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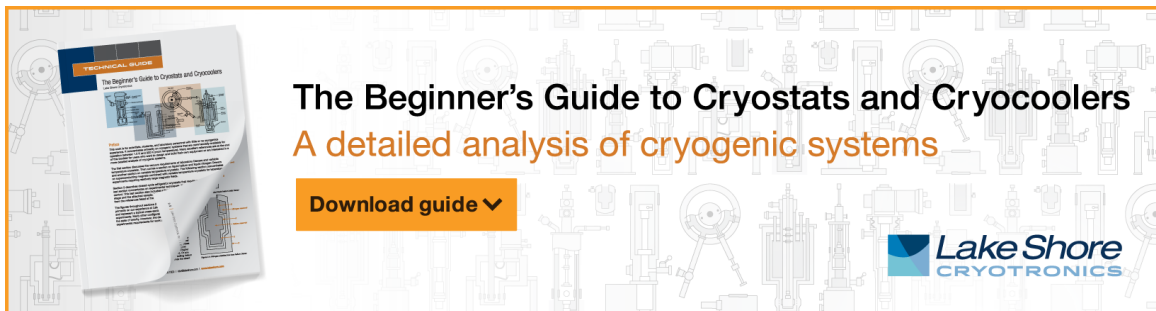


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# Threshold effect in Mg-doped lithium niobate

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Optical absorption spectra were obtained after reducing (i.e., vacuum annealing) a series of  $\text{LiNbO}_3$  crystals grown from melts having various Mg concentrations and Li/Nb ratios. A band peaking at 500 nm, and assigned to oxygen vacancies containing two electrons, was the only absorption present in one set of crystals following reduction. In contrast, two overlapping bands peaking near 1200 and 760 nm were present in the other set of crystals immediately after the reduction. The 1200-nm band is assigned to a previously unreported electron trap and the 760-nm band to oxygen vacancies containing only one electron. These data are interpreted in terms of a threshold level for Mg doping; however, the threshold Mg doping level is not a constant but depends on the ratio of Mg ions to Li vacancies.

Recently, Bryan *et al.*<sup>1</sup> reported that the damage resistance of lithium niobate is increased by a factor of 100 when the crystals are heavily doped with MgO. Even more important, their results indicate the presence of a threshold effect wherein the improvement in damage resistance occurs for doping levels greater than approximately 4.5 at. %. This dramatic improvement in the properties of lithium niobate crystals was unexpected and represented a significant deviation from earlier attempts to eliminate optical damage by reducing the total impurity content of the material.

It is important to further understand the nature of the point defects produced in Mg-doped  $\text{LiNbO}_3$  and to determine the reasons for the existence of a threshold behavior in the Mg doping level. In the present letter, we describe optical-absorption results obtained after reducing (i.e., vacuum annealing) a series of  $\text{LiNbO}_3$  crystals having various magnesium concentrations and Li/Nb ratios. Two types of optical absorption behavior were observed, one of which was similar to that previously reported for undoped  $\text{LiNbO}_3$  and another was new and only found in several of the more heavily doped crystals. We interpret our data in terms of a threshold effect, since there was not a gradual transition between the two behaviors, and we conclude that the threshold doping level for Mg ions is not a constant but depends directly on the concentration of lithium vacancies in the crystal.

The McDonnell Douglas Astronautics Company engaged the services of Crystal Technology, Inc. of Palo Alto, California to grow a series of Mg-doped lithium niobate crystals for use in an earlier investigation.<sup>1</sup> We have used four crystals from that series in the present study: these were a 3% Mg-doped sample, grown from a stoichiometric melt, and three 5% Mg-doped samples, grown from melts with lithium atomic percentages of 50% (stoichiometric), 48.6% (congruent), and 47.6% (lithium deficient). For comparison, an undoped lithium niobate crystal grown from a congruent melt was included in our study. We reduced these various crystals by holding them for one hour at 1000 °C in a vacuum

of  $10^{-5}$  Torr and then slowly cooling to room temperature. Optical absorption spectra were subsequently taken with a Perkin-Elmer model 330 spectrophotometer. All measurements were made at 85 K with unpolarized light propagating along the *c* axis.

