

Chemical bonding and atomic structure of Rb^+ exchanged KTiOPO_4 waveguides probed by micro-Raman spectroscopy

David D. Tuschel^{a)} and Gustavo R. Paz-Pujalt
Eastman Kodak Company, Rochester, New York 14650-2017

William P. Risk
IBM Research Division, Almaden Research Center, San Jose, California 95120-6099

(Received 12 September 1994; accepted for publication 13 December 1994)

Channel waveguides of Rb^+ exchanged single-crystal KTiOPO_4 were studied by micro-Raman spectroscopy. Rb^+ exchange causes a disruption of the long-range translational (crystal) symmetry of the lattice and a tilting of the TiO_6 octahedra. The ability to nondestructively map the chemical and physical structure related to the optical properties of channel waveguides is demonstrated. © 1995 American Institute of Physics.

Partial ion exchange of the alkali cation in single-crystal transition metal oxides that have a high nonlinear susceptibility is a convenient way of fabricating waveguides for second harmonic generation.¹⁻³ Understanding how ion exchange and subsequent thermal treatments affect the chemical and physical structure, which are related to the refractive index and optical nonlinearity, reveals the most favorable conditions for the fabrication of ion exchange waveguides. Recent studies have demonstrated the utility of micro-Raman spectroscopy and optical microscopy for the structural characterization of proton-exchanged LiNbO_3 waveguides.⁴⁻⁶ Here we report on the structural characterization of Rb^+ exchanged KTiOPO_4 (R/KTP) waveguides.

An Al mask was deposited on the Z face of a flux-grown KTP crystal. Channel waveguides were then fabricated by carrying out a partial ion exchange of K^+ in pure RbNO_3 at 350 °C for 20 min. The Y faces were subsequently polished to remove exchanged material generated by migration along the Y axis and produce an optically smooth surface. A Z-polarized, 1.6 mW, 488.0 nm laser beam was focused (0.6 μm diameter) with an Olympus MS Plan 100 (0.95 NA) objective at various positions on the Y face of the device. Back scattered light was collected with the same objective, guided into an Instruments SA S3000 spectrometer, and detected with a Hamamatsu R943-02 photomultiplier tube. No polarization analyzer was used. The Porto notation for the experimental arrangement described above is $Y(X,XZ)\bar{Y}$, where the first and second symbols outside the parenthesis correspond to the excitation and scattering propagation directions, respectively. The first and second symbols within the parenthesis denote the excitation and scattering polarizations, respectively.

Micro-Raman spectra of a R/KTP waveguide obtained at 0.4, 1.1, and 1.8 μm from the Z face and a spectrum of KTP from the center of the device are shown in Fig. 1. In general the Raman band structure is predominantly due to the vibrational motions of the TiO_6 octahedra and the PO_4 tetrahedra.⁷ More specifically, the regions from approximately 200–400 cm^{-1} and 600–850 cm^{-1} are associated with TiO_6 octahe-

dral torsional and stretching modes, respectively. The bands in the 900–1200 cm^{-1} region are due to the PO_4 tetrahedra. The greatest amount of Rb^+ exchange is expected to occur near the Z face of the crystal and diminish with increasing depth. Consequently, the most significant changes in the Y face Raman spectra should be observed near the Z face. Indeed, the most significantly altered spectrum of R/KTP in Fig. 1 is that obtained at a depth of 0.4 μm . Specifically, the Raman scattering strength is significantly attenuated, band positions are shifted, bandwidths are moderately increased, and relative band strengths are significantly altered. Attenuation of Raman scattering strength and increased bandwidth are attributed to the disruption of long-range translational (crystal) symmetry by partial Rb^+ exchange. The band shifts and changes in relative band strengths do not correspond to a linear progression between the limits of KTP and RbTiOPO_4 (RTP) as shown in Fig. 2. For example, the 699 and 750 cm^{-1} bands from the waveguide are at higher frequencies than the corresponding ones from either KTP or RTP and the 739/786 cm^{-1} relative band strengths of KTP and RTP are reversed in R/KTP. In particular, the position of the ν_1 band of R/KTP (699 cm^{-1}) is unexpected because it is at a higher energy than either of the corresponding bands in KTP (696 cm^{-1}) and RTP (691 cm^{-1}). Note from Table I that

