Articles

Determination of Li and Nb in Congruent Lithium Niobate by ICP-MS

R. Fernández-Ruiz* and V. Bermúdez

*Departamento de Física de Materiales, Facultad de Ciencias,
Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain*

This paper reports the study undertaken to obtain a quantification method of Li and Nb in lithium niobate (LN) through an analytical chemical method. With use of a specifically designed digestion protocol, the contents of both lithium and niobium in a congruent LN monocrystalline compound have been systematically quantified by means of ICP-MS. HF and HNO_3 acid mixtures in proportions 8:2 and 6:4 turn out to be most favorable to obtain the total digestion of the compound. Under these experimental conditions, Li and Nb recovery factors between 95% and 108% together with coefficients of variation around 1% were obtained. The resulting data are enough to suggest a new model of vacancies for the congruent lithium niobate based on the combination of both lithium and oxygen vacancies.

Introduction

The precise and accurate determination of the Li/Nb fraction is a necessary condition for further use of lithium niobate (LN) in both scientific investigations and industrial applications. LN presents a combination of unique electrooptical, acoustic, piezoelectric, pyroelectric, and nonlinear optical properties which make it especially suitable for scientific and technological devices. Recent interest is mainly focused on LN nonlinear optical properties for application to laser technology[1,2] when its ferroelectric domain structure is adapted to a periodic fashion. It is well-known that many LN physical properties, such as the Curie temperature, density, refractive indexes, lattice parameters, and domain structure, are affected by the Li/Nb ratio.[3,4] These variations in the physical parameters of this material have been usually employed to determine the Li/Nb ratio through indirect techniques, such as lattice parameters or refractive index measurements.[5] However, highly precise independent determinations of both lithium and niobium contents in a crystal pose considerable difficulties when a direct chemical analysis is proposed.[6,7] Total digestion of the LN compound is the main difficulty. To the best of the authors' knowledge,

complete digestion of the LN compound and precise analytical determinations of both lithium and niobium concentrations have not yet been reached. An ongoing research project involving the study of the relationship between LN stoichiometry and physical properties of both pure and doped LN matrixes is now being carried out. As a preliminary result, the rare-earth niobium mass ratio in doped LN compounds was determined by means of TXRF.[8] Therefore, the following step of the research was to obtain a complete digestion of this kind of compound and undertake the independent quantification of Li and Nb. The main goal of this work was to obtain the independent quantification of both lithium and niobium in a LN matrix in order to understand the pattern of vacancies associated to the congruent LN crystalline lattice.

Background. In the field of physics of materials, the accepted expression for the stoichiometric composition of LN is as follows: when both the lithium and niobium concentrations in a LN compound are normalized to 100 mol %, the $Li_1 Nb_1$ stoichiometry would suppose a composition of 50 mol % for lithium and 50 mol % for niobium. If vacancies for lithium do exist, e.g., $Li_{0.97}$, the molar proportion for lithium would be then 48.5 mol %, which supposes in turn 50.3 mol % for niobium. This is due to the condition of electroneutrality as is shown in the currently accepted nonstoichiometric lithium vacancies model $[Li_{1-x}Nb_{x/5}\square_{4x/5}]NbO_3$.

Almost all commercially available LN crystals are grown from a melt of congruent by the Czochralski

* To whom correspondence should be addressed: D. Ramón Fernández Ruiz, Universidad Autónoma de Madrid, Facultad de Ciencias, Servicio Interdepartamental de Investigación, Modulo C-9, Laboratorio de TXRF, Crta. Colmenar, Km 15, Cantoblanco, 28049 Madrid, Spain. E-mail: ramon.fernandez@uam.es. Fax: +34 914973529.

(1) Agulló-López, F.; Cabrera, J. M.; Agulló-Rueda, F. *Electrooptics: Phenomena, Materials and Applications*; Academic Press: New York, 1994.
(2) Prokhorov, M.; Zuz'minov, Yu S. *Physic and Chemistry of Crystalline Lithium Niobate*; Adam Hilger: Bristol, 1990.
(3) Abrahams, S. C.; Marsh, P. *Acta Crystallogr. B* **1986**, *42*, 61.
(4) Furukawa, Y.; Sato, M.; Kitamura, K.; Yajima, Y.; Minakata, M. *J. Appl. Phys.* **1992**, *72*, 3250.
(5) Serrano, M. D.; Bermúdez, V.; Arizmendi, L.; Dieguez, E. *J. Cryst. Growth* **2000**, *210*, 670−676.

