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Use of Piezoelectric Ceramics in Detection and Measurement of Pulsed Laser Radiation

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In many analytical applications there is a need for a device to measure the energy or spatial profile of a laser pulse. Such a detector is also useful as a trigger for synchronizing various electronic devices with the laser pulse. Pyroelectric detectors, which are frequently used for these purposes, have been reviewed extensively (*1–3*). They have the advantages of high sensitivity, very fast rise times, and broad spectral response. They have the limitation, however, of being fragile devices, subject to damage when exposed to the high laser intensities commonly obtained in the laboratory. In contrast we have found that large piezoelectric ceramics (*4*) have a much higher damage threshold than pyroelectric crystals, while still maintaining a response time and sensitivity that are suitable for many laboratory applications. In this note we describe the performance of a PZT ceramic detector that is used to measure the output of pulsed CO_2, dye, and excimer lasers.

EXPERIMENTAL SECTION

We have studied the response of commercially supplied PZT piezoelectric ceramics (Edo-Western EC-64 and EC-65) to pulsed laser radiation. All samples were either cubes or disks with dimensions ranging from 0.3 to 1.2 cm. In all cases the ceramics were irradiated in a normal configuration, i.e. with the laser beam striking an area perpendicular to the surface electrodes. The irradiated surface was not conditioned, and all ceramic elements were used as supplied by the manufacturer. The samples were either freely suspended from leads soldered to the electrodes or clamped between two brass bars that also served as a heat sink. Electrical output was observed directly with a 150-MHz oscilloscope. For more quantitative measurements the signal was recorded by a transient digitizer (Biomation 805) and averaged over several pulses with a microcomputer.

In a typical experiment radiation from a TEA CO_2 laser (Lumonics 201K, 10.62 μm), a Rhodamine B dye laser (Lambda Physik FL2002, 608 nm), or a XeCl excimer laser (Lambda Physik EMG 102E, 308 nm) was collimated by a circular aperture 0.15–0.25 cm in diameter before striking the detector. Typical pulse energies and widths were 1–50 mJ and 150 ns fwhm for the CO_2 laser, 1–4 mJ and 15 ns for the dye laser, and 2–4 mJ and 15 ns for the excimer laser. For a fixed aperture size the laser energy was varied with attenuating filters (CaF_2 for the IR and neutral density filters for the visible lasers). For the highest IR fluences the pulse energy was varied by changing the operating parameters of the laser. Absolute measurements of incident energy were performed with either a calibrated calorimeter (Scientech 362) or a pyroelectric detector (Molectron J3-05).

RESULTS AND DISCUSSION

For CO_2 and dye laser excitation the detected signal was characterized by a very fast initial rise ($\sim$25 ns for the dye

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laser) to $\sim$80% of the peak, followed by a slower growth to a broad maximum at approximately 2 μs and then by a long decay (1.5–2.0 msec) to the base line. These temporal characteristics were insensitive to the ceramic dimensions and to the diameter of the collimating aperture. Superimposed on the signal were rapid piezoelectric (PZE) oscillations (*5*) with frequencies ranging from 100 to 500 kHz. The exact appearance and frequency of the PZE oscillations were a function of the ceramic composition, shape, and dimensions (*6*) and was not analyzed in this work. In the case of UV excitation the very rapid rise was absent. Instead, a broad maximum occurred at approximately 45 μs after the laser pulse, modulated by the rapid PZE oscillations.

In all three cases the maximum signal amplitude was strictly proportional to the incident pulse energy. With a TEA CO_2 laser, for example, pulse energies from 1 to 50 mJ produced a linear response with a porportionality constant of 55 V/J. When the detector was used in the clamped configuration, the sensitivity increased by a factor of 2.5. For visible and UV radiation the sensitivity was 34% lower. A UV laser pulse energy of 15 μJ was easily detected with a single shot signal to noise (S/N) of 8, without any amplification. This sensitivity is approximately 1% that obtained with a typical commercial pyroelectric detector and amplifier but at a very small fraction of the cost.

The PZT ceramic detectors have the advantage of extreme ruggedness. In the IR measurements the energy density routinely exceeded 1 J/cm^2, yet no visible deterioration of the sample surface or detector performance was observed. With 2.5-mJ output of the dye laser focused onto the surface of the sample to a $\sim$10^{-5} cm^2 spot, we observed intense light emission from the surface. The temporal characteristics of the output changed so that very strong PZE oscillations dominated the signal. Nevertheless, the maximum amplitude was unchanged and the detector was undamaged. One PZT sample that had been used extensively in this laboratory for over 6 months showed only slight signs of surface wear but no deterioration of sensitivity.

