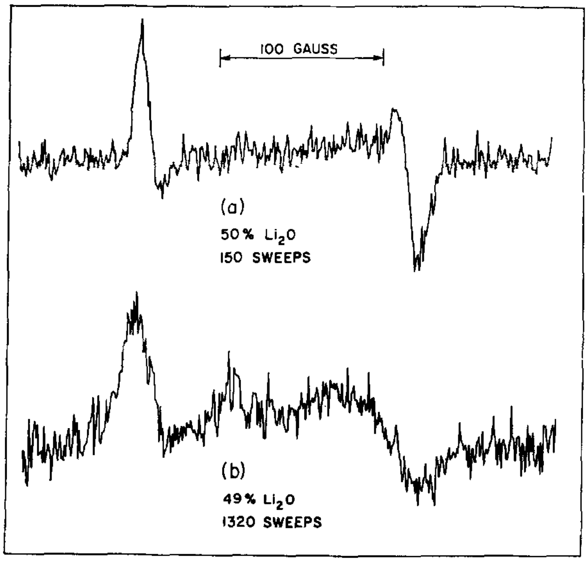

FIG. 1. ^{93}Nb NMR for (a) 50% Li_2O and (b) 49% Li_2O. The derivatives of the spectra are plotted. The oscillator frequency is ~19.24 MHz.

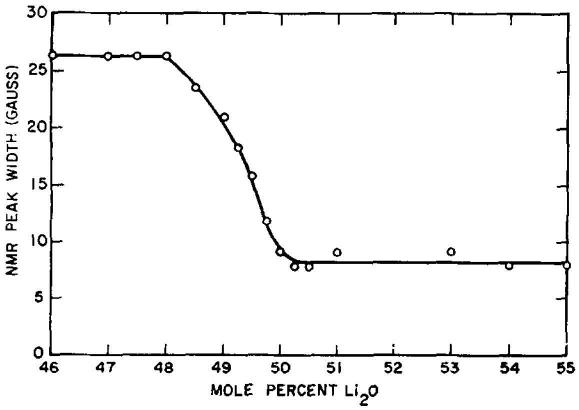

FIG. 2. Half-width of low field derivative peak as a function of composition for lithium niobate. Note that the width remains constant, as expected, outside the single-phase solid-solution region.

composition is shown in Fig. 2. The positions of the phase boundaries as determined by X-ray powder diffraction (in a Guinier camera) of the powders are near 48 and 50% Li_2O. The minimum linewidth occurs at 50% (the stoichiometric compound) indicating that the niobium nuclei all see nearly the same electric field gradients. The increase in linewidth for the niobium excess (nonstoichiometric) $LiNbO_3$ is quite remarkable and corresponds to the effects of removing lithium atoms from and inserting extra niobium atoms in the $LiNbO_3$ structure. In the two-phase regions, (20–48% and 50–75%) resonance lines from the other phase are observed in addition to that of $LiNbO_3$. The niobium resonance spectrum for the compound at 75% Li_2O is quite simple and shows a coupling constant of 11.9 MHz and quite uniform electric field gradients.

A number of $LiNbO_3$ single crystals were ground into powders and examined for comparison to Fig. 2. The most striking observation has been that all crystals grown by the Czochralski technique are lithium deficient. This verifies a recent redetermination of the phase diagram in this region (*1*) which places the congruently melting composition at 48.6% Li_2O. Such a shift in composition from the stoichiometric value of 50% Li_2O is expected if lithium vacancies form with relatively less energy than niobium vacancies (*2*). We expect such behavior on the basis of the differences between the Li–O and Nb–O bonds in $LiNbO_3$ (*3*). The phase diagram also indicates that it will be quite difficult to grow a 50% Li_2O crystal by the Czochralski technique. Growth from a liquid composition of 54% Li_2O gives crystals with niobium resonances corresponding to 49.6% Li_2O. We have prepared $LiNbO_3$ crystals from a LiCl flux and found that the stoichiometric composition (50.0%) has been achieved on the basis of the niobium resonances. However, all pulled crystals on which measurements have been published are undoubtedly lithium deficient and this may have some bearing on their susceptibility to laser damage. Previous physical properties of $LiNbO_3$ which have been measured as a function of melt composition must be related to solid composition to be meaningful. The technique described here allows this to be done.

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