Concentration Dependence of the Octahedral Ti⁴⁺ Center in LiNbO₃: Its Effect on Refractive Indices

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X-ray absorption spectra of titanium-diffused LiNbO₃ indicate that a strong change in the Ti center appears as the concentration is increased above 5×10^{20} cm⁻³, involving a tendency toward displacement in the x-y plane and disorder. This change in the Ti center occurs within the concentration range used for integrated-optical-device fabrication, and may account for the abrupt decrease in rate of change of the ordinary optical index (n₀) with increasing Ti concentration reported in the literature.

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Ti-diffused LiNbO₃ is the most widely used technology for ferroelectric optical-waveguide device fabrication. Yet there is little basic understanding of how titanium is incorporated into the LiNbO3 lattice, and how the incorporation center is related to optical and electro-optical properties. In this Letter we report on the nature of the diffused titanium site and its concentration dependence in LiNbO₃ as determined by extended x-ray absorption fine structure (EXAFS) and x-ray absorption near-edge structure (XANES) measurements¹ and by secondaryion mass spectroscopy (SIMS). More generally, our results provide an important experimental demonstration of the relationship between optical properties and the local bonding configuration of dopant atoms. Near the conclusion of this Letter we make use of linear combination of atomic orbitals (LCAO) theory to account for specific features of this relationship.

Both x-cut and y-cut polished single-crystal congruent LiNbO₃ substrates were used to allow the electric-field vector of the linearly polarized incident x rays to be aligned with the X, Y, and Z, axes of the crystal lattice.² Diffusion was carried out in a quartz-tube Lindberg furnace with dry flowing O₂ at temperatures from 900 to 1050 °C. Fluorescent x-ray detection¹ was used for Ti absorption-edge measurements on the single-crystal samples (diffused LiNbO₃). The fluorescence sampling depth was between 2 and 3 μ m. The Ti edge position was calibrated with Cr foil and scanning across both the Ti and the Cr edges. The transmission detection method¹ was used for powdered model compounds (including TiO₂ and SrTiO₃).

SIMS depth profiles were obtained with a Perkin-Elmer (Physical Electronic Division) model PHI-6300 with a 6-keV, $0.6-\mu A O_2^+$ primary beam rastered over a $500 \times 500-\mu m^2$ area and charge neutralized with a $12-\mu A$ electron beam. An average sputter rate of 150 Å/min was achieved. Quantitation was made possible with a double-isotope implant of ⁴⁸Ti and ⁵⁰Ti in LiNbO₃. Normalization to the Nb matrix signal was used to determine the Ti concentration both in the diffusion source layer and after diffusion into the LiNbO₃ crystal.

For Ti in a site with with octahedral symmetry and zero displacement, the 1s-to-3d dipole transition is forbidden, but the quadrupole transition is allowed. This gives rise to some weak pre-edge structure (-5 to 0 eV), relative to edge) as seen in SrTiO₃ [see Fig. 1(a)]. Kutzler et al.³ have pointed out that as the inversion symmetry of the octahedral site is broken, (e.g., with ferroelectric displacement), dipole transitions from the 1s core to the 3d bands can be allowed. This leads to a large pre-edge peak for the Ti-1s edge of PbTiO₃, in which the Ti is displaced by 0.30 Å from the center of octahedral symmetry [see Fig. 1(b)]. In the series SrTiO₃, BaTiO₃, and PbTiO₃, the pre-edge peak increases linearly with Ti displacement.⁴ The lack of a strong pre-edge peak in the Ti-diffused LiNbO3 data when the incident x-ray polarization is along the z axis [see Fig. 1(c)] thus indicates an octahedral-oxygen-cage site for the titanium, as expected, but without detectable displacement (< 0.05 Å) along the polar axis. This is in contrast to the Li and Nb ions, which are displaced along the polar axis by ≈ 0.45 Å and ≈ 0.25 Å, respectively, from their oxygen-cage centers.²

However, the pre-edge, XANES, and EXAFS data show marked changes as a function of Ti concentration. The amplitude of the EXAFS component at low Ti concentration ($<10^{21}$ cm⁻³ Ti; for comparison, stoichiometric LiNbO₃ has 1.89×10^{22} cm⁻³ Nb) is typical in size for titanium compounds, indicating a well-defined radial distribution of atoms surrounding the diffused Ti in LiNbO₃ [see Fig. 2(a)]. As the near-surface concentration is increased from 5×10^{20} cm⁻³ ("400-Å" Ti,



