

Light-Induced Absorption and Holographic Recording in Pr:LiNbO₃

Van-Thai PHAM

Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland

Sun-Kyun LEE, Minh-Tuan TRINH and Ki-Soo LIM*

*Department of Physics and Basic Science Research Institute,
Chungbuk National University, Cheongju 361-763*

D. S. HAMILTON

Department of Physics, University of Connecticut, CT 06268, U.S.A.

(Received 3 May 2006)

With ultraviolet illumination, we have found a broad UV-induced absorption in the blue and some involvement of Pr ions in Pr:LiNbO₃. Transient and stable absorption induced by UV illumination was analyzed at 457, 514, and 633 nm and could be explained by hole trap centers and iron ions. We also studied the effects of UV illumination and boundary conditions during holographic recording in the visible. In ultraviolet-gated short-circuit holographic recording, we obtained a high sensitivity and a high diffraction efficiency.

PACS numbers: 42.70.Ln, 71.55.-i, 78.55.-m, 78.40.-q

Keywords: Induced absorption, Pr, LiNbO₃, Holographic recording, Short circuit

I. INTRODUCTION

Lithium niobate (LiNbO₃) crystals doped with transition-metal or rare-earth ions have been extensively studied for holographic data storage and other applications [1]. Recently, nonvolatile two-color holographic recordings have been demonstrated in congruent LiNbO₃ doped with Pr ions [2]. Addition of Pr ions was found not to alter the absorption spectrum of LiNbO₃ much, but the roles of the Pr ions and the deep ultraviolet (UV) absorption centers [3] are little understood yet. In general, rare-earth ions have weak transitions in the visible region because the 4f-4f dipole transitions are forbidden and, thus, reveal few electron-phonon coupled absorption bands. However, the positions of the 5d levels of trivalent rare-earth ions strongly depend on the interaction of 5d electrons with the surrounding anion ligands, producing broad absorption bands in the UV region. Thus, the UV illumination can excite Pr ions to 5d levels, as well as to the conduction band. However, it is not clear if Pr ions are involved in holographic recording and how the UV illumination affects holographic recording in Pr:LiNbO₃. In this work, we studied the UV-induced absorption and the role of Pr ions to find the mechanism of the UV-gated holographic recording process. In addition, we consid-

ered two boundary conditions, short and open circuits, during recording.

II. EXPERIMENT

The LiNbO₃ crystal with a congruent composition doped by 0.15 % Pr⁺³ was grown by using the Czochralski method. The dimensions $a \times b \times c$ of the crystal were 10 × 10 × 10 mm. Except for two faces perpendicular to the c -axis, the others were polished to high optical quality. Photoluminescence (PL) was measured using a SPEX 1403 Double spectrometer. Photoluminescence excitation spectra were measured with a system consisting of a 1-kW xenon arc lamp and a monochromator in the range of 400 – 750 nm with a Spectra Pro 300i data acquisition system. The excitation spectra were corrected for the spectral dependence of a xenon lamp and the detection system. The light source for the UV-induced absorption was a mercury lamp at 365 nm. The absorption spectra were measured by using an Ocean Optics S 2000 fiber spectrometer within the wavelength range of 350 – 1000 nm. The light was controlled by using an electromechanical shutter, and variations of the light intensity were achieved by adjusting neutral density filters. To observe the temporal behavior of the induced absorption, we used weak argon laser beams at 457 and

*E-mail: kslim@chungbuk.ac.kr; Fax: +82-43-271-1653

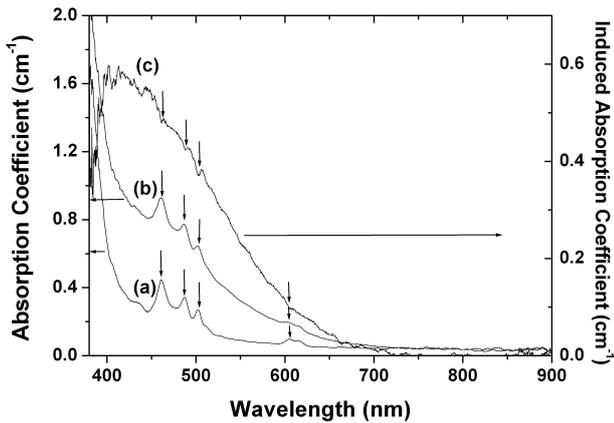


Fig. 1. Absorption spectra of Pr: LiNbO₃ measured before and after illumination at 365 nm: (a) before UV illumination, (b) after UV illumination, and (c) absorption difference. The crystal was irradiated for 2 h with an intensity of 25 mW/cm² at room temperature.

