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Lattice site of Mg ion in LiNbO₃ crystal determined by Raman spectroscopy

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Abstract. The defect structure of Mg-doped lithium niobate crystals was studied with varying Mg doping concentration by means of Raman scattering measurements. The Mg content dependences of both the frequency and damping of the two lowest-frequency A₁(TO) phonon modes were used to derive the Mg incorporation mechanism in the LiNbO₃ lattice. Results indicated that Mg ions are located on the Li site for low doping and then replace both Li and Nb ions for larger concentration.

1. Introduction

When grown from the melt, LiNbO₃ (LN) crystals usually present a large Li₂O deficiency in the congruent composition (i.e. 48.45 mol% Li₂O and 51.55 mol% Nb₂O₅) and therefore contain a large amount of intrinsic defects produced to maintain the charge neutrality [1].

As a consequence, the LiNbO₃ lattice is a host for the incorporation of dopants such as rare earth or metal ions, even in a large concentration. It is known that doping can significantly change the physical properties of LiNbO₃ [2].

Among other dopants, Mg addition in LiNbO₃ is the object of particular interest and extensive investigations, since it was found to be responsible for varying the resistance of LN to optical damage. It was thus discovered that the laser damage threshold was increased 100-fold in a crystal doped with 4.5 mol% MgO, compared with undoped LiNbO₃ [3].

Despite many studies, the defect structure of the Mg-doped LiNbO₃ crystal is still an unsolved question and has been generally discussed on the basis of a defect model in the undoped crystal, which is always the object of controversies [4, 5]. The Li-deficient lattice can be thus described generally in terms of Li vacancies [4] or Nb vacancies [5] according to different charge compensation mechanisms.

The measurements of the crystal density with varying composition (or ratio [Li]/([Li]+[Nb])) are consistent with both models and exclude the oxygen–vacancy model. Within the niobium site vacancy model [5], a fraction of the Nb ions in excess occupy vacant Li sites (the so-called Nb antisites) and the electrical charge compensation is insured by vacant Nb sites. The lithium site vacancy model [4] also suggests the Nb antisites but the neutrality charge is then achieved by unoccupied Li sites.

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The main differences between these two descriptions are thus in the electrical compensation mechanism and in the amount of Nb antisites.

Structural investigations led to contradictory interpretations of the average structure of LN. Recent x-ray and neutron diffraction data reported by Iyi *et al* [6], as well as by Zotov *et al* [7], were in favour of the Li-site vacancy model and opposed to the conclusion derived from earlier x-ray studies of Abrahams and Marsh [5] which supported the Nb-vacancy model.

Only a few studies were concerned with the analysis of defect structure in Mg-doped LN. A model was suggested by Donnerberg *et al* [8] from computer simulations based on lattice energy minimization among the possible defect structures of LN.

Other investigations were devoted to lattice parameter [9] and density [9,10] measurements. In each investigation, an Mg doping mechanism was proposed as constructed on the basis of one of the above models suggested for the undoped lattice [4,5]. Recently, Donnerberg [11] stated that a realistic description would be independent of a particular model for intrinsic defects.

The present study deals with the experimental characterization of Mg ion incorporation into the LN lattice using Raman scattering measurements, which are proved to provide a more direct substitution site probe, compared with other techniques used in earlier studies.

It was recently shown that the Raman spectrum is very sensitive to the crystal composition or the amount of intrinsic defects related to the non-stoichiometry [12]. Thus frequencies of phonon modes for both A_1 and E symmetries in the LN lattice have been clearly established from Raman scattering measurements on a stoichiometric crystal (i.e. 50 mol% LiO_2 and 50 mol% Nb_2O_5). The attribution of each phonon mode to a particular displacement of ions was achieved only very recently by Postnikov *et al* [13].

In the present study we use this assignment of the $A_1(\text{TO})$ phonons to interpret the changes of the Raman spectrum recorded in Mg-doped crystals with varying Mg concentration in terms of the defect substitution model. We thus show that Raman spectroscopy can be used as a site-spectroscopy technique.

2. Lattice dynamics

At room temperature, the ferroelectric phase LN lattice belongs to the space group symmetry $R3c$. The perfect structure is given by oxygen octahedra stapled along the polar z axis, with central ions (in fact slightly displaced from the centre of the octahedron) in the sequence as follows: Li, Nb, \square , Li, Nb, \square , . . ., where \square denotes the vacant site. These sites are privileged places for introduction of impurities and are labelled hereafter A, B and C.

