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UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

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WINTER COLLEGE ON
LASER PHYSICS: SEMICONDUCTOR LASERS
AND INTEGRATED OPTICS

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PROTON EXCHANGE

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Proton Exchange in Lithium Niobate and Lithium Tantalate

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Proton-exchanged layers on planar single-crystal substrates

Proton-exchange in Lithium Niobate

1) Initial discovery by J.Jackel and C.E.Rice

2) 'Standard Process': immerse polished single crystal sample in molten benzoic acid (more generally carboxylic acids).

$$LiNbO_3 \rightarrow Li_xH_{1-x}NbO_3$$

3) 150°C to 240°C in open system (300°C plus in enclosed system) for 3minutes to several hours (days)

4) Inorganic acids ,e.g. pyrophosphoric acid

5) Other proton sources.........!

6) X-cut, Y-cut (slightly more sophisticated approach), Z-cut, 128°-rotated Y-cut (Saiga et al)

7) $\delta n_e \sim 0.12$, $\delta n_0 \sim -0.04$ (note the minus sign) at $\lambda = 0.6328$ µm. $\delta n_e \sim 0.09$ at $\lambda = 1.15$ µm

8)Approximately step-index profile, with or without melt dilution and even after short anneal.

Proton-Exchange Process Options

1) **Source:** acid, organic or inorganic? Non-acid?

2) **Temperature:** 160°C to 240°C (benzoic acid) in unsealed vessel. Up to at least 300°C in sealed ampoule.

3) **'Melt-dilution':** buffering using a small mole percentage of lithium benzoate in benzoic acid. 0 to 5% (very slow above about 2%).

4) **Annealing:** Temperature range from 250°C to 400°C. Time: a few minutes to several hours.

5) **Titanium In-Diffusion plus Proton-Exchange (TIPE):**
a) Strain compensation (particularly for Y-cut $LiNbO_3$)
b) Both TE and TM modes may be supported.

6) **Double (Multiple)-Diffusion:** Profile synthesis (buried waveguides), lenses.

Materials Analysis Techniques applied to Proton-Exchanged single-crystal

1) Rutherford Back-scattering Spectrometry (RBS):
1.8MeV alpha-particles elastically scattered mainly by niobium atoms (largest atomic number). PE-induced lattice distortion shown by increased yield in aligned mode along substrate major-axis channeling direction. Energy loss provides a measure of depth.

2) X-ray Diffractometry (double-crystal): rocking-curves indicate amounts of lattice-strain and extent of region in which there is lattice strain

3) Infra-red (IR) absorption spectroscopy: OH (OH^1) and OD (OH^2) absorption peaks and related bands, absorption peak-shifts associated with modifications to crystallographic local-environment

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4) Nuclear Reactions:

a) Resonant interaction:

$$^{15}N + {}^{1}H \rightarrow {}^{12}C + \alpha + \gamma$$

E_R = 6.385 MeV. ΔE = 3 keV (20 Angstrom resolution). Measure γ- ray yield as function of ^{15}N input energy. Particles lose energy in penetrating material until they reach energy for resonant interaction with protons. Obtain proton concentration as a function of depth.

b) Non-resonant interaction:

$$^{1}H + {}^{7}Li \rightarrow {}^{4}He + \alpha$$

Low resolution estimate (1000 Angstrom) of Lithium concentration. Incident proton energy 1.5MeV. Measure α-particle yield.

Devices

1) **Passive Bragg-grating beam-splitter** (Glasgow)

2) **Stripe-waveguide electrooptic frequency shifter** (Glasgow)

3) **Acoustooptic devices** (Korablev et al, Davis)

4) **Lenses**: chirp-grating, analogue Fresnel, simple (concave(inverse) and convex), lenslet arrays (Chang, Suhara, Yu, Tsai)

5) **Second Harmonic Generation (SHG):** phase-matched planar (DeMicheli), stripe-guide leaky 'Cerenkov' (Taniuchi and Yamamoto)

6) **Temperature Sensor:** 180° arc Mach-Zehnder (Haruna)

7) **Ring-resonator:** also temperature sensitive ! (Mahapatra)

8) **Waveguide Polarizer:** (Veselka and Bogert)

9) **etc**

Lithium Tantalate

Bulk material properties:

a) Electrooptic effect close to that of niobate.
b) Birefringence and piezoelectricity smaller.
c) Ferroelectric Curie temperature lower.
d) Pyroelectric coefficient significantly larger.
e) Photorefractive effect smaller.

Proton-Exchange:

1) Planar waveguides possible in both X-cut and Z-cut by benzoic acid PE. Single or multimode.
2) Annealing is (almost) essential. Melt dilution is useful.
3) Refractive-index difference (after annealing) is small: at 0.6328 micron, δn_{eff} =0.0174 (X-cut), δn_{eff} = 0.0033 (Z-cut).
4) Stripe guides may be realised by masking the exchange process
5) Typical fabrication conditions for single-mode guides (X-cut): 0.6328 micron
a) PE 1hourat 210°C + anneal 1 hour at 325°C
b) 0.5% dilute melt, PE 6 hours at 230°C, with no annealing

1.15 micron

c) PE 1hour at 210°C + anneal 2hours at 325°C

6)Acousto-optic device: Narrowband (10.5 finger pair IDT), 22% diffraction efficiency from electrically unmatched structure at 203 MHz, with 640 mW electrical input power.

Conclusions

1) A wide range of devices and applications have already been demonstrated in PE-$LiNbO_3$.

2) Proton-Exchange enhances the flexibility of $LiNbO_3$-based integrated optics.

3) Proton-Exchange is already used in advanced systems development (polarization control).

4) Proton-Exchange is likely to increase the use of $LiTaO_3$-based integrated optics.

5) A wide-ranging and thorough study of the electro-optic performance of PE-$LiNbO_3$, covering all process options, is still needed.