514 nm, as well as a HeNe laser beam at 633 nm, with ordinary polarizations. The probe beams passed along the a-axis just below the UV-illuminated surface because most of UV light was absorbed near the surface. The UV beam with diameter of 2 mm and the probe beam with diameter of 0.5 mm were made to well overlap inside the crystal. The temperature dependence of the UV-induced absorption was obtained by heating the sample in the temperature range of 20 – 164 °C. The signal from a photodiode attached to a cut-off filter was monitored on a LeCroy 9310A digital oscilloscope. Holographic recording was performed with and without UV illumination. In addition, different boundary conditions of open and short circuits were applied for holographic recording. Good electrical contact between a copper plate and the crystal was achieved by using silver paste for the short circuit.

III. RESULTS AND DISCUSSION

Fig. 1 shows the unpolarized absorption spectra of the crystal before and after UV illumination at room temperature. The spectrum before UV illumination consists of several bands corresponding to visible transitions between the ³H₄ ground state and excited multiplets belonging to the 4f² configuration of Pr³⁺. The band edge of LiNbO₃ is at 320 nm [4], and the broad band in the 330 – 520 nm range comes from impurities or defects. Typical impurities in undoped LiNbO₃ are known to be Fe²⁺ and Fe³⁺ ions [5]. The intervalence transfer of Fe²⁺ - Nb⁵⁺ is located at 490 nm, and the charge-transfer band edge of Fe³⁺ starts at 410 nm and extends to near-ultraviolet region [6]. The absorption spectrum in Fig. 1 implies that the concentration of Fe³⁺ ions in the unexposed crystal is much larger than that of Fe²⁺ ions because of little absorption at 490 nm, which is expected in a

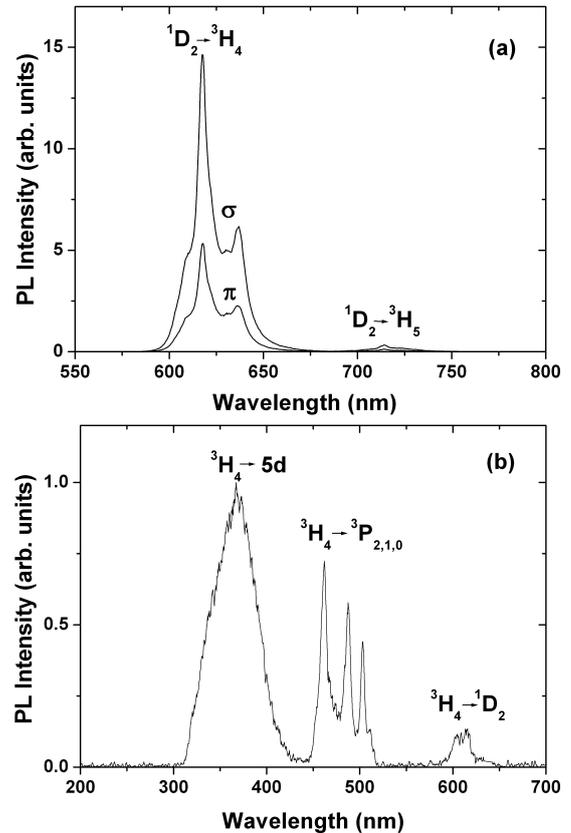


Fig. 2. (a) Photoluminescence spectrum for different polarizations of the exciting beam (514 nm), and (b) excitation spectrum for the emission at 710 nm.

sample grown in oxygen environment. The UV-induced absorption spectrum obtained after two hours illumination of 25 mW/cm² at 365 nm shows a broad band in the blue with several dips at the positions of Pr³⁺ ions. The four small dips in the induced absorption around 500 nm correspond to three transitions from the ground state ³H₄ to ³P_J ($J = 0, 1, 2$) and a transition at 610 nm from ³H₄ to ¹D₂. This slightly decreased absorption of Pr³⁺ ions indicates a reduction in the Pr³⁺ ion density. The electrons removed from Pr³⁺ ions could be trapped in defect or impurity centers.

