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SPECIAL TOPICS

Effect of optical damage resistant dopants on the dielectric properties of LiNbO₃: Insight from broadband impedance spectroscopy and Raman scattering

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Optical damage limits the application range of congruent LiNbO₃. This problem is commonly overcome by adding optical-damage-resistant cations. Here, the influence of doping with optical-damage-resistant Mg and Zn on the ionic and piezoelectric contributions to the dielectric permittivity is investigated in a broad frequency range (1 mHz–2 THz). It is shown that the two dopants have radically different influences on the variation of ionic permittivity with doping, in spite of their similarities with respect to the crystallographic structure. Raman spectroscopy reveals that the difference in permittivity can be traced to the effect of Mg and Zn doping on the susceptibility of the phonon modes. Both observations point to differences in the defect incorporation mechanisms. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5021758>

I. INTRODUCTION

Since its first growth in the 1960s,¹ lithium niobate LiNbO₃ (LN), has attracted a lot of interest owing to its large variety of properties ranging from ferroelectricity to electro-optic properties or photorefractivity.² It was already realized at that time that congruently grown LN deviated strongly from the stoichiometric composition. Indeed, congruent LN exhibits a [Li]/[Nb] ratio of about 0.94, i.e., 6% off the stoichiometric composition. Despite this large number of defects, congruent LN has been used in a variety of applications such as surface acoustic wave devices.

This lower content of Li can be understood in terms of outdiffusion of Li₂O during the growth process.³ Several mechanisms of charge compensation can be envisioned and have been debated in the early 1990s.^{4,5} Today, the so-called *Li site vacancy model* is the one favored. In this model, some of the Li vacancies are replaced by Nb atoms in the antisite. In this case, using Kröger-Vink notations, the chemical formula of congruent LN can be written as

where the braces group the atoms on the Li site.

It was very soon recognized that these defects make LN extremely sensitive to optical damage.^{6,7} To overcome this limitation, enormous efforts were deployed to grow defect-free stoichiometric LN. Simultaneously, different dopants were incorporated in congruent LN not only to reduce optical damage (Mg, Zn, Sc, and In) but also to tailor its properties to one's need, like Fe is used to enhance the bulk photovoltaic effect.⁸

Doping with these specific cations has proven very successful in strongly decreasing the optical damage induced by high laser power without any deterioration of the optical properties of interest. The ability to reduce optical damage while maintaining exceptional optical properties has allowed to design compact laser systems at high wavelengths^{9,10} and optical parametric oscillators.¹¹ Additionally, doping with damage-resistant cations causes a decrease in the coercive field and a shift of the absorption edge to shorter wavelengths.¹² The former is particularly advantageous for the preparation of periodically poled LN (PPLN) used for quasi-phase matching frequency conversion, while the latter becomes an asset for holographic recording.

Reduction of optical damage appears abruptly at the doping level above a *threshold* composition, which itself depends on the cation used as a dopant (e.g., ~5 mol. % for Mg doping and ~7 mol. % for Zn doping). At low concentrations, dopants are incorporated on the Li site. Notably, their incorporation decreases the Nb in the antisite up to the threshold composition above which this type of defect disappears. Above the threshold composition, dopants sit on both the Li and Nb sites. Despite the extensive research on the influence of dopants on the defect structure,^{13–16} the exact mechanism for defect compensation when doping with damage resistant ions is not fully understood yet and may depend on the nature of the dopants and the growth conditions.³

Naturally, the impact of doping on the optical and electro-optic properties of LN has been at the center of numerous research studies, whereas its effect on other properties of LN has attracted less attention. In particular, the influence of dopants on the dielectric permittivity at low

frequencies has attracted only sporadic interest,^{17–19} in spite of the relevance of dielectric measurements for discussions on defects in general and defect mobility in particular.

