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Growth and Characterization of LiNbO$_3$ Single Crystals Doped with Cu and Fe Ions

Single crystals of lithium niobate doped with 0.03 and 0.1 at.% of Cu or Fe ions were grown by the Czochralski technique. Optical absorption spectra in visible and infrared regions before and after • irradiation with doses up to 10^5 Gy were measured and positions of both dopants in LiNbO$_3$ lattice were analyzed according to changes in optical absorption in the range of OH$^-$ group absorption. Some properties of crystals doped with Cu during the growth processes were compared to those for specimens doped by thermodiffusion. It was observed that doping with Cu results in an increase of crystal resistance to radiation.

Keywords: LiNbO$_3$; Optical properties; photorefractivity; doping

1. Introduction

Lithium niobate (LiNbO$_3$) is commonly used in nonlinear optics, and is frequently investigated as an interesting material owing to its good electrooptic and acoustooptic properties. It also offers technologically important possibilities for planar waveguide lasers and amplifiers (SCHMIDT et al., 1974; KOZLOWSKY et al., 1988). Construction of waveguiding structures as well as of electrooptic modulators and miniature bulk lasers has increased interest in high-quality LiNbO$_3$ single crystals doped with rare earths and co-doped with MgO which leads to enhanced resistance to optical damage (LALLIER et al.,1991; SOCHTING et al., 1995). For the construction of such sophisticated elements a high quality, lowly defected material is necessary. Hence, there has been a noticeable interest in research works dealing with single-crystal growth of stoichiometric LiNbO$_3$ (KITAMURA et al., 1992) theoretically free from lithium vacancies (POLGAR et al., 1997). Also considerable attention has been paid to the photorefractive properties of this crystal doped with transition metal ions (Fe, Cu, Ce, Zn) (KURZ et al., 1997; STURMAN et al., 1996). The photorefraction phenomenon exploited in holographic memories seems to be connected with defects generated by these ions. It is expected that position of these defects in the crystal lattice as well as their ionization, especially the ratio of 3$^+$ to 2$^+$ ions, plays here the most important role (ZHAO, CHIN, 1994). The influence of these metallic dopants on the photorefraction phenomenon should be correlated to their sites in the crystal lattice. By investigation of absorption spectra, especially the location of peak associated with the OH$^-$ group (3485 cm^{-1}) it is possible to correlate a specific site with a particular dopant (PRACKA et al., 1997). It is assumed that proton migration caused by the space charge field is the basic mechanism in photorefractive memory operation in LiNbO$_3$.

In this work we investigate the optical quality of LiNbO$_3$ single crystals, and by

analysing the absorption spectra of Fe- and Cu-doped crystals before and after γ irradiation we also determine radiation-induced defects. In the case of Cu doping we find the possible sites occupied by the dopant in the crystal lattice.

2. Crystal Growth

Z-oriented $LiNbO_3$ crystals doped with Cu with diameters up to 40 mm and lengths up to 70 mm, and Y-oriented Fe-doped crystals with diameters up to 85 mm and lengths up to 70 mm were grown by the Czochralski technique from the congruent melt (51.4 mol. % LiO_2 : 48.6 mol. % Nb_2O_5). The dopant concentrations were: 0.03 and 0.1 at.% Fe, and 0.03, 0.05, 0.06, 0.07 and 0.1 at.% Cu. In the majority of cases the doping ions were naturally incorporated in the crystal lattice during the growth process. On the contrary to these, as grown crystals, in few cases, however, the so-called thermodiffusion process was applied for the modification of the dopant location in the crystal lattice. In this case undoped $LiNbO_3$ wafers were subjected to hot vapours of Cu which evapourated onto their surfaces. By increasing temperature of the wafers it was possible to incorporate a certain amount of the dopant into the crystal in a controlable way.

In order to obtain single domain crystals doped with Cu an electric field was applied for 30 min. at 20°C above the Curie temperature (ca 1140°C). Afterwards the crystals were cooled down to room temperature for 24 hours (the electric field was switched off when the temperature decreased to 1050°C) (Pracka et al., 1988). The dopant concentration was uniform and electrodiffusion was not observed. In the case of Fe doping uniform dopant distribution was achieved by applying the electric field to the crystal in two successive runs with opposite field directions. The treatment was the same as in the case of Cu doping.