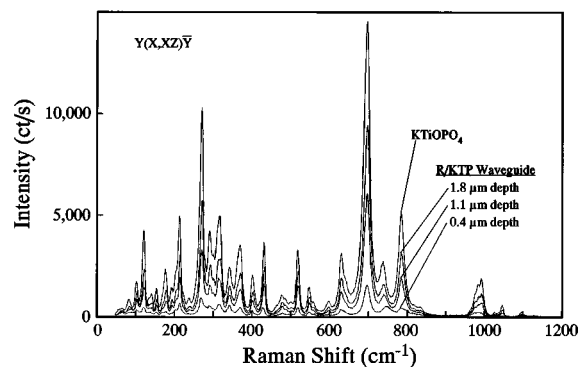


FIG. 1. Micro-Raman spectra of the Y face of an R/KTP channel waveguide obtained at the indicated distances from the Z face.

^{a)}Electronic mail: dtuschel@kodak.com

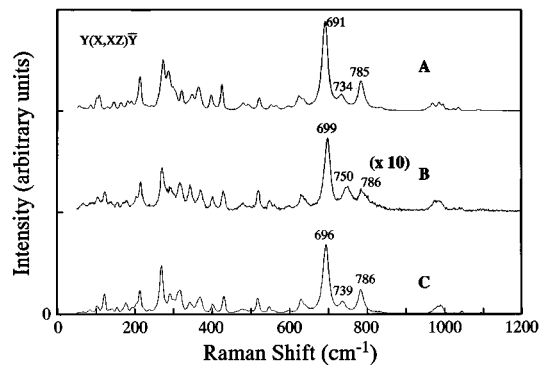


FIG. 2. Micro-Raman spectra of the Y face of (A) RbTiOPO_4 , (B) R/KTP channel waveguide obtained at $0.4 \mu\text{m}$ from the Z face, and (C) KTiOPO_4 .

the ν_1 band of RTP is lower in energy than that of KTP for all crystal faces.

The greatest amount of Rb exchange is expected to occur at the corner of the crystal. Consequently, the most significant changes in the Raman spectra should be observed there. Micro-Raman spectra of the R/KTP Z face were obtained approximately $5 \mu\text{m}$ from the corner with X -polarized excitation. The KTP and R/KTP X -polarized spectra are plotted on the same scale in Fig. 3 for comparison. Most of the R/KTP bands are attenuated relative to their KTP counterparts although not all to the same degree; e.g., $\Delta I_{376} > \Delta I_{172}$. The interesting and significant exceptions are at 327 cm^{-1} , where $\Delta I = 0$, and at $204, 216, 270, 637,$ and 700 cm^{-1} where $I_{\text{R/KTP}} > I_{\text{KTP}}$. To account for these spectral changes, we consider the directional dispersion present in the KTP and RTP spectra.

The directional dispersion can be attributed to two components, the classical directional dispersion of phonons and selective probing of the two distinct octahedra. One can envision a Raman experiment in which the laser beam is originally incident upon one of the crystallographic faces. As the crystal is rotated about a crystallographic axis orthogonal to that of the incident beam, some relative intensities and band frequencies will change. For example, if the laser beam is originally incident upon the Y face, as in Fig. 2, ν_1 will necessarily shift to a higher energy as the crystal is rotated off the Y axis. The spectral changes that occur in conjunction with Rb^+ exchange coincide with those for a directional dispersion where the strength and frequency of Raman bands vary with the phonon-mode propagation direction. Therefore, we propose a mechanism by which Rb^+ exchange, because

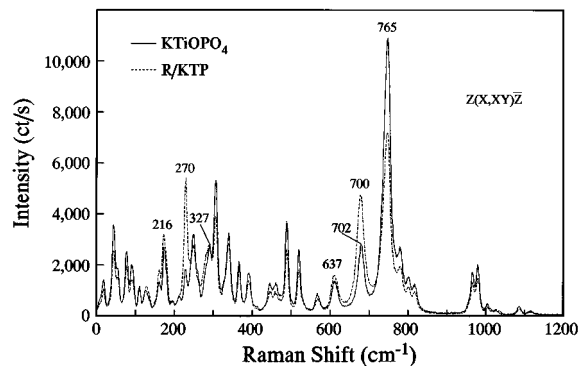


FIG. 3. Micro-Raman spectra of the Z face of an R/KTP channel waveguide device. The R/KTP and KTP spectra were obtained $5 \mu\text{m}$ from the corner of the crystal and from an unexchanged region between the R/KTP channel waveguides, respectively.

