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Defect Structure Model of MgO-Doped $LiNbO_3$

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To study the defect structure of MgO-doped lithium niobate, single crystals of lithium niobates ($LiNbO_3$, "LN") with varying MgO content were characterized by chemical analysis, lattice parameters, and density measurements. An Mg-incorporation mechanism was assumed on the basis of the chemical formulae derived from the data and in light of our recently proposed defect model of nondoped LN. At first, Mg would replace the Nb ion at the Li site and complete replacement would take place at 3% MgO doping keeping the molar ratio Li/Nb = 0.94. This corresponds to the formula $[Li_{0.94}Mg_{0.03}\square_{0.03}][Nb_{1.0}]O_3$. Further Mg ions are incorporated into the Li site, replacing Li ions, with accompanying vacancy creation, down to Li/Nb = 0.84, which corresponds to the Nb-rich side limit of the LN solid solution range. The number of vacancies would reach a maximum at this composition and the formula would be $[Li_{0.84}Mg_{0.08}\square_{0.08}][Nb_{1.0}]O_3$. Beyond this point, Mg ions enter the Nb and Li sites simultaneously, maintaining the Li/Nb ratio, leading to a decrease in vacancies. Two thresholds in the change of composition and properties reported so far in the literature can be interpreted by this model. Improved optical damage resistance due to MgO-doping was attributed to the increase in vacancies, and not by its decrease as was generally supposed.

INTRODUCTION

Optical properties of congruent lithium niobate (LN) are known to be improved by doping 5–6% MgO into the starting composition for the CZ (Czochralski) growth (1). So far, many investigations have been performed on MgO-doped LN (2–5); however, most of them have focused on changing optical and other properties by MgO doping. Only a few studies deal with the change in defect structure of LN by doping with MgO.

Since the structural study by Abrahams and Marsh (6) on nondoped congruent LN, the defect structure of MgO-doped LN has been interpreted on the basis of their model (7–10). According to Abrahams and Marsh (6), congruent LN (Li/Nb = 0.942) was expressed by $[Li_{0.951}Nb_{0.049}][Nb_{0.961}\square_{0.039}]O_3$, where 4.9% of the Li sites are occupied by Nb ions and vacancies exist at the Nb site (Nb-site vacancy model). Mg ions were assumed to replace the Nb ions at the Li site (hereafter denoted Nb_{Li}), and all Nb_{Li} would be replaced by 4.9% doped MgO. The resulting compound contains the minimum number of vacancies at the Nb site because further addition of MgO results in an increase in vacancies by the replacement of Li at the Li site (Li_{Li}) with divalent Mg ions. As optical absorption and damage were attributed to the number of vacancies, this scheme was supposed to be consistent with the well-known fact that the optical properties were most improved at around 5% MgO doping. Therefore it was regarded as a reasonable structural model for MgO-doped LN.

The above-mentioned simple model was not, however, consistent with the recent work of Grabmaier *et al.* (11) on MgO-doped LN. They have grown LN single crystals with various MgO-doping levels by the CZ method and analyzed their compositions. According to their chemical analysis, the Li/Nb ratio *does* change with 4.9% doping of MgO. At this doping level, the Li/Nb ratio is 0.90, so the composition would be $[Li_{0.90}Mg_{0.049}Nb_{0.051}][Nb_{0.949}\square_{0.051}]O_3$. This means that 5.1% Nb still remains at the Li site, and also the Nb site has as much as 5.1% vacancies. This is contradictory to the idea that Nb_{Li} is completely replaced by Mg when the vacancy minimum is attained at 4.9% MgO content.

Recently, we proposed a new model for nondoped LN on the basis of single-crystal X-ray diffraction data and powder neutron diffraction data (12). Our model was in agreement with Lerner *et al.*'s assumption (13) that vacancies exist at the Li site (Li-site vacancy model), which was different from that of Abrahams and Marsh (6) with respect to the position of the vacancy. The congruent LN can be expressed as $[Li_{0.951}\square_{0.039}Nb_{0.0098}][Nb_{1.0}]O_3$ in our model.

