LA-UR- 96-3605

CONF-961070--2

Pyroelectricity and its role in optical damage of potassium titanyl phosphate crystals

D. W. Cooke, B. L. Bennett, R. E. Muenchausen, J. C. Thomas, N. J. Cockroft, J. R. Quagliano,
R. R. Petrin, C. J. Maggiore, M. T. Paffett, D. M. Wayne, T. N. Taylor and M. Hawley

Materials Science and Technology Division, MST-4, MS E546
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

J. C. Jacco and M. P. Scripsick
Crystal Associates, Inc., 15 Industrial Park, Waldwick, New Jersey 07463

RECEIVED
DEC 2 5 1996
OSTI

ABSTRACT

The origin of optical damage in potassium titanyl phosphate (KTP) crystals has been vigorously investigated since its introduction as a nonlinear optical material in 1976. It is well known that this material exhibits a laser damage threshold that limits its use in many high average-power applications, especially frequency doubling of Nd-doped lasers. Both photochromic and electrochromic damage can be induced in KTP. Until recently, it was thought that these two types of damage were distinctly different, possibly involving different mechanisms; however, new data show that electrochromic-like damage can be induced in KTP by laser irradiation only, implying the existence of an internal electric field. We have recently observed bursts of light (optical scintillations) when heating KTP crystals at 0.1 - 1.0 K/s in the temperature range 8 - 675 K. The scintillations correspond to molecular nitrogen emission occurring during the electrical breakdown of air near the crystal surface, and imply the existence of pyroelectric fields in KTP exceeding 30 kV/cm. These fields (and concomitant currents) were induced by 10.6 μm laser irradiation. The observation of pyroelectric effects, heretofore not considered in KTP damage models, provides an important new insight into the possible cause of the recently observed "electrochromic-like" photochromic damage in KTP.

Keywords: KTP, photochromic damage, electrochromic damage, pyroelectric effects, optical scintillations, nonlinear optical crystals, second harmonic generation, optical damage

1. INTRODUCTION

Potassium titanyl phosphate (KTP) is the most commonly used nonlinear optical crystal for frequency doubling near-infrared lasers, especially Nd:YAG. It possesses large nonlinear optical coefficients, broad temperature and spectral bandwidth, good chemical and mechanical properties, and low dielectric constant.[1] And although KTP is the material of choice for frequency doubling Nd-doped lasers, it is limited to low power-density *pulsed*, and moderate power-density *cw* operation because of laser-induced optical damage.[2] Since its introduction as a nonlinear optical material in 1976, it has been known that above-threshold laser excitation of KTP produces optical damage (often referred to as "gray tracking"), manifested as enhanced optical absorption in the green spectral region. The sequence of second harmonic generation, coupled with concomitant enhanced green absorption, results in catastrophic damage to the KTP crystal and limits its usefulness in high average-power applications. In addition to these frequency-doubling applications, KTP is also used in conjunction with mid-infrared lasers as an optical parametric oscillator capable of producing tunable radiation in the 1 - 5 μm region.

In addition to the optically-induced photochromic (PC) damage in KTP, it has been demonstrated that application of an *external* electric field will also induce electrochromic (EC) damage.[3,4] Originally, it was thought that PC and EC damage were distinctly different; however, new results presented in the present work show that EC-like damage can be induced by optical excitation alone. This type of damage points to the existence of an *internal* electric field in KTP whose origin, we believe, can be directly linked to the pyroelectric properties of the crystal.

We have recently discovered that KTP emits bursts of light (optical scintillations) when heated or cooled at a rate of 0.1 - 1.0 K/s in the interval 8 - 675 K. The scintillations correspond to molecular nitrogen emission occurring during the electrical breakdown of air near the crystal surface, and implies the existence of electric fields exceeding 30 kV/cm. Generation of these large fields is attributed to the temperature-dependent change in the crystal's spontaneous polarization. These pyroelectric effects have not been previously included in proposed damage models of KTP; however, similar observations have been made on other pyroelectric materials.[5-7] In the present work we demonstrate that laser excitation can in fact produce the small heating rates necessary to generate large surface fields (and concomitant currents) in KTP and suggest that these thermally-induced fields play an important role in optical damage of this technologically important material.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

