Hydrostatic-pressure dependence of Raman-active optical phonons in Nd:Mg:LiNbO$_3$

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Abstract

In this work, we report the frequency variation of Raman phonon modes of a doped Nd:Mg:LiNbO$_3$ crystal under high hydrostatic pressure up to 6.5 GPa. Whereas most of the phonon modes are not affected by doping, showing the same pressure dependence of their frequency as for undoped LiNbO$_3$, there are three exceptions: The A$_1$(TO)$_2$, the A$_1$(TO)$_3$ and the E(TO)$_4$ phonons. These modes exhibit a considerably different pressure coefficient, which is mainly attributed to the influence of Mg ions occupying Nb-sites in the lithium niobate matrix.

Lithium niobate (LNB) is a ferroelectric crystal with a high Curie temperature, which has several technological applications in optical communications, photonics, acousto-optics, etc. In general, LNB is mainly used as a substrate for waveguide fabrication, being a key element in different integrated photonic devices [1,2]. The ~~Nd- doping~~ Nd-doping makes this material an useful luminescent system for lasing action and frequency doubling [3,4] ~~[3–5].~~ Complementary, the Mg-ions are commonly added to the LiNbO$_3$ lattice because this increases the resistance to optical damage originated by the photo-refractive effect [5,6] ~~[6]~~. Due to these properties, Nd:Mg:LiNbO$_3$ has been massively used as bulk material for waveguide fabrication employing different techniques such as proton exchange, Zn or Ti diffusion and femtosecond laser writing [7–10]. Among these techniques, femtosecond laser writing is relatively novel (1996, [11]) and is in constant development. Within this feasible "one-step" method, a kind of a so-called "type II" waveguide was extensively studied [12], because it can be generated in several optical materials and can also preserve its optical guidance properties after high temperature treatment [13]. This kind of waveguide ("type II") is produced by the mechanical expansion during/after the non-linear interaction between the writing laser and the bulk material. As it is well known, the residual strain field after this interaction leads to waveguide formation [14]. To characterize this microscopic waveguiding region, μ-Raman spectroscopy was used in various works ~~papers~~[12,14] ~~[12,14–16]~~. However, to carry out a quantitatively computing of the residual strain field ~~and~~, thus, to estimate the refractive index variation in the mentioned waveguides, the phonon deformation potentials or, at least, the phonon frequency shifts under hydrostatic pressure are needed [15] ~~[16]~~. Also, the phonon frequency shifts under hydrostatic pressure are useful to determine the phonon deformation potential constants by using pseudo-numerical methods [15] ~~[16]~~.

The Nd:Mg:LiNbO$_3$ Raman spectrum has been analyzed in various papers [16-18], ~~[17–19]~~ where the Mg location in the LiNbO$_3$ lattice and its phonon frequency behaviour as a function of different Mg concentrations was explored, among other important features of this material. Despite the important technological applications of Mg:Nd:LiNbO$_3$ mentioned before, the pressure dependence of the Raman spectrum of this material has not been reported yet.

In this work, the hydrostatic pressure dependence of the Nd:Mg:LiNbO$_3$ Raman spectrum was determined and compared to previous results obtained for pure LiNbO$_3$ crystals [19] ~~[20]~~.

Raman measurements under pressure were carried out using a gasketed diamond anvil cell (DAC). A 4:1 mixture of methanol and ethanol was employed as pressure-transmitting medium. The sample was a y-cut of a ~~Nd- and~~ Nd-

and Mg-doped LiNbO$_3$ single crystal with 0.3% and 5% mol concentration, respectively. This was thinned down by mechanical polishing to about 40 μm and its surface perpendicular to the y-axis was polished up to optical quality. To this end, a diamond power with 1/4-micron grain size was used. Pressure was monitored in situ by the Raman shift of the main optical phonon mode of a small piece of single crystalline Si, loaded together with the sample. The dependence on pressure of the Si optical phonon frequency was accurately calibrated using the ruby luminescence method by Qin et al.[15]. The main advantage of using the Si phonon rather than the ruby emission to monitor the pressure is the following: the first method allows for higher accuracy in the determination of the Raman peak positions by avoiding errors introduced, when using ruby luminescence, by moving the spectrometer back and forth. So, the latter was kept at a fixed spectral position throughout the whole pressure run. Raman spectra were collected in backscattering geometry with a high resolution LabRam HR800 spectrometer using a grating with 1800 lines/mm and equipped with a liquid-nitrogen-cooled charge coupled device detector. The 514.5 nm line of an Ar$^+$-ion laser was used for excitation, which was focused onto the sample inside the DAC using a long distance 20× Olympus objective. All measurements were performed at room temperature.

