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Transmutation-induced tritium in $LiNbO_3$ single crystals

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Irradiation of $LiNbO_3$ single crystals with thermal neutrons has produced tritium ions by transmutation of ^6Li atoms. Following subsequent heat treatments, infrared-absorption measurements have been used to identify bands attributed to OH^- and OT^- ions; additional OD^- bands have also been produced, and all three species exhibit similar behavior under heat treatment.

Hydrogen exists in many "as-grown" oxide crystals as an ubiquitous impurity and has been the subject of many recent investigations. It is known to have a profound effect on the optical and electronic characteristics of oxide crystals, especially for device applications.[1] Due to its excellent electro-optic, piezoelectric, and optical properties, $LiNbO_3$ has become widely used for linear, nonlinear, and laser-based electro-optic devices.[2–4] In $LiNbO_3$, the introduction of hydrogen increases its resistance to optical damage[5] and may prevent the out-diffusion of Li_2O which would otherwise occur during the heat treatments which are necessary in forming Ti-doped surface layers.[6] Additionally, hydrogen is of great significance in the thermal fixing of holograms in $LiNbO_3$.[7]

Previously we have monitored, by infrared-absorption measurements, the presence of hydrogen in the form of OH^- ions in $LiNbO_3$ and in addition have produced OD^- ions by heating $LiNbO_3$ samples in D_2O vapor.[8] The experimental isotope ratio between the OH^- and OD^- stretching frequencies is 1.36, which is close to the theoretical expected value of 1.37 and was strong evidence of the successful introduction of deuterons. Diffusion coefficients and activation energies have been also measured in $LiNbO_3$.[8]

Experiments with radioactive tritium are difficult and expensive. Very little data are available concerning the infrared characteristics and diffusion properties of tritium in oxides,[9–11] in spite of the importance of tritium in advanced energy devices. We report here the successful production of tritium ions following transmutation of ^6Li ions in $LiNbO_3$ single crystals by thermal neutrons. Tritium is produced by the following nuclear reaction:

$$^6_3\mathrm{Li} + {}^1_0n \rightarrow {}^3_1\mathrm{T} + {}^4_2\mathrm{He} \quad (1)$$

with a production cross section of 910 b.[12] The natural abundance of the ^6_3Li isotope is 7.4%.

Crystals from boule no. 14N142, obtained from the Crystal Systems Division, Union Carbide Corporation, were cut perpendicular to the crystallographic z axis. Neutron irradiations were performed in a dry tube immersed in a D_2O tank (D3-1) in the Oak Ridge Bulk Shielding Reactor. The thermal-neutron flux was $\sim 5\times 10^{12}$ $n\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$, the neutron flux with energy exceeding 1 MeV was 0.6×10^{11} $n\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$, and the γ flux was 0.7×10^8 R/h. The duration of the irradiation was 40.8 h. The irradiation temperature was ~40 °C. Optical-absorption measurements were performed with a Perkin-Elmer model 983G infrared spectrophotometer and a Perkin-Elmer Lambda-9 spectrophotometer. In all cases, unpolarized light propagating along the crystallographic z axis was used. Samples were heated in air, or in flowing D_2O vapor, inside a quartz tube inserted in the horizontal, axial hole of a Sentry Furnace model 7 AV.

Subsequent ionizing irradiations in liquid nitrogen were performed in a ^{60}Co γ source with a dose rate of $\sim 5\times 10^5$ R. The irradiated samples were transferred directly to a quartz flowing-gas cold finger inside the microwave cavity of a conventional homodyne X-band electron paramagnetic resonance (EPR) spectrometer without any intervening warmup. The spectrometer cavity (rectangular Varian Associates V-4531 operating in the TE_{102} mode) and cold-finger Dewar afforded a vertical sample entry hole, facilitating a rapid change of samples in order to maintain the irradiated samples at low temperature.

After irradiation with thermal neutrons, the initial transparent crystals exhibited a slight brownish coloration, probably induced by the concomitant γ rays and fast neutrons during the neutron irradiation. Such broad absorption bands with maxima near 500 nm have been previously observed in crystals irradiated with either γ rays or electrons.[13–16] The most significant changes occurred in the infrared region of the spectrum. The "as-grown" crystals exhibited a OH^- vibration band at ~ 3480 cm^{-1} with a full width at half maximum (FWHM) of ~ 30 cm^{-1}. After the neutron irradiation, this band was absent and two new bands at 3500 ad 3550 cm^{-1} appeared in the OH^- region. Their FWHM are ~ 40 and 15 cm^{-1}, respectively. In addition, two very weak bands at 2180 and 2211 cm^{-1} were observed (Fig. 1, bottom).