FIG. 1. X-ray absorption near-edge structure (XANES) spectra, with the averaged step height across the absorption edge normalized to unity. Zero energy is defined at the metallic Ti absorption threshold, 4966 eV. Curve *a*, SrTiO₃ powder; curve *b*, PbTiO₃ single crystal, with x-ray polarization along the axis of Ti displacement; curve *c*, high-concentration Ti-diffused x-cut LiNbO₃ ($c = 2 \times 10^{21}$ cm⁻³), x-ray polarization along the polar *z* axis; and curve *d*, same as *c* except x-ray polarization along the *y* axis of the crystal.

1050 °C, 10 h)⁵ to 2×10^{21} cm⁻³ (930-Å Ti, 1050 °C, 10 h) the amplitude of the EXAFS is greatly diminished [see Fig. 2(b)], suggesting a tendency toward disorder. Furthermore, at concentrations of 2×10^{21} cm⁻³ and higher, a pre-edge peak is seen which is x-ray-polarization dependent [compare the pre-edge region of Fig. 1(d) to 1(c)]. Comparison with the x-ray-polarization-dependent pre-edge peak from single-crystal lead titanate indicates that this asymmetry (probably a displacement) of Ti in LiNbO₃ is in the x-y plane.

Because of the nature of titanium diffusion in LiNbO₃, the high-concentration data should be compared to similar EXAFS and XANES data from the surface layer of chemically reacted Ti and LiNbO₃, which forms at lower temperatures and acts as the source for the diffusion. Armenise *et al.*⁶ report that a "Ti_{0.65}Nb_{0.35}O₂" diffusion source layer is formed after 400 Å of Ti has reacted with LiNbO₃ at 900 °C for 1 h in dry oxygen, and that the diffusion source layer is essentially consumed by diffusion after 10 h at 950 °C. Since the present diffusions [samples associated with Figs. 1(c), 2(a), and 2(b)] were performed at 1050 °C for 10 h, it is expected that no Ti remains on the surface as a diffusion source layer.^{6,7} This is confirmed by SIMS analysis of the samples. As expected, the 450-Å Ti sample processed at 900 °C for l h has an oxide layer about ≈ 1200 Å thick at the surface consisting mainly of Ti and Nb oxide with some Li [see Fig. 3(a)—only Ti concentration shown]; only a shallow diffusion of Ti into the LiNbO₃ is seen. In contrast, the diffusion of the 400-Å Ti and 930-Å Ti samples is complete, as judged by the smooth, relatively flat concentration profile and the lack of a Ti-Nb oxide layer on top of the LiNbO₃ [see Figs. 3(b) and 3(c)]. Thus the change in Ti EXAFS as a function of concentration [see Figs. 2(a) and 2(b)] is due to a change in the geometry or degree of order of the Ti center, and not due to residual Ti oxide [see Fig. 2(d)] or diffusion source layer^{6,7} [see Fig. 2(c)] on the surface. Work is currently under way to determine the specific site of Ti at low concentration $(< 10^{21} \text{ cm}^{-3})$ from the EXAFS.

A change in the Ti center should also be reflected in the fundamental optical properties as a function of Ti concentration. In earlier work it was noted that the change in ordinary index versus a measure of concentration was found to be a simple linear relationship over a limited concentration range, but it was suspected to be nonlinear at lower concentration because the extrapolated relationship did not pass through the origin.⁸ Recently, Ctyroky *et al.*⁹ summarized the experimental data on



FIG. 2. Extended x-ray absorption fine structure (EXAFS) spectra, with a $\times 3$ expanded absorption scale at energies above 60 eV. The averaged step height is again normalized to unity: Curve *a*, low-concentration Ti-diffused *y*-cut LiNbO₃ ($c = 5 \times 10^{20}$ cm⁻³); curve *b*, high-concentration Ti-diffused *y*-cut LiNbO₃ ($c = 2 \times 10^{21}$ cm⁻³); curve *c*, diffusion source layer; and curve *d*, TiO₂ powder (rutile phase).

the changes in ordinary and extraordinary indexes as functions of mass concentration. They show an abrupt decrease in slope of the ordinary index occurring at a Ti mass concentration in the range 0.2% to 0.7% $(1.3 \times 10^{20}$ cm⁻³ to 4×10^{20} cm⁻³), the exact value being different for different workers. This concentration range is in good agreement with our own observations, in which the strong EXAFS structure associated with the low-concentration Ti center fades within the atomic concentration range 5×10^{20} cm⁻³ to 2×10^{21} cm⁻³, leaving the relatively featureless EXAFS structure of the highconcentration Ti center.