Within their calculations, Postnikov *et al* [13] have used the full potential linearized augmented plane wave method and have deduced phonon characteristics from the total energy curvature. It is to be mentioned that calculations were obviously performed on the ideal stoichiometric structure in the ferroelectric phase of LN.

A fairly good agreement can be noted in zone centre phonon frequencies, for both symmetry modes A_1 and E, between the values predicted by the *ab initio* model and the experimental data deduced from Raman scattering. The deviation which appeared in the lowest- and highest-frequency $A_1(\text{TO})$ modes was attributed as due to anharmonic effects which are not accounted in the model. Among the nine calculated E(TO) phonon frequencies, only two display a shift from the experimental value. A large anharmonicity was invoked for one mode whereas for the remaining phonon, some controversies persist in the attribution of the Raman spectrum in the frequency range close to this mode. In addition these lattice dynamical calculations provide displacement patterns for each mode, which can be useful in the present context regarding the effect of doping in the structural and vibrational properties of LiNbO_3 .

Within our study, we do not retain the results on the E(TO) modes since the associated eigenvectors are quite complicated.

It is found that A₁(TO₁) phonon corresponds to antiphase motion, along the ferroelectric *z* axis, of Nb ions against the oxygen octahedron whereas Li ions are nearly at rest. Both highest-frequency modes, i.e. A₁(TO₃) and A₁(TO₄) exhibit the vibrations of oxygen ions only. The TO₃ mode is a rigid rotation of the whole oxygen octahedra along *z*, whereas the TO₄ mode is a stretching of individual octahedra. The A₁(TO₂) phonon is associated with a large displacement, along the *z* axis, of Li ions in antiphase to Nb ions, whereas oxygen ions do not move. It is to be noted that this is the sole mode which implies a significant motion of Li ions. This attribution corroborates previous experimental data which have shown that the A₁(TO₂) frequency is shifted by the isotope change from ⁷Li to ⁶Li [14].

3. Experiment

We have performed Raman scattering measurements in five LN samples: a 'pure' crystal with a congruent composition and four crystals doped by introduction of various amounts of MgO in the congruent melt. In order to discard the influence of other involuntary kinds of impurity, the crystals have been prepared in the same conditions and thus belong to the same series. As the Mg concentration in the crystal differs from its content in the melt, it was correctly determined regarding the segregation coefficient *k_{eff}*. Hao-Ran Tan *et al* reported that *k_{eff}* during growth changed from 1.3 to 0.95 at around 8 mol% Mg content [15]. Raman scattering experiments have been performed in right angle geometry using a Spex double monochromator and the 5145 Å exciting line of an Ar-ion laser with 400 mW output power. Raman spectra were recorded within a resolution of 0.2 cm⁻¹ in the same experimental conditions for all crystals. The scattering configuration X(ZZ)Y was chosen since it is appropriate to provide the pure A₁(TO) phonon.

4. Results

Figure 1 exhibits the A₁(TO₁), A₁(TO₂) and A₁(TO₄) Raman line shapes obtained from different samples. The A₁(TO₃) line is not reported since it is much less intense than the other bands so that the scattered intensity can be more hidden by the background.

The A₁(TO₄) line appears to be only slightly affected by Mg doping. Its maximum position does not shift whereas its integrated intensity regularly decreases with increasing Mg doping, leading to an increase of the linewidth.

These features can be interpreted consistently with the predicted eigenvectors associated with the A₁(TO₄) mode, which exhibit motion of oxygen ions only. Mg ions clearly do not substitute for oxygen ion locations and their introduction in the lattice gives rise to a rising anharmonic contribution of the oxygen octahedron.

In contrast to the effect on the A₁(TO₄) mode, Mg doping significantly affects the low-frequency spectrum containing A₁(TO₁) and A₁(TO₂) phonons. As these lines are lying close to each other (253 cm⁻¹ for A₁(TO₁) and 276.5 cm⁻¹ for A₁(TO₂) in the undoped congruent crystal) a fit of the spectrum to two damped harmonic oscillators is needed to deduce the frequency and damping characterizing each phonon. Results derived from this spectrum adjustment are reported in figure 2. The TO₂ mode shows a large and monotonic decrease of its frequency Ω(TO₂) with increasing Mg concentration whereas its damping is nearly constant up to a 4 mol% concentration and then exhibits a huge increase in the 4.6 mol% doped crystal. The A₁(TO₁) frequency Ω(TO₁) shows a small decrease with raising Mg content and then a

