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TWO-DIMENSIONAL SPATIALLY RESOLVED RAMAN SPECTROSCOPY OF SOLID MATERIALS

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### Authors

Veirs, D.K.  
Rosenblatt, G.M.  
Dauskardt, R.H.

### Publication Date

1988-03-01



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials & Chemical Sciences Division

To be presented at the Microbeam Analysis Society Annual Meeting, Milwaukee, WI, August 8-11, 1988

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D.K. Veirs, G.M. Rosenblatt, R.H. Dauskardt, and R.O. Ritchie

March 1988

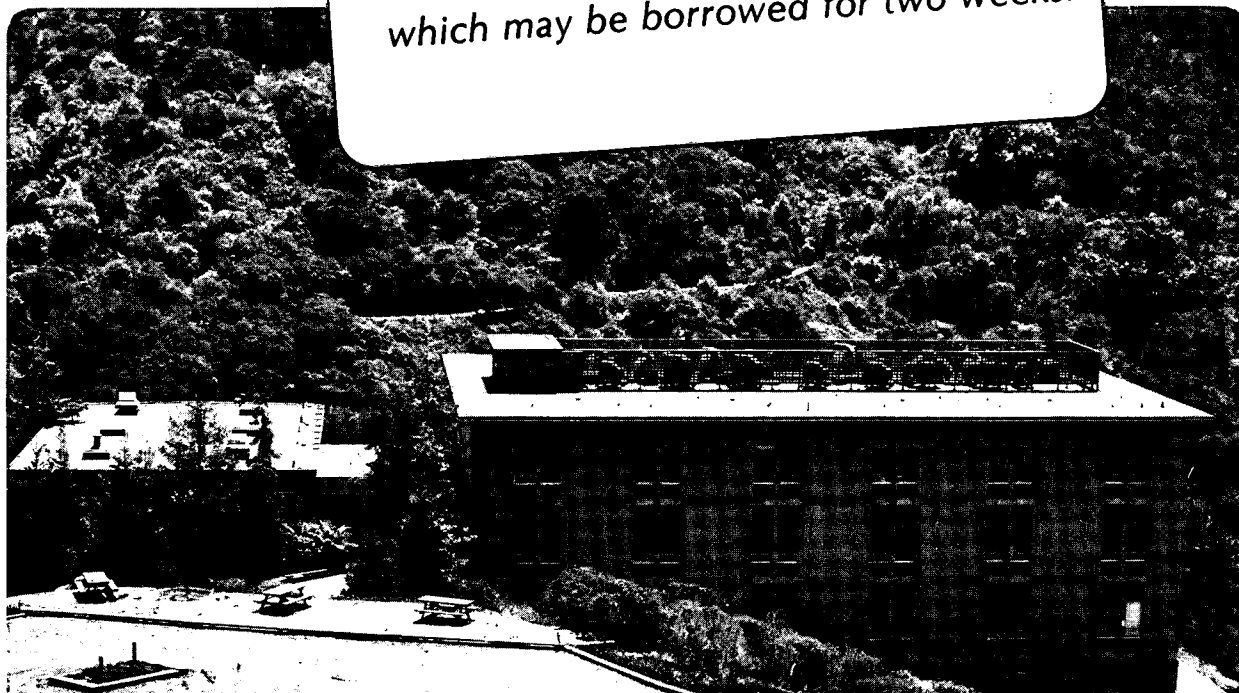
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## TWO-DIMENSIONAL SPATIALLY RESOLVED RAMAN SPECTROSCOPY OF SOLID MATERIALS

D.K. Veirs, G.M. Rosenblatt, R.H. Dauskardt, and R.O. Ritchie

Chemical compositional analysis of solid materials often is based upon vibrational spectroscopy, either infrared or Raman. Vibrational analysis is particularly valuable when information about molecular form, not only atomic composition, is desired. Many applications require analysis of small volumes necessitating sensitive instrumentation and spatial resolution. The development of multichannel detection systems for Raman spectroscopy coupled with microscopic techniques has resulted in a number of commercial Raman microprobes (from Spex Industries, Jobin-Yvon ISA, Dilor, for example)<sup>1</sup> capable of probing areas on the order of  $100 \mu\text{m}^2$  routinely. For macroscopic samples, with dimensions of thousands of microns on a side, an instrument which multiplexes both the spatial domain and wavelength would enhance the capability of Raman spectroscopy. We report on the development of such a Raman instrument and describe, as an example, its application to the investigation of the phase transformation accompanying crack growth in partially stabilized zirconia (PSZ).

### EXPERIMENTAL

A Raman spectroscopy system employing an imaging photomultiplier tube (PMT) detector has been constructed. The instrument produces a one-dimensional

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The authors are at the Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720. R.H. Dauskardt and R.O. Ritchie are also with the Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720. The work was supported by the Director, Office of Energy Research, U.S. Department of Energy under Contract No. DE-AC03-76SF-00098.