Defect structure models for MgO-doped LN thus far

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proposed are all based on the Nb-site vacancy model. Now that this basic model has proved doubtful, the Mg-incorporation mechanism must be reconstructed in light of our new defect model of nondoped LN. The purpose of the present paper is to construct a new defect model for MgO-doped LN, for which single crystals of LN, with various degrees of MgO-doping, were characterized by chemical analysis, lattice parameters, and density measurements.

EXPERIMENTAL

Nondoped congruent LN (CG) and four kinds of MgO-doped LN single crystals with varying MgO content were grown by the CZ method. For the MgO-doped samples, 1, 3, 5, and 9% MgO were added to congruent LN and used as the starting material. The specimens were denoted MG01, MG03, MG05, and MG07, respectively. The grown crystals were characterized by chemical analysis, density measurements, and lattice parameter determinations.

Chemical analysis was conducted as follows: The crushed samples were dissolved with HNO_3–HF solution in a closed Teflon vessel at 150°C for one night. After being filtered for the separation of precipitated MgF_2, the yielded solution was passed through an SA-1 anion exchanger for further separation of Li and Nb ions. The Li and Mg contents were analyzed by ICP-AES (inductively coupled plasma atomic emission spectrometry). Nb ions eliminated from the resin by HCl–HF solution were precipitated by Cuperon, and the precipitate was dried and incinerated. The weight of the yielded Nb_2O_5 gave the Nb content.

The density was measured by the method of Archimedes, using highly pure water (ion-exchanged, Millipore-filtered, and degassed under vacuum; resistivity > 17 MΩ/cm) as the floating medium. The samples were cut in a rectangular shape and the faces were polished with a diamond polisher. The accuracy of the measurement was checked by density measurements of a single crystal of α-alumina.

The lattice parameters were calculated from the 2θ data obtained on single crystals mounted on a computer-controlled four-circle X-ray diffractometer (AFC-3, Rigaku Co., Ltd.), which was calibrated using a tiny sphere of Si single crystal as the standard. The radiation source was Mo$K\alpha_1$ and the 2θ range was 65–90° for 24 reflections for each sample.

RESULTS AND DISCUSSION

The results of the characterization of the five LN specimens with various MgO-doping amounts are listed in Table 1. On the basis of these data, the chemical formulae were obtained. Two calculation methods were tried: one is based only on the lattice parameters, chemical composition, and density data; the other used the first two types of data, fixing the oxygen per unit formula to 3. The latter treatment is equivalent to the assumption of no oxygen vacancy. The preconditions of charge neutrality and no change of valence were common to both. The number of oxygens per unit formula obtained for each sample was 3.00 with an error of less than 0.3% when the first method was applied, so the obtained formulae were essentially the same for both methods. This means that an oxygen vacancy, even if it existed, was not the major defect in MgO-doped LN. The number of vacancies was calculated by subtraction of the amount of Li, Nb, and Mg from the total amount of cation sites (=2.0) as was done by Grabmaier *et al.* (11). The errors in the formulas obtained were estimated to be 0.5% for Li, 0.1% for Nb, and 0.7% for Mg, which were accurate enough for discussing the number of vacancies. In Table 2, the fundamental chemical formulae thus obtained by the second method are given. Our data on the number of vacancies and Li/Nb ratio are plotted against the Mg content in the diagram

TABLE 1
Crystallographic Data for Congruent and MgO-Doped Lithium Niobates

Specimen	Composition Nb_2O_5 : Li_2O : MgO (wt%)	Lattice parameters[a] (Å)	Density ($g\,cm^{-3}$)
CG	90.4 : 9.57 : 0.00	a = 5.1499(1) c = 13.8647 (4)	4.6454
MG01	90.3 : 9.56 : 0.20	a = 5.1498(4) c = 13.8652 (7)	4.6454
MG03	89.8 : 9.30 : 0.86	a = 5.1501(4) c = 13.8668 (7)	4.6419
MG05	89.6 : 9.00 : 1.21	a = 5.1507(4) c = 13.8699 (6)	4.6408
MG07	89.3 : 8.78 : 1.92	a = 5.1520(4) c = 13.8737 (7)	4.6370

[a] The crystal symmetry is rhombohedral, and space group is $R3c$. The parameters are expressed in the hexagonal system.

