Suppression of mid-infrared light absorption in undoped congruent lithium niobate crystals

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Received December 9, 2009; accepted January 27, 2010;
posted February 25, 2010 (Doc. ID 121144); published March 31, 2010

Absorption measurements on 5 mol. % MgO-doped and undoped congruent lithium niobate ($LiNbO_3$) crystals revealed absorption bands in the wavelength range of 2500–2800 nm, caused by incorporated hydrogen ions. High-temperature annealing was applied to the congruent $LiNbO_3$ (CLN) crystals, which decreased the absorption significantly. Then the annealed CLN crystals were periodically poled. As an application of the low-loss annealed CLN crystal, the operation of a 1550 nm pumped singly resonant CW optical parametric oscillator, resonant around 2600 nm, using a periodically poled crystal was demonstrated. © 2010 Optical Society of America

OCIS codes: 160.3730, 190.4970, 190.4400.

Optical parametric oscillators (OPOs) have been established as attractive sources of tunable coherent radiation in the mid-IR [1]. The availability of highly nonlinear and noncritically phase-matched materials such as periodically poled $LiNbO_3$ (PPLN) has greatly expanded the practical range of operation of these devices, especially for CW singly resonant oscillators (SROs) [1,2]. Low absorption for the resonant wave is important in these applications, as the threshold pump power P_{thr} is proportional to the total round-trip loss in the cavity [3]. To date, CW mid-IR SROs have been pumped with 1 μm radiation, with resonant wavelengths around 1400–1900 nm. Pumping at the wavelength of 1550 nm is of interest in order to take advantage of convenient tunable telecommunication-band pump technology and for signal processing applications such as transferring the amplitude and phase modulation of a pump onto a long-wave idler. Correspondingly longer resonant wavelengths, typically in the wavelength range of 2500–2700 nm for idler outputs in the 3600–3850 nm wavelength range, are required in these applications. In a previously published work [4] as well as with efforts in our own laboratory, it has not been possible to obtain CW singly resonant operation with resonant waves in this range using 5 mol. % MgO-doped periodically poled $LiNbO_3$ (PPMgOLN), even for pump powers as large as 20 W. In this Letter we report on the observation of a broad weak absorption band in the wavelength range 2500–2800 nm related to the concentration of protons in $LiNbO_3$, reduction of this absorption through a high-temperature annealing process, and successful operation of a CW 1550 nm pumped singly resonant OPO (SROPO) in an annealed periodically poled congruent $LiNbO_3$ (PPCLN) crystal. To the best of our knowledge, this is the first time any CW SROPO has been pumped with a wavelength longer than 1100 nm.

It is well known that hydrogen ions, which are always incorporated into $LiNbO_3$ and MgO-doped $LiNbO_3$ during crystal growth in air [5,6], generate an OH-vibration peak in the absorption spectrum at $\lambda = 2871$ nm in congruent $LiNbO_3$ (CLN) and shifted to $\lambda = 2826$ nm in 5 mol. % MgO-doped $LiNbO_3$ (MgOLN) [6]. In CLN combined OH-vibration-libration absorption bands can be found, in the wavelength range 2200–2500 nm [7,8]. In the wavelength range from 2500 to 2800 nm there is no absorption band known so far for CLN and MgOLN. However, since $P_{\mathrm{thr}} \propto \alpha_s$, where α_s is the absorption coefficient of the signal wavelength, an absorption coefficient in the range of only 0.005 cm^{-1} in a several-centimeter-long crystal would add significantly to the total loss of a well designed cavity and therefore increase P_{thr} substantially.

To ascertain whether losses of this magnitude were present, we conducted careful light absorption measurements in CLN and MgOLN. The samples used in our experiments were provided by Crystal Technology, Inc. Absorption measurements were performed with a 5 mol. % MgO-doped $LiNbO_3$ crystal with the dimensions of $25\ \mathrm{mm} \times 25\ \mathrm{mm} \times 25\ \mathrm{mm}$ and four CLN crystals with the dimensions of $20\ \mathrm{mm} \times 20\ \mathrm{mm} \times 20\ \mathrm{mm}$. Two CLN crystals were cut from the top part of a CLN boule, and two crystals were cut from the bottom part of the same boule. The y- and x-faces of every crystal were polished to high optical quality. Using crystals from the top and bottom parts of the boule was useful for determining whether impurities causing absorption are distributed inhomogeneously within the crystal during growth. Two CLN crystal cubes, one from the top part and one from the bottom part of the boule, were subjected to a high-temperature annealing treatment, at 1000 °C in a dry oxygen atmosphere for 24 h, before polishing. The purpose of the annealing step was to drive hydrogen out of the crystal [9]. After annealing, back at room temperature, the diffusion coefficient of hydrogen was too low for the significant incorporation back into the crystal [9].

0146-9592/10/071070-3/$15.00

High-precision light transmission measurements were performed with a Varian Cary 500 absorption spectrophotometer in the wavelength range of 2400–2950 nm. The spectrophotometer was purged with dry air to avoid atmospheric absorption and to make the measurement less sensitive to changes in atmospheric humidity that occur over time. To be able to distinguish between ordinarily and extraordinarily polarized light, a Glan–Taylor polarizing prism was used. The light transmission data were corrected for Fresnel reflection losses according to [10]. The wavelength dependence of the reflection coefficient was taken into account by using the Sellmeier equations for CLN and MgOLN according to [11].