The effects of reduction on the optical properties of undoped  $\text{LiNbO}_3$  are described in the literature,<sup>2,3</sup> and, as background information, we provide a brief summary of these observations in this and the next paragraph. A primary result of reduction is the introduction of an intense black coloration in the crystals. This absorption spectrum peaks at 500 nm and extends, with little change, to the band edge near 300 nm. When a reduced sample is optically bleached near liquid nitrogen temperature, the band initially at 500 nm decreases and a different band peaking near 760 nm appears. The 760-nm band is only stable at the lower temperatures, i.e., it disappears and the 500-nm band is restored upon warming the sample to room temperature.

The optical absorption bands peaking at 500 and 760 nm in the undoped crystals have previously been assigned to oxygen vacancies.<sup>2</sup> Specifically, the peak at 500 nm has been attributed to neutral oxygen vacancies (containing two electrons) while the peak at 760 nm has been attributed to positive-charged oxygen vacancies (containing one electron). These are referred to as F and F<sup>+</sup> centers, respectively. The low-temperature optical bleach removes one of the electrons from the F center, thus forming an F<sup>+</sup> center. The removed electron becomes trapped elsewhere in the crystal, and electron spin resonance (ESR) data have suggested that this trap is a Nb<sup>4+</sup> ion.<sup>4</sup>

As part of our present investigation, we observe that reduction causes the same effects in 3% Mg-doped (stoichiometric) and 5% Mg-doped (Li-deficient) crystals as in the undoped  $\text{LiNbO}_3$ . Figure 1 shows the optical absorption data taken at 85 K from the 3% Mg-doped (stoichiometric) sample after reduction. To illustrate the light-induced conversion of F to F<sup>+</sup> centers which was described in the pre-

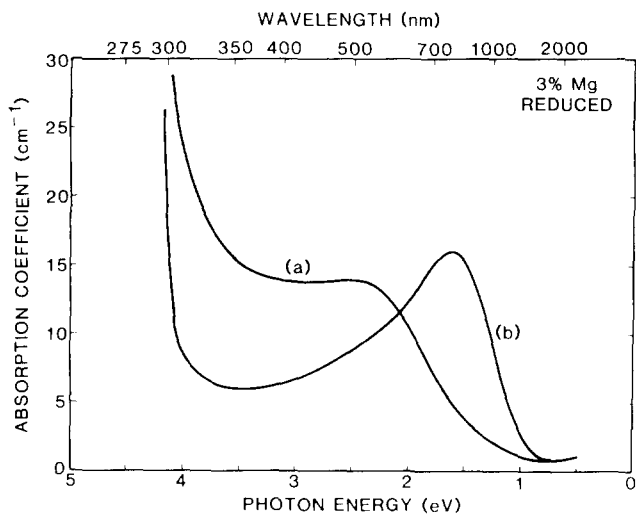


FIG. 1. Optical absorption from a reduced 3% Mg-doped (stoichiometric) crystal. Trace (a) represents the F centers and was taken at 85 K after a vacuum anneal at 1000 °C for 1 h. Trace (b) represents the F<sup>+</sup> centers and was taken after the F to F<sup>+</sup> conversion by a xenon lamp at 85 K.

ceding two paragraphs, we took trace (a) before and trace (b) after an optical bleach at 85 K with the full output of a 150-W xenon lamp.

A new and quite different behavior was found when we reduced the 5% Mg-doped crystals grown from the stoichiometric or congruent melts. This is illustrated in Fig. 2 where traces (a) and (b) represent the optical absorption spectrum obtained at 85 K before and after reducing the 5% Mg-doped (stoichiometric) crystal. Instead of a peak at 500 nm, as found in the 3% Mg-doped case and shown in trace (a) of Fig. 1, the dominant peak now occurs at 1200 nm with a shoulder on the high-energy side.