Fig. 2 shows the photoluminescence of Pr ions and the excitation spectrum. The excitation spectrum for the ¹D₂ emission at 710 nm shows a broad band at 370 nm, which is overlapped with the conduction band and was also observed in other Pr:LiNbO₃ [7]. It can be associated with an exciton bounded on Pr³⁺ or a ³H₄ → 5d electronic configuration of the Pr³⁺ ion because the locations of the 5d bands of Pr³⁺ ions in LiNbO₃ are lower than they are in other oxide crystals [8]. Thus, most excited electrons from Pr³⁺ ions by illumination at 365 nm recombine with Pr⁴⁺ ions to produce photoluminescence. However, a small number of the electrons from the conduction band in the Pr³⁺ ions are assumed to migrate and be trapped in small electron polarons for less than

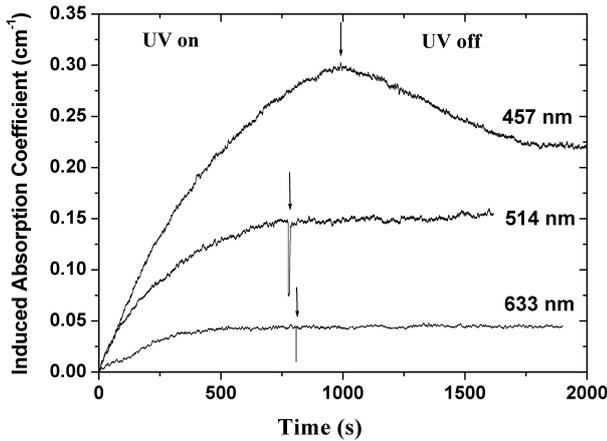


Fig. 3. Temporal evolution and decay of the UV-induced absorptions at 457, 514 and 633 nm. The UV intensity was 15 mW/cm^2 .

1 s [9] and eventually in defects or Fe^+ ions, resulting in the dips in the spectrum. Pr ions are known to be shifted from the regular Li^+ position towards the nearest oxygen plane for charge compensation [10], which may also contribute to the quasi-stability of tetravalent Pr ions.

The 365 nm light can also excite electrons in the valence band or deep UV centers [3] to Fe^{3+} ions naturally existing in this crystal directly or via the conduction band, producing Fe^{2+} ions which have their broad absorption band at 490 nm. However, the shape of the induced absorption indicates the existence of another band at 410 nm. The holes created by the UV light migrate in the valence band. Some of them are recombined with electrons, and others may be captured at defect centers. Recently, the 320 – 410 nm light illumination in Mg:LiNbO_3 [11] was reported to have produced a new broad absorption band at 410 nm, which was attributed to the O^- hole polarons created by holes trapped at O^{2-} sites near lithium vacancies [12].

Fig. 3 shows the buildup and the decay of the induced absorption. When we used a probe at 457 nm where the absorption bands of the O^- centers and the Fe^{2+} ions overlap, the induced absorption grows and reaches a strong absorption. When the UV light is off, an unstable absorption is seen in the first 12 min and then stable absorption. This is expected because the populations of both centers are detected at 457 nm. The stable component shows the absorption of Fe^{2+} ions. The initial decay is assumed to originate from O^- centers, which are known to be relatively unstable. The decay time of the transient absorption centers is larger than that of O^- centers in Mg:LiNbO_3 , which has a lifetime of 71 s [13]. Pr ions may stabilize O^- centers because they are located close to oxygen sites. In another rare-earth-ion doped crystal, Tb:SLN , Tb ions were reported to stabilize the induced absorption band [3]. When we used a probe beam of 514 nm to study the dynamic behavior of Fe^{2+} ions, excluding O^- centers at 410 nm, the UV-

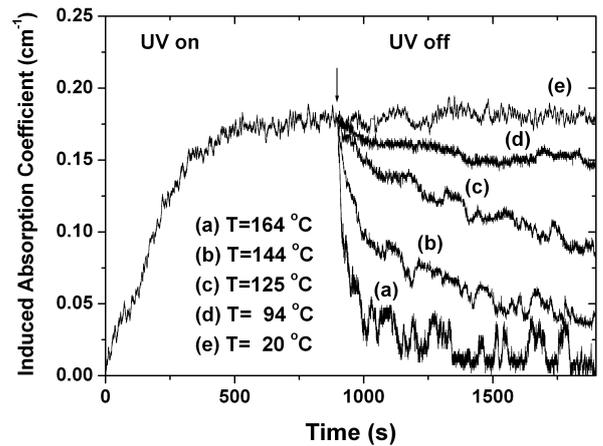


Fig. 4. Buildup of UV-induced absorption at 633 nm and its decay at different temperatures. The UV intensity was 37 mW/cm^2 .