As a result, Raman spectra were collected in backscattering geometry from the y-crystallographic direction- for different pressures up to 6.5 GPa in the phonon wavenumber range between 200 and 700 cm^{-1}. Two different groups of spectra were collected, with different linear polarization of the incident laser; the incidence polarization along the z-axis corresponds to the data of group A (Figs. 1(a) and 2(a)), whereas the incidence polarization along the x-axis corresponds to group B (Figs. 1(b) and 2(b)). The detection of the scattered photons proceeded unpolarized. Then, the excited Raman phonons in group A are those corresponding to y(zz)y and y(zx)y configuration, and in group B, those corresponding to y(xz)y configuration[12]. A representative spectrum from group A at a pressure of 0.1 GPa is shown in Fig. 1(a) and one of group B at a pressure of 6.0 GPa is shown in Fig. 1(b). For these spectra each phonon was fitted with a Lorentzian function, as indicated by the orange lines. The phonon modes are labelled according to the analysis performed in Ref. [20].
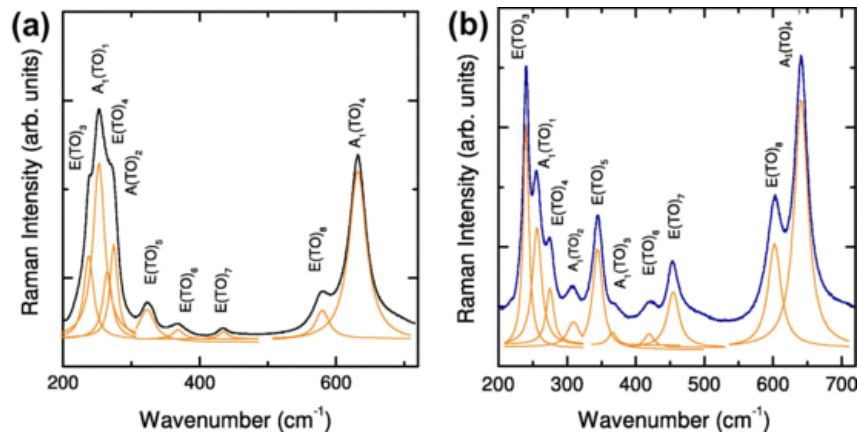

Fig. 1 Representative Raman spectra of (a) group A and (b) group B, corresponding to the different incident linear polarization. The orange lines represent lineshape fits to the measured spectra using a Lorentzian function for each phonon mode. The phonons are labelled according to Ref. [20].
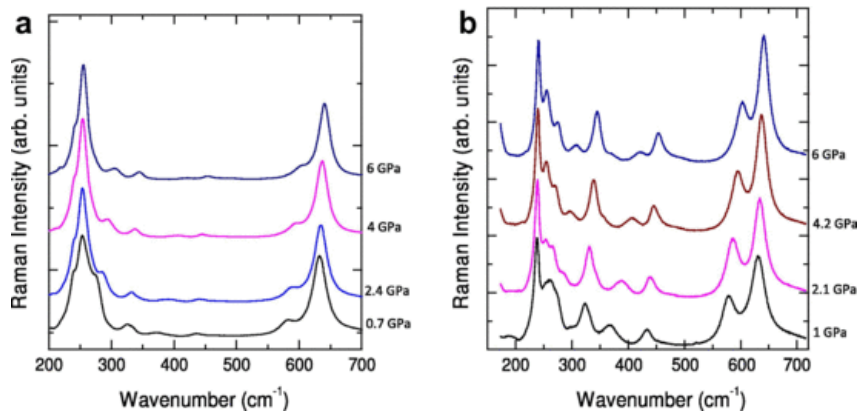
Fig. 2 Pressure dependence of the Raman spectra corresponding to the polarization group A (a) and group B (b).