In this work, the effect of optical damage resistant dopants, namely Zn and Mg, on the dielectric properties is systematically investigated. It is shown that these two dopants influence the ionic permittivity differently. These results are put in perspective with Raman spectroscopy in order to get a better understanding of the origin of these differences.

II. EXPERIMENTAL DETAILS

In this study, plates of congruently grown single crystals of undoped, Zn- and Mg-doped LN provided by Impex GmbH (Rheine, Germany) were used. Mg-doped LN was characterized as square plates ($10 \times 10 \times 0.5 \text{ mm}^3$) with doping concentrations ranging from 1.5 mol. % to 5.5 mol. %, whereas the properties of Zn-doped LN were determined using rectangular plates ($10 \times 8 \times 1 \text{ mm}^3$) with doping concentrations between 5.5 mol. % and 9 mol. %. The crystals were oriented along either the z or x axes depending on the composition. Both z and x -oriented plates were employed for the characterization of pure LN.

The two room temperature components of the dielectric permittivity $\epsilon_{11}^* = \epsilon'_{11} + j\epsilon''_{11}$ and $\epsilon_{33}^* = \epsilon'_{33} + j\epsilon''_{33}$ were determined based on impedance measurements from 1 mHz to 10 MHz carried out using a Novocontrol Concept 40 dielectric spectrometer. At higher frequencies, the dielectric permittivity was evaluated based on refractive index measurements: $n^* = \sqrt{\epsilon^* \mu^*}$ with $\mu^* = 1$ in the case of LN. The refractive index was determined in the free-space quasi-optical setup, in the W-band (70–110 GHz),²⁰ and using a commercial Menlo terahertz time domain spectrometer (THz-TDS) from 200 GHz to 1.5 THz.

Raman scattering experiments were performed at room temperature on a Renishaw inVia spectrometer using a red excitation (633 nm).

III. RESULTS AND DISCUSSION

The dispersion of the real part of the dielectric permittivity ϵ' over the entire frequency range is similar for all doping concentrations. It is exemplified in Fig. 1 with the

FIG. 1. Example of dielectric dispersion for congruent LN, LN doped with 4.5% Mg, and LN doped with 6.5% Zn at room temperature.

presentation of ϵ'_{11} for undoped LN, and LN doped with 4.5 mol. % Mg and with 6.5 mol. % Zn. Regardless of the doping, the same features can be observed: two plateaus separated by piezoelectric resonances. At high frequencies ($>100 \text{ MHz}$), the dielectric permittivity results from the electronic and ionic contributions. At the highest frequency limit measured here, the permittivity increases slightly due to the onset of a phonon mode. At low frequencies ($<40 \text{ kHz}$), the piezoelectricity of LN adds another contribution to these two.²¹

To detail the effect of Mg and Zn doping on these contributions, the ionic and the piezoelectric contributions to the permittivity are plotted separately as a function of doping concentration in Figs. 2 and 3, respectively, and will be discussed individually in the following. For simplicity, we call here “ionic contribution” to the permittivity ϵ_{ion} a value that in fact contains the sum of the ionic and electronic contributions. Since the latter shows no dependence on Mg or Zn doping,^{22,23} the discussion remains correct nonetheless.

A. Ionic contribution

Our previous work²¹ on undoped congruent LN single crystals demonstrates that no dielectric relaxation is observed between the resonances associated with piezoelectricity

FIG. 2. Effect of Mg and Zn doping on the ionic contribution to the room temperature dielectric permittivity. The green circles represent ϵ'_{11} and the orange squares represent ϵ'_{33} . The open and filled symbols depict data obtained at 90 GHz and 0.75 THz, respectively. The dielectric permittivity measured at 0.75 THz reported in Ref. 24 is displayed in darker triangles for comparison. The dashed lines are a guide to the eye.

