

Gray track formation in KTiOPO_4 by swift ion irradiation

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Potassium titanyl phosphate single crystals were irradiated with 48 MeV lithium ions at fluences varying from 5×10^{12} to 10^{16} ions/cm². The defects created in the crystal have been characterized using x-ray rocking curve measurements, optical transmittance, and photoluminescence spectroscopy. From x-ray rocking curve studies, the full width at half maximum for the irradiated samples was observed to increase, indicating lattice strain caused by the energetic ions. Optical transparency of these samples was found to decrease upon irradiation. The irradiated samples exhibited a broadband luminescence in the 700–900 nm region, for fluences above 5×10^{13} ions/cm². The results indicate that ion-beam-induced optical effects in KTiOPO_4 single crystals are very similar to the ones obtained for crystals with “gray tracks,” which are attributed to the electronic transitions in the Ti^{3+} levels.

Ion implantation is a promising alternative to the conventional ion exchange and diffusion processes for fabricating optical waveguides and waveguide lasers, so also for tailoring the electro-optic and nonlinear properties of important materials of modern optics.¹ Lighter ions such as H, He, etc. have been used extensively to form waveguides by ion implantation in several optoelectronic materials including lithium niobate,² potassium niobate,³ and potassium titanyl phosphate (KTiOPO_4 or KTP).⁴ Several reports on ion implantation in KTP are associated with its projected range, damage production, and distribution of ions^{5–7} and waveguide formation by light ions.^{4,8–10} Apart from Rutherford backscattering and channeling experiments on damage distribution in this crystal,^{5–7} defect related characterization is limited. In an earlier investigation,¹¹ it has been observed that KTiOPO_4 crystals exposed to laser, x-ray irradiation as well as electric fields developed “gray tracks,” which is a much discussed defect in this crystal.¹² These defects have their microscopic origin in the electronic transitions of titanium in the Ti^{3+} state. In this communication, we analyze the defects created in KTP due to varying doses of lithium ion irradiation using rocking curve measurements, optical transmission, and photoluminescence (PL) spectroscopy and correlate them with the defects produced by other irradiation experiments.

KTP crystals grown by spontaneous nucleation as well as by top seeded solution growth were cut using a diamond saw to yield (100), (010), and (001) plates of ~ 0.7 – 1.2 mm thickness and then were carefully polished to optical finish. Ion irradiation was carried out at the Nuclear Science Center, New Delhi, using a 15 UD 16 MV Pelletron accelerator. Lithium (Li^{3+}) ions of energy 48 MeV and different fluences ranging from 5×10^{12} to 1×10^{16} ions/cm² were used for the

purpose at room temperature. In order to ensure uniformity over the irradiated area, the ion beam was magnetically scanned. The beam current was maintained below 10 nA.

X-ray rocking curve measurements were carried out before and after irradiation using a high resolution Siemens D5005 powder diffractometer with $\text{Cu } K\alpha$. Optical transmission on mirror polished thin plates of KTP (0.7 mm with no antireflection coating) was recorded prior to and after irradiation using a Hitachi 330 spectrophotometer. These samples were later analyzed to detect the induced defects using photoluminescence spectroscopy. Luminescence was excited by the 514.5 nm line of a 0.5 W argon ion laser of a MIDAC Fourier transform photoluminescence spectrometer. Signals from the samples were detected using a liquid nitrogen-cooled germanium detector. The depth profile of lithium ions in KTP lattice has been simulated using transport of ions in matter (TRIM) code. The mean projected range and the straggling of 48 MeV Li ions in KTP determined by TRIM98 are 242.5 and 10.8 μm , respectively.

Rocking curve measurements carried out on a sample irradiated to a dose of 10^{15} ions/cm² showed an increase in the full width at half maximum (FWHM) from a value of 195 in. (in the pristine state) to 223 arcsec for (800) reflection. This is depicted in Fig. 1. To look into the effect of this high energy ion beam on the optical properties of KTP crystals, optical transmission spectra were recorded in the wavelength range 200–900 nm. As shown in Fig. 2, the crystal transmittance decreased, while the absorption edge remained unchanged at ~ 340 nm, after exposure to the ion beam.