2. EXPERIMENTAL ASPECTS

Measurement of optical scintillations in KTP was done by mounting the specimen on the cold finger of a continuous-flow liquid helium cryostat maintained under ambient pressure, irradiating at selected temperatures by an 8-W CO_2 laser, and recording the emission with an optical multichannel analyzer, as depicted in Fig. 1. A Ge window was used to maintain a light-tight chamber and to allow entry of the laser beam into the cryostat; an aperture provided appropriate collimation to ensure that only the sample was illuminated during the experiment. Application of silver electrodes to the sample also allowed measurement of thermally-induced currents as a function of temperature. The CO_2 laser was chosen to excite the sample because its energy is insufficient to produce electronic excitation across the bandgap, but is sufficient to provide heating via absorption into the phosphate group of KTP.

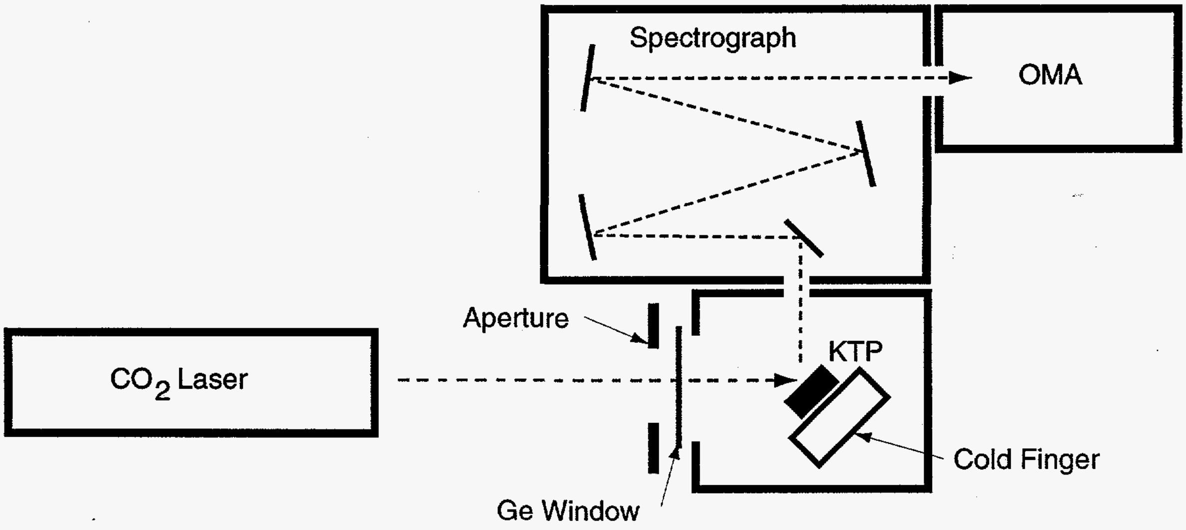

Fig. 1. Experimental apparatus utilized to measure optical scintillations in KTP.

3. EXPERIMENTAL RESULTS

3.1 Optical scintillations

Shown in Fig. 2 is a typical scintillation spectrum occurring in KTP during a heating or cooling cycle (0.1 - 1.0 K/s). The KTP spectrum is shown as the solid line and the dashed line depicts a nitrogen discharge spectrum obtained in the absence of a sample. The spectrum is identified as the second positive system of molecular nitrogen ($C^3\pi_u \rightarrow B^3\pi_g$) and results from the electrical breakdown of air near the KTP surface. This implies the existence of surface fields greater than 30 kV/cm, which is ten times larger than fields routinely used to induce EC damage in KTP.[4] Evolution of these large fields is due to the pyroelectric nature of KTP.