FIG. 3. Piezoelectric contribution to the dielectric permittivity as a function of Mg (yellow) and Zn (blue) doping normalized to the threshold value (doping concentration/threshold composition). The piezoelectric contribution is calculated as the difference between the ionic permittivity and the permittivity measured at 1 kHz. The markers are of the size of the errorbars.

around 5 MHz and the resonances observed due to phonons (above 5 THz), indicating that the ionic permittivity can be determined measuring either the *clamped* permittivity (characterized at frequencies above piezoelectric resonances) or permittivity at higher frequencies. In this study, the ionic contribution to the permittivity is determined based on measurements performed at 90 GHz and 0.75 THz, since the two values are far from any resonances. These two values are in good agreement with one another and with the available literature²⁴ (Fig. 2).

For both dopants, the ionic contribution $\epsilon'_{33,ion}$ is not strongly affected by doping although a limited decrease in the permittivity can be observed when increasing the Mg content in LN. On the other hand, the Zn and Mg dopants affect $\epsilon'_{11,ion}$ differently. Indeed, Zn-doped LN presents a permittivity that is constant up to a threshold composition, where it increases abruptly. Above the threshold composition, the dielectric constant of LN:Zn shows again no dependence on the Zn content. In the case of Mg doping, the permittivity increases steadily up to the threshold composition where it reaches its maximum and decreases suddenly for larger Mg doping.

Thus, it appears that the two components of the ionic permittivity are influenced very differently by the doping and that Mg and Zn doping have different effects on the permittivity.

B. Piezoelectric contribution

Piezoelectricity contributes to the permittivity at frequencies below the piezoelectric resonances, i.e., below 40 kHz. Hence, the piezoelectric contribution to the low-frequency permittivity can be determined as the difference between the dielectric constant measured at frequencies below the piezoelectric resonances (e.g., 1 kHz) and the ionic permittivity: $\epsilon'_{piezo} = \epsilon'(1 \text{ kHz}) - \epsilon'_{ion}$. The influence of Zn and Mg doping on the piezoelectric permittivity is presented in Fig. 3.

The increase in either Mg or Zn concentration has the same effect on the piezoelectric contribution to permittivity: $\epsilon'_{11,piezo}$ decreases while $\epsilon'_{33,piezo}$ remains constant. This effect

of doping on the two components of ϵ' differs owing to their contrasting magnitude: $\epsilon'_{33,piezo}$ is nearly negligible due to the low corresponding piezoelectric coefficients d_{31} and d_{33} .²¹ In contrast, LN is known for its large d_{15} and d_{22} inducing the large value of $\epsilon'_{11,piezo}$, making it more sensitive to doping. Nevertheless, it appears clearly that the two optical-damage resistant dopants considered here, Zn and Mg, have similar impacts on the piezoelectric contribution to the permittivity.

C. Raman spectroscopy

Raman spectroscopy can probe subtle changes in the structure²⁵ and, in polar crystals, where polar phonon modes are also Raman active, the dielectric contribution of each phonon mode can be calculated from the experimentally obtained spectra.²⁶ Both are intimately linked, because the ionic permittivity describes the response/movement of the ions to an electric field. In simple cases, and in particular, in the case of LN, the dielectric response of the phonons can be modeled as the superposition of damped harmonic oscillators (DHOs), so that the dielectric contribution ϵ_i of the i th transverse optical phonon can be written as

$$\epsilon_i(\omega) = \frac{\Delta\epsilon_i \omega_{TO_i}^2}{\omega_{TO_i}^2 - \omega^2 - j\omega\gamma_i}, \quad (2)$$

where ω_{TO_i} is the frequency of the phonon, γ_i is its damping, and $\Delta\epsilon_i$ is the oscillator strength. For frequencies far below the phonon frequencies, the dielectric contribution of the i th phonon is given by the oscillator strength $\Delta\epsilon_i$, whereas γ_i and ω_{TO_i} are of major influence only for frequency close to ω_{TO_i} . The contribution of a specific phonon mode to the permittivity depends on its symmetry: in LN, the longitudinal A_1 -modes contribute to ϵ'_{33} , while the transverse E-modes lead to the development of ϵ'_{11} .