3. Crystal Characterization

3. 1. Sample preparation

There were two types of samples used in experiments: the boule itself with plane-parallel optically-polished surfaces for conoscopic investigations, and plane-parallel plates (wafers) cut out from the boules. In the preceding case, after cutting off the cone and the bottom part of the boule, the adequate surfaces were lapped and polished. A pair of plane-parallel surfaces were also cleaved, lapped and polished on the perimeter of the boule, thus making two pairs of perpendicular planes for conoscopic investigations. In the case of wafers they were cut out from the boule either perpendicularly or parallely (for certain spectroscopic measurements) to the growth direction. Both sides were optically polished.

3. 2. Etch pit density

Etch pit densities were determined for undoped and Cu or Fe-doped wafers cut out perpendicularly to the polar Z-axis. The wafers were cut from the middle part of each crystal and were both sides mechanically polished to optical grade. The etching was carried out in the mixture $2HNO_3$: $1HF$ at the boiling point (ca 110°C) for 30 min (Nassau et al., 1966). After washing the wafers in destilled water and drying them, they were next positioned in a scaled optical microscope and etch pits were then counted. For undoped $LiNbO_3$ crystals the etch pit density increased from $2 \times 10^3/cm^2$ in the center to a maximum of $9 \times 10^3/cm^2$ located approximately at 2/3 of the wafer's radius, and then decreased to $4 \times 10^3/cm^2$ at the perimeter.

For crystal doped with 0.1 at. % Fe this distribution was similar but density of etch pits varied from $5x10^4/cm^2$ to $4x10^5/cm^2$. And in the case of Cu doping (0.1 at. %) the etch pit density varied from $5x10^4/cm^2$ to $2x10^5/cm^2$. Since etch pits densities are closely related with dislocation densities it can be concluded that Fe or Cu doping has noticeable influence on crystalline imperfections in doped $LiNbO_3$.

3. 3. Optical quality of crystalline boules

The conoscopic observations and measurements were performed for two orientations of the incident light versus the crystallographic directions in the boules. Firstly, Z-oriented boule was placed in the conoscope with its optical Z-axis parallely to the axis of the convergent beam of light (wavelength 632.8 nm) and the extinction ratio was measured. It was found that the extinction ratio in Cu-doped crystals was noticeably smaller than in undoped $LiNbO_3$. For example, in the crystal doped with 0.03 at. % of Cu the extinction ratio was between 3.7 and 51, whereas in the crystal doped with 0.1 at. % of Cu the corresponding figures were between 2.7 and 142. Usually, in an undoped $LiNbO_3$ crystals the extinction ratio in different points on the front face exceeded 100 and was rarely less than 50.

Secondly, in conoscopic observations of the interference patterns for Y direction on the perimeter (mirror reflected hyperbolas and parabolas) it was found that the patterns were more deformed in doped crystals. Such observations along the perimeter of the crystal enabled to choose areas of fairly good optical quality that were later utilized for preparing crystalline wafers.

3. 4. Optical quality of wafers

The wafers were cut out from the most homogeneous parts of the boules, chosen on the basis of conoscopic measurements and observations. Each wafer was placed in a computerized imaging polarimeter (BAJOR, BAJOR et al., 1995). The polarimeter enables to acquire in one measurement step three different maps of sample: birefringence spread on wafer area (natural or stress-induced), principal azimuth distribution (one of the principal residual stress directions), and transmission. A typical birefringence distribution associated with residual stresses (Z-oriented samples) in $LiNbO_3$ wafer doped with 0.05 at. % of Cu is presented in Fig. 1 a, whereas another one in 0.03 at. % Fe-doped wafer is shown in Fig. 1 b, respectively.
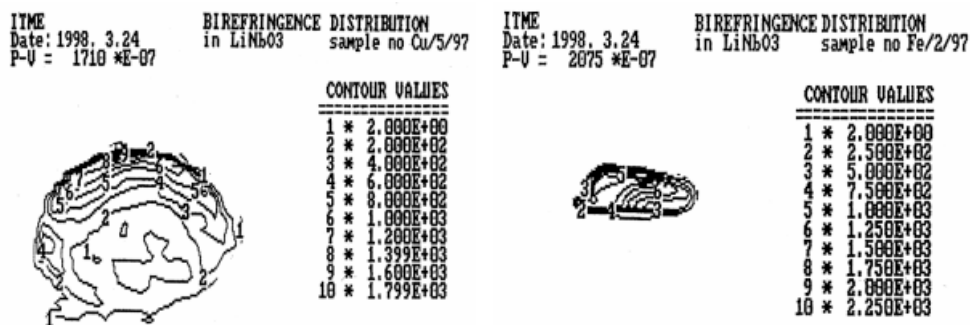

a)   b)