In Fig. 1 the absorption spectra of the as-grown MgOLN crystal are shown for ordinarily and extraordinarily polarized light. The maximum absorption coefficient at $\lambda = 2826$ nm is 0.7 cm^{-1} for ordinary and 0.08 cm^{-1} for extraordinary light polarization. Besides the well-known OH-vibration band at $\lambda = 2826$ nm, broad absorption bands between $\lambda = 2500$ and 2750 nm can be seen. The magnitude of the absorption coefficient is similar between ordinary and extraordinary light polarizations within these absorption bands; however, the wavelength dependence is somewhat shifted for the two polarizations. Another narrower absorption peak is located with its center at $\lambda = 2447$ nm. It is interesting to note that the amplitude of this peak does not depend on the light polarization, and the newly discovered absorption bands depend only weakly on it, while the OH-vibration peak at $\lambda = 2826$ nm is $\sim 9\times$ larger for ordinarily than for extraordinarily polarized light. The small negative absorption coefficients in Fig. 1 can easily be explained by an imperfect Fresnel correction due to uncertainties in the angle of the incident light, thickness of the sample, and surface scattering, which can lead to an offset and are representative of the limiting resolution of the measurement. The shape of the graph is unaffected by these errors within the measurement accuracy, which is about $\Delta\alpha = 0.0005$ cm^{-1}.

In Fig. 2 the absorption spectra of an as-grown (not annealed) and an annealed CLN crystal are shown for ordinarily [Fig. 2(a)] and extraordinarily [Fig. 2(b)] polarized light. There is no significant difference

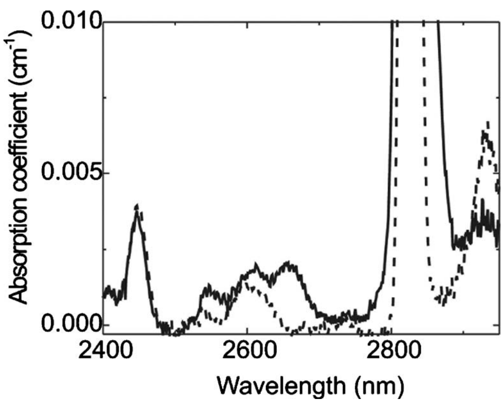

Fig. 1. Absorption coefficient versus wavelength for a 5 mol. % MgO-doped $LiNbO_3$ crystal for ordinarily (solid curve) and extraordinarily (dashed curve) polarized light.

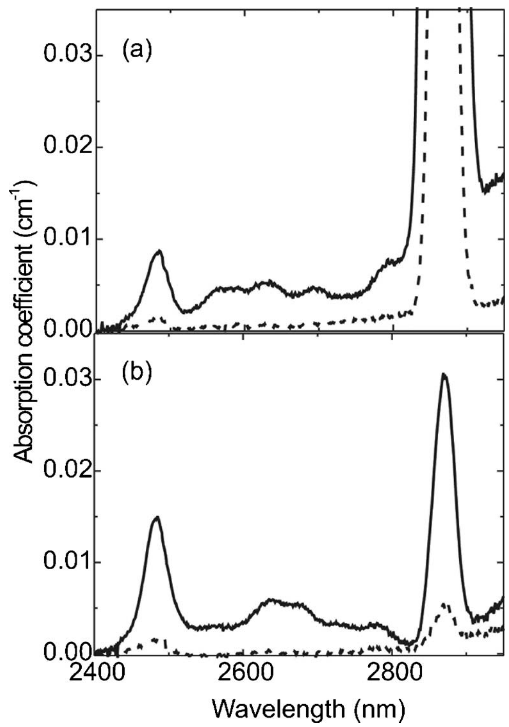

Fig. 2. Absorption coefficient for (a) ordinarily and (b) extraordinarily polarized light versus wavelength for undoped congruent $LiNbO_3$ in the as-grown state (solid curve) and after high-temperature annealing (dashed curve).

in the absorption spectra in this wavelength range between the crystals from the top and bottom parts of the boule. The maximum absorption coefficient of the OH-vibration peak at $\lambda = 2870$ nm is 1.5 cm^{-1} for ordinary and 0.03 cm^{-1} for extraordinary light polarization. In Fig. 2 it can be seen that CLN in the as-grown state exhibits absorption bands between $\lambda = 2500$ and 2800 nm that are similar to those in MgOLN. The main difference between CLN and MgOLN is that the bands for both ordinarily and extraordinarily polarized light are shifted by about 40 nm with respect to those in MgOLN. This shift is similar to the well-known shift of the OH-vibration peak [6]. There is also a peak centered at $\lambda = 2483$ nm which can be compared to the peak at $\lambda = 2447$ nm for MgOLN.