Pyroelectricity occurs in crystals that lack inversion symmetry and possess an electric dipole moment. If the dipoles throughout the crystal are aligned in such a way as to avoid self cancellation, the material will exhibit spontaneous polarization P_s. Maintaining a constant crystal temperature for some time period will allow accumulation of surface charges and consequent masking of the internal P_s. An increase or decrease in sample temperature may change the magnitude of the dipoles by altering atomic positions, thus changing the net polarization and thereby causing a concomitant redistribution of surface charges, which can be measured in an external circuit.[8]

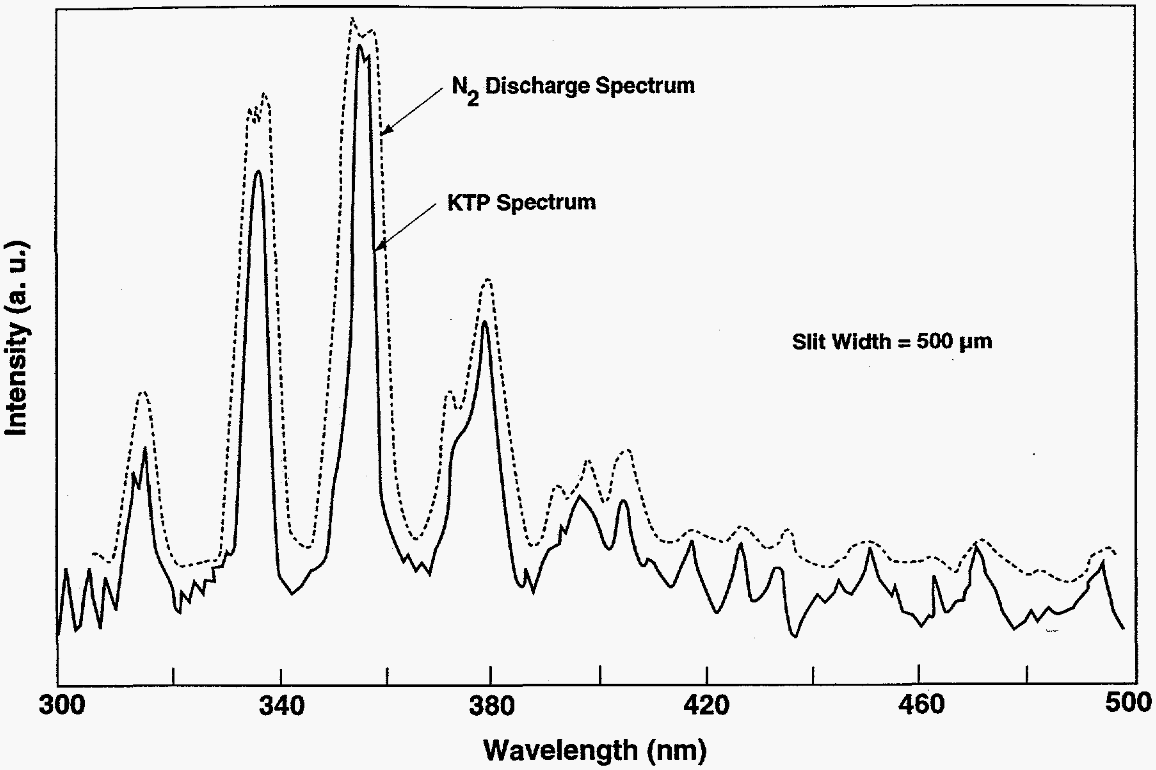

Fig. 2. Spectrum of scintillations occurring in KTP. A nitrogen discharge spectrum is shown for comparative purposes.

Fundamentally, P_s and the dielectric permittivity ε of the crystal determine the spontaneous polarization field. In general we can write

$$E \propto \frac{dP_S}{dt} = \frac{dP_S}{dT}\frac{dT}{dt} \tag{1}$$

and define the terms in the usual way,

$$\frac{dP_S}{dT} \equiv \lambda_T, \qquad \frac{dT}{dt} \equiv \beta, \tag{2}$$

with λ_T being the pyroelectric coefficient and β the heating rate. Thus, if a KTP sample is heated or cooled, it is possible to generate surface electric fields that may be of sufficient magnitude to break down air and cause scintillations. Indeed, scintillations (sometimes referred to in the literature as "pyroelectric luminescence") have been observed in several pyroelectric samples, and a simple model has been proposed to explain the results.[9]

3.2 Thermally-induced currents

Laser excitation of KTP at 12 K produces a current as shown in Fig. 3. A transient current is always observed during initial laser irradiation; however, no steady-state current is observed that is proportional to the heating rate. This is consistent with the known pyroelectric properties of KTP–the pyroelectric coefficient vanishes below approximately 20 K, as shown in