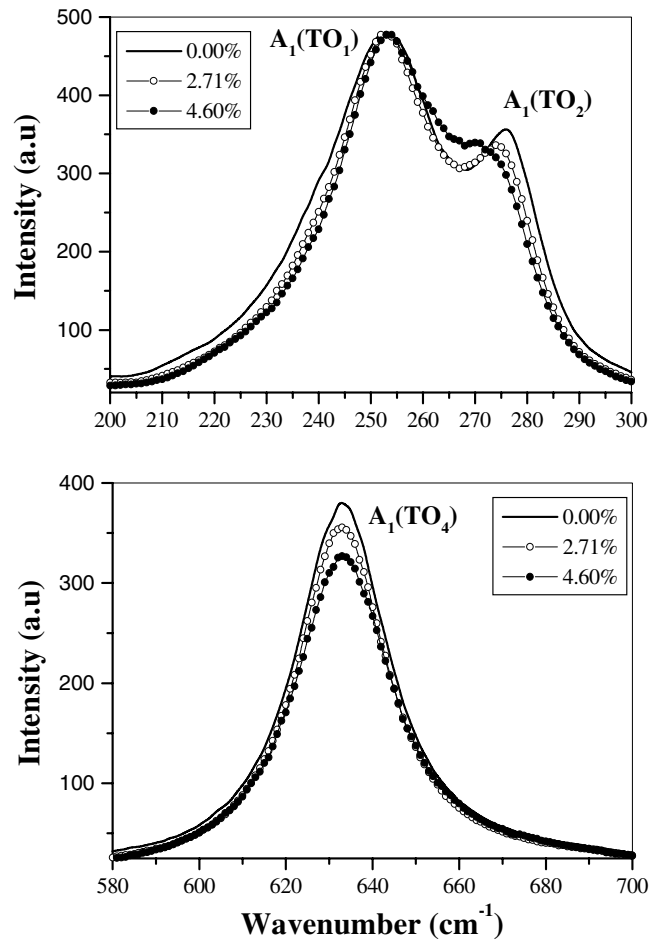


Figure 1. Raman spectra recorded on different Mg-doped LiNbO₃ crystals in the X(ZZ)Y configuration.

significant increase for the highest doped crystal. Its damping continuously diminishes with increasing concentration.

5. Discussion

These results are interpreted below in terms of the Mg substitution process in the LN lattice, in the light of the respective displacement patterns associated with TO₁ and TO₂ phonons.

The eigenvector patterns, as obtained by Postnikov *et al* [13], provide the kind of motion involved in a particular mode according to symmetry rules but regardless of whether the site is occupied or not. Their results can be therefore used in the off-stoichiometric LN lattice as well as in the doped LN crystal. This means that the A₁(TO₁) mode is mainly the vibration of ions in the B site with respect to oxygen ions, whereas the A₁(TO₂) mode corresponds to the antiphase motion of ions in A and B sites. The most important feature detected in our experiments is the large decrease of Ω (TO₂) in the whole investigated Mg concentration range. As the TO₂ is the sole mode which involves Li ion motion, this result can be related to Mg ion