As an example of the application of large PZT ceramic detectors we have measured the spatial profile of the CO_2 laser beam. In this measurement the laser beam was collimated with a 1.38-mm diameter aperture. The ceramic detector, masked by a 0.20 mm diameter pinhole, was mounted on a translation stage and placed 13.3 cm away from the collimating aperture. The profile shown in Figure 1 was obtained by scanning the detector across the laser beam.

The initial rapid rise of the detected signal for IR and visible radiation is most likely a localized pyroelectric effect (*5*). The rise time in the case of CO_2 radiation (70 ns) corresponds
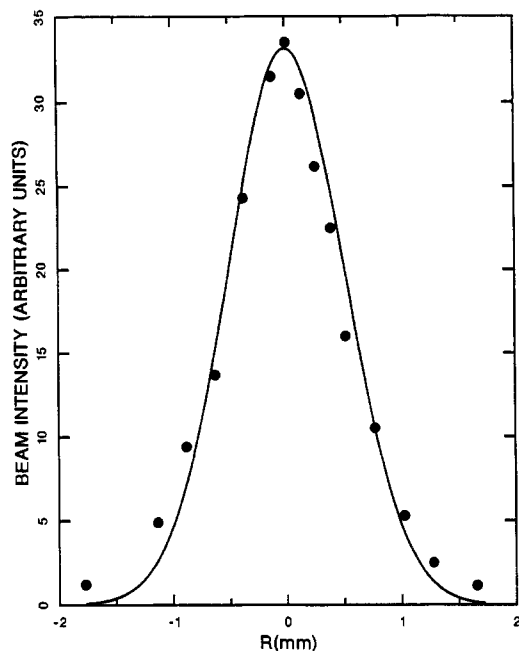
Figure 1. Profile of CO_2 laser beam measured by scanning with a masked PZT detector. The curve is a Gaussian function.

approximately to that of the laser pulse, whereas for dye laser radiation (25 ns) it is several times longer than the pulse rise time and is independent of laser spot size. The PZE oscillations that follow the transient pyroelectric signal are due to strain developing from the heating of the element. This combination of pyroelectric followed by piezoelectric response has also been seen by Glass and Abrams (6) and by Simhony and Bass (7, 8) in the case of CO_2 irradiation of very thin ferroelectric crystals. The broad maximum observed for IR

and visible radiation at ~2 μs is a bulk pyroelectric effect resulting from eventual heating of the entire element.

In the case of UV excitation a different mechanism is operating. The transient pyroelectric signal is completely absent and the bulk pyroelectric effect is delayed substantially. Crystalline PLZT is known to absorb strongly below 500 nm (9). The absorbed energy is possibly stored in a long-lived electronic state, the relaxation of which produces the delayed pyroelectric signal (10). The identity of this electronic state, which may be due to an impurity in the ceramic (9), requires further investigation.

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Chemiluminescence Sulfur Detection in Capillary Supercritical Fluid Chromatography

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The need for selective detectors in supercritical fluid chromatography (SFC) is particularly evident for the sensitive analysis of sulfur-containing species. These sulfur species are of interest to the environmental community, for the analysis of pesticides (1) and atmospheric pollutants (2), as well as to the petroleum industry (3). Various detectors have been employed for the analysis of sulfur. Among these are the Hall electrolytic conductivity detector (HECD) (4–6), a microwave-induced plasma detector (7), a helium after glow plasma detector (8), a nonflame source induced S_2 fluorescence detector (9), and a dc plasma detector (10). The most popular sulfur-selective detector for gas chromatography (GC) is the flame photometric detector (FPD) (11) which has also been applied to capillary SFC (12). When used as an SFC detector, the FPD suffers from several limitations. Among these limitations is a signal that has a squared dependence on sulfur concentration (as in GC). While this nonlinear response can be electronically compensated, the ideal analytical instrument provides linear calibration. Another major drawback in ap-

plication of the FPD to SFC is a limited dynamic range. Poor sensitivity (detection limits of about 25 ng on-column), a severe response dependence on pressure, and a significant base-line shift during pressure programming are also among the SFC–FPD limitations that had been initially reported (12). It should be pointed out that the FPD–SFC results were found during a preliminary study and that further optimization has produced detection limits (13) approaching those for an FPD–GC system. While optimization of the FPD has produced improved detection limits, the detector still suffers from the disadvantage of a squared dependent response and a base-line perturbation with pressure programming.

Multidetector compatibility is a major advantage of SFC over either GC or high-pressure liquid chromatography (HPLC). Fluid phase optical detectors such as the ultraviolet–visible (UV–vis) spectrophotometric detector and the fluorescence detector have been employed successfully in capillary SFC (14, 15). While gas-phase detectors such as the flame ionization detector (FID) (16) and the dual flame