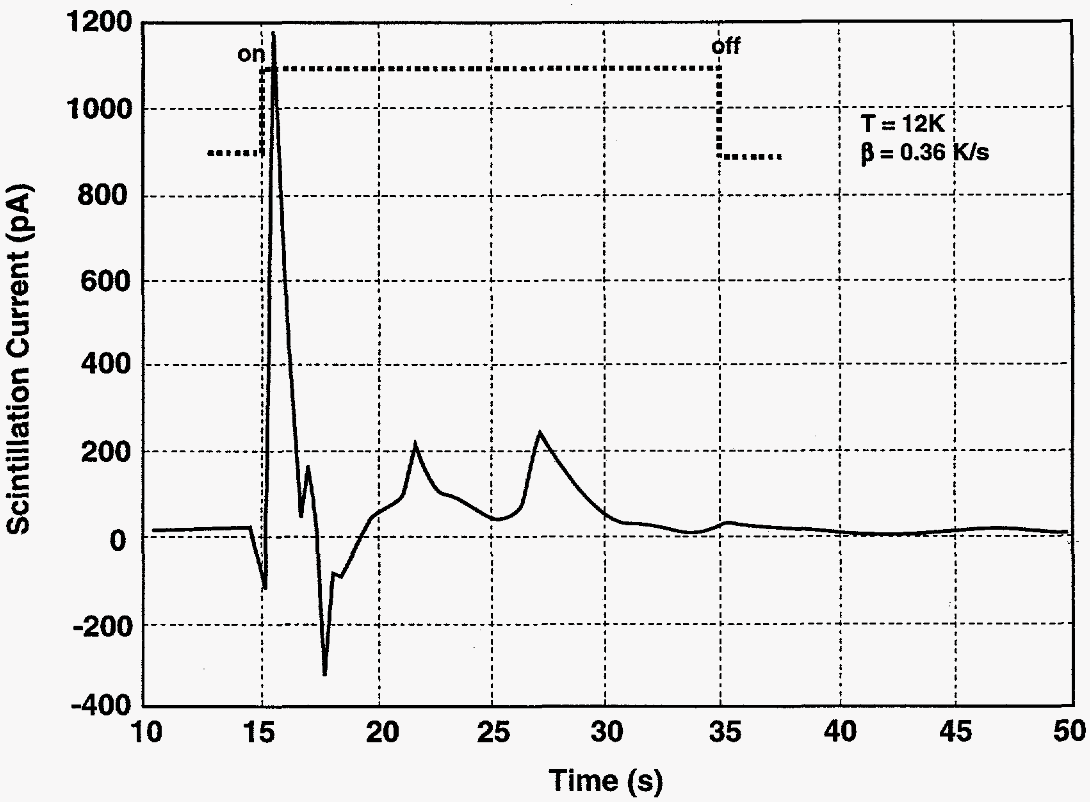

Fig. 3. Current generated in KTP at 12 K by a CO_2 laser pulse. The laser cycle is shown by the dashed line.

the inset of Fig. 4. This behavior is in contrast to that observed at 80 and 295 K, as shown in Figs. 4 and 5, which clearly demonstrate peak currents that are correlated with the laser on-off cycle. Note the sharp polarity change that occurs when the laser pulse is terminated. From Eq. (2) we expect large surface fields to occur when β is large, as is the case when the laser beam initially strikes the sample or is terminated. As the KTP temperature increases during constant laser excitation, β decreases and the magnitude of the current decreases. Concomitant with the peak current pulses are optical scintillations, implying a surface electric field in excess of 30 kV/cm. Note that even at 295 K, heating rates as small as 0.1 K/s can induce these surprisingly large fields. And although we have employed a long wavelength (10.6 μm) laser for heating purposes, it is reasonable to expect similar effects from Nd-doped laser irradiation. In the severe case of transient absorption (t ~ 0.01 s), presumably associated with hole traps, we expect significant heating of KTP during high rep-rate irradiation.

