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Photoconductivity parameters in lithium niobate

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Measurements on a variety of doped (magnesium and/or iron) and undoped lithium niobate crystals in the oxidized state demonstrate an Arrhenius dependence of dark conductivity on reciprocal temperature between 460 and 590 K. All of the crystals had roughly the same conductivity and activation energy (1.21 eV) over the temperature range, implying that all have about the same free-carrier concentration and mobility. The enhanced photoconductivity of magnesium-doped lithium niobate is attributed to a greatly reduced trapping cross section of Fe³⁺ for electrons, the smaller cross section being due to a changed substitutional site for Fe³⁺. The Fe³⁺ trapping cross section is calculated from photoconductivity data to be of order 10^{-18} m² in undoped lithium niobate. This implies a photoelectron lifetime of order 6×10^{-11} s in a relatively pure (2-ppm Fe) oxidized crystal.

INTRODUCTION

Lithium niobate (LN) crystals of excellent optical quality and with strong electro-optic coefficients are grown by the Czochralski method. The compound has been widely used in electro-optic devices, both of the bulk type, such as modulators, and the waveguide type, such as binary switches. Such applications are partially limited, however, by two effects related to the semiconductive properties of the crystal, its conductivity and its absorptivity. Both of these properties may have their origin in the intrinsic behavior of crystals, or be due to impurities and defects. Two particularly important aspects of electronic behavior in LN, the photorefractive effect and photoconductivity, have been shown to be primarily due to iron impurities, present at the parts per million level in even the purest crystals.^{1,2} The complete analysis of these effects has been hindered because the value of some important electronic parameters, such as the mobility and the photoelectron lifetime, are uncertain.

Within the past few years it has been ascertained that the addition of five mole percent of magnesium oxide to LN raises its photoconductivity by two to three orders of magnitude, while most of its other properties are relatively unchanged.^{3,4} This finding was quite unexpected. Magnesium oxide at the one mole percent level has been commonly used to alter the phase-match temperature of LN by slightly changing its extraordinary refractive index,⁵ but other major effects had not been seen. Even after the discovery of the enhanced photoconductivity, it was not immediately clear whether it was due to increased photoionization, increased mobility of the photoelectrons, or to a greater photoelectron lifetime. Further experimentation was necessary to distinguish among these three possibilities.

A very useful measurement to promote understanding of electronic processes in pure LN is the determination of the electron mobility. In polar oxides similar to LN, the measured room-temperature mobilities are often found to be about 10^{-4} m²/V s, a value considered to be in the transition region between band and hopping conduction. Oxidized LN is an excellent insulator, where the combination of low mobility and few charge carriers makes the measurement of mobility impossible. Three reported mobility values⁶⁻⁸ were found by reducing the oxide crystals and introducing stoichiometric defects, which enhanced the conductivity and photoconductivity and made Hall effect measurements possible. The drawback to this method is that the heavily reduced crystal may not have the same mobility as the pure crystal. Ohmori et al.6 measured the mobility of photoexcited carriers, principally below room temperature, while Nagels⁷ and Jösch et al.⁸ both used heavily reduced crystals and worked at high temperatures to further increase the conductivity. Ohmori reported that the mobility increased with decreasing temperature, while the other authors found the opposite. Both Nagels' and Jösch's data supported the hypothesis that they had observed hopping conductivity. It is possible that strong reduction causes a transition from band to hopping mobility. In the calculations to follow, Ohmori's results will be used, since his more lightly reduced LN should better approximate the oxidized or slightly reduced crystals commonly used in photorefractive effect and photoconductivity experiments.