Photoluminescence measurements carried out on the irradiated samples at 4.2 K for different excitation power levels showed a broadband luminescence in the energy range 1–1.8 eV, with a maximum at 1.41 eV (corresponding to a wavelength of 880 nm). As expected, the pristine sample did not exhibit any luminescence in this region.¹³ Moreover, only above a dose of 5×10^{13} ions/cm², was there any observable luminescence from the crystal, though crystals irra-

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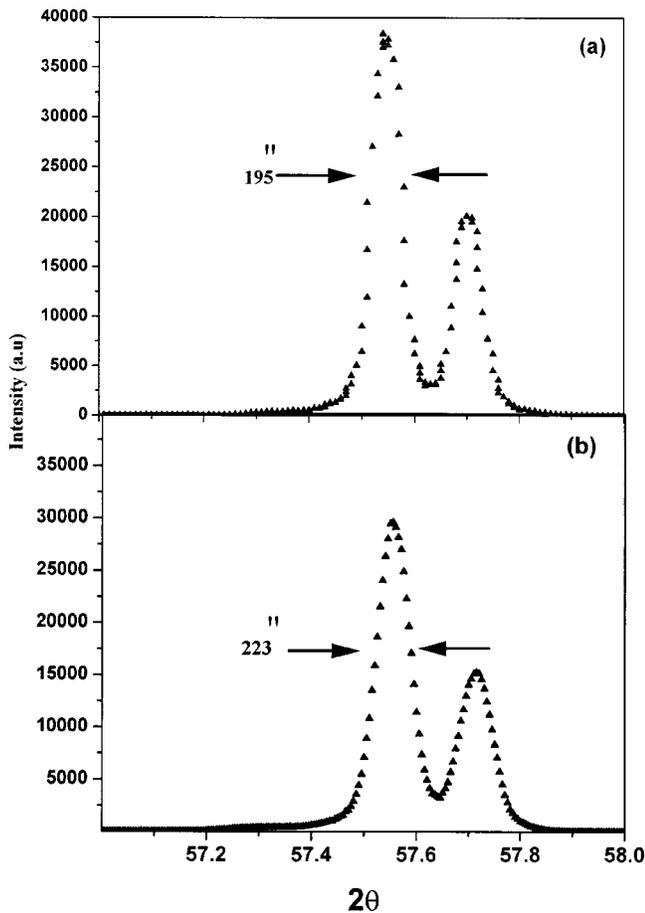


FIG. 1. X-ray rocking curves for KTP samples (a) before irradiation and (b) after irradiation.

diated at lower fluences were checked for PL at high excitation power levels. This is understandable because for low damage levels, annealing of the defects can occur even during implantation. However, in highly disordered materials, movement of larger defect clusters is inhibited. This sets a threshold for the occurrence of luminescence from the sample. Figure 3 shows the variation in intensity of the luminescence peak for several fluences with an excitation power of 200 mW. The intensity is found to saturate for higher fluences.

Luminescence intensity was also found to increase monotonically with increasing power levels of the excitation source. Typical spectra recorded for a sample irradiated to a fluence of 10^{15} ions/cm² for different power densities of the excitation source are given in Fig. 4. From these spectra, it is evident that there is neither any split in the broad luminescence peak, nor any relative shift in the peak position for various power levels applied. This indicates that the defect states produced in these samples are not related to donor-acceptor pairs. Luminescence from these samples when studied as a function of temperature revealed a gradual decrease in intensity and a broadening of the peak, with increasing temperature. As with power variation, the peak showed no shift in position with changing temperature which clearly shows that the defects created in the crystal due to irradiation are not excitonic in nature. A similar variation has been ob-