(6) Räuber, A. *Current Topics in Material Science*; North-Holland: Amsterdam, 1978; Vol. 1, p 481.
(7) Bordui, P. F.; Norwood, R. G.; Birnd, C. D.; Calvert, G. D. *J. Cryst. Grown* **1991**, *113*, 61.
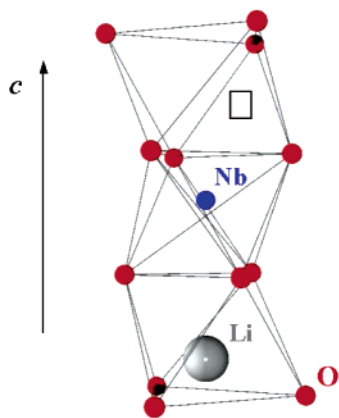(8) Fernández-Ruiz, R.; Capmany, J. *J. Anal. At. Spectrom.* **2001**, *16*, 867.

Figure 1. Polyhedral networks of the LN crystal structure along the *c* axis. The periodicity O−Li−O−Nb−O−□−O ...., where □ represents the octahedral vacant position, is shown.

Table 1. Main Defect Models in the LN Compound[a]

defect model	site structure formula	empirical formula
oxygen vacancies	$[Li_{1-2x}\square_{2x}][Nb][O_{3-x}\square_x]$	$Li_{1-2x}NbO_{3-x}$
lithium vacancies	$[Li_{1-x}Nb_{x/5}\square_{4x/5}][Nb]O_3$	$Li_{1-5x}Nb_{1+x}O_3$
niobium vacancies	$[Li_{1-5x}Nb_{5x}][Nb_{1-4x}\square_{4x}]O_3$	

[a] Site structure formula: square brackets represent lithium, niobium, and oxygen respective site crystal positions, while □ represents the vacancies in their respective site atomic positions. Empirical formula: atomic abundance by each atom without crystal position.

technique.[9] The resulting crystals are of good quality and present a high compositional uniformity. The LN can be crystallized in the range 47−50 mol % Li, as is shown in its phase diagram.[10] This fact indicates that an excess of niobium is present in the crystal, causing defects in the LN crystalline microstructure. Such defects strongly affect the properties of this crystal and may vary both the congruent and the stoichiometric composition. As Figure 1 shows, the open nature of the LN structure is apparent, as various types of polyhedral networks of the crystal structure contain large voids or interstices, which provide obvious sites for accommodated atoms.

An open field of scientific discussion is, at this point, the nature of these punctual defects. There are several models for explaining the LN vacant structure.[11] As Table 1 shows, the condition of electroneutrality in the crystal can be explained by three main models: oxygen vacancies, lithium vacancies, and niobium vacancies, respectively.

Experimental Section

Reagents. In this work, a commercial LN of congruent composition (Johnson Matthey Co, Karlsruhe, Germany) with a purity of 99.9995% and a nominal Li molar proportion of $48.55 \pm 0.04\%$ (batch no. M691902) has been used. The resulting theoretical formula, considering the lithium vacancies model (Table 1), was $Li_{0.971(1)}Nb_{1.006(1)}O_3$, whose stoichiometry supposes 4.54 ± 0.01 wt % of lithium and 63.1 ± 0.2 wt % of niobium.

Both suprapure quality reagents (Merck, Darmstadt, Germany) and ultrapure quality water (Milli-Q-Element, 18.2 MΩ)

(9) O'Bryan, H. M.; Gallagher, P. K.; Brandle, C. D. *J. Am. Ceram. Soc.* **1985**, *68*, 493.
(10) Carruthers, J. R.; Peterson, G. E.; Grasso M.; Bridenbaugh, P. M. *J. Appl. Phys.* **1971**, *42*, 1846.
(11) Zotov, N.; Boysen, H.; Frey, F.; Metzger, T.; Born, E. *J. Phys. Chem. Solids* **1994**, *55*, 145.

Table 2. Acid Mixtures Evaluated in the LN Digestion Process

acid mixture	HF (mL)	HNO_3 (mL)
AM-19	1	9
AM-28	2	8
AM-37	3	7
AM-46	4	6
AM-55	5	5
AM-64	6	4
AM-73	7	3
AM-82	8	2
AM-91	9	1

were used in this study. Nb, Li, Rh, and Be certified ICP-MS mono-elemental standards from Merck (Merck, Darmstadt, Germany) were used for calibration of the ICP-MS instrument.

Instrumentation. LN samples were digested through a high-pressure microwave digester, model Milestone ETHOS SEL, equipped with a HPR-1000/10S high-pressure rotor, with control of both temperature and pressure (Milestone, Sorisole, Italy). The same digestion program (5 steps with temperature control) was used for all the samples. The first step raised the temperature up to 140 °C in 3 min. The second step raised the temperature up to 210 °C in 5 min. The third step raised the temperature up to 225 °C in 10 min. The fourth step maintained the temperature at 225 °C for 20 min. Finally, the fifth step cooled the system for 20 min.