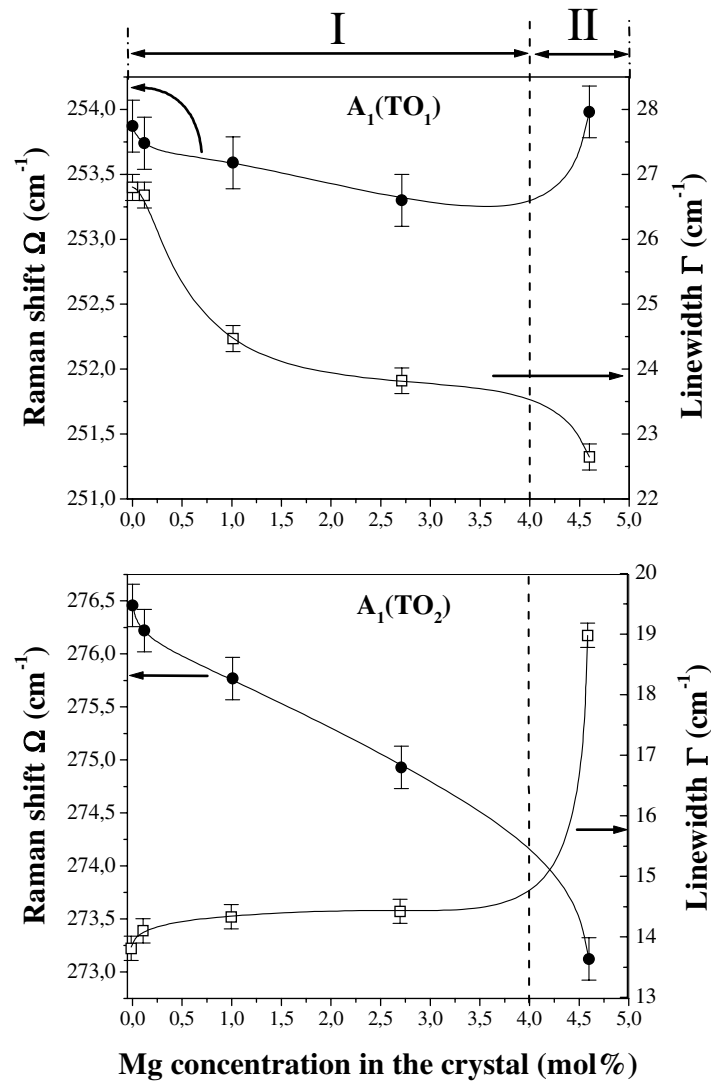


Figure 2. Mg concentration dependence of frequency (—●—, solid circle) and damping (open square, —□—) for the A₁(TO₁) and A₁(TO₂) phonon modes.

introduction in the A sites. As these sites can be occupied by Li ions, Li vacancies and/or Nb ions (the so-called Nb antisites), the dependence of $\Omega(\text{TO}_2)$ on the Mg concentration can be understood by successive processes within the Mg ion substitution mechanism. Whatever is the model proposed to describe the undoped crystal, vacant Li (A) sites are occupied by Nb ions in the congruent LN lattice. As they are particularly unstable, these positions should be consequently firstly affected by the Mg introduction. Under Mg doping, Mg ions push Nb ions out of the antisites. Since the Mg mass is larger than the Li mass, the continuous decrease of $\Omega(\text{TO}_2)$ can be related to the successive processes as follows: (i) the filling by Mg ions of Li vacancies and (ii) the partial replacement of Li ions in their proper sites.

This picture is corroborated by the behaviour of the A₁(TO₁) mode which consists of Nb vibration against oxygen ions. For low Mg concentration, the small decrease of $\Omega(\text{TO}_1)$ is not

in contradiction with the fact that more Nb (B) sites are occupied by Nb ions which are pushed out from Li sites by Mg doping. For larger Mg content, the increase of $\Omega(\text{TO}_1)$ reveals the substitution of Mg for Nb and thus reflects a change in the doping process. The positive sign of the frequency shift is in agreement with the respective masses of Nb and Mg.

As a consequence we can define clearly two ranges in the Mg doping mechanism, (i) range I for Mg concentration smaller than 4 mol% in the crystal; the Mg ions are located on the A-sites only; (ii) range II for Mg content larger than 4 mol%; the Mg ions are lying on both A and B sites. We have furthermore some indications about the three different kinds of Li site since with increasing Mg doping Mg ions substitute successively for Nb_{Li} , V_{Li} (in range I) and Li_{Li} (in range II).

The concentration dependence of the damping for both modes TO_1 and TO_2 can be interpreted in terms of ordering in the LN lattice, according to the above description of the Mg substitution dynamics. Indeed the damping of TO_1 and TO_2 mainly reflects the order in the site Nb and sites Li respectively. In range I, Mg substitution of unstable Nb_{Li} and V_{Li} in an empty and thus deformable octahedron, is in favour of ordering. Subsequently, as revealed by the $\Gamma(\text{TO}_2)$ decrease, the order in the Nb site is indirectly enhanced by Mg ions since the occupation number of Nb ions on their own sites is probably larger.

For higher concentrations, i.e. in range II, Li ion substitution by Mg ions causes a large disorder of the Li sites whereas the order in the Nb sites is unaffected by a partial replacement of Nb ions by Mg ions.

6. Conclusion

We have discussed the mechanism of Mg ion incorporation in the defective LN lattice from the Raman data recorded in crystals with varying Mg content and in the light of recent lattice dynamical calculations. It was pointed out that two Mg concentration ranges can be derived from this investigation. In range I for Mg content smaller than 4 mol%, Mg ions are lying on the Li site and substitute from niobium antisites and Li vacancies. These processes contribute to an increasing ordering of the lattice. In range II, for Mg concentrations larger than 4 mol%, Mg ions replace both Li and Nb ions on their own sites.

The present interpretation is independent of the defect model chosen to describe the undoped crystal.

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