CONDUCTIVITY

While the direct measurement of mobility in oxidized LN is impossible, we present conductivity data permitting the comparison of mobilities in crystals of different doping. To do this the resistivity of well oxidized crystals was measured in the crystallographic c direction (it was also found that *a*-direction resistivities were approximately equal to those in the c direction). All of the crystals tested were grown from congruent melts by Crystal Technology, Inc., but the dopant concentration differed significantly. Two

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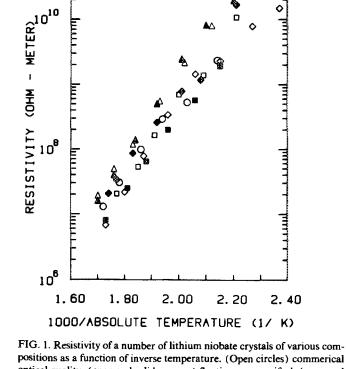
crystals were grown from starting materials purified by the floating zone technique; one was a commercial, optical quality crystal; two had an addition of five mole percent of MgO: one had five mole percent MgO and 100 ppm of iron; and one was doped with five mole percent of MgO and 200 ppm of iron. The sample dimensions were about $6 \times 6 \times 2$ mm, the c axis corresponding to one of the long dimensions and the other two crystallographic axes along the other edges. Silver paste electrodes were applied to faces normal to the c direction, and the resistance of the samples was measured with a Keithley 616 electrometer. Measurements were made between 190 and 315 °C, but pyroelectric effects made for larger uncertainties below 220 °C.

Figure 1 shows the results of the measurements. It is seen that the data for log resistivity as a function of reciprocal temperature can be fit by straight lines for each crystal, particularly at temperatures above 220 °C. Within the reproducibility of the measurements, all of the slopes are approximately the same. The samples which are magnesium doped and have no other additive have a somewhat higher resistivity than the rest, while the crystals which are zone purified have a slightly lower resistivity. It is not certain whether these minor variations, which may be associated with stoichiometry fluctuations as found by Bollmann and Gernand,⁹ are reproducible. All of the data may be adequately represented, in terms of conductivity, by the equation

$$\sigma = 1620 \exp[-(1.94 \times 10^{-19})/kT], \qquad (1)$$

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where $\sigma =$ conductivity $(\Omega m)^{-1}$, T =temperature (K), and $k = \text{Boltzmann's constant} = 1.38 \times 10^{-23} \text{ J/K}.$



positions as a function of inverse temperature. (Open circles) commerical optical quality; (open and solid squares) floating zone purified; (open and solid triangles) 5-mol % MgO; (open diamonds) 5-mol % MgO + 100ppm Fe; (solid diamonds) 5-mol % MgO + 200-ppm Fe.

The energy, 1.94×10^{-19} J, corresponds to 1.21 eV. To the extent that Eq. (1) satisfactorily represents the data, all of the crystals have approximately the same conductivity parameters. That is, it is reasonable to conclude that there are no large differences in activation energy, mobility, or effective mass among the LN crystals we have studied, in spite of their large compositional differences. This result is surprising for both the magnesium and the iron dopants.

Several models could be considered to explain the conductivity given by Eq. (1). One model takes the conductivity as extrinsic. The crystals measured were all congruent, and have lithium and oxygen vacancy concentrations of order 1%. A model of conductivity based on doubly ionizing oxygen vacancies containing trapped electrons, with the ionization energy approximately equal to the optical energy gap, can account for Eq. (1) in undoped LN. One would expect, however, that either magnesium or iron doping should substantially alter the crystal's conductivity if this model is correct, because magnesium doping changes the vacancy equilibria.¹⁰ Iron doping introduces numerous trapped electrons, substantially altering the photoconductivity and optical absorption, and might also be expected to change the extrinsic conductivity.

An alternate model assumes that the conductivity describd by Eq. (1) is intrinsic. The immediate objection to this idea is that the optically determined energy gap of LN at 200 °C is 3.7 eV,¹¹ about three times greater than the activation energy in Eq. (1), whereas in an intrinsic model the two energies should differ by a factor of 2. The intrinsic model could be valid if LN were an indirect gap semiconductor with an energy gap of 2.4 eV. A rough calculation of the intrinsic conductivity for this case, using Ohmori's value of the mobility, gives results within an order of magnitude of Eq. (1). This does not prove the intrinsic model correct, but shows that it is not ruled out. In addition, small polaron hopping conductivity is possible.

Some semiconductors can be identified as indirect gap materials by examining details of the optical absorption edge. Redfield and Burke¹¹ measured the absorption edge of LN as a function of temperature and stoichiometry at optical energies between 3.2 and 4.4 eV. They found the spectrum to have "unique curvature and great breadth at low temperature," and attributed this to the internal electric fields of charge defects, a very plausible explanation in congruent LN. Unfortunately, under these circumstances it becomes difficult to use the spectrum to decide between direct and indirect gap absorption.