Although we do not fully understand the behavior of thermally-induced pyroelectric currents in KTP, especially their apparent modulation by the ionic conductivity above 200 K, it is clear that they are associated with laser heating. Moreover, the magnitude of the corresponding surface fields are sufficient to break down air, which is ten times larger than fields normally used to induce EC damage. We suggest that these pyroelectric fields, which, to our knowledge have not been previously considered in the development of damage models for KTP, may play an important role in the process and must be included in any comprehensive model. In fact, support for this assertion is provided by the recent observation of EC-like damage being induced in KTP by the usual PC method. Shown in Fig. 6 is a micrograph of a KTP crystal that has been optically damaged by exposure to a high-rep-rate laser. The beam enters the sample perpendicular to the plane of the paper and covers a region shown by the dotted line. In separate experiments the sample received sequential exposures of 7 and 17

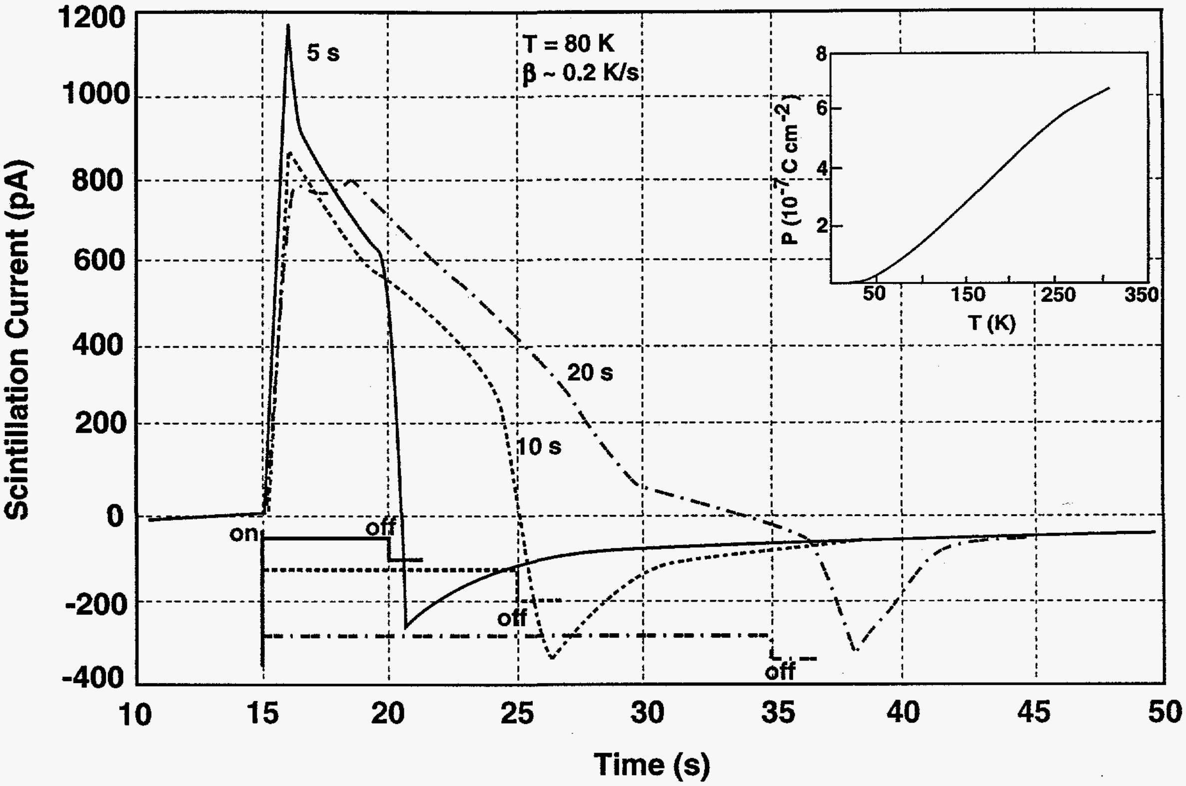

Fig. 4. Current generated in KTP at 80 K by a CO_2 laser pulse. Currents corresponding to excitation times of 5, 10, and 20 seconds are shown. The inset depicts the polarization of KTP as a function of temperature (taken from ref. 10).

hours duration; the left portion of the micrograph corresponds to the heavily damaged specimen. The beam characteristics are: 3 mJ/p, 15 ns pulse length, 300 Hz rep-rate, and 350 μm beam diameter. The calculated fluence is approximately 3.1 J/cm^2 with a corresponding intensity of approximately 210 MW/cm^2. Note that the darkened (damaged) regions are concentrated near the left portion of the beam area. Previous work has shown the EC-damaged bulk region of KTP to be deficient in both K and Ti ions relative to the pristine region, implying the existence of an internal electric field.[3] We suggest that the EC-like damage induced by optical excitation results from the pyroelectric fields generated by the laser beam.