LCAO theory, which is well suited to describe the localized states of impurity atoms, relates the optical index to local bond-antibond orbitals. Pantelides has pointed out that the mechanism determining the dielectric susceptibility of an ionic crystal is based on coupling between states on *adjacent* ions, and that the traditional theory of summing the "polarizability" of the isolated constituent elements (e.g., the Clausius-Mossotti relation) is not well founded physically.¹⁰ Harrison¹¹ uses the view of Pantelides to describe the dielectric susceptibility in terms of universal matrix elements between atomic orbitals on neighboring ions. Polarization is then the charge transfer from the filled valence states on one ion to the empty states on the neighboring ion due to an applied electric field.¹¹

The LCAO perspective on polarizability is directly applicable to the question of how the Ti displacement is related to the optical index. The optical index is associated with virtual transitions between valence-band and conduction-band states, with the states near the valenceband maximum and the conduction-band minimum being the most important. In Ti-diffused LiNbO₃, the states near the valence-band maximum are primarily the oxygen 2p states, while those near the conduction-band minimum are primarily Nb 4d and Ti 3d states.

From this it is expected that a shift of the titanium atom only in the x-y plane of the LiNbO₃ lattice, which changes mainly the coupling and symmetry of 3d orbitals associated with that plane, will influence only the ordinary optical index (n_0 ; associated with the electric field in the x-y plane). Since the orbitals oriented along the polar axis are essentially unchanged, there is no corresponding influence on the extraordinary optical index (n_e). In this way, the pre-edge peak of the LiNbO₃:Ti x-ray absorption spectroscopy data is seen to be closely related to the optical index. Both are derived from transitions involving the d states near the conduction-band minimum. Thus the theory is consistent with our experimental results, and we conclude that the change in the Ti center observed by EXAFS can account for the previous-



FIG. 3. SIMS depth profiles of LiNbO₃:Ti normalized to the Nb matrix signal, plotted with the logarithm of Ti concentration as a function of depth below the surface. Curve a

tration as a function of depth below the surface. Curve a, diffusion source layer; curve b, 400-Å Ti diffused into LiNbO₃ with near-surface concentration 5×10^{20} cm⁻³; and curve c, 930-Å Ti diffused into LiNbO₃, with near-surface concentration 2×10^{21} cm⁻³.

ly reported Ti-concentration-dependent ordinary optical index in LiNbO₃.

In summary, we have performed the first EXAFS and XANES measurements of Ti in LiNbO₃. The data show that the Ti center is concentration dependent, with a well-defined site that dominates the EXAFS region at or below 5×10^{20} cm⁻³ Ti, and a more disordered center which dominates the EXAFS at or above 2×10^{21} cm⁻³ Ti. This change in the Ti center involves a displacement (or asymmetry) in the x-y plane but no apparent displacement along the polar z axis. LCAO theory was used to relate the Ti displacement qualitatively to the optical-index dependence on Ti concentration. It was concluded that the Ti displacement, which is limited to the x-y plane, accounts for the bilinear dependence of n_0 and the simple linear dependence of n_e on Ti concentration.

In relationship to this, we note that the lack of knowledge of dopant site geometries has inhibited the development of theories relating the optical and dielectric properties of solids to the local bonding configuration of dopant elements. The connection between the concentration-dependent x - y-plane displacement of Ti in LiNbO₃ and the similarly concentration-dependent bilinear behavior of the optical index associated with the x - y plane is a *key example* of how directly the optical prop-

erties depend on impurity-site geometry. Proper development of theory should allow one to make some detailed conclusions about site geometry based on a combination of careful optical measurements of refractive index (as well as absorption) together with XANES and EXAFS measurements.

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⁵This thickness is in a range for which our thickness measurement method gives reproducible results, but probably not a true reading. The concentration determined by SIMS provides a more accurate measure.

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