We expect oxygen vacancies to be introduced during the reduction of these latter two 5% Mg-doped crystals, and the shoulder in the 500–800-nm region of trace (b) in Fig. 2 implies that we have produced more than one band. A possible form for these oxygen vacancies is F<sup>+</sup> centers. To explore this suggestion, we subtracted an F<sup>+</sup>-center absorption band from the total absorption for the reduced 5% Mg-doped stoichiometric crystal. A symmetrical band peaking at 1200 nm remained after the F<sup>+</sup> band was subtracted. Specifically in Fig. 2, trace (c) which represents the F<sup>+</sup>-center band was subtracted from trace (b) with the remainder being trace (d). This separation of bands suggests that reduction creates two types of defects in the 5% Mg-doped crystals grown from the stoichiometric or congruent melts, one being oxygen vacancies containing only one electron (F<sup>+</sup> centers) and the other being an electron trap peaking at 1200 nm. The F<sup>+</sup>-center band used in our subtraction was obtained from trace (b) of Fig. 1 with no adjustments being made in its shape or magnitude. Thus, trace (b) in Fig. 1 and trace (c) in Fig. 2 are identical. The two samples used in Figs. 1 and 2 were vacuum annealed under identical conditions and presumably contain the same concentrations of oxygen vacancies, which accounts for our successful band separation without the need to introduce arbitrary adjustable parameters.

Little if any absorption from a 1200-nm band was found in the 3% Mg-doped crystal after reduction [see trace (b) in Fig. 1], whereas an intense 1200-nm band was present in the

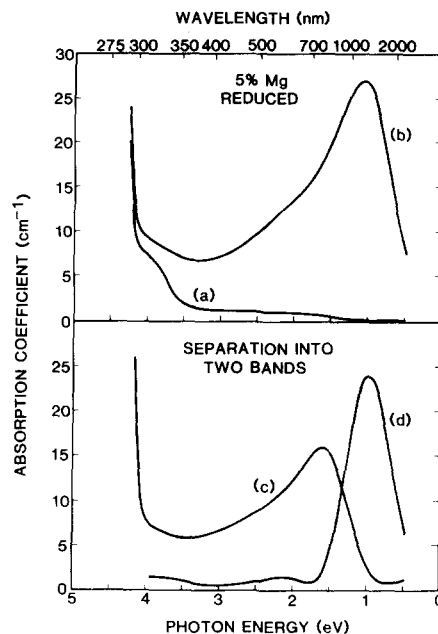


FIG. 2. Optical absorption from a reduced 5% Mg-doped (stoichiometric) crystal. Trace (a) was taken from the as-received crystal and trace (b) was taken after a vacuum anneal at 1000°C for 1 h. The F<sup>+</sup> center band obtained from Fig. 1 is reproduced as trace (c). The 1200-nm band illustrated in trace (d) is the result of subtracting the F<sup>+</sup> center band from the initial absorption [i.e., subtracting trace (c) from (b)].

5% Mg-doped crystal after a similar reduction. This shows that there is no simple scaling of the 1200-nm band intensity with the magnesium doping level which, in turn, suggests the existence of a threshold level. However, this threshold level does not depend on the magnesium concentration alone, as illustrated when we compare the 5% Mg-doped Li-deficient crystal with the 5% Mg-doped stoichiometric crystal. Although the Mg doping level is the same for these two crystals, their concentrations of lithium vacancies (i.e., Li/Nb ratios) are quite different and they exhibit different reduction behaviors. This implicates lithium vacancies as an important parameter.

Thus, our data indicate that the threshold level depends upon both the magnesium concentration and the lithium-vacancy concentration. To understand these dependences, we consider possible defect behaviors resulting from the magnesium doping. The divalent charge and the ionic size of the magnesium strongly suggest that this ion occupies a lithium site in LiNbO<sub>3</sub>. Because of their excess positive charge relative to this lattice site, these substitutional Mg<sup>2+</sup> ions can act as charge compensators for lithium vacancies which are present in the crystal at high (up to 3%) concentrations.<sup>5</sup> Since the lithium vacancy concentration is normally very large, early investigators proposed that the charge compensation in undoped LiNbO<sub>3</sub> is accomplished by “antisite” niobium ions, either via a simple one-for-one substitution<sup>6</sup> or through replacement of extended sequences of ions.<sup>7</sup> We suggest the off-site niobium ions are no longer needed for charge compensation of the lithium vacancies when the Mg<sup>2+</sup> ions are present. This means that the lithium vacancy concentration can stay constant and the off-site niobium concentration can decrease as magnesium is added to the crystal.