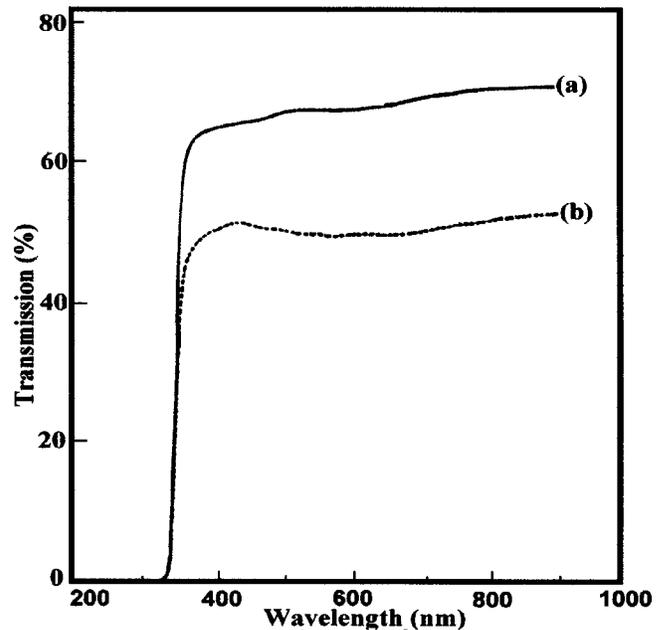


FIG. 2. Optical transmission spectra of KTP (a) before irradiation and (b) after irradiation.

served earlier for the samples in which gray tracks have been produced by electric and laser fields and x-rays.¹¹ The luminescence observed in the irradiated samples was found to be unaffected even after a lapse of a few months. However, heat treatment at a temperature of ~ 400 °C for 3 h annihilated the luminescence peak, which can be associated with the annealing of the defects introduced. Variation in the intensity maxima of the luminescence band at 1.41 eV with temperature revealed that PL intensity changes only marginally up to 70 K after which it decreases rapidly until it gets quenched above 110 K. A least squares fit to the Arrhenius plot gives the activation energy for thermal quenching as

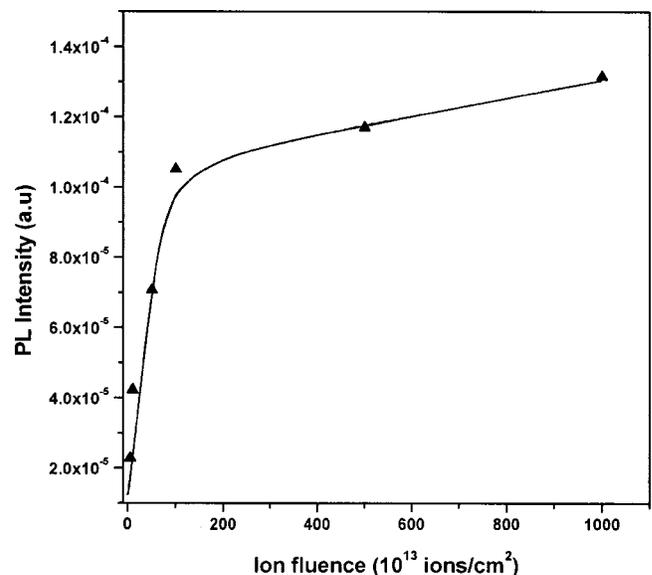


FIG. 3. Luminescence intensity vs ion fluence for a laser power of 200 mW.