Many of the properties of LN will continue to be obscured by the nonstoichiometry of the compound. It may thus not be easy to establish definitely whether Eq. (1) represents intrinsic or extrinsic conductivity. However, if a doped composition can be found with a lower conductivity and a higher activation energy over a significant temperature range than is given by Eq. (1), then Eq. (1) must describe extrinsic behavior.

PHOTOCONDUCTIVITY

While most of the basis concepts describing photoconductivity in LN have been understood for some time^{1,2,12-17} (at least, at light intensities low enough so that nonlinear processes are not significant), some of the microscopic parameters involved were unknown. We shall show that Ohmori's measurement of the mobility can be used to derive a set of parameters which are in reasonable agreement with data on photoconductivity and the photorefractive effect. Furthermore, an explanation is given below for the high photoconductivity of magnesium-doped LN.

The photoconductivity of LN is primarily due to iron impurity. In iron-doped LN, irradiated with light lower in frequency than the absorption edge, the main source of photoelectrons is the photoionization of Fe^{2+} .

$$Fe^{2+} + photon \rightarrow Fe^{3+} + electron$$
. (2)

The photoelectron contributes to the photoconductivity until it is retrapped by an Fe^{3+} ion in the process

$$Fe^{3+} + electron \rightarrow Fe^{2+} + phonon$$
. (3)

The magnitude of the free-electron concentration is established by the condition that the rate of free-electron creation must equal the rate of trapping. The free-electron creation rate is

$$(I/h\nu)N_2S_2\phi, \qquad (4)$$

where I = light intensity (W/m²), h = Planck's constant = 6.63×10^{-34} J s, $\nu = \text{light}$ frequency (Hz), $N_2 = \text{Fe}^{2+}$ ion concentration (ions/m³), $S_2 = \text{cross section}$ of Fe²⁺ion for light of frequency ν (m²), and $\phi = \text{quantum}$ efficiency, photoelectrons created per absorbed photon.

The rate of electron capture is

$$nN_3S_3v, (5)$$

where $n = \text{free-electron concentration (electrons/m³)}, N_3 = \text{Fe}_3^+$ ion concentration (ions/m³), $S_3 = \text{cross section}$ of Fe^{3+} for electron capture (m²), and v = thermal velocity of electrons (m/s).

Equating (4) and (5)

$$n = \left(\frac{I}{h\nu}\right) \frac{\phi}{\nu} \frac{S_2}{S_3} \frac{N_2}{N_3}.$$
 (6)

The photoconductivity $\Delta \sigma$ is given by

$$\Delta \sigma = n e \mu , \qquad (7)$$

where $e = \text{electronic charge} = 1.60 \times 10^{-19} \text{ C and } \mu = \text{electron mobility (m²/V s)}$. Then, from (6) and (7)

$$\Delta \sigma = \frac{Ie}{h\nu} \left(\frac{\mu \phi}{v} \frac{S_2}{S_3} \frac{N_2}{N_3} \right). \tag{8}$$

We shall try to determine S_3 by estimating the other terms in Eq. (8) from experimental data. μ , the electron mobility, is approximately 0.8×10^{-4} m²/V s at room temperature.⁶ v, the electron thermal velocity, is about 1.2×10^5 m/s at room temperature.

The value of ϕ , the quantum efficiency, can be approximated by using the idea that the scattering distance for electrons in the photorefractive effect should be of comparable magnitude to the scattering distance calculated from the mobility, since similar electron-phonon interactions govern both processes. Now

$$\mu = e\tau_s/m_e = eL_s/m_e v, \qquad (9)$$

where τ_s = electron collision time(s), L_s = mean scattering

distance between collisions (m), and m_e = electron effective mass $\approx 9.1 \times 10^{-31}$ kg.