TABLE 2
The Obtained Chemical Formulas

Specimen	Formula
CG	$Li_{0.951}\square_{0.039}Nb_{1.010}O_3$
MG01	$Li_{0.949}Mg_{0.0074}\square_{0.037}Nb_{1.007}O_3$
MG03	$Li_{0.924}Mg_{0.032}\square_{0.042}Nb_{1.003}O_3$
MG05	$Li_{0.896}Mg_{0.045}\square_{0.0566}Nb_{1.003}O_3$
MG07	$Li_{0.872}Mg_{0.071}\square_{0.060}Nb_{0.997}O_3$

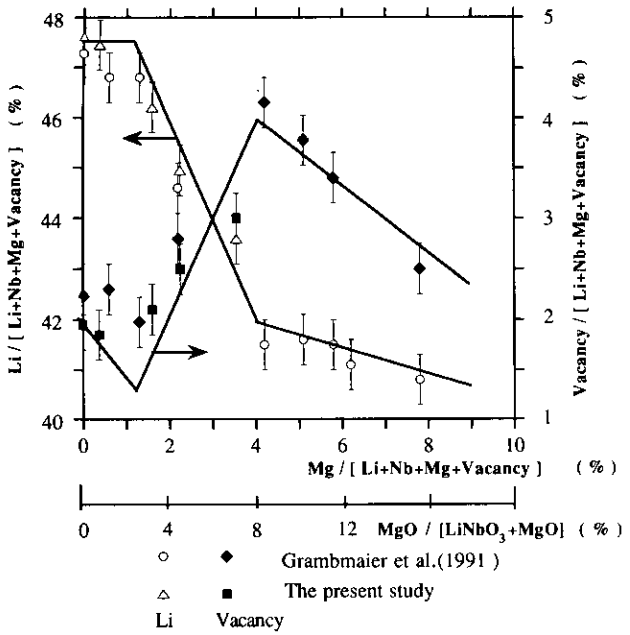

FIG. 1. Change in Li and vacancy contents by MgO-doping into congruent lithium niobate. Solid symbols correspond to vacancies and open symbols correspond to Li.

used by Grabmaier *et al.* (11) in Fig. 1 together with their data. Here [Li] + [Nb] + [Mg] + [vacancy] = 100%. Our data are consistent with their observations. According to Grabmaier *et al.* (11), the Li/Nb ratio was nearly constant up to 2% MgO doping, and then decreased steeply up to 8% MgO-doping, followed by a sluggish decrease in Li/Nb beyond this concentration. They also recognized that the Mg-replacement mechanism changed twice and designated the first "threshold 1," and the second "threshold 2." The threshold phenomenon can also be recognized in the diagram.

As mentioned in the Introduction, the simple model based on Abrahams and Marsh's model of nondoped LN, which assumed the replacement of all Nb_{Li} by doping with 4.9% MgO, is contradicted by the experimental result that the Li/Nb ratio changes with MgO doping. As the Li/Nb ratio becomes 0.90, the composition will be $[Li_{0.90}Mg_{0.049}Nb_{0.051}]\ [Nb_{0.949}\square_{0.051}]O_3$. This formula is not consistent with the idea that Nb_{Li} is completely replaced by Mg, attaining the vacancy minimum at 4.9% MgO content. As long as it is based on the Nb-site vacancy model, the only reasonable model thus far proposed is that of Grabmaier *et al.* (11). They proposed an Mg-incorporation mechanism on the basis of the LN structure model of Abrahams and Marsh (6) in keeping consistency with the chemical formulas they obtained. According to them, Mg ions replace Nb_{Li} up to 3%, which corresponds to threshold 1. (At this point Nb ions still remain at the Li site.) Then Mg ions replace Li_{Li}, repelling Nb_{Li} to the Nb site until the MgO amount reaches 8% (threshold 2). The formula at threshold 1 would be $[Li_{0.951}Mg_{0.030}Nb_{0.019}]\ [Nb_{0.979}\square_{0.021}]O_3$, and that at threshold 2 would be $[Li_{0.84}Mg_{0.08}\square_{0.08}]\ [Nb_{1.0}]O_3$. At threshold 2, no vacancies exist at the Nb site, though a vacancy has been generated at the Li site. The problems with this model are (i) that the reason for Mg to replace Li beyond 3% doping of MgO in spite of the existence of remaining Nb_{Li} is unclear, and (ii) that there is no reason for the change in vacancy site from the Nb site to the Li site. Donnerberg *et al.* (9, 10) also proposed a scheme for MgO doping, which is essentially the same as Grabmaier *et al.*'s model. As long as the model is based on Abrahams and Marsh's LN model, it is difficult to explain the increase in vacancies and the existence of two thresholds.