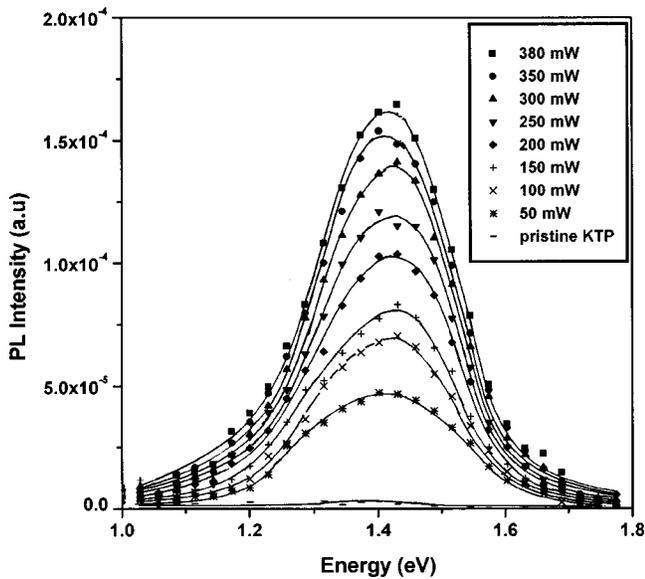


FIG. 4. PL spectra of pristine and ion irradiated KTP at 4.2 K for varying power levels (ion fluence: 10^{15} ions/cm²).

$\Delta E = 0.011$ eV. This compares reasonably well with the value of $\Delta E = 0.016$ eV obtained for an optically gray tracked KTP sample.¹¹

Our x-ray studies on the ion irradiated samples mimic the behavior of KTP crystals subjected to electric fields. Rocking curves recorded for crystals with an increasing static electric field along the polar axis showed a strong enhancement in diffracted intensity as well as FWHM for the (400) and (800) reflections.¹⁴ This indicates the presence of an inhomogeneous lattice strain due to the applied field, which has been established earlier using synchrotron x-ray topography on electrically gray tracked KTP crystals.¹⁵ Similarly, the strain developed in the crystal lattice due to ion irradiation has contributed to its increased rocking curve width. As regards the optical transmission, a broad absorption in the range 400–750 nm is evident for the irradiated crystal from Fig. 2. A similar reduction in transmitted intensity has been reported for KTP samples subjected to x-ray irradiation, which later got reverted upon annealing in air at 800 °C for 48 h.¹⁶ For hydrogen as well as electric-field treated samples, Roelofs¹⁷ concluded that the observed optical absorption is due to the formation of Ti^{3+} ions in the crystal lattice. For Ti-doped phosphate glasses also, a similar absorption in the 400–700 nm region with a peak at 450 nm has been reported, which is ascribed to the ${}^2T_2 \rightarrow {}^2E$ transition in Ti^{3+} ions.¹⁸ Comparison of these optical absorption spectra allows us to conclude that the broad absorption in ion irradiated samples can also be attributed to the transitions between the electronic levels of Ti^{3+} . Such a transition is the manifestation of the defect centers produced by high energetic beams incident on the crystal. Wang *et al.*¹⁹ in their investigations on $KTiOPO_4$ implanted with 3.0 MeV erbium ions to a dose of 7.5×10^{14} ions/cm² at 10 K observed that the PL spectrum exhibited a peak around 860 nm. This was in sharp contrast to the expected characteristic luminescence of Er^{3+} around 1530 nm, though the presence of erbium in the crystal lattice was confirmed by reflective x-ray spectroscopy.

However, for samples implanted with 300 keV Er ions to a dose of 2×10^{15} ions/cm² and later annealed in flowing oxygen at 750 °C for 4 h, light emission occurred at a wavelength of 1530 nm, which is rightly attributed to the presence of Er ions.²⁰ In this case, the luminescence at 860 nm might have been annealed due to the high temperature treatment, which otherwise would have appeared in their spectrum. Hence, irrespective of the ion beam used and its energy, a luminescence characteristic of gray tracks is observed in these samples for irradiation at high fluences. Thus, we generalize by saying that the damage effect called gray tracks, can be caused by several radiation fields including swift ion beams with wide ranging energies. For integrated optical devices, frequency doubling of waveguide lasers should be performed in the waveguide structure which is obtained by ion implantation.¹⁰ However, gray tracking results in a deterioration of its nonlinear optical properties and, hence, ion implantation at higher ion fluences is detrimental to device performance.