The resulting digestions were analyzed by an ELAN-6000 (Perkin-Elmer Sciex, Ontario, Canada) ICP-MS unit under the following instrumental conditions: RF power of 1000 W, nebulizer gas flow of 0.8 L/min, lens setting as auto lens, cross-flow nebulizer, and nickel cones. The ICP-MS acquisition settings were as follows: dwell time of 50 ms, number of sweeps equal to 30, 5 replicates, peak hopping scan mode, 1 MCA channels per peak, and dual detector mode. All the samples were analyzed under the same instrumental conditions.

Samples Preparation. The first problem to solve was the determination of the suitable acid mixture for the digestion of the LN compound. Previous studies demonstrated that the acid mixture composed of HF and HNO_3 seemed to be suitable for digesting this kind of compound.[12,13] The LN samples were dried at 80 °C for 120 min. Once the samples were cooled, aliquots around 10 mg were taken. After that, the aliquots were transferred to previously cleaned PTFE reactors. Table 2 shows the different acid mixtures used throughout the digestion process.

Once the digestion process was concluded, the reactors were then introduced into a bath of cold water for condensing the gassy phases. The content of the reactors was diluted up to 25 mL in flasks of PTFE with HNO_3 at 1%. Finally, the sample was diluted in a proportion of 1:20 for Li analysis and 1:1000 for Nb analysis. The obtained concentration of sample implies that the Li and Nb waited concentrations in the analysis were 908 and 252 ppb, respectively. Under these conditions, the samples were analyzed by ICP-MS.

ICP-MS Analysis. The quantification was carried out using external calibration curves from dilutions of certified ICP-MS mono-elemental standards (Merck, Darmstadt, Germany). The calibration curves were made as follows: ^7Li: 1000, 800, 500, and 100 ppb; ^{93}Nb: 500, 250, 100, and 50 ppb. The certified standards were diluted with a 0.5% HNO_3 and 0.5% HF dissolution. The quadratic correlation coefficients obtained in the regression lines were r^2 (^7Li) = 0.99998 and r^2 (^{93}Nb) = 0.99994. These coefficients assured the linearity in the range of concentrations investigated. Both rhodium and beryllium were used as internal standards for correcting possible instrumental drifts. As far as the lithium analysis is concerned, both ^6Li and ^7Li isotopes were focused on. To maximize the accuracy

(12) Furukawa, Y.; Kitamura, K.; Alexandrovski, A.; Route, R. K.; Fejer M. M.; Foulon, G. *Appl. Phys. Lett.* **2001**, *78*, 1979.
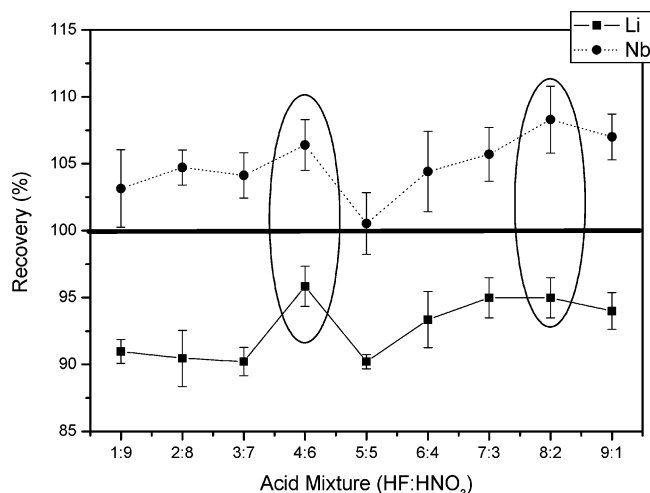(13) Collin, S.; Sakellaris, M.; William, B.; Robert, E.; Owen, J. *J. Mater. Chem.* **2002**, *12* (2), 295.

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Figure 2. Recoveries obtained as a function of the acid mixture used. Error bands represent the standard deviation associated with five digestions and analysis of each sample. Central thick line represents the 100% recovery level.

in the lithium measurements, the calibration curve was built using [7]Li intensities because it is the most abundant isotope (92.5%). The [93]Nb isotope was focused on the niobium analysis. Five replicates were carried out for each isotope analyzed. The RSD mean obtained was 1.0% for the lithium ([7]Li) and 1.3% for the niobium ([93]Nb). Each digestion was analyzed under those conditions exposed above.