Raman profile of a sample's chemical composition along the path illuminated by a focused slit-like laser beam. The system as presently configured achieves a resolution of 40  $\mu\text{m}$ ; theoretically, the spatial resolution can be improved to the diffraction limit with appropriate collection optics.<sup>2</sup> The one-dimensional Raman profile is acquired continuously without moving the sample or illuminating laser beam, and without scanning the spectrometer. By translating the sample perpendicular to the focused illumination, a two-dimensional Raman map of the chemical composition can be obtained.

Fig. 1 presents a schematic of the Raman apparatus used for obtaining spatially-resolved Raman spectra. The 488 nm cw  $\text{Ar}^+$  laser line passes through a six-cavity narrow bandpass interference filter which reduces the plasma line intensities by  $10^{-6}$ . The laser is incident on a sample and the scattered light is collected and imaged onto the entrance slit of a single monochromator. A six-cavity interference filter is used to pass the spectral region of interest and to reject the Rayleigh scattered light by  $10^{-6}$  before the monochromator. The dispersed light is detected by an imaging PMT consisting of a photocathode that generates photoelectrons with a quantum efficiency of 10-16%, 5 amplifying microchannel plates, and a resistive anode. The position of each arriving photon that generates a current is determined to an accuracy of 70  $\mu\text{m}$  in both the X- and Y-directions. The computed position the photon is digitized in real time and passed to a digital data acquisition system. Each detected photon increments one element in a memory array which has a one-to-one correspondence with a map of the surface of the detector. Wavelength is dispersed along the X-direction.

The illumination and collection optics must be configured appropriately to obtain multiplexed spatial resolution. Fig. 2 shows the optical design used for obtaining one-dimensional Raman profiles, in this case, on the surface of PSZ. The laser beam is expanded with a telescope to the desired diameter and then

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focused in one dimension using a cylindrical lens. The laser beam is incident on the sample at  $70^\circ$  from the surface normal. This angle can be varied as needed. The laser optics form a slit-like illumination at the sample with  $\approx 400:1$  aspect ratio. The scattered light is collected with a  $f/1.3$  camera lens and focused onto the entrance slit of the monochromator. Rotation of the cylindrical lens allows the slit-like laser beam to be aligned so that the image formed by the collection lens is parallel to the entrance slit. There is a one-to-one correspondence of the Y-position at the sample to the position along the entrance slit; this correspondence is maintained at the detector. Magnification of the laser illuminated area onto the detector is determined by the focal length of the collection lens. In the present arrangement each vertical (or Y-direction) pixel (row in the data array) corresponds to  $28 \mu\text{m}$  at the sample. Spatial resolution in the X-direction is determined by the spectrometer entrance slit width coupled with the magnification of the collection lens. In the present experiments, a  $50 \mu\text{m}$  slit width corresponds to a spatial resolution  $17 \mu\text{m}$  in the X-direction. Increasing the magnification by using a shorter focal length collection lens (such as a microscope lens) will increase the spatial resolution in both the X- and Y-directions.

A two-dimensional Raman map of the specimen surface is obtained by data collection at successive incremental sample translations. The procedure is applicable to gaseous, liquid, and solid systems; here we describe application to a technologically important ceramic.

### SAMPLE APPLICATION

Partially stabilized zirconia (PSZ) has been referred to as the "first ceramic material in which microstructural design was explicitly used to achieve optimum properties".<sup>3</sup> When stress is applied to a crack in PSZ, material in the tetragonal phase near the crack tip undergoes transformation to the monoclinic phase, which results in a dilation, thereby relieving the tensile stress near the crack tip. Compositional mapping of the phases surrounding the crack and crack tip helps to

elucidate the mechanisms of crack growth and failure in these ceramic materials.

The Raman spectra of PSZ containing both tetragonal and monoclinic phases is shown in Fig. 3. Well resolved Raman peaks for each phase (identified in the accompanying table)<sup>4</sup> can be used to determine the relative intensity of the two phases. An integrated peak intensity entirely associated with the monoclinic phase is determined by subtracting the average background at positions indicated as 1 and 2 from the integrated area between 1 and 2. Likewise an integrated area centered at the  $264\text{ cm}^{-1}$  peak and corrected for the average background determined at 2 and 3 yields an intensity associated solely with the tetragonal phase. The relative intensity of the monoclinic phase is computed from the intensity of the monoclinic phase divided by the sum of the intensities of the tetragonal and monoclinic phases. This calculation is carried out for each Y-position (row in the data array) and yields a one-dimensional Raman profile. Fig. 4 shows two such 1-D Raman profiles, one across a crack grown in PSZ and a second parallel to the first profile but in front of the crack tip. The data for each profile were collected using 100 mWatts of laser power and a collection time of 7.5 minutes. The laser power was limited by scattered light saturating the detector. A series of such 1-D profiles can be used to determine a 2-D surface compositional map of a sample of PSZ as previously discussed. Spectra were acquired at 12 positions separated by  $250\ \mu\text{m}$ . Interpolation between the resulting 12 profiles was used to generate a 2-D Raman compositional map of the extent of transformation surrounding a crack, as shown in Fig. 5. An additional profile, taken parallel to and centered on the crack, was used to check the interpolation and add data in the dimension parallel to the crack. The experiment took about 1.5 hours.