induced absorption grew slowly and reached a constant value where the competition of creation and bleaching of Fe^{2+} ions were stabilized. It did not decrease even after removing the UV light, which means that the thermal excitation rate of traps formed by UV illumination was negligible at room temperature. With a probe beam of 633 nm, we also obtained almost the same growth rate of the absorption and the same stability as in the case of 514 nm. These features indicate that 514 and 633 nm correspond to the same band and that Fe^{2+} ions are stable at room temperature. The slower growing rate at 457 nm than at 514 nm may be due to the hole trapping being slower than the electron trapping. The Fe^{2+} ions are very stable at room temperature, but show a population decay at high temperatures.

Fig. 4 shows the rise and the decay processes of the induced absorption at 633 nm at various temperatures after UV light of 37 mW/cm^2 is switched on and off. The decay curve was not a single exponential because the decay process may involve a few shallow traps. The decay time τ was defined as the time taken to decay to $1/e$ of the original induced absorption. The temperature dependence in the range of 20 – 164 °C appears to obey the Arrhenius law $1/\tau = Ae^{-E/kT}$, where A is a pre-exponential factor, E is the activation energy for dark decay, k is the Boltzmann constant, and T is the temperature in Kelvin. The activation energy for dark decay was found to be 1.1 eV, which is very close to the values reported for other low-concentrated Fe:LiNbO_3 [5].

The hologram was recorded at different recording wavelengths. Fig. 5 shows the recording and the read-out curves for writing wavelengths of 633, 514, and 457 nm. The recording sensitivity is defined as

$$S = \frac{\partial \sqrt{\eta}}{\partial t} \frac{1}{I_w L} \quad (1)$$

where η , L , and I_w are the diffraction efficiency, the overlapped length of the two crossing beams, and the

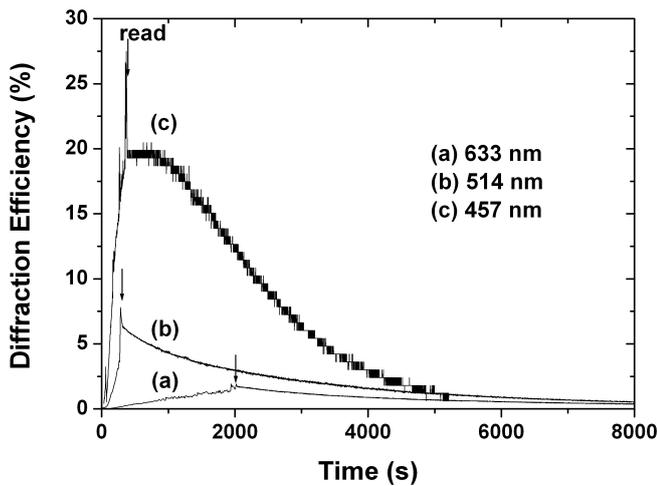


Fig. 5. Holographic recording and read-out at different recording wavelengths. All holograms were recorded with a total recording intensity of 750 mW/cm^2 .

writing intensity, respectively [1]. The observed sensitivities are $1.7 \times 10^{-2} \text{ cm/J}$, $6.5 \times 10^{-3} \text{ cm/J}$, and $1.1 \times 10^{-3} \text{ cm/J}$ for blue, green, and red recording lights, respectively. The higher diffraction efficiencies and higher sensitivities in the blue are obviously due to the higher absorption cross-section from the recording centers. Although Pr ions have some absorption at 514 and 457 nm, it is not plausible that they are the main photorefractive centers because the holograms are recorded at 633 nm where there is no absorption of Pr ions. Instead, the charge-transfer bands of Fe ions or other defects are candidates for photorefractive centers. During the reading process, a grating of 457 nm erases differently from those of 514 and 633 nm, which is similar to the typical case of Fe-doped LiNbO_3 and implies that not only residual Fe^{2+} ions but also other defects may be involved in recording and reading at 457 nm. Further investigation is necessary to clarify the origin.