4. CONCLUSIONS

We have demonstrated that large electric fields (and associated currents) are generated in KTP as a result of modest heating and cooling. Peak currents and optical scintillations are coincident with the rapid heating of KTP encountered during the on-off cycle of the laser pulse. Temperature behavior of the thermally-induced current pulses suggests that ionic currents modulate the overall signal in KTP above 200 K. We conclude that pyroelectric properties of KTP are responsible for these effects, and should be considered in the formulation of KTP optical damage models.

5. ACKNOWLEDGMENTS

The authors kindly acknowledge T. Shimada for lending us the waveguide CO_2 laser. The Research at Los Alamos National Laboratory was sponsored by Laboratory Directed Research and Development funds.

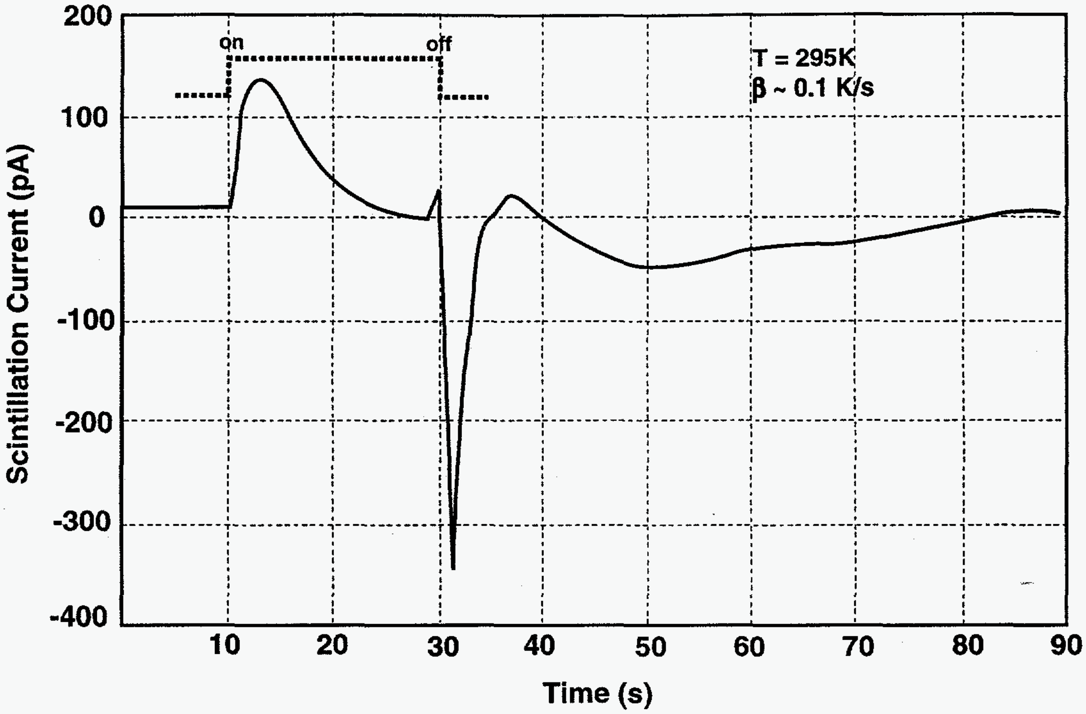

Fig. 5. Current generated in KTP at 295 K by a CO_2 laser pulse; the duration is shown by the dashed line.