## CONCLUSIONS

Two-dimensional detection, coupled with appropriate illumination and collection optics, yields Raman data which can be used to generate a 1-D Raman profile of the chemical composition at a surface. Successive 1-D Raman profiles



can be acquired by translating the sample and can be used to generate an accurate 2-D Raman compositional map of a surface. Advances in detector technology and microcomputer capabilities are responsible for this new direction in Raman microprobe analysis.

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#### Figure captions

FIG. 1.--Schematic of Raman spectroscopy experimental apparatus.

FIG. 2.--Optical arrangement used to obtain spatially-resolved Raman spectra from the surface of partially stabilized zirconia samples.

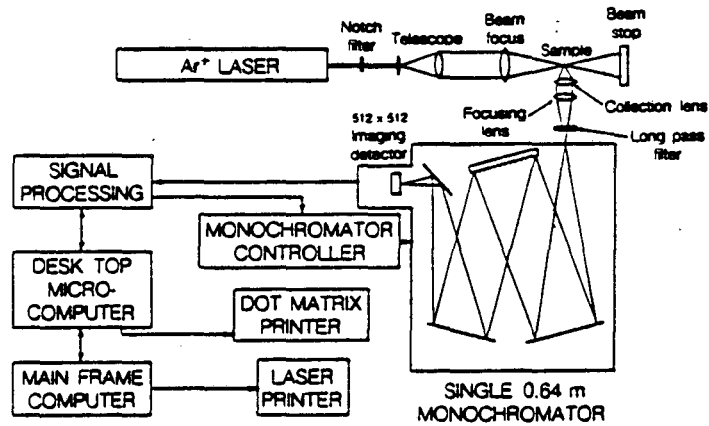
FIG. 3.--Raman spectrum of partially stabilized zirconia sample containing both tetragonal and monoclinic phases. Peak positions are identified in table.

Regions used for evaluating background intensities are numbered.

FIG. 4.--One-dimensional Raman profiles of PSZ. Spatial resolution is estimated to be 40  $\mu\text{m}$ .

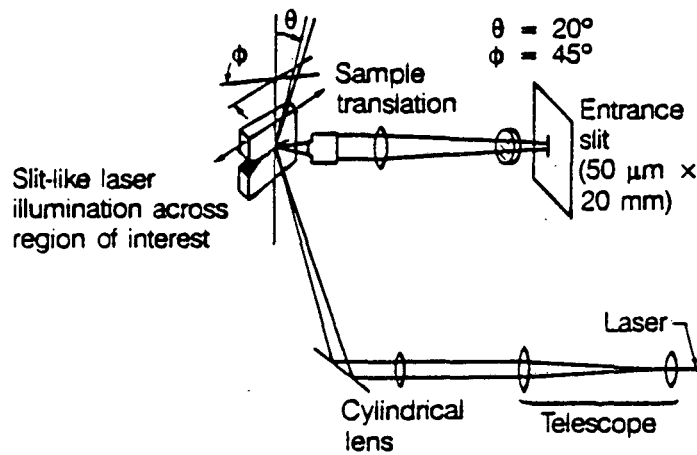
FIG. 5.--Two-dimensional Raman map of the surface of PSZ. A crack was grown partway through material. The map shows increased relative intensities of the monoclinic phase which decay to bulk values both ahead of crack tip and to the sides of the crack.

RAMAN SPECTROSCOPY EXPERIMENTAL APPARATUS



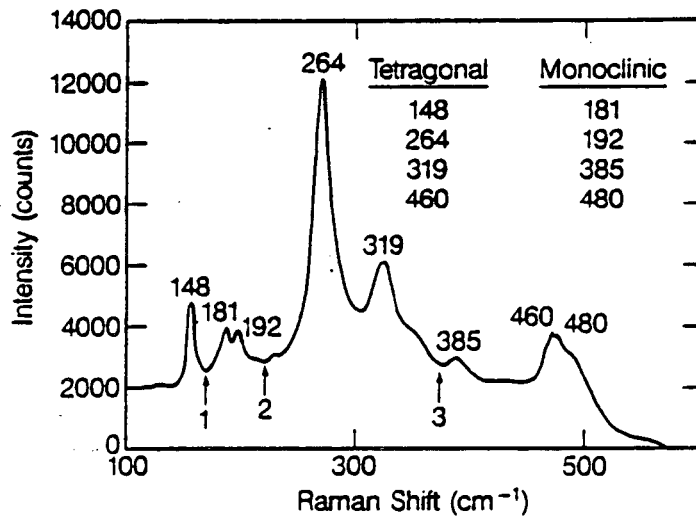
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Fig. 1