The holographic diffraction efficiency was reported to be much higher in a short circuit than in an open circuit for Fe:LiNbO_3 [14]. Fig. 6 shows the holographic recording and read-out curves at 514 nm in short and open circuits for Pr:LiNbO_3 . The observed maximum diffraction efficiency is about 12 % in a short circuit, which is 11 times higher than that in an open circuit. However, the sensitivity is $6.5 \times 10^{-2} \text{ cm/J}$ in the short circuit and $7.3 \times 10^{-2} \text{ cm/J}$ in the open circuit. During the reading process, the diffraction efficiency in the open circuit decreases more rapidly than it does in the short circuit, which is in good agreement with the theory [14], because there is charge accumulated on the surfaces in the open circuit.

More pronounced enhancements in the sensitivity and the diffraction efficiency at 514 nm were obtained with UV gating in a short circuit, as shown in Fig. 7. The crystal was irradiated with UV light of 26 mW/cm^2 from

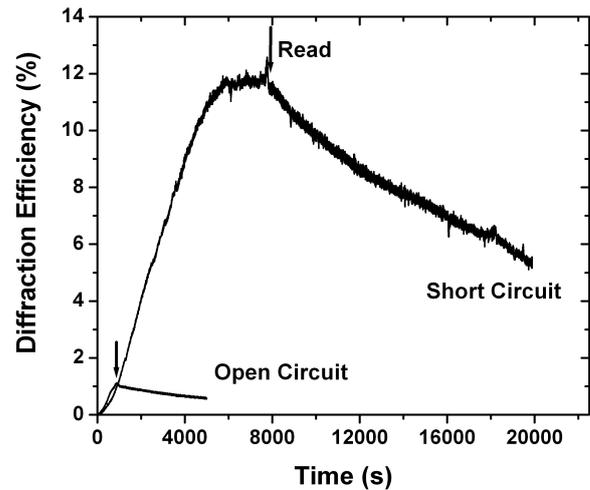


Fig. 6. Typical holographic recording and read-out curves in short and open circuits. In both cases, holograms were recorded with the same recording intensity of 120 mW/cm^2 , wavelength of 514 nm, extraordinary polarization, and external incident angle of 40° .

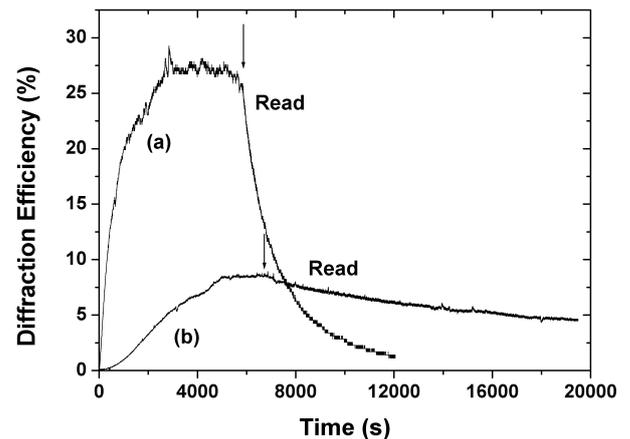


Fig. 7. Typical holographic recording at 514 nm (a) with UV and (b) without UV in a short circuit. The UV intensity was 26 mW/cm^2 . Read-out started at the arrows and was performed by one of the recording beams without UV.

a mercury lamp at 365 nm for 1 h before recording. The recording intensity was 160 mW/cm^2 , and the incident angle, 2θ , was 20° . A small crossing angle was chosen for a large overlap of the two beams. The decay time was estimated as 70 min, and the non-volatile diffraction efficiency was observed as 0.5 %, which may be improved by controlling the ratio of the gating to the recording light intensity [15]. The diffraction efficiency in UV-gated recording is much enhanced, and the sensitivity is a few times larger than the value reported for Pr-ion-doped stoichiometric LiNbO_3 with a UV gating of 20 mW/cm^2 and near-infrared recording light [16]. The enhancement can be explained by effective formation of Fe recording centers in the UV-gated hologram. The problem of fast erasing during reading holograms recorded

with UV gating can be removed by optimizing the ratio of the UV gating and the visible recording intensities. As mentioned before, UV illumination creates both long-lived O^- centers and Fe^{2+} ions. However, when we record at 514 or 633 nm, only Fe^{2+} ions can provide electrons to the conduction band because O^- centers cannot absorb the recording light. The electrons migrate and are trapped finally at either Fe^{3+} centers or O^{2-} sites in the dark area of the grating. It is evident that the hologram stored on O^- centers will decay in the dark and finally disappear. Further detailed investigations in this direction are currently underway.