In general, the Raman scattered intensity is expressed as^{26,27}

$$I(\omega) = K[n(\omega) + 1]\epsilon''(\omega), \quad (3)$$

where ϵ'' is the imaginary part of the permittivity, $[n(\omega) + 1]$ is the Bose-Einstein population factor for the Stokes scattering, and K is a factor dependent on the experimental conditions. Replacing $\epsilon''(\omega)$ in Eq. (3) by the value derived from the DHO [Eq. (2)], the oscillator strength can be derived

$$\Delta\epsilon_i = I(\omega_{TO_i}) \frac{\gamma_i}{\omega_{TO_i} K [n(\omega_{TO_i}) + 1]}. \quad (4)$$

Therefore, it appears clearly that the dielectric contribution of a phonon mode is given by the intensity of the Raman mode, as well as its position and damping. A detailed study of the effect of doping on the different Raman modes is then a natural starting point to the understanding of the different effects of Zn or Mg doping on the ionic contribution of LN.

Figure 4 presents the Raman spectra for all samples considered in this study. With our crystal orientations and scattering geometries, it is expected from the selection rules that all Raman active mode except for E(LO) can be observed (Table I). Actually, despite the fact that the E(LO) modes

FIG. 4. Examples of Raman spectra measured at room temperature obtained in this study. The spectra were chosen to exemplify all possible selection rules available in our experiment (Table I): (a) $A_1(LO) + E(TO)$, (b) $E(TO)$, (c) $A_1(TO)$, (d) $E(TO)$, and (e) $A_1(TO) + E(TO)$. The $E(LO)$ modes^{25,37} that are forbidden by symmetry are highlighted in (e) by arrows. Relevant details for the discussion are highlighted in Figs. 5–7.

should not be accessible, they are clearly visible in the $X(YY)\bar{X}$ spectrum when LN is doped with either Zn or Mg [Fig. 4(e)]. Therefore, it appears that doping leads to a breaking of the selection rules in LN.

In addition, Raman bands present the usual broadening related to doping. It can be seen for example in Figs. 5 and 6. It is particularly interesting to note that the $A_1(TO_2)$ mode is more affected by doping than the $A_1(TO_1)$ mode. This has been attributed in the past to the fact that the two modes

probe different movements of Li or Nb.²⁵ In fact, the $A_1(TO_2)$ mode describes essentially the z vibration of Li ions in antiphase to Nb with respect to a relatively rigid oxygen cage, whereas the TO_1 mode can be seen as Nb vibrating in antiphase with the oxygen sublattice while leaving Li relatively static²⁸ so that it is naturally less affected by substitution on the Li site.

Furthermore, changes in the position can be observed for some Raman bands (see, for example, the inset of Fig. 5).

TABLE I. Expected modes according to selection rules accessible in the present experiment.

Configuration	Expected modes according to selection rules
$X(Y\bar{Y})\bar{X}$	$A_1(\text{TO}) + E(\text{TO})$
$X(Z\bar{Z})\bar{X}$	$A_1(\text{TO})$
$X(Y\bar{Z})\bar{X}$	$E(\text{TO})$
$X(Z\bar{Y})\bar{X}$	$E(\text{TO})$
$Z(X\bar{X})\bar{Z}$	$A_1(\text{LO}) + E(\text{TO})$
$Z(Y\bar{Y})\bar{Z}$	$A_1(\text{LO}) + E(\text{TO})$
$Z(X\bar{Y})\bar{Z}$	$E(\text{TO})$
$Z(Y\bar{X})\bar{Z}$	$E(\text{TO})$

FIG. 5. Comparison of $A_1(\text{TO})$ Raman spectra in Zn-, Mg-doped, and undoped LN crystals. The spectra were all normalized to the intensity of the $A_1(\text{TO}_1)$ mode. (Inset) illustration of the shift in the peak position induced by doping. The spectra were normalized to the maximum intensity. FIG. 6. Comparison of $E(\text{TO})$ Raman spectra in Zn-, Mg-doped and undoped LN crystals. Spectra were normalized to the maximum intensity and shifted for clarity.