For $\mu = 0.8 \times 10^{-4} \text{ m}^2/\text{V} \text{ s}$, $L_s = \text{is found to be 0.054}$ nm. Grousson *et al.*¹⁶ recently measured the photorefractive anisotropy constant K for iron-doped LN at 2.9 eV, just below the photon energy at which the anisotropy constant is a maximum. They then calculated ϕL_p by using the equation

$$K = (e/h\nu)\phi L_p , \qquad (10)$$

where K = anisotropy constant (A m/W) and $L_p =$ photorefractive scattering distance (m).

 ϕL_p was found to be 0.06 nm. Therefore, at this wavelength, ϕL_p is about equal to L_s . If in addition $L_p \simeq L_s$, ϕ is of order unity. The value of ϕ decreases at longer wavelengths, as shown by a decreasing anisotropy constant.¹⁶ At 2.5 eV, $\phi \simeq 0.5$, the value we shall use.

The ratio N_2/N_3 depends on the state of oxidation of the crystal, and has been determined, by Mössbauer spectroscopy and by photrefractive measurements, to be approximately 0.05 in oxidized crystals and 10 in reduced crystals.¹⁴

 S_2 can be estimated from the absorption coefficient α of LN crystals by using the equation $\alpha = S_2N_2$. However, the literature data on α as a function of divalent iron content vary widely, partly because of the difficulty in determining divalent iron concentration and partly because in highly reduced crystals, where the divalent iron concentration is known, a second strong absorption appears, possibly associated with Nb⁴⁺.¹⁸ For oxidized crystals containing 200 ppm Fe, we found $\alpha = 70 \text{ m}^{-1}$. If $N_2/N_3 = 0.05$, $S_2 = 1.5 \times 10^{-22} \text{ m}^2$, close to most of the literature values.

Substituting in Eq. (8) the values for μ , ϕ , v, and S_2 indicated above,

$$\Delta \sigma = \frac{2 \times 10^{-32}}{S_3} \frac{N_2}{N_3} I.$$
 (11)

Krätzig's measured value for $\Delta \sigma$, as a function of iron valency, is, in S. I. units¹⁵:

$$\Delta \sigma = 1.5 \times 10^{-14} (N_2/N_3) I.$$
⁽¹²⁾

From (11) and (12) we calculate $S_3 = 1.3 \times 10^{-18} \text{ m}^2$. There is an approximate theoretical relationship that can also be used for estimating S_3 . It is known from Mössbauer spectroscopy¹⁴ and from field annealing experiments¹ that the principal site for iron substitution is the lithium site, with Fe³⁺ replacing Li⁺. The electron capture cross section is then that of a + 2 impurity relative to its lattice site, given by¹⁹

$$S_3 = \left[2(9\pi)e^4 \right] / \left[16(4\pi\epsilon)^2 (kT)^2 \right], \tag{13}$$

where ϵ = dielectric constant (F/m).

For LN the average value of the clamped dielectric constant is 3.3×10^{-10} F/m,²⁰ leading to $S_3 = 8 \times 10^{-18}$ m² at 300 K, a factor of 6 higher than the value calculated above from Eq. (8) and Krätzig's data [although there is a correction of magnitude 0.1 to 0.01 which should be applied to the S_3 calculation from Eq. (13) because of the short electron scattering distance in LN]. In view of the many rough approximations in these calculations, and the approximate nature of Eq. (13), the agreement of the two values for S_3 indicates that 1.3×10^{-18} m² is a reasonable magnitude.

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Several other tests of Eq. (8) may be cited. For heavily reduced LN doped with 0.2-wt. % Fe, Glass *et al.*²¹ have measured $\Delta \sigma = 1.5 \times 10^{-13} I$. Equation (8), with $N_2/N_3 = 10$ (reduced conditions) and $S_3 = 1.3 \times 10^{-18} m^2$, gives the same result. For oxidized LN with 0.015-wt. % Fe, Grousson *et al.*¹⁶ found $\Delta \sigma = 2.6 \times 10^{-16} I$, while Eq. (8), with $N_2/N_3 = 0.05$ and $S_3 = 1.3 \times 10^{-18} m^2$, gives $\Delta \sigma = 7.7 \times 10^{-16} I$, within a factor of 3 of the experimental result. Our previous measurements on undoped oxidized crystals⁴ agree with Eq. (8) to within a factor of about 4.