In a previous paper (12), we proposed a new model for nondoped LN on the basis of single crystal X-ray diffraction data and powder neutron diffraction data, in which vacancies exist at the Li site (Li-site vacancy model). On the basis of our data, the Mg-incorporation model was reconstructed in the light of our Li-site vacancy model. Our model of the Mg-incorporation is schematically shown in Fig. 2. At first, Mg would replace Nb_{Li}, maintaining the ratio of Li/Nb at 0.94; complete replacement takes place at 3%. This corresponds to the formula $[Li_{0.94}Mg_{0.03}\square_{0.03}]\ [Nb_{1.0}]O_3$. Further Mg ions are incorporated into the Li site, replacing Li ions up to Li/Nb = 0.84 with creation of vacancy. This ratio corresponds to the Nb-rich side limit of the LN solid solution range. Here, the number of vacancies reaches a maximum and the formula is $[Li_{0.84}Mg_{0.08}\square_{0.08}]\ [Nb_{1.0}]O_3$. Beyond this point, Mg ions enter the Nb and Li sites simultaneously, maintaining the Li/Nb ratio constant. This leads to a decrease in vacancies. The expected values for the models are also plotted as a solid line in Fig. 1. This clearly shows that our model is in good agreement with the experimental data. On the basis of the Li-site vacancy model, the experimental formulae shown in Table 2 can be rewritten to be, for example, $[Li_{0.949}Mg_{0.0074}Nb_{0.007}\square_{0.037}]\ [Nb_{1.0}]O_3$ for

MgO-content	Formula
0.0%	$[Li_{0.95}Nb_{0.01}\square_{0.04}][Nb]O_3$
	↓ Li/Nb = 0.94
3.0%	$[Li_{0.94}Mg_{0.03}\square_{0.03}][Nb]O_3$
	↓ Mg → Li
8.0%	$[Li_{0.84}Mg_{0.08}\square_{0.08}][Nb]O_3$
	↓ Li/Nb = 0.84
28%	$[Li_{0.79}Mg_{0.21}][Nb_{0.931}Mg_{0.069}]O_3$

FIG. 2. Ideal scheme of MgO-incorporation in congruent LN (lithium niobate).

MG01, and $[Li_{0.872}Mg_{0.068}\square_{0.060}]$ $[Nb_{0.997}Mg_{0.003}]O_3$ for MG07. In the study of crystal growth of MgO-doped LN, Hu *et al.* (14) reported that the distribution coefficients (k) of Mg during growth changed from $k = 1.2$ to $k = 0.95$ at around 7.5% Mg content. The distribution coefficient is related to the site preference for incorporated Mg ions from the melt, which implies that a change in the Mg site takes place at 7.5% Mg concentration. This behavior is consistent with the present model. In contrast to Grabmaier *et al.*'s model the vacancy site does not change in our model, so the existence of two thresholds can be explained in a simpler way. Indeed, the chemical formulas we obtained in the present study cannot indicate the vacancy site, but a new Mg-doping model could be obtained from these data in the light of Li-site vacancy model. In this sense, our trial is an extension of our Li-site vacancy model.

There may be a third position, which assumes that vacancies would exist at both sites and that the vacancy distribution between two sites depends on the growth conditions. Donnerberg *et al.* (9, 10) asserted that the difference in energy in these models was small, considering the partial "ilmenite" structure or domain as the cause of Nb site vacancy. In the present study, however, we did not consider these possibilities. This is because (i) no evidence has been found thus far about the dependence of defect structure on growth conditions, and (ii) no quantitative data showing the closeness in energy for two models have been published. Also, for the ilmenite structure, thus far, no experimental evidence, such as electron microscopic observations, has been published to support this assumption.