IV. CONCLUSION

UV illumination at 365 nm of 0.15 % Pr doped congruent $LiNbO_3$ revealed the formation of Fe^{2+} ions and O^- hole polarons in the blue region. A change in the Pr^{3+} population under UV illumination was also found. In addition, we performed UV-gated short-circuit holographic recording at 514 nm and obtained a high sensitivity larger than the value reported for UV-gated near-infrared holographic recording in Pr-doped stoichiometric $LiNbO_3$. However, further experimental data will be necessary to identify precisely the roles of the Pr ions and the ultraviolet centers.

ACKNOWLEDGMENTS

This work was supported by a Chungbuk National University grant in 2004. We thank Prof. L. Hesselink and Dr. R. R Neurgaonkar for providing the crystal used in this study.

REFERENCES

- [1] J. Ashley, M.-P. Bernal, G. W. Burr, H. Coufal, H. Guenther, J. A. Hoffnagle, C. M. Jefferson, B. Marcus, R. M. Macfarlane, R. M. Shelby and G. T. Sincerbox, *IBM J. Res. Develop.* **44**, 341 (2000); Yeung Lak Lee, Chang-soo Jung, Young-Chul Noh, Do-Kyeong Ko and Jongmin Lee, *J. Korean Phys. Soc.* **44**, 267 (2004); Min-Ji Jin, Oc-Yeub Jeon, Byeong-Joo Kim and Myoungsik Cha, *J. Korean Phys. Soc.* **47**, S336 (2005).
- [2] Y. S. Bai, R. R. Neurgaonkar and R. Kachru, *Opt. Lett.* **22**, 334 (1997).
- [3] M. Lee, S. Takekawa, Y. Furukawa and Y. Uchida, *J. Appl. Phys.* **88**, 4476 (2000).
- [4] T. P. J. Han, A. Hill, H. G. Gallagher and F. Jaque, *Chem. Phys. Lett.* **364**, 323 (2002).
- [5] P. Günter and J. P. Huignard, *Photorefractive Materials and Their Applications I* (Springer, Berlin, 1988).
- [6] S. A. Basun, D. R. Evans, T. J. Bunning, S. Guha, J. O. Barnes, G. Cook and R. S. Meltzer, *J. Appl. Phys.* **92**, 7051 (2002).
- [7] A. Lorenzo, L. E. Bausa and G. Sole, *Phys. Rev. B* **51**, 16643 (1995).
- [8] P. Dorenbos, *J. Lumin.* **91**, 91 (2000).
- [9] D. Berben, K. Buse, S. Wevering, P. Herth, M. Imlau and Th. Woike, *J. Appl. Phys.* **87**, 1034 (2000).
- [10] A. Lorenzo, H. Jaffrezic, B. Roux, G. Boulon, L. E. Bausa and J. Garcia Solé, *Phys. Rev. B* **52**, 6278 (1995).
- [11] Guoquan Zhang and Yasuo Tomita, *J. Appl. Phys.* **91**, 4177 (2002).
- [12] P. Herth, T. Granzow, D. Schaniel, Th. Woike, M. Imlau and E. Kra'tzig, *Phys. Rev. Lett.* **95**, 067404 (2005).
- [13] K. L. Sweeney, L. E. Halliburton, D. A. Bryan, R. R. Rice and Robert Gerson, *J. Appl. Phys.* **57**, 1036 (1985).
- [14] C. Gu, J. Hong, H. Y. Li, D. Psaltis and P. Yeh, *J. Appl. Phys.* **69**, 1167 (1991).
- [15] Ali Adibi, Karsten Buse and Demetri Psaltis, *J. Opt. Soc. Am. B* **18**, 584 (2001).
- [16] H. Guenther, G. Wittman and R. M. Macfalane, *Opt. Lett.* **22**, 1305 (1997).