Fig. 1: Residual birefringence distributions in Z-oriented $LiNbO_3$ wafers doped with 0.05 at. % Cu (a), and 0.03 at. % Fe (b)

In Fig. 1a a deformed quasi-radial residual birefringence pattern can be observed, and this is a typical case for wafers cut perpendicularly to the growth direction in (quasi)cylindrical boules pulled by the Czochralski technique. The largest birefringence up to 1.71×10^{-4} can be observed only at the perimeter areas of this wafer, whereas its central part is almost free from residual stresses. The quasi-radial residual birefringence pattern is also evidenced from the principal azimuth map (residual stress direction), however, not shown in this work. The observed patterns are in good agreement with theory of residual stress formation in crystals grown by the Czochralski method (INDENBOM, OSVIENSKY, 1986). On the contrary to Fig. 1 a, a slightly larger birefringence (up to $2,075 \times 10^{-4}$) has been found in 0.03 at % Fe-doped LiNbO₃ (Fig. 1b).

3.5. Optical absorption measurements

Cu- or Fe-doped LiNbO₃ wafers cut perpendicularly to either Z or Y directions were both sides mechanically polished to the thickness of 1 mm. Optical spectra were measured using UV-VIS Lambda 2 and Fourier transform IR 1705 Perkin Elmer spectrophotometers. Fig. 2 a shows the absorption (K) spectrum of Cu-doped LiNbO₃ crystals of Z orientation for different Cu concentrations. In Fig. 2 b an additional absorption (ΔK) in LiNbO₃:Cu specimens with the content of 0.03 and 0.1 at. % after gamma irradiation with doses of 10^3 Gy and 10^5 Gy is presented. A comparison of absorption in Z- and Y-oriented samples is shown in Fig. 2 c.
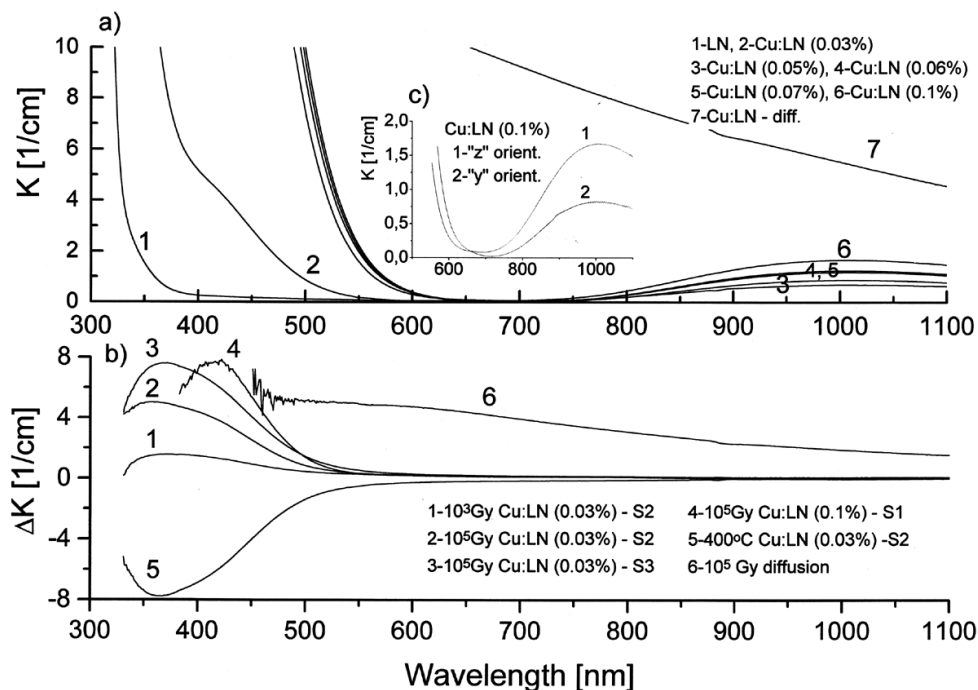

Fig. 2: Absorption in LiNbO₃:Cu Z-oriented crystals (a) and additional absorption after gamma irradiation with doses 10^3-10^5 Gy (b); comparison of absorptions in Z- and Y-oriented samples (c)