Following an anneal, the band at 3500 cm^{-1} was re-

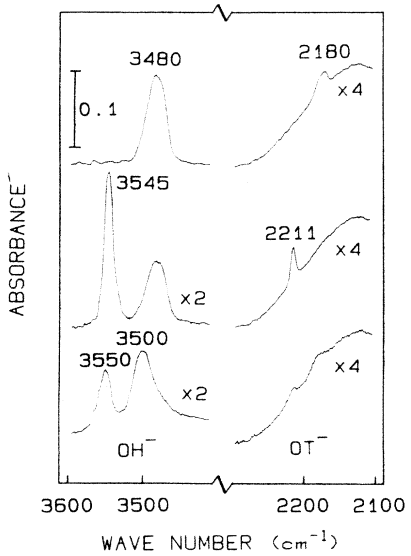

FIG. 1. Absorption spectra of a $\mathrm{LiNbO_3}$ crystal: bottom, irradiated with thermal neutrons ($\sim 7.5\times10^{17}$ n cm^{-2}); center, after subsequent annealing for 1 h at 625 K in air; top, after additional annealing for 1 h at 775 K in air. The thickness of the sample was 1 mm.

placed by one at 3480 cm^{-1} (FWHM 30 cm^{-1}). The band at 3550 cm^{-1} disappeared and a new band at 3545 cm^{-1} (FWHM of ~ 15 cm^{-1}) appeared. In the lower-energy region, the band at 2211 cm^{-1} (FWHM of ~ 7 cm^{-1}) is now well resolved and the band at 2180 cm^{-1} almost disappeared (see Fig. 1, center). This overall spectrum was not noticeably modified by annealing the sample for two more hours at 625 K. A subsequent annealing for 1 h at a higher temperature (775 K) greatly increased the intensity of the 3480-cm^{-1} band and annihilated that at 3545 cm^{-1}. Correspondingly, the band at 2211 cm^{-1} disappeared and the band at 2180 cm^{-1} became more prominent (see Fig. 1, top).

The frequency ratios between the two OH^- bands at 3545 and 3480 cm^{-1} and their analogs at 2211 and 2180 cm^{-1} are both 1.61, which corresponds well to the theoretical expectation of $[\mu(\mathrm{OT}^-)/\mu(\mathrm{OH}^-)]^{1/2}=1.64$. Here μ is the reduced mass of the radicals. Consequently, we attribute these two bands to OT^- stretching vibrations.

As mentioned earlier, after neutron irradiation, two peaks at 3550 and 3500 cm^{-1} appeared in the OH^- region instead of the single peak at 3480 cm^{-1} observed in the "as-grown" crystals. This observation suggests that during the n irradiation, protons were mobile under the effect of the concomitant γ irradiation and migrate to different OH^- configurations. Anneals at 775 K restored the initial configuration. The enhancement of proton diffusion by ionizing radiation has been previously observed in MgO single crystals.[17]

The tritium concentration in the neutron-irradiated crystals can be estimated by taking into account that the original $^6\mathrm{Li}$ concentration in the crystals was $\sim 1.4\times10^{21}$ atoms cm^{-3} and the total neutron dose was $\sim 7.5\times10^{17}$ n cm^2. Using the cross section of 910 b, the resulting tritium concentration was $n(\mathrm{T})\simeq 9.5\times10^{17}$ cm^{-3}. Assuming that after the short thermal annealing at 625 K all the tritium remained in the crystal and was in the OT^- configuration corresponding to the 2211-cm^{-1} band, the relationship between the tritium concentration and the peak absorption coefficient at 2211 cm^{-1} can be written as

$$n(\mathrm{OT}^-)\approx(1.4\times10^{16}\ \mathrm{cm}^{-2})\alpha_{\max}(\mathrm{OT}^-)\ . \qquad (2)$$

We proceeded to produce a crystal which contained all three hydrogenic isotopes, as exemplified by OH^-, OD^-, and OT^- infrared bands. The procedure involved heating a neutron-irradiated crystal, whose spectrum is shown at the bottom of Fig. 2, in $\mathrm{D_2O}$ vapor at 625 K for 1 h.