Statistical Study. To estimate the grade of precision of the individual recovery measurements R, the applicable uncertainties for the R values due to the propagation of errors were calculated. Equation 1 shows the results obtained:

$$\Delta R^2 = \left(100\frac{\Delta[X]_{\text{exp}}}{[X]_{\text{theo}}}\right)^2 + \left(100\frac{[X]_{\text{exp}}}{[X]_{\text{theo}}^2}\Delta[X]_{\text{theo}}\right)^2 \quad (1)$$

where $[X]_{\text{exp}}$ and $[X]_{\text{theo}}$ are the experimental and the expected concentration obtained for lithium or niobium while $\Delta[X]_{\text{theo}}$ and $\Delta[X]_{\text{exp}}$ are the respective uncertainties for each of them. If a total recovery of the sample is assumed, it may be then supposed that $[X]_{\text{exp}} \approx [X]_{\text{theo}}$. Based upon these conditions, it can be eventually written that $100(\Delta[X]_{\text{exp}}/[X]_{\text{theo}}) \approx 100(\Delta[X]_{\text{exp}}/[X]_{\text{exp}}) = \text{RSD}_{\text{ICP-MS}}$, where $\text{RSD}_{\text{ICP-MS}}$ is the instrumental standard deviation of the ICP-MS measurements expressed as a percentage. On the other hand, the theoretical uncertainty associated with the composition of the commercial LN as $\Delta[X]_{\text{theo}}/[X]_{\text{theo}} \approx 10^{-3}$ can also be estimated. Therefore, the final error equation that has been used for estimating the uncertainty associated with each of the individual recoveries obtained was

$$\Delta R = \sqrt{(\text{RSD}_{\text{ICP-MS}})^2 + 0.01} \quad (2)$$

When multiple replicates of the recovery measures were made, the statistical average value and standard deviation were used.

Results and Discussion

Like the first approach to the problem, nine different samples and acid compositions were evaluated. Each one of them was digested and analyzed five times. The blank used in each digestion had the same acid mixture as the sample and later it was digested as a sample. Such a procedure assured that the possible interferences of N^{2+} were compensated by the blank since the high HNO_3 concentrations could affect the values of the [7]Li isotope. Therefore, if this potential interference was not corrected, the lithium determinations could be affected.
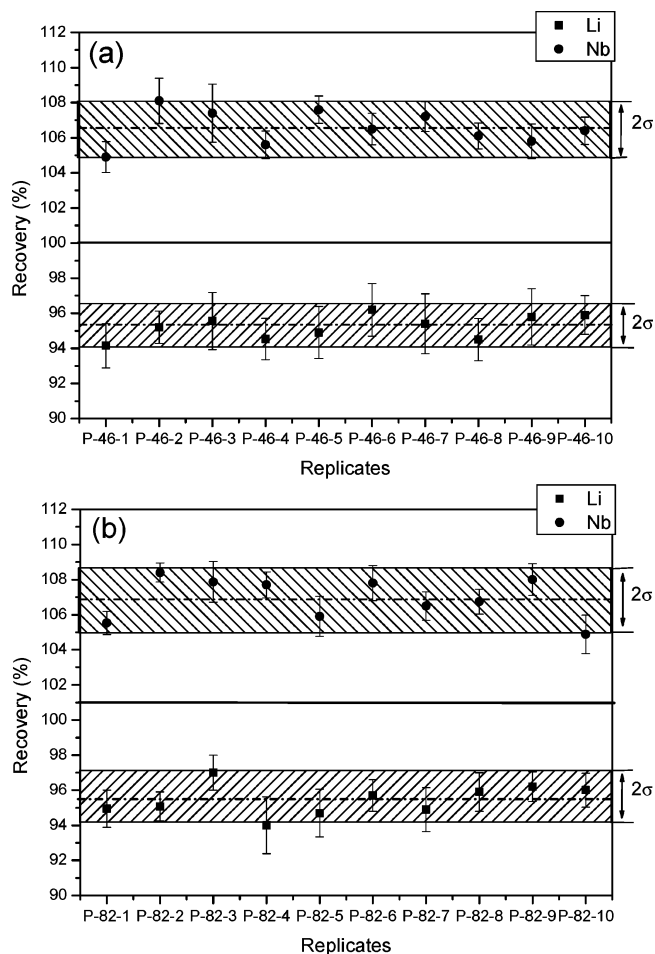

Figure 3. Lithium and niobium recoveries obtained for the acid mixture 4:6 (a) and 8:2 (b) (HF:HNO₃). Error bands represent the uncertainty associated with each digestion according to eq 2. Dotted lines represent the mean associated with the 10 independent measures and dashed areas represent their standard deviation ($n = 10$).