With Zn and Mg doping, evolution in the relative intensity between several Raman bands can be indubitably observed. For example, the intensity of all $A_1(\text{TO})$ peaks decreases in comparison with the $A_1(\text{TO}_1)$ mode in Fig. 5. Changes in relative intensity are also observed for bands with different symmetries: Fig. 7 not only highlights the changes in relative intensities between different $A_1(\text{LO})$ modes, but also

FIG. 7. Comparison of $A_1(\text{LO})$ and E Raman spectra in Zn-, Mg-doped and undoped LN crystals. The spectra were all normalized to the intensity of the $E(\text{TO}_3)$ mode (236 cm^{-1}).

between these modes and the E modes. In summary, doping with Zn or Mg influences very strongly the Raman spectra in terms of the peak position, width, and relative intensity.

It is also clear that Zn and Mg influence differently the position of the phonon modes, indicating that indeed these two dopants have different effects on the structure. Our observations are consistent with similar systematic investigations in the literature,^{29–31} with shifts of the order a few wavenumbers at most, and a behaviour that may be linear or non-linear as a function of the doping concentration (spectra are given as the [supplementary material](#)). For both types of dopants, it was found that the width of the bands shows almost no dependence for below threshold compositions and increases with larger doping. On the other hand, the position of the peaks varies differently depending on the phonon modes considered and the dopant: Mg keeps the position of most bands unaltered except the $A_1(\text{TO}_2)$ and $A_1(\text{TO}_3)$, which are shifted to lower frequencies, whereas Zn tends to favor a decrease in the frequency of most phonon modes.

In principle, it should be possible to quantify the contribution of each phonon mode and identify their atomic vibration patterns in order to gain more insight into the structural aspects of doping. However, this is particularly challenging here for a number of reasons. First, the transverse permittivity ϵ_{11} is more complex than the longitudinal ϵ_{33} because of the larger number of phonons involved (9 E modes vs. 4 A_1 modes). Besides, examination of the eigenvectors for the E modes calculated in Ref. 28 shows that they do not have very clearly distinguishable atomic displacements patterns, but more or less involve motions of all atoms, and as such are less sensitive to modifications at a specific atomic site. Last, experimentally comparing Raman intensities from sample to sample is always challenging and comes with many uncertainties (absorption corrections, possible miscuts, etc.), while the change in permittivity remains relatively modest (about 10%–20% at most). At this stage, it appears unlikely that the variations in permittivity can be reduced to a simple contribution; this is left for future studies.

D. Consequences for the dopant incorporation mechanism

Literature usually indicates that both Zn and Mg tend to incorporate in LN in a similar way above and below their threshold composition, and as such have a very similar effect on the crystal structure of LN.⁸ Both tend to increase the unit cell volume^{32,33} and sit on the Li-site for doping concentration below the threshold and on both sites above it.^{34,35} Yet, to this date, the precise incorporation mechanism related to this substitution is not fully understood.³ At doping levels below the threshold, the dopant goes on the Li site and favors a decrease in the niobium in antisite $\text{Nb}_{\text{Li}}^{4+}$. Two possible scenarios can be considered. The first is a two-step process where the dopant first substitutes all $\text{Nb}_{\text{Li}}^{4+}$ and only then starts to replace lithium on its site Li_{Li} . The second scenario assumes that these two substitutions happen simultaneously, leading ultimately to the disappearance of all $\text{Nb}_{\text{Li}}^{4+}$. In this picture, already at the threshold, the dopant will be situated on both Li and Nb sites, in a ratio that depends on their respective energetic cost.