of the relatively larger ionic radius of Rb^+ ($r_{\text{Rb}} = 1.49 \text{ \AA}$, $r_{\text{K}} = 1.33 \text{ \AA}$), causes a reorientation or tilting of the octahedra to accommodate the larger cation, thereby causing spectral changes similar to those of a directional dispersion.

The information obtained by micro-Raman spectroscopy can be practically applied to the characterization of R/KTP device chemical bonding and crystal structure which are related to the optical nonlinearity. Micro-Raman studies can also reveal optimal fabrication conditions for the more efficient design of R/KTP devices. In particular, the Raman polarizability tensor, and therefore the strengths of the Raman bands, can be related to the nonlinear susceptibility of a crystal.⁸ Raman bands of certain symmetries can be correlated to specific nonlinear coefficients through crystal symmetry. Consequently, R/KTP waveguide depth (or lateral) profiles of Raman band strength relative to KTP can yield corresponding optical nonlinearity profiles. Also, the nonlinear susceptibility tensor is determined by the crystal symmetry. Disruption of the long-range translational (crystal) symmetry and tilting of the TiO_6 octahedra caused by ion exchange can therefore alter the values of specific tensor elements. Micro-Raman (band shifts and/or strengths) two-dimensional (2D) profiles of R/KTP waveguides can be generated to map the degree and direction of disrupted symmetry and TiO_6 octahedral tilt which depend on the extent and spatial distribution of Rb^+ exchange. Our micro-Raman studies show that 2D Rb^+ exchange profiles of waveguide top and endfaces can be mapped. Vibrational modes associated with the alkali cation appear in the region below 200 cm^{-1} , and the spectral differences between KTP and RTP in this region are as great as those observed in the region associated with the TiO_6 octahedral torsional and stretching modes. Therefore, the alkali cation Raman bands can also be used to monitor *in situ* the migration of cations, induced by device operation, over time and correlate changes to the performance of the device.

We thank Dr. John D. Bierlein of Du Pont for use of the RbTiOPO_4 single crystal.

¹ J. L. Jackel, C. E. Rice, and J. J. Vasselka, *Appl. Phys. Lett.* **41**, 607 (1982).

² J. D. Bierlein, A. Ferretti, L. H. Brixner, and W. Y. Hsu, *Appl. Phys. Lett.* **50**, 1216 (1987).

TABLE I. Band energy of ν_1 as a function of crystal orientation and incident polarization.

Orientation	RTP $\nu_1(\text{cm}^{-1})$	KTP $\nu_1(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$
$X(Y,YZ)\bar{X}$	696	701	+5
$X(Z,ZY)\bar{X}$	694	698	+4
$Y(X,XZ)\bar{Y}$	691	696	+5
$Y(Z,ZX)\bar{Y}$	691	695	+4
$Z(X,XY)\bar{Z}$	696	703	+7
$Z(Y,YX)\bar{Z}$	697	703	+6

- ³W. P. Risk, Appl. Phys. Lett. **58**, 19 (1991).
- ⁴G. R. Paz-Pujalt and D. D. Tuschel, Appl. Phys. Lett. **62**, 3411 (1993).
- ⁵D. D. Tuschel and G. R. Paz-Pujalt, Ferroelectrics **151**, 85 (1994).
- ⁶G. R. Paz-Pujalt, D. D. Tuschel, G. Braunstein, T. Blanton, S.-T. Lee,
and L. Salter, J. Appl. Phys. **76**, 3981 (1994).
- ⁷G. E. Kugel, F. Bréhat, B. Wyncke, M. D. Fontana, G. Marnier, C.
Carabatos-Nedelec, and J. Mangin, J. Phys. C **21**, 5565 (1988).
- ⁸W. D. Johnston, Jr., Phys. Rev. B **1**, 3494 (1970).