Equation (8) is not new. Grousson *et al.*¹⁶ presented almost the same equation in a different form. However, the use in this article of Ohmori's value of mobility, and the argument for a high quantum efficiency, leads to a set of parameters which are consistent with most of the experimental data.

MAGNESIUM-DOPED LITHIUM NIOBATE

It is found that very large quantities of magnesium, an ion of charge +2, are able to substitute for lithium, of charge + 1, with little effect on many electronic properties, including the photorefractive anisotropy current. However, the photoconductivity is increased by two to three orders of magnitude. If one evaluates the factors entering Eq. (8), the only one that can be expected to be markedly affected by magnesium substitution without also affecting the anisotropy current is S_3 , the trapping cross section for Fe³⁺. ESR data have shown that the Fe³⁺ site in the magnesium-doped crystal differs from that in nominally pure LN.²² In the latter, S_3 is relatively large because the Fe³⁺ ion functions as a doubly positive impurity in an Li⁺ site, and both Mössbauer and ESR spectra indicate that there is no compensating negative impurity nearby. In the new site of Fe^{3+} in the magnesium-doped crystal, the ion could be a neutral or negative substituent, which would have a much lower cross section for electron trapping. To increase the photoconductivity by a factor of 100, S_3 would have to decrease to an average trapping cross section of 1.3×10^{-20} m², somewhat larger than the area presented by an Fe²⁺ ion, in the magnesiumdoped crystal.

Considered as a chemical process, the addition of magnesium as a substituent for lithium results in an excess of positive charge in the crystal, which may be compensated for by lithium expulsion and the incorporation of negative oxygen ions in the lattice. However, compensation by any other chemical change which will introduce negative charge to the lattice is also favored. One such change would be for iron to substitute for Nb⁵⁺, rather than for Li⁺. It has not been determined that this occurs. The ESR data show that the environment of the iron ion is changed by the magnesium addition, however, and the above chemical considerations dictate that the change should tend to make the iron a neutral or negative substituent. The complex defect chemistry of LN does not permit a definite assignment of the new iron site.

PHOTOEXCITED CARRIER LIFETIME

The lifetime of the excited electron, τ_e (s), is given by²³

$$\tau_e = (N_3 S_3 v)^{-1}. \tag{14}$$

$$\tau_e = (e/\mu kT)L^2, \qquad (15)$$

where L = diffusion length (m).

For nominally pure, oxidized LN, with an iron concentration of 2 ppm, $N_3 \approx 10^{23}$ ions/m³, S_3 is 1.3×10^{-18} m², and v is 1.2×10^5 m/s. This leads to a photoelectron lifetime of 6×10^{-11} s in the crystal. For a reduced crystal, the lifetime is an order of magnitude greater, since the Fe³⁺ concentration is reduced by 10.

In oxidized, magnesium-doped LN with 2 ppm of iron content, the photoconductivity is enhanced by two or more orders of magnitude. Taking S_3 as 1.3×10^{-20} m², the lifetime in this crystal is about 6×10^{-9} s. For the same crystal in the reduced state, the lifetime should be 6×10^{-8} s. It should be emphasized that all of these quoted lifetimes are order of magnitude estimates.

The photoconductivity model presented here can be tested by a direct measurement of either the photoelectron lifetime or the diffusion length in these crystals. The larger values of these parameters in magnesium-doped LN may make the measurement easier in this material. A partial test of the lifetime values would be to measure the rise time of the photoconductivity, which is equal to or greater than the photoelectron lifetime, depending on the trap level energies. A laser emitting radiation pulses appreciably shorter than the rise time will induce a correspondingly reduced photoconductivity, and should have a higher hologram writing efficiency.

SUMMARY

A simple theory has been given in which approximate cross sections are calculated for photoionization and retrapping of electrons in lithium niobate. The theory is based on conductivity measurements and on the use of a value of the electron mobility which was determined by the photoexcitation of reduced samples.⁶ In order to make more precise determinations of the cross sections presented here, and to test the theory further, it would be useful to have both an Ohmori-type direct experimental determination of the charge carrier mobility in magnesium-doped lithium niobate, and a measurement of the photoelectron lifetime.

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