Figure 3 is another diagram plotting the Mg amount against the Li/Nb ratio. The solid diagonal line ("boundary line") corresponds to the formula $[Li_{1-2x}Mg_x\square_x]$ $[Nb_{1.0}]O_3$, which represents the state without Nb_{Li} or Mg_{Nb}. So the region above the line can be expressed as the "Mg_{Nb}-region" and the below as the "Nb_{Li}-regions." The vertical line at around Li/Nb = 0.84 indicates the limit of the Li/Nb ratio, which was taken from the phase diagram (15). Data from all samples were plotted in this diagram. The above-mentioned scheme for Mg incorporation can be plotted as the dotted line in this diagram. As can be seen in the figure, the experimental data are a little off from the ideal scheme. The plotted data in the series of Mg-doped LN show bends near 3 and 8%; however, the change does not exactly follow the diagonal line as stated in the above scheme, but crosses the boundary line at about 6%. At the crossing, a drastic change in the defect structure occurs and a change in the properties of LN can be expected. The information on number of vacancies is also included as contour lines. By using this diagram, the defect structure of a certain composition can be recognized visually, as can the relation between properties and

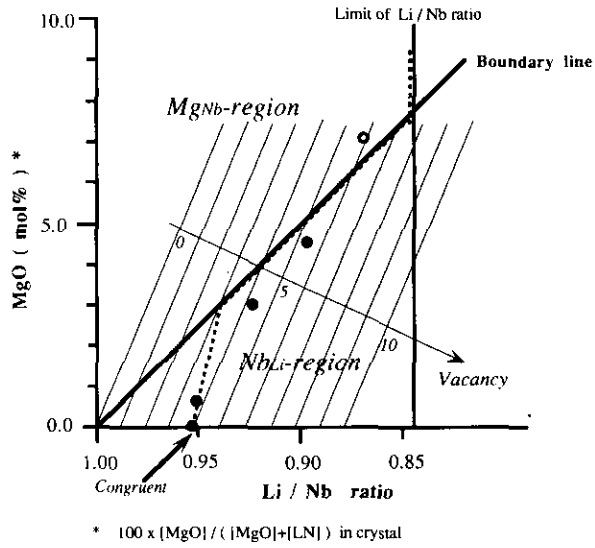

FIG. 3. The diagram showing MgO content plotted against Li/Nb ratio. The specimens are plotted in the diagram as circles: The solid circles show the specimen with lower wavenumber of the OH stretching vibration, and the open circle the specimen with the higher wavenumber. Details are given in text.

structure. For example, the frequency of the O–H bond stretching vibration, due to the small number of protons, is known to shift to a higher wavelength beyond several percent MgO doping (4). In our case, only MG07, which is the only sample in the Mg_{Nb}-region, is shifted. This suggests the close relationship between the frequency of the O–H bond and defect structure. The environment of the proton site may change in a different defect structure. The details are discussed in a separate paper (16).

Thus far, optical damage has been thought to be caused by vacancies in the LN structure, which is the main idea of the defect structure models based on Abrahams and Marsh's model. However, the experimental data revealed that the vacancy increased with the addition of MgO. Grabmaier *et al.* (11) tried to solve this contradiction by assuming that the damage was caused only by the vacancy at the Nb site. In other words, Li-site vacancies were assumed to have no influence on the optical properties, though vacancies increase at the Li site by doping MgO. In our model, the vacancy is only at the Li site, and it was assumed that the optical-damage resistance increases as the vacancies increase. So far, some researchers (17, 18) have pointed out that the optical-damage resistance increases as Nb/Li ratio increases, i.e., vacancy increases, in the case of nondoped LN. The increase in vacancies would make the photoconductivity higher, which may lead to the higher optical-damage resistance. By the present model, the cause of the optical damage resistance can be explained consistently for nondoped and doped LN.

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