He and Xue³⁶ showed using the bond valence model that the energy cost is lower for Zn to sit on the Li site than for Mg and conversely that it costs more energy for Zn to be located on the Nb site than for Mg. These (small) differences in energy cost might lead to slight differences in the substitution and defect compensation mechanisms. Indeed, below the threshold, Zn would simultaneously replace $\text{Nb}_{\text{Li}}^{4+}$ and Li_{Li} , while Mg would favor a two step substitution mechanism. Above the threshold, the difference in energy cost for Zn and Mg to go on the Li or Nb sites can lead to a slightly different amount of Zn or Mg going on either of the sites.

It is worth noting that this difference between the incorporation mechanism of Zn and Mg is consistent with the fact that the two dopants exhibit different threshold compositions. Indeed, it is usually considered that the threshold composition corresponds to the value above which there is no Nb in antisite left. As Mg would favor taking the place of Nb atoms, all incorporated Mg atoms would decrease the amount of $\text{Nb}_{\text{Li}}^{4+}$, whereas all Zn would not push the Nb back on its site as Zn substitutes simultaneously both $\text{Nb}_{\text{Li}}^{4+}$ and Li_{Li} necessitating a larger amount of Zn to annihilate all antisite Nb.

Here, our data both from dielectric measurements and Raman spectroscopy point out differences between Zn and Mg-doped samples, visible in the values of the ionic contribution to the dielectric constant, and the alterations of the Raman spectrum. Even though our analysis does not allow for a quantification of defect populations, it clearly supports the hypothesis of two different incorporation mechanisms for Zn and Mg.

IV. SUMMARY AND CONCLUSION

The dielectric properties of congruently grown undoped, Zn- and Mg-doped LN crystals were measured in a wide frequency range: 1 mHz to 2 THz. The influence of doping on the different contributions to the two components of permittivity was systematically investigated. It was shown that Zn and Mg have similar effects on ϵ'_{33} , while they have different

effects on the ionic contribution of ϵ'_{11} . This dopant dependence comes as a surprise as it is usually accepted that Zn and Mg have similar effects on the crystallographic structure.

Investigation using Raman spectroscopy was undertaken to get a better understanding of the origin of this difference. It appears that the difference is reflected in changes in the oscillator strengths of the phonon modes. This corroborates the dielectric measurements and supports the idea of differences in the defect incorporation mechanism for Zn and Mg. However, it was not possible to single out a particular mode responsible for the effect.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the raw Raman spectra obtained during the course of this work.