Fig. 2 shows several Raman spectra for both polarization groups at different hydrostatic pressures in a range up to 6 GPa. All the phonon modes shift to higher frequencies when increasing pressure but, with different pressure coefficients. In fact, the four lowest-frequency modes ~~which~~ at low pressure merge into a broad band (see spectra of group A) but are clearly resolved at higher pressures (e.g. spectra of group B in Fig. 2(b))~~.~~ This indicates that their spectral separation increases when pressure is increased. Their full width at half maximum (FWHM), though, seems to be fairly independent of pressure.

Fig. 3 displays the extracted Raman shift corresponding to the peak position for each measured phonon mode of Nd:Mg:LiNbO$_3$ as a function of hydrostatic pressure. For all phonons, a linear dependence on pressure was obtained for the whole pressure range, despite the Mg doping.
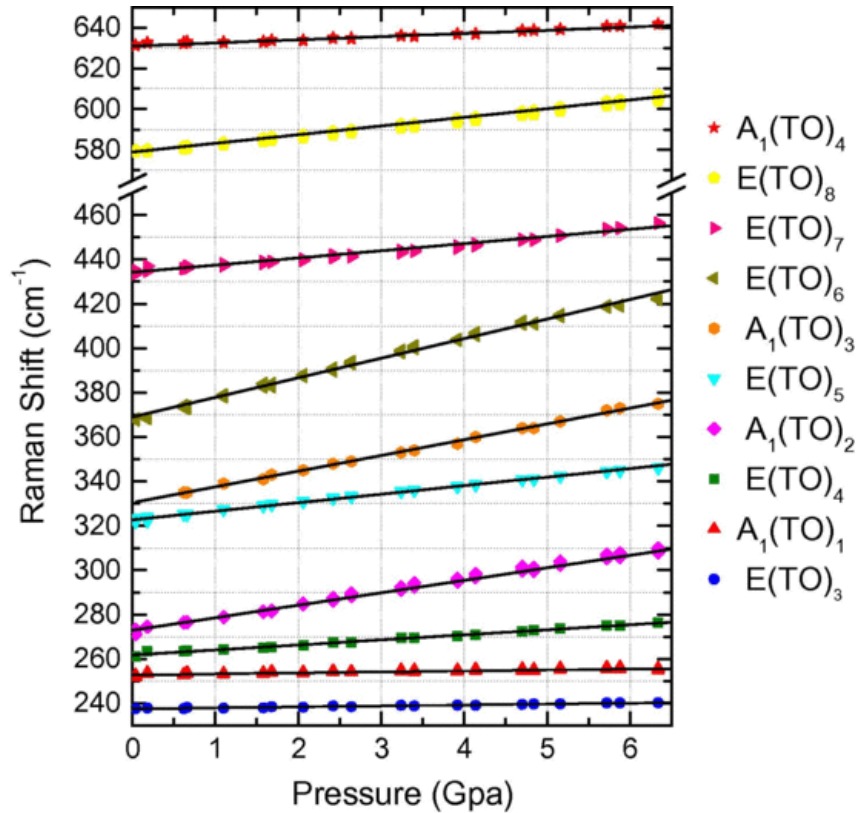

Fig. 3 Raman shift corresponding to the peak position of each phonon mode plotted against applied hydrostatic pressure for the Nd:Mg doped LNB sample. Full lines represent least squares fits to the data points using linear functions. The error bars for the peak position values are smaller than the marker symbols.

In Table 1, the values of the phonon pressure coefficient ($d\omega/dp$) corresponding to the slopes of the linear fitting functions are listed for each measured mode. For comparison, data from Ref. [19]~~[20]~~ obtained for undoped LNB are also shown. It can be seen that for the E1(TO)$_3$, A1(TO)$_1$, E1(TO)$_5$, E1(TO)$_6$, E1(TO)$_7$, E1(TO)$_8$ and A1(TO)$_4$ vibrational modes, the values of $d\omega/dp$ are coincident, within experimental uncertainty, for Nd:Mg-doped and undoped LiNbO$_3$. In previous works [16-18]~~[12,13]~~, it was found that a 5% Nd:Mg-doping do not modify the mentioned phonon frequencies at atmospheric pressure. Then, a constant pressure coefficient $d\omega/dp$ with respect to doping can be expected for those phonons.

Table 1 Measured values of phonon frequencies at ambient conditions and their linear pressure coefficient $d\omega/dp$ corresponding to the Raman modes of Nd:Mg:LiNbO$_3$ crystals.