A characteristic absorption band with a maximum at λ = 1000 nm may be seen in Fig. 2 a. The intensity of the band increases with an increase in Cu concentration from 0.03 at. % through 0.05, 0.06, 0.07, up to 0.1 at %. Line no. 1 is for an undoped crystal, whereas line 7 is for a specimen doped by thermodiffusion (in this case high optical density was observed in UV-VIS region). The values of ΔK factor due to irradiation were calculated according to formula

$$\Delta K(\lambda) = \frac{1}{d} \ln \frac{T_1}{T_2} \tag{1}$$

where λ is the wavelength, d is the sample thickness, and T_1 and T_2 are the transmissions of the sample measured before and after gamma irradiation, respectively. The intensity of ΔK peaks also increases with increasing doses. At least one band of ΔK with a maximum at 370 nm for 0.03 at. % Cu, and at 440 nm for 0.1 at. % Cu is observed. The position of this maximum shifts to higher wavelengths with an increase in Cu concentration. Similarly the fundamental absorption edge (FAE) shifts to 320 and 380 nm for 0.03 at. % and 0.1 at. %, respectively. FAE of thermodiffusively doped specimen is shifted further than 420 nm. It seems that in Cu-doped specimens of Z orientation the absorption is twice as high as in the case of Y-oriented samples (Fig. 4 c). This phenomenon, however, requires further studies for its explanation. To compare the as-grown and thermodiffusive doping the transmission spectra in UV-VIS and IR regions for two as-grown specimens with 0.03 and 0.1 at.% Cu, and one doped by thermodiffusion are shown in Fig. 3. A higher optical density for the latter in the UV-VIS region can be observed.
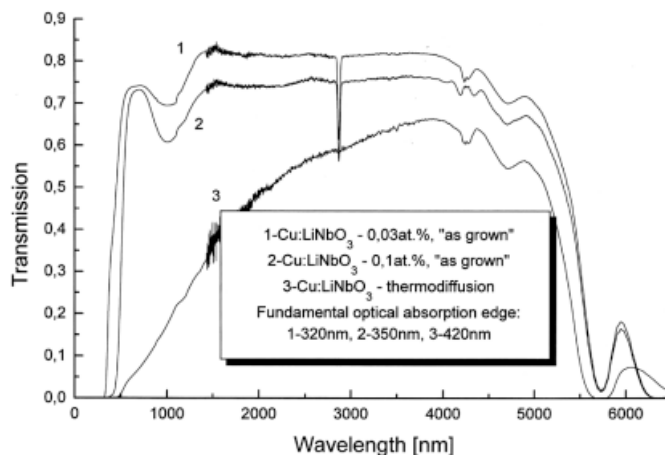

Fig. 3: Transmission spectra of as-grown LiNbO$_3$:Cu compared to that obtained by thermodiffusion

Fig. 4 illustrates absorption spectra of Y-orientated undoped and Cu-doped (from 0.03 to 0.1 at.%) specimens in UV-VIS and IR regions. The maximum of the band at 1000 nm is lower than in the case of Z-oriented samples (see also Fig. 2). A very clear line due to the OH$^-$ ions absorption at 2870 nm is observed. The intensity of this line and its position practically do not depend on Cu ion concentration. This observation of no significant change in the position and intensity of OH$^-$ absorption band with an increase in Cu concentration is associated with the location of Cu^{2+} in LiNbO$_3$ lattice, which does not retard the formation of OH$^-$ ions.

The observation of the OH$^-$ absorption band at 2870 nm can be used to analyze the location of Cu^{2+} ions in LiNbO$_3$ lattice. It is known that OH$^-$ ions located at the O^{2-} site