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- ¹A. A. Ballman, "Growth of piezoelectric and ferroelectric materials by the Czochralski technique," *J. Am. Ceram. Soc.* **48**(2), 112–113 (1965).
- ²K. K. Wong, *Properties of Lithium Niobate* (INSPEC, 2002).
- ³T. Volk and M. Wöhlecke, *Lithium Niobate Defects, Photorefractive and Ferroelectric Switching* (Springer, 2008).
- ⁴H. Donnerberg, S. M. Tomlinson, C. R. A. Catlow, and O. F. Schirmer, "Computer-simulation studies of intrinsic defects in LiNbO_3 crystals," *Phys. Rev. B* **40**(17), 11909–11916 (1989).
- ⁵A. P. Wilkinson, A. K. Cheetham, and R. H. Jarman, "The defect structure of congruently melting lithium niobate," *J. Appl. Phys.* **74**(5), 3080–3083 (1993).
- ⁶H. B. Serreze and R. B. Goldner, "Study of the wavelength dependence of optically induced birefringence change in undoped LiNbO_3 ," *Appl. Phys. Lett.* **22**(12), 626–627 (1973).
- ⁷A. Ashkin, G. D. Boyd, J. M. Dziedzic, R. G. Smith, A. A. Ballman, J. J. Levinstein, and K. Nassau, "Optically-induced refractive index inhomogeneities in LiNbO_3 and LiTaO_3 ," *Appl. Phys. Lett.* **9**(1), 72–74 (1966).
- ⁸T. Volk, M. Wöhlecke, N. Rubinina, A. Reichert, and N. Razumovski, "Optical-damage-resistant impurities (Mg, Zn, In, Sc) in lithium niobate," *Ferroelectrics* **183**(1), 291–300 (1996).
- ⁹J. Q. Yao, W. Q. Shi, J. E. Millerd, E. Garmire, and M. Birnbaum, "Room-temperature 1.06-0.53- μm second-harmonic generation with $\text{MgO}:\text{LiNbO}_3$," *Opt. Lett.* **15**(23), 1339–1341 (1990).
- ¹⁰J. L. Nightingale, W. J. Silva, G. E. Reade, A. Rybicki, W. J. Kozlovsky, and R. L. Byer, "Fifty percent conversion efficiency second harmonic generation in magnesium oxide doped lithium niobate," *Proc. SPIE* **0681** (1987).
- ¹¹M. Bode, P. K. Lam, I. Freitag, A. Tunnermann, H. Bachor, and H. Welling, "Continuously-tunable doubly resonant optical parametric oscillator," *Opt. Commun.* **148**, 117–121 (1998).
- ¹²T. Volk, M. Wöhlecke, and N. Rubinina, "Optical damage resistance in lithium niobate," in *Photorefractive Materials and Their Applications* (Springer, 2007), Vol. 2, pp. 165–203.
- ¹³T. S. Chernaya, B. A. Maksimov, T. R. Volk, N. M. Rubinina, and V. I. Simonov, "Zn atoms in lithium niobate and mechanism of their insertion into crystals," *JETP Lett.* **73**(2), 103–106 (2001).
- ¹⁴H. Donnerberg, "Comments on the defect chemistry of magnesium-doped lithium niobate (LiNbO_3)," *J. Solid State Chem.* **123**(2), 208–214 (1996).
- ¹⁵S. Sulyanov, B. Maximov, T. Volk, H. Boysen, J. Schneider, N. Rubinina, and Th. Hansen, "Neutron and X-ray study of stoichiometric and doped $\text{LiNbO}_3:\text{Zn}_{0.08}$," *Appl. Phys. A* **74**, s1031–s1033 (2002).