In addition, any other matrix effect might be corrected to ensure that all the measurements were as exact as possible. The experimental recoveries for Li and Nb were evaluated using the following equations:

$$R_{\text{Li}} = 100\frac{C_{\text{Li}}^{\text{exp}}}{C_{\text{Li}}^{\text{theo}}}, \quad R_{\text{Nb}} = 100\frac{C_{\text{Nb}}^{\text{exp}}}{C_{\text{Nb}}^{\text{theo}}} \quad (3)$$

To evaluate the recovery values, the statistical average values and the standard deviations ($n = 5$) were used. Figure 2 shows the recoveries obtained as a function of the acid mixture used.

Figure 2 shows that the concentration of Nb is systematically superior to the one of Li in the nine analyzed samples. In particular, it is appraised that for HF:HNO₃ acid mixtures 4:6 and 8:2, the recoveries for Li and Nb are superior or on the order of the other acid mixtures. Therefore, we chose these mixtures to make a more exhaustive statistical study. In the second step of the study, five additional LN samples were prepared using HF:HNO₃ 4:6 and 8:2 acid mixtures, respectively. The estimation of the bands of error for each one of the measures was calculated by means of eq 3. The Figure 3a shows lithium and niobium recoveries obtained from the acid mixture 4:6 (HF:HNO₃), while Figure 3b shows

the same element recoveries obtained for the acid mixture 8:2 ($HF:HNO_3$).

The mean recoveries ($n = 10$) obtained were as follows: (a) for an acid mixture 4:6, $R(Li) = 95.2 \pm 0.6\%$ and $R(Nb) = 106.6 \pm 0.9\%$. (b) For an acid mixture 8:2, $R(Li) = 95.3 \pm 0.9\%$ and $R(Nb) = 106.9 \pm 1.2\%$. From these results one can appreciate that recoveries obtained are nearly the same, even as far as the experimental errors are concerned. The standard deviation concerning $HF:HNO_3$ acid mixture 4:6 are smaller than those obtained with $HF:HNO_3$ acid mixture 8:2. From the safety point of view, the mixture $HF:HNO_3$ 8:2 is less dangerous than the $HF:HNO_3$ 4:6 since the first reaches a pressure of 24 bar while the latter reaches 32 bar in the digestion processes. Accordingly, both acid mixtures are suitable ones for undertaking the complete digestion of the LN samples. The fact that recovery results do not change no matter the acid mixture used, even as far as the experimental errors are concerned, it is indicative that, in both cases, the digestion of the LN compound is complete. Consequently, Figures 3a and 3b suggest that the initial stoichiometry ($Li_{0.971(1)} Nb_{1.006(1)}O_3$) is not correct. The new proposed stoichiometry will be, therefore, 0.925 ± 0.008 atoms of lithium and 1.07 ± 0.01 atoms of niobium per molecule of LN. The atomic oxygen content was obtained by a difference of masses and the result was of 2.64 ± 0.02 atoms per molecule. The LN formula can then be written as $Li_{0.925(8)}Nb_{1.07(1)}O_{2.64(2)}$. This result is not in agreement with the models of vacancies shown in Table 1. The results suggest the coexistence of lithium and oxygen vacancies. Therefore, it seems necessary to review the models of vacancies proposed up to now for the LN. An exhaustive study by means of neutron diffraction is being carried out by the authors to verify the compatibility of these results with a suitable model of vacancies.

Conclusion

The spectroscopic technique of ICP-MS may provide precise and accurate enough independent determinations to characterize the composition and stoichiometry of Li and Nb in LN compounds. The study carried out in this work shows that a total digestion of the lithium niobate compound with around 100% recoveries can be obtained with coefficients of variation around 1%. A specifically designed high-pressure microwave digestion protocol seems to be an efficient method to completely digest the lithium niobate when HF and HNO_3 acids, in the relation 8:2 or 4:6, respectively, are used. The 1% variation coefficient obtained in the recoveries of both lithium and niobium are enough for questioning the lithium niobate models of vacancies currently in use in the physics of materials science. The chemical formula $Li_{0.925(8)}Nb_{1.07(1)}O_{2.64(2)}$ obtained in this study suggest the coexistence of lithium and oxygen vacancies. There were no experimental evidences, up today, that different models of vacancies could coexist. A new detailed study of the models of vacancies by means of neutron and X-ray diffraction is necessary. The developed analytical method will allow analyzing this type of material as well as similar materials like the lithium tantalate (LT) and the mixed phases LN−LT.

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