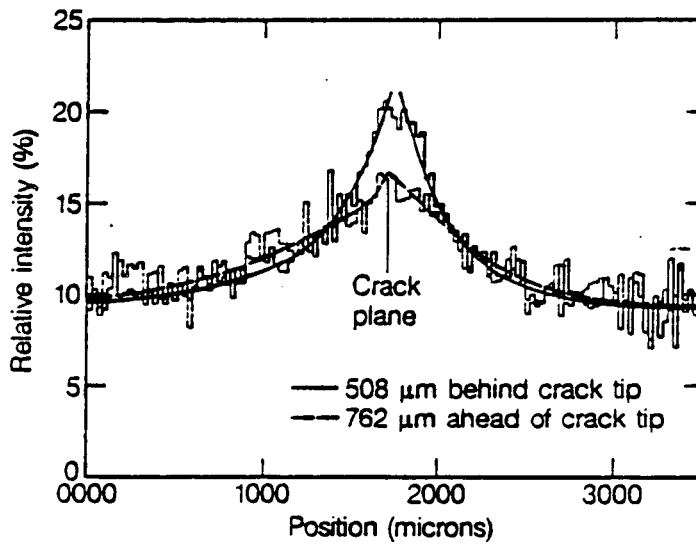
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Fig. 2



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Fig. 3



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Fig. 4

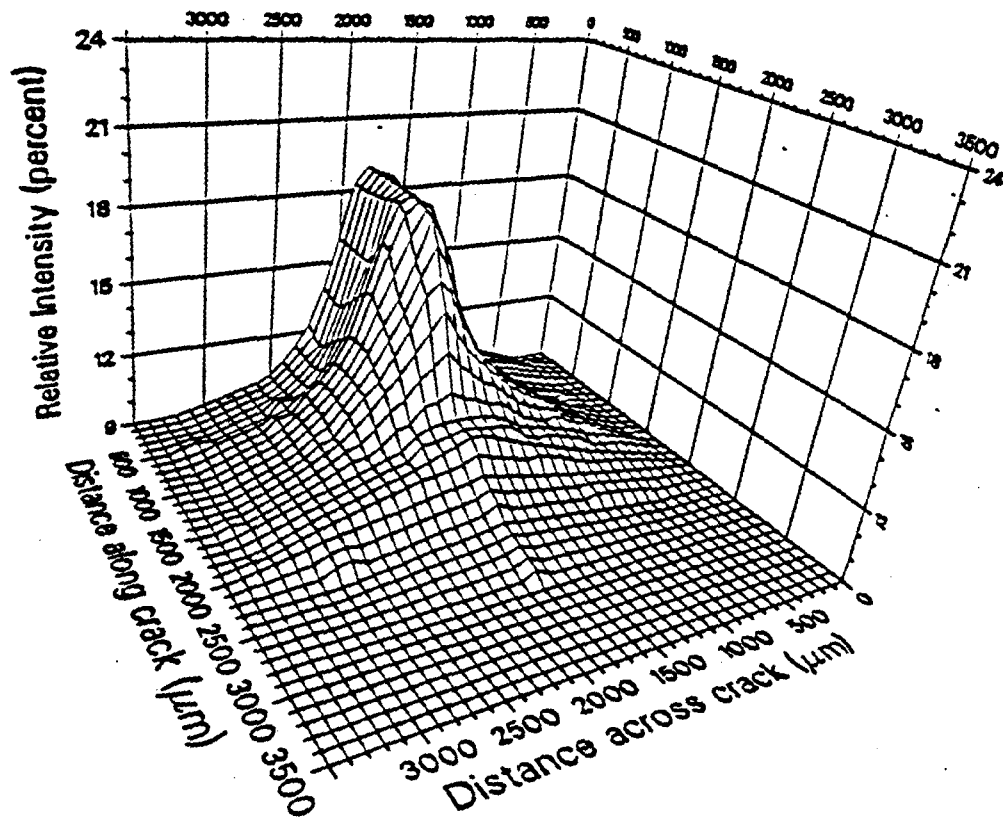


Fig. 5

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*LAWRENCE BERKELEY LABORATORY  
TECHNICAL INFORMATION DEPARTMENT  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720*