- ¹⁶B. C. Grabmaier, W. Wersing, and W. Koestler, "Properties of undoped and MgO-doped LiNbO₃: correlation to the defect structure," *J. Cryst. Growth* **110**, 339 (1991).
- ¹⁷P. C. Barbosa, J. A. C. de Paiva, J. M. Filho, A. C. Hernandez, J. P. Andreeta, and A. S. B. Sombra, "Dielectric relaxation process and pyroelectric currents in LiNbO₃: Fe single crystals," *Phys. Status Solidi* **125**, 723–729 (1991).
- ¹⁸T. Granzow, "Polaron-mediated low-frequency dielectric anomaly in reduced LiNbO₃: Ti," *Appl. Phys. Lett.* **111**, 022903 (2017).
- ¹⁹N. Meyer, G. F. Nataf, and T. Granzow, "Field induced modification of defect complexes in magnesium-doped lithium niobate," *J. Appl. Phys.* **116**(24), 244102 (2014).
- ²⁰C. Cochard, T. Spielmann, M. K. Matters-Kammerer, A. R. van Dommele, A. Halpin, J. Gomez-Rivas, and T. Granzow, "Tunable polar dielectrics for applications at millimeter wavelengths," in *2016 41st International Conference on Infrared, Millimeter, Terahertz Waves* (IEEE, 2016), pp. 1–2.
- ²¹C. Cochard, T. Spielmann, A. Halpin, and T. Granzow, "Broadband characterization of congruent lithium niobate from mHz to optical frequencies," *J. Phys. D: Appl. Phys.* **50**, 36LT01 (2017).
- ²²U. Schlarb and K. Betzler, "Influence of the defect structure on the refractive indices of undoped and Mg-doped lithium niobate," *Phys. Rev. B* **50**(2), 751–757 (1994).
- ²³U. Schlarb, B. Matzas, A. Reichert, K. Betzler, M. Wöhlecke, B. Gather, and T. Volk, "Refractive indices of Zn/In-co-doped lithium niobate," *Ferroelectrics* **185**(1), 269–272 (1996).
- ²⁴M. Unferdorben, Z. Szaller, I. Hajdara, J. Hebling, and P. Laszlo, "Measurement of refractive index and absorption coefficient of congruent and stoichiometric lithium niobate in the terahertz range," *J. Infrared, Millimeter, Terahertz Waves* **36**(12), 1203–1209 (2015).
- ²⁵M. D. Fontana and P. Bourson, "Microstructure and defects probed by Raman spectroscopy in lithium niobate crystals and devices," *Appl. Phys. Rev.* **2**(4), 040602 (2015).
- ²⁶A. Ridah, M. Fontana, and P. Bourson, "Temperature dependence of the Raman modes in LiNbO₃ and mechanism of the phase transition," *Phys. Rev. B* **56**(10), 5967–5973 (1997).
- ²⁷M. DiDomenico, S. H. Wemple, S. P. S. Porto, and R. P. Bauman, "Raman spectrum of single-domain BaTiO₃," *Phys. Rev.* **174**(2), 522–530 (1968).
- ²⁸V. Caciuc, A. Postnikov, and G. Borstel, "Ab initio structure and zone-center phonons in LiNbO₃," *Phys. Rev. B* **61**(13), 8806–8813 (2000).
- ²⁹K. Lengyel, L. Kovács, Á. Péter, K. Polgár, and G. Corradi, "The effect of stoichiometry and Mg doping on the Raman spectra of LiNbO₃:Mg crystals," *Appl. Phys. B: Lasers Opt.* **87**(2), 317–322 (2007).
- ³⁰M. L. Hu, C. T. Chia, J. Y. Chang, W. S. Tse, and J. T. Yu, "Low-temperature Raman study of zinc-doped lithium niobate crystal powders," *Mater. Chem. Phys.* **78**(2), 358–362 (2003).
- ³¹R. Mouras, M. D. Fontana, P. Bourson, and A. V. Postnikov, "Lattice site of Mg ion in LiNbO₃ crystal determined by Raman spectroscopy," *J. Phys.: Condens. Matter* **12**, 5053–5059 (2000).
- ³²F. Abdi, M. Aillerie, M. Fontana, and P. Bourson, "Influence of Zn doping on electrooptical properties and structure parameters of lithium niobate crystals," *Appl. Phys. B* **68**, 795–799 (1999).
- ³³N. Iyi, K. Kitamura, Y. Yajima, S. Kimura, Y. Furukawa, and M. Sato, "Defect structure model of MgO-doped LiNbO₃," *J. Solid State Chem.* **118**, 148–152 (1995).
- ³⁴T. Volk, B. Maximov, T. Chernaya, N. Rubinina, M. Wöhlecke, and V. Simonov, "Photorefractive properties of LiNbO₃: Zn crystals related to the defect structure," *Appl. Phys. B* **72**, 647–652 (2001).
- ³⁵A. V. Yatsenko, S. V. Yevdokimov, D. Y. U. Sugak, and I. M. Solskii, "NMR analysis of Mg ion localization in LiNbO₃ crystal," *Acta Phys. Pol., A* **117**(1), 166–169 (2010).
- ³⁶X. He and D. Xue, "Doping mechanism of optical-damage-resistant ions in lithium niobate crystals," *Opt. Commun.* **265**, 537–541 (2006).
- ³⁷S. Margueron, A. Bartaszyte, A. M. Glazer, E. Simon, J. Hlinka, I. Gregora, and J. Gleize, "Resolved E-symmetry zone-centre phonons in LiTaO₃ and LiNbO₃," *J. Appl. Phys.* **111**(10), 104105 (2012).