For both CLN crystals in the as-grown state the absorption bands between $\lambda = 2500$ and 2800 nm exhibit absorption coefficient maxima of about 0.005 cm^{-1} which would raise P_{thr} by at least 7 W in typical 1550 nm pumped OPO configurations. However, Fig. 2 also shows that high-temperature annealing decreases the absorption bands between $\lambda = 2500$ and 2800 nm by at least a factor of 10. The hydrogen content in both annealed samples also decreases due to annealing, which, e.g., can be seen in Fig. 2(b) in the amplitude decrease of the OH-vibration peak at $\lambda = 2870$ nm before and after annealing [6]. For ordinarily polarized light the OH-vibration peak also decreases by 1 order of magnitude. Furthermore, experiments show that the observed absorption bands in both MgOLN and CLN are related to the bulk crystal and not to the crystal surface or anything that is adsorbed to the surface. These observations lead to the strong indication that the observed absorption bands between $\lambda = 2500$ and 2800 nm in the as-grown CLN and the MgOLN crystals are also caused by hydrogen ions and therefore are reduced by the annealing procedure. For ordinarily polarized light, the ratio of the maximum absorption coefficient of the OH-vibration peak to the maximum absorption coefficient of the absorption bands between 2500 and 2800 nm is ≈ 300 for both CLN and MgOLN crystals. Applying this relation, the magnitude of these absorption bands can be easily inferred from the amplitude of the OH-vibration peak for ordinarily polarized light, and since the absorption bands between 2500 and 2800 nm are similar in magnitude for both light polarizations, the magnitude of these absorption bands for extraordinary light polarization can also be estimated.

The observed absorption bands cannot be attributed to the already known combined OH-vibration-librations [7]. Further experiments have to be performed in order to investigate if the origin of these absorption bands can be explained by, e.g., defects in the vicinity of the hydrogen atoms, different hydrogen sites, or combination bands similar to OH-vibration-librations [8] or coupled phonon-OH-vibrations. As a next step the effect of annealing on MgOLN is under study. Preliminary results indicate a decrease in absorption due to annealing similar to that seen in CLN. Details will be reported elsewhere.

We fabricated a SRO using as-grown PPMgOLN and annealed PPCLN crystals, pumped with a tunable 1550 nm source based on an external cavity diode laser amplified in an erbium-doped fiber amplifier, which could deliver up to 20 W of CW single-frequency radiation around $\lambda = 1550$ nm. The OPO was of conventional bowtie type, designed for resonance at 2600 nm, with a spot size of 80 μm at the center of the 1-mm-thick 5-cm-long periodically poled crystal, which was antireflection coated at the signal and pump wavelengths. The output coupler had 99.9% reflectivity at 2600 nm and 3% reflectivity at the 3800 nm idler wavelength. The entire bowtie was contained in a vacuum chamber ($P = 5 \times 10^{-5}$ Torr) to eliminate absorption by water vapor in the cavity or adsorbed on the surface of the optics.

As noted in the introduction, the OPO operation using as-grown PPMgOLN crystals could not be obtained with any of our PPMgOLN samples, indicating that P_{thr} exceeded the available 20 W over the entire tuning wavelength range from 2500 to 2700 nm. However, with a 5-cm-long 1-mm-thick *annealed* CLN crystal subsequently poled with a 32.8 μm period by conventional electric-field poling methods, the OPO reached its threshold at 6.5 W pump power. At 15 W pump power it achieved an output of 3 W at 3800 nm. OPO operation was obtained with several annealed PPCLN crystals. Details of this OPO will be reported elsewhere. The absorption coefficient in the as-grown PPMgOLN crystals around 2600 nm could be estimated to be about 0.0075 cm^{-1}. This was deduced from the OH-vibration peak amplitude and the calibration factor of 300. Therefore P_{thr} was theoretically more than 10 W larger than in an annealed PPCLN crystal. The OPO operation with annealed PPMgOLN will be studied next.

In conclusion, new absorption bands in the wavelength range of 2500–2800 nm were found in CLN and 5 mol. % MgO-doped $LiNbO_3$, which are present for both ordinary and extraordinary light polarizations. These absorption bands precluded the operation of a CW SRO with a 20 W 1550 nm pump source. A high-temperature annealing treatment was applied to CLN crystals. During this treatment, incorporated hydrogen ions diffused out of the crystals, which indicates that the newly discovered absorption bands depend on the hydrogen content within the crystals. Thus a decrease in hydrogen content by 1 order of magnitude in CLN decreased the absorption bands by 1 order of magnitude and therefore reduced P_{thr} of the CW SRO into a range accessible to our pump source. To test the influence of the annealing on the OPO operation, CLN wafers were periodically poled after the annealing procedure. Using the annealed PPCLN crystals, the operation of above-mentioned 1.5 μm pumped CW SRO was obtained.

J. R. Schwesyg gratefully acknowledges financial support of the Deutsche Telekom Stiftung. This research was supported in part by Crystal Technology, Inc.; Defense Advanced Research Projects Agency (DARPA) under prime contract W911QX-06-C0101 through Celight, Inc.; and U.S. Air Force Office of Scientific Research (AFOSR) under grants FA9550-09-1-0233 and FA9550-05-1-0180.

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