To clarify the interrelationship between the concentra-

TABLE I. A summary of the estimated concentrations of magnesium ions and lithium vacancies for the five LiNbO<sub>3</sub> crystals used in the present investigation. The concentrations are given as percentages of the total number of lithium sites in the crystal. The lithium-vacancy values were obtained from the initial Li/Nb ratio in the melt and reference to the phase diagram. The magnesium values represent the amount of MgO added to the melt.

Mg concentration	Type of melt	Li-vacancy concentration	Behavior observed
0%	congruent	3%	below threshold
3%	stoichiometric	3%	below threshold
5%	Li-deficient	5%	below threshold
5%	stoichiometric	3%	above threshold
5%	congruent	3%	above threshold

tion of magnesium ions and lithium vacancies, we have tabulated their values in Table I for those crystals used in the present study. It should be emphasized that only the approximate values of these concentrations are known, but the expected uncertainties do not detract from our conclusions. The samples which showed below-threshold behavior had lithium vacancy concentrations greater than or similar to the magnesium levels. Conversely, above-threshold behavior was found only in samples where the magnesium ions significantly exceeded the number of lithium vacancies. Thus, we conclude from our data that the threshold doping level (i.e., defined in our present case to be production of the 1200-nm optical absorption band during reduction) depends directly on the ratio of magnesium ions to lithium vacancies.

The identity of the defect responsible for the 1200-nm absorption band has not been revealed in the present study although we can conjecture that it is an electron trapped by a magnesium ion. Radiation studies involving luminescence, optical absorption, and electron spin resonance techniques presently under way will provide additional information about this defect.<sup>8</sup> Assuming that our proposed assignment is correct, the threshold for observation of the 1200-nm band implies the existence of two distinct environments for the magnesium ions. We envision the magnesium ions to be at

lithium sites in both cases, but with different nearby point defects causing the distinct environments. Until the threshold doping level is reached, apparently only one of the environments is occupied by magnesium ions, and this is not a stable electron trap at the higher temperatures involved in the reduction process. When the magnesium concentration exceeds the threshold doping level, the additional ions enter the other environment where they act as stable electron traps and result in the 1200-nm absorption band.

The existence of two magnesium environments is supported by the work of Bryan *et al.*<sup>1</sup> wherein they reported two trapping sites for OH<sup>-</sup> molecules. One of the OH<sup>-</sup> infrared bands, at 2.87 μm, was observed only in below-threshold LiNbO<sub>3</sub> crystals and the other band, at 2.83 μm, occurred only in above-threshold crystals. We expect that the environments for a proton (in the form of the OH<sup>-</sup> molecule) and for a substitutional magnesium ion will be similar since both have an effective positive charge relative to the lattice.

While the data presented in this letter clearly show significant changes in defect structure caused by Mg addition to LiNbO<sub>3</sub>, the interpretation of the data is not unambiguous at this time. A paper discussing alternate interpretations is in preparation.

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<sup>1</sup>D. A. Bryan, Robert Gerson, and H. E. Tomaschke, *Appl. Phys. Lett.* **44**, 847 (1984).

<sup>2</sup>K. L. Sweeney and L. E. Halliburton, *Appl. Phys. Lett.* **43**, 336 (1984).

<sup>3</sup>L. Arizmendi, J. M. Cabrera, and F. Agullo-Lopez, *J. Phys. C* **17**, 515 (1984).

<sup>4</sup>J. L. Ketchum, K. L. Sweeney, and L. E. Halliburton, *Phys. Lett. A* **94**, 450 (1983).

<sup>5</sup>M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Oxford University, Oxford, 1977), pp. 275–280.

<sup>6</sup>P. Lerner, C. Legras, and J. P. Dumas, *J. Cryst. Growth* **3/4**, 231 (1968).

<sup>7</sup>K. Nassau and M. E. Lines, *J. Appl. Phys.* **41**, 533 (1970).

<sup>8</sup>K. L. Sweeney, L. E. Halliburton, D. A. Bryan, R. R. Rice, Robert Gerson, and H. E. Tomaschke (unpublished).