generate O^{1+} charge defect in the lattice (PRACKA et al., 1997). Occupation of Li$^+$ sites by X^{2+} or X^{3+} ions also generates 1$^+$ or 2$^+$ positively charged defects, thus their incorporation should be in some way competitive for the generation of OH$^-$ ions.
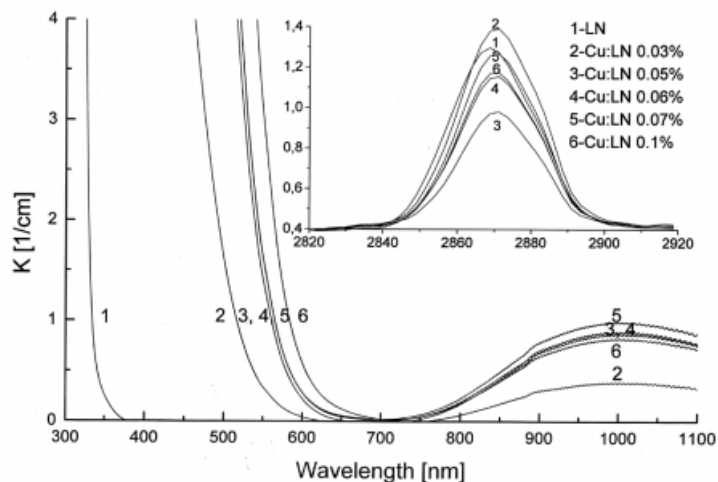

Fig. 4: Absorption in (1) undoped and (2-6) Cu-doped Y-oriented samples. In the inset OH$^-$ absorption band is depicted for different samples
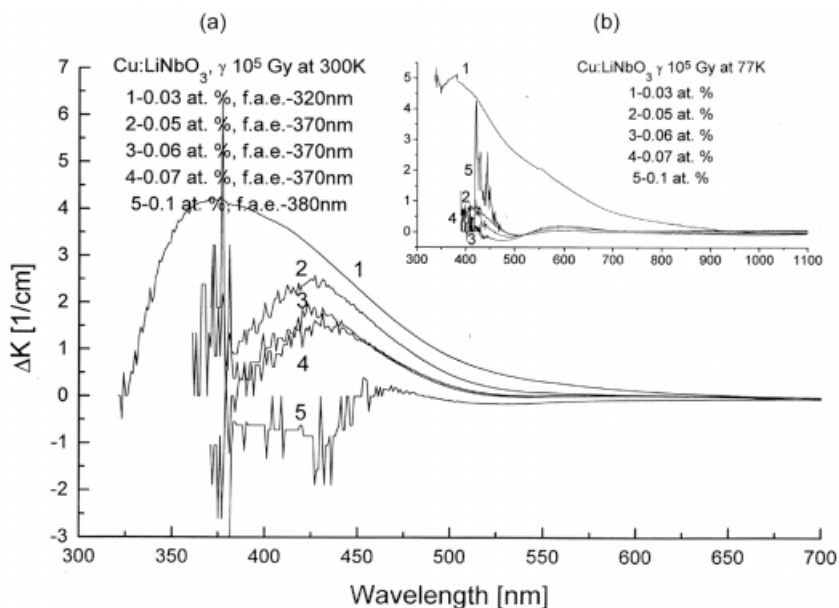

Fig. 5: Additional absorption bands for Y-oriented LiNbO$_3$: Cu single crystals after γ irradiation with a dose 10^5 Gy at (a) 300K and (b) 77K

The location of X^{2+} or X^{3+} ions at Nb^{5+} site generates a 3$^-$ or 2$^-$ negatively charged defects and should not retard the incorporation of OH$^-$ ions. In the case of LiNbO$_3$ crystals doped with Cu ions the intensity of OH$^-$ absorption band depends on the method of doping. When Cu ions are incorporated into the crystal during growth, the intensity of OH$^-$ absorption is

relatively strong in contrast to doping by thermodiffusion. Fig. 5 shows additional absorption in Y-oriented $Cu:LiNbO_3$ specimens with Cu contents from 0.03 at.% to 0.1 at.% after • irradiation at temperatures of 300 K (Fig. 5 a) and 77 K (Fig. 5 b).

Some conclusions concerning the defective structure of as-grown crystals can be drawn. Single crystals with low dopant contents are more defected. With an increase in Cu concentration the intensity of additional absorption bands decreases. The influence of γ irradiation on $Cu:LiNbO_3$ specimens at liquid nitrogen temperature confirms that it leads to an increase in the additional absorption for low Cu concentration only. Cu also increases the resistance of $LiNbO_3$ to radiation defects.
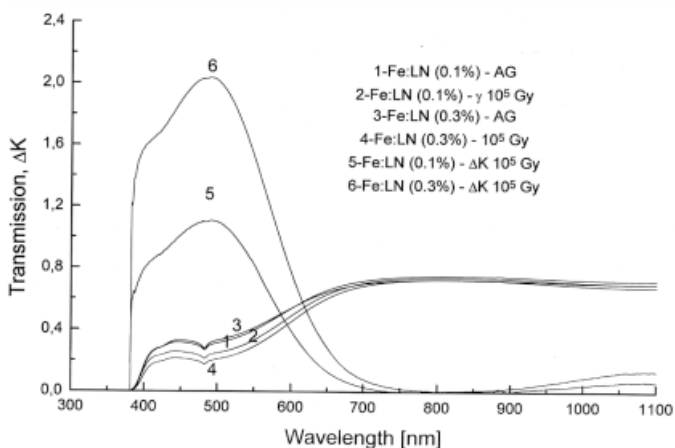