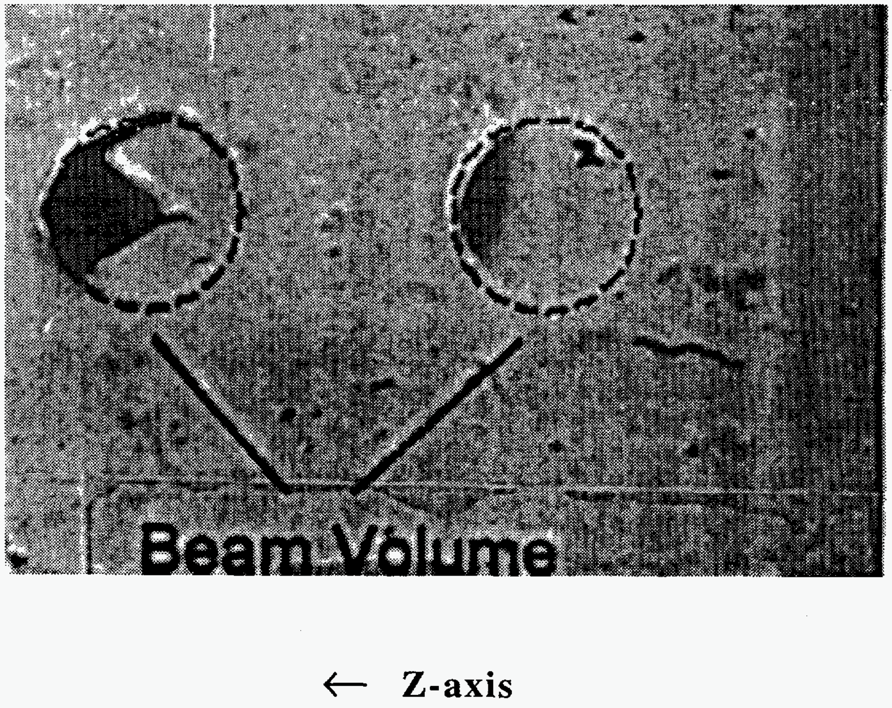

Fig. 6. Micrograph of a high-rep-rate damaged KTP sample. The laser beam enters the sample perpendicular to the plane of the paper. The PC damage occurs primarily in the z-direction and looks similar to the EC damage normally induced by the application of an external electric field.

6. REFERENCES

1. J. D. Bierlein and H. Vanherzeele, "Potassium titanyl phosphate: properties and new applications," *J. Opt. Soc. Am. B*, **6**(4), 662 (1989).

2. J. C. Jacco, D. R. Rockafellow and E. A. Teppo, "Bulk-darkening threshold of flux-grown $KTiOPO_4$," *Optics Letters* **16**(17), 1307 (1991).

3. J. R. Quagliano, R. R. Petrin, T. C. Trujillo, R. Wenzel, L. J. Jolin, M. T. Paffett, C. J. Maggiore and N. J. Cockroft, "Materials characterization, optical spectroscopy, and laser damage studies of electrochromically and photochromically damaged $KTiOPO_4$ (KTP)", *Proc. SPIE* **2428**, 4-11 (1994).

4. J. R. Quagliano, R. R. Petrin, T. C. Trujillo, N. J. Cockroft, M. T. Paffett, C. J. Maggiore and J. C. Jacco, "An investigation of the chemical and physical properties of pristine, electrochromically damaged and photochromically damaged $KTiOPO_4$ (KTP) using surface analytical and optical spectroscopic techniques," *OSA Proceedings on Advanced Solid-State Lasers* **24**, 528-532 (1995).

5. J. S. Patel and D. M. Hanson, " Pyroelectric luminescence," *Nature* **293**, 445-447 (1981).

6. H. P. Yockey and C. L. Aseltine, "Development of high voltages in potassium dihydrogen phosphate irradiated by γ rays", *Phys. Rev. B* **11**, 4373-4382 (1975).

7. D. W. Cooke and C. Alexander, Jr., "Observations of intense scintillations in unirradiated glycine", *Phys. Rev. B* **14**, 1333-1335 (1976).

8. S. B. Lang, *Sourcebook of Pyroelectricity* (Gordon and Breach, New York, 1974).

9. J. Kalinowski and Z. Dreger, "Simple model for pyroelectric luminescence," *Phys. Rev. B* **36**, 7840-7848 (1987).

10. J. Mangin, G. Jeandell and G. Marnier, "Temperature dependence of polarization in $KTiOPO_4$ single crystals," *Phys. Stat. Sol. (a)* **117**, 319 - 323 (1990).