Phonon	Wavenumber (cm^{-1})	$d\omega/dp$ (cm^{-1}/Gpa) Nd:Mg:LiNbO$_3$ current work	$d\omega/dp$ (cm^{-1}/Gpa) pure LiNbO$_{3[19]}$ [20]
E(TO)$_3$	@236	0.6 ± 0.1	0.5 ± 0.1
A$_1$(TO)$_1$	@253	0.2 ± 0.1	~0
E(TO)$_4$	@261	2.2 ± 0.5	0.4 ± 0.1
A$_1$(TO)$_2$	@273	5.7 ± 0.1	5.2 ± 0.1
E(TO)$_5$	@323	3.5 ± 0.1	3.4 ± 0.2
A$_1$(TO)$_3$	@330	7.0 ± 0.1	2.1 ± 0.1
E(TO)$_6$	@368	8.8 ± 0.3	8.3 ± 0.3
E(TO)$_7$	@436	3.5 ± 0.1	3.5 ± 0.1
E(TO)$_8$	@578	4.3 ± 0.1	4.2 ± 0.3
A$_1$(TO)$_4$	@631	1.6 ± 0.1	1.5 ± 0.1

On the other hand, an increase of around 15% and 200% in the $d\omega/dp$ values is noticed for the A$_1$(TO)$_2$ and A$_1$(TO)$_3$ phonons, respectively, when comparing the doped Mg:LiNbO$_3$ and pure LiNbO$_3$ with each other. At ambient pressure conditions, the frequency of these vibrational modes is changed because of a 5% Mg-doping[16-18] [12], hence, the observed difference in the $d\omega/dp$ values can be ascribed to doping and be expected beforehand [11].

Furthermore, the most significant variation in the $d\omega/dp$ coefficient because of the Nd:Mg-codoping is observed for the E$_1$(TO)$_4$ phonon. For this vibrational mode the linear pressure coefficient is increased by 450%. As a wavenumber variation of this phonon was found by S.C.Kim Kim et al.[21] [17] because also for 5% Mg-doping, a change in the E$_1$(TO)$_4$ pressure coefficient (dw/dp) ($d\omega/dp$) can be expected in our case.

For E(TO)$_4$, A$_1$(TO)$_2$ and A$_1$(TO)$_3$ phonons, the amount of the pressure coefficients variation because of 5% Mg-doping do not show correlation with the amount of phonon wavenumber variation because of this doping.

We believe these results from the fact that the Mg ions are mainly substitutionally located at Nb-sites and the incorporation of this atoms modifies the internal vibrations related to the NbO$_6$ octahedral[21,22] [23,24]. As the Mg mass is smaller than the Nb mass, the frequencies of phonon modes corresponding to the NbO$_6$ octahedral might also increase, as previously published[21] [24]. This behaviour due to Mg-doping is completely analogous to the so-called "local vibrational modes" which generally posses higher pressure coefficients than the related phonon mode of the host lattice[23,24] [25,26].

In brief, the Nd:Mg:LiNbO$_3$ phonon wavenumber variation as a function of hydrostatic pressure is reported for several Raman active modes in the range from 200 to 700 cm^{-1} and compared to that of undoped LiNbO$_3$. As expected, the studied phonons exhibit a linear wavenumber variation with the applied pressure within the analyzed range. No change was evident in the pressure behaviour for most of the phonon modes. However, increments of about 15%, 200% and 450% in the linear pressure coefficients of the A$_1$(TO)$_2$, A$_1$(TO)$_3$ and E(TO)$_4$ phonons with respect to the case of pure LiNbO$_3$ was found and discussed. Taking into account that the phonon pressure coefficient (dw/dp $d\omega/dp$) is a key parameter to retrieve the residual strain field in femtosecond-laser written waveguides[15] [10], this work provides valuable information which can be useful for integrated photonics device fabrication.

1 Uncited references

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Highlights

- Optical phonon shift versus hydrostatic pressure from 0 to 6 GPa in Mg:LiNbO$_3$ crystal.

- Comparison of Raman response of Mg doped and undoped ~~Lithium Niobate~~ lithium niobate crystal.

- Local vibrational mode is the responsible of large Raman variation with hydrostatic pressure.

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