Fig. 6: Changes in transmission and additional absorption in $LiNbO_3$:Fe single crystals after γ irradiation with a dose 10^5 Gy

Fig. 6 presents the transmission and additional absorption in $LiNbO_3$ crystals doped with Fe with concentrations 0.1 to 0.3 at % after γ irradiation with a dose 10^5 Gy. With an increase in Fe content an intensity of these bands (at least at 400, 480 and over 1000 nm) increases, but its value is lower (2 cm^{-1}) than in the case of Cu-doped samples (4 - 5 cm^{-1}). A change in the band with its maximum at 480 nm after γ irradiation duly suggests that Fe^{2+} ions are also incorporated into the as-grown crystals, which undergo ionization after irradiation, and, therefore, the final content of Fe^{3+} is increased.

4. Conclusions

The quality of Cu or Fe doped $LiNbO_3$ single crystals is lower than for undoped ones. The location of Cu^{2+} ions in the crystal lattice depends on the method of doping. During thermodiffusive doping Cu is introduced into Li^+ sites whereas other sites seem to be more favorable for location of Cu^{2+} ions in as-grown crystals. From the fact of different kinds of defects generated during Cu doping by these two methods, which is also confirmed by fundamental absorption edge measurements, it can be concluded that doping with Cu leads to an increase of crystal resistance for radiation defects.

From absorption measurements of Fe doped $LiNbO_3$ crystals one may derive a conclusion that Fe should be present also at other than Fe^{3+} valence, since after γ irradiation the increase in the absorption related to the intracenter transition of Fe^{3+} ions is observed. It is then possible that by irradiating the crystals, i.e. by changing the valence of Fe and Cu ions, the photorefractive properties depending on the ratio of Fe^{2+}/Fe^{3+} can be improved.

This hypothesis, however, needs an experimental verification.

References

Bajor, A.L.: Rev. Sci. Instrum., **66** (1995) 2977

Bajor, A.L., Kukla, M.J., Pitkowski, T., Sabut, L., Spik, A., Szwedowski, A.: Rev. Sci. Instrum., **66** (1995) 2991

Indenbom, V.L., Osvensky, V.B.: Growth of Crystals, **13** (1986) 279

Kitamura, K., Yamamoto, J.K., Iyi, N., Kimura, S., Hayashi, T. : J.Cryst. Growth **116** (1992) 327

Kozlovsky, W.J., Nabors, C.D., Byer, R.L. : IEEE J. Quant. Electron., **24** (1988) 913

Kurz, H., Kratzing, E., Keune, W., Engelman, H.,. Gonser, K., Dischler, K., Rauber, A.: Appl. Phys. Lett., **12** (1970) 355

Lallier, E., Pochole, J.P., Papuchon, M., He, Q., De Micheli, M., OStrovsky, D.B., Grezes-Besset, G, PElletier, E. : Electron. Lett. **27** (1991) 9361

Polgar, K., Peter, A., Kovacs, L., Corrodi, G., Szaller, Z.S. : J. Cryst. Growth **177** (1997) 211

Pracka, I., Malinowski, M., Bajor, A.L., Surma, B., Gazka, Z., Wirkowicz, M., Modonek., M.: SPIE, **3178** (1997) 295

Pracka, I., Giersz, W., Wirkowicz, M., Janusz, Cz. : Patent No 272663 (1988), Poland

Schmidt, R. V., Kaminow, I. P. : Appl. Phys. Lett. **25** (1974) 458

Sochtig, J., Gros, R., Bauman, I., Sohler, W., Schutz, H., Widmer. R. : Electron. Lett. **31** (1995) 551

Sturman, B.I., Goulkov, M.Yu., Odoulov, S.G. : J. Opt. Soc. Am. B. **13** (1996) 557

Zhao, M..G., Chin, M. : Phys. Rev. **49** (1994) 12556

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