In conclusion, the present studies in lithium ion irradiated KTP reveal that interaction of high energy ions with the crystal lattice results in the modification of the electronic levels associated with titanium ions leading to gray track formation.

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- ¹P. D. Townsend, Nucl. Instrum. Methods Phys. Res. B **65**, 243 (1992).
- ²P. J. Chandler, L. Zhang, and P. D. Townsend, Appl. Phys. Lett. **55**, 1710 (1989).
- ³T. Bremer, W. Heiland, B. Hellermann, P. Hertel, E. Kratzig, and D. Kollwe, Ferroelectr. Lett. Sect. **9**, 11 (1988).
- ⁴L. Zhang, P. J. Chandler, P. D. Townsend, and P. A. Thomas, Electron. Lett. **28**, 650 (1992).
- ⁵K. M. Wang, F. Lu, M. Q. Meng, B. R. Shi, D. Y. Shen, Y. G. Liu, and D. Fink, Nucl. Instrum. Methods Phys. Res. B **145**, 271 (1998).
- ⁶W. Wesch, Th. Opfermann, and T. Bachmann, Nucl. Instrum. Methods Phys. Res. B **141**, 338 (1998).
- ⁷K. M. Wang, B. R. Shi, Z. L. Wang, X. D. Liu, Y. G. Liu, and Q. T. Zhao, Phys. Rev. B **50**, 770 (1994).
- ⁸K. M. Wang, F. Lu, M. Q. Meng, B. R. Shi, W. Li, F. X. Wang, D. Y. Shen, and N. Cue, Jpn. J. Appl. Phys., Part 2 **37**, L1055 (1998).
- ⁹Th. Opfermann, T. Bachmann, W. Wesch, and M. Rottschalk, Nucl. Instrum. Methods Phys. Res. B **148**, 710 (1999).
- ¹⁰L. Zhang, P. J. Chandler, P. D. Townsend, Z. T. Alwahabi, S. L. Pityana, and A. J. McCaffery, J. Appl. Phys. **73**, 2695 (1993).
- ¹¹A. Deepthy, M. N. Satyanarayan, K. S. R. K. Rao, and H. L. Bhat, J. Appl. Phys. **85**, 8332 (1999).
- ¹²M. N. Satyanarayan, A. Deepthy, and H. L. Bhat, Crit. Rev. Solid State Mater. Sci. **24**, 103 (1999).
- ¹³G. Blasse, G. J. Dirksen, and L. H. Brixner, Mater. Res. Bull. **20**, 989 (1985).
- ¹⁴M. T. Sebastian, H. Klapper, and R. J. Bolt, J. Appl. Crystallogr. **25**, 274 (1992).
- ¹⁵M. N. Satyanarayan, H. L. Bhat, M. R. Srinivasan, P. Ayyub, and M. S. Multani, Appl. Phys. Lett. **67**, 2810 (1995).
- ¹⁶K. Terashima, M. Takena, and M. Kawachi, Jpn. J. Appl. Phys., Part 2 **30**, L497 (1991).
- ¹⁷M. G. Roelofs, J. Appl. Phys. **65**, 4976 (1989).
- ¹⁸L. E. Bausa, J. G. Sole, A. Duran, and J. M. F. Navarro, J. Non-Cryst. Solids **127**, 267 (1991).
- ¹⁹K. M. Wang, M. Q. Meng, F. Lu, X. D. Liu, T. B. Xu, P. R. Zhu, D. Y. Shen, and Y. H. Tian, Mater. Sci. Eng., B **52**, 8 (1998).
- ²⁰Th. Opfermann, T. Bachmann, E. Lux, and W. Wesch, Nucl. Instrum. Methods Phys. Res. B **127/128**, 483 (1997).