The resulting infrared spectrum is shown in the center of Fig. 2. In the OH^- region, a prominent band at 3547 cm^{-1} and a smaller one at 3480 cm^{-1} were observed. In the OD^- region, two bands at 2615 and 2570 cm^{-1} were apparent with FWHM of ~ 9 and 22 cm^{-1}, respectively. In the OT^- region, only the band at 2211 cm^{-1} was apparent, similar to Fig. 1 (center). When this sample was further heated in $\mathrm{D_2O}$ vapor at 750 K (see Fig. 2, top), the band at 3547 cm^{-1} shifted at 3545 cm^{-1} and its intensity diminished; instead, the 3480-cm^{-1} band increased significantly. In the OD^- region, the absorbance at 2615 cm^{-1} remained unchanged while that at 2570 cm^{-1} increased. In the OT^- region, the intensity of the band at 2211 cm^{-1} diminished while that at 2180 cm^{-1} became more intense.

The existence of all three isotopic species (tritons, deuterons, and protons) in the same crystal is clearly demonstrated in Fig. 2 (top). Thermal annealing permits

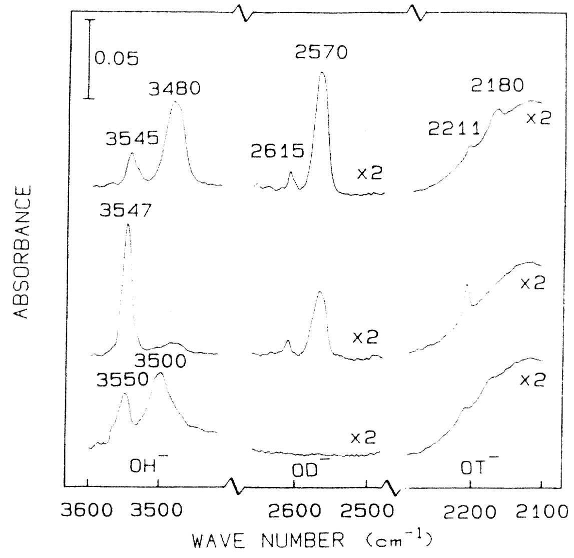

FIG. 2. Absorption spectra of a $\mathrm{LiNbO_3}$ crystal: bottom, irradiated with neutrons ($\sim 7.5\times10^{17}$ n cm^{-2}); center, after subsequent annealing for 1 h at 625 K in $\mathrm{D_2O}$ vapor; top, after additional annealing for 1 h at 750 K in $\mathrm{D_2O}$ vapor. The thickness of the sample was 1 mm.

these isotopes to become mobile and seek the same configurations corresponding to the lowest potentials of OT^-, OD^-, and OH^- ions. That this was indeed achieved is evidenced by the emergence of a set of double bands for all three isotopic ions. The isotopic frequency ratios for both ionic configurations should be $\nu(OH^-)/\nu(OD^-)=1.37$ and $\nu(OH^-)/\nu(OT^-)=1.64$. The frequency ratios noted in Fig. 2 (top) were 1.36 and 1.61, respectively. The frequency and the FWHM of the OH^-, OD^-, and OT^- bands are summarized in Table I. The slight departure from the theoretical values is indicative of the anharmonicity of the oscillators. The fact that two configurations with the same isotopic ratios is unambiguous evidence for the existence of all three isotopes in the $LiNbO_3$ crystal.

We also used EPR to search for paramagnetic hydrogenic defects under different conditions, but to no avail. All measurements were made at 77 K. Initially the neutron-irradiated crystals exhibited no EPR signals. In order to produce magnetic resonance signals with a possible relation to hydrogen, ionizing radiation experiments were initiated. Following a γ irradiation at 77 K, large-EPR signals were observed. These signals were similar to those observed by Halliburton, Sweeney, and Chen[14] and completely vanished following warmup to room temperature. After annealing in either air or D_2O at 775 K, again no EPR signals were observed. Following γ irradiation at 77 K, the same EPR signals were observed but with a reduced intensity.

In summary, single crystals of $LiNbO_3$ have been irradiated with thermal neutrons in order to produce tritons resulting from transmutation of ^6Li atoms. Infrared-absorption measurements have identified the bands due to OT^- ions, based primarily on isotopic frequency ratios of the corresponding OH^- and OD^- bands. We have been successful in diffusing deuterons into a crystal containing protons and tritons, so that the infrared absorptions of OH^-, OD^-, and OT^- ions were observed. The growth and decay of the bands corresponding to the three isotopes were similar upon thermal annealing.

TABLE I. Frequencies (ν) and bandwidths (δ) of the OH^-, OD^-, and OT^- bands in $LiNbO_3$ (units of cm^{-1}).

$\nu(OH^-)$	$\delta(OH^-)$	$\nu(OD^-)$	$\delta(OD^-)$	$\nu(OT^-)$	$\delta(OT^-)$
3550	20				
3547	15				
3545	15	2615	9	2211	7
3500	40				